University of Cincinnati

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I, Ranaweera Arachchilage Ajantha Upul Ranaweera, hereby submit this original work as part of the requirements for the degree of Doctor of Philosophy in Chemistry.

It is entitled:
Photo-induced Nitrogen and Carbon Based Radicals; A study on triplet nitrenes, triplet 1,2 and 1,3-biradicals

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Photo-induced Nitrogen and Carbon Based Radicals; A study on triplet nitrenes, triplet 1,2 and 1,3-biradicals

A dissertation submitted to the Graduate School of the University of Cincinnati in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry of the College of Arts and Sciences by

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ABSTRACT

This research project looked into different types of carbon and nitrogen based organic radicals. It summarizes following research studies.

1. Intramolecular sensitized triplet nitrene formation.
2. Efficient trans-cis isomerization through a 1,2-triplet biradical
3. Photo-induced 1,3-triplet biradical
4. Corannulene as a singlet oxygen generator and a singlet sensitizer
5. Ethynyl alcohols as a triplet sensitizer for 1-azidoadamantane

In Chapter 02, we look at alkynitrenes with the focus of building high spin units. We demonstrated that geminal diazido alkane form high spin triplet iminenitrene (which is also a triplet 1,3-biradical) at cryogenic temperature but undergo mainly azido cleavage at ambient temperature.

In Chapter 03, we have analyzed the completion between the triplet nitrene formation and azido cleavage in azidomethylacetophenones using product studies, laser flash photolysis and Gaussian calculations.

In Chapter 04, we demonstrated that vinylketone undergo trans-cis isomerization via triplet 1,2-biradicals. We found the lifetime of the triplet 1,2-biradical varies from ~3 μs to 30 μs depending on the substituent group attached to the phenyl ring. Further, We showed that trans-cis isomerization via triplet-1,2-biradicals are efficient at cryogenic temperatures. We revealed the
mechanism for the trans-cis isomerization using time resolved UV/Visible and time-resolved IR spectroscopy, matrix isolation and DFT calculations.

In Chapter 05, we have designed corannulene derivatives that can be used as singlet sensitizers. We have shown that these corannulene derivatives can be used to generate singlet oxygen from triplet oxygen.

In Chapter 06, we have utilized triplet-1,2-biradicals to form triplet vinylnitrene from vinyl azides. We found the lifetime of the triplet-1,2-biradical is ~5 μs for one vinyl azide where as the lifetime of the triplet vinyl nitrene could range from 4 – 12 μs depending on the substitution of the ring.

In Chapter 07, we studied the solid-state reactivity of the vinyl azides by performing laser flash photolysis of nanocrystals in water suspension, and correlated the kinetics and the crystal packing of the vinyl azides to explain the solid-state reactivity.

In Chapter 08, we demonstrated formation of triplet-1,3-biradicals through laser flash photolysis. We have shown that the lifetime of the triplet 1,3-biradical for the cyclopropyl phenyl ketones is ~2 μs.

In Chapter 09, we demonstrated that vinylketones with an electron withdrawing substituent like –C(O)OCH₃ undergo trans-cis isomerization via triplet 1,2-biradicals. These molecules undergo 100% conversion into their cis-adduct upon irradiation.
In Chapter 10, we demonstrated the generation of a carbon based radical upon azido cleavage with small amount of triplet alkyl nitrene formation. This carbon based radical has a lifetime ~16 ms in argon-saturated solutions which increases upon the increase of oxygen concentration suggesting a formation of a peroxy radical.

In Chapter 11, we have shown that ethynyl alcohol derivatives can be used as a triplet sensitizer for 1-azidoadamantane. We have shown with product studies, laser flash photolysis, phosphorescence and DFT calculations that one out of the four ethynyl alcohols functions as a triplet sensitizer where as another functions as both triplet and singlet sensitizers.
DEDICATION

…………..To my loving parents and my wife, who were standing as strong pillars behind me and giving all the blessings………..

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Chapter 01

Introduction, Background, Experimental Methods and Calculations
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Introduction to Molecular Photochemistry

Molecular Photochemistry is a science concerned with description of physical and chemical processes induced by the absorption of photons, in terms of a concrete mechanistic model based on molecular structures and their implied properties.¹

Let’s consider the following fundamental reaction.

\[
\text{A} + \text{B} \xrightarrow{\text{hv}} \text{C} \rightarrow \text{D}
\]

**Figure 1. General reaction**

When reactant A and B expose to light, it converts to D. We are interested in characterizing D to determine what it really is. We then propose how A and B could possibly convert to D, hence we look into the mechanism of formation of D. This involves identification of intermediates like C which may require ultra-fast techniques to detect and also the trapping methods to determine the structure of the intermediates. We employ laser flash photolysis, matrix isolation, time-resolved IR and time-resolved EPR techniques to characterize the intermediates formed from photo-reactions. This helps us to come up with a reasonable mechanism of how A and B convert to C and D or C or D upon irradiation (Figure 2). This also allows us to design molecular systems which selectively give the function that we want them to have upon exposing to light.
Figure 2. Progress of a reaction

Fundamental research in chemistry had laid the foundation for the discovery of new materials with fascinating magnetic and electric properties. There is a need to form magnets that are more flexible and lighter than the more traditional metallic magnets. Currently, scientists have been successful in making magnetic materials using organic ligands and a metal / metal oxide centers. However, most of the metal or metal oxides used in making these materials are transition metals which are not as lighter in weight as organic polymers. To build lighter devices, it is important to have access to lighter components, including magnets. By making use of organic magnets, these devices can be made. In addition, organic magnets are more flexible than traditional magnets, so that the devices that use potential organic magnets will be more flexible; therefore, it is easier to carry them.
The pursuit of organic magnetic material has sparked interest in nitrene, which are intermediates that have unpaired electrons. In a nitrene (R-N:), the nitrogen atom has only 6 electrons available in its outer shell. Two out of 6 valence electrons are involved in the bond with R group, which leave one lone pair of electrons and two unpaired electrons (Figure 02). Therefore a nitrene is a reactive intermediate and is involved in many chemical reactions. However, recent studies in our laboratory show that alkyl nitrene can be formed selectively and these intermediates are stable since they highly un-reactive and thus long lived. These results have open up the possibility to use triplet alkyl nitrenes as building blocks for high spin units.

![Figure 3. Configurations of alkyl nitrenes](image)

However, the mechanism of formation of alkyl nitrene is not well understood. By understanding the mechanism of forming alkyl nitrenes, we could make better building blocks having high paramagnetic properties in order to use in potential organic magnets. Based on how the remaining 4 electrons of the nitrogen atom of a nitrene arranged in orbitals, there are 3 sub configurations of nitrenes and they are namely triplet configuration, singlet-closed shell
configuration and singlet open shell configuration (Figure 02). Out of the 3 sub configurations of the nitrene, the one that gives the paramagnetic properties which lead to magnetism is the triplet configuration. In triplet configuration, there are two unpaired electrons in two different p orbitals of nitrogen aligned in the same direction, which gives the magnetic momentum in the direction perpendicular to the spin of two electrons. The ground state of triplet alkyl nitrenes has triplet configuration and are intrinsically highly unreactive because the energy of the triplet state is much lesser than the other two states of the nitrene (Figure 02). Thus, by connecting two alkyl nitrene units together to form high spin quintet di-nitrenes could be used as building blocks for organic magnets. Therefore, di-nitrenes will be even more paramagnetic and very neat candidate to make potential organic magnets, which in turn could use to make different electrical and optical devices.

We also focus on trans-cis isomerization of vinyl alkenes. Vinyl alkenes are compounds which has carbon-carbon double bonds. We have developed a method to make vinyl alkenes with and without electron donating and withdrawing substituent that undergo trans\(\rightarrow\)cis isomerization upon exposure to light. Trans – cis isomerization is used in chemical applications such as dyes, organic photo-switches and optical-data storage devices. Photoinduced trans - cis isomerization can also be used for release of fragrances in household goods and in biological applications like drug and gene delivery systems.
Figure 4. Exposure to light causes large conformational changes “ON” and “OFF” states of a photoswitch.\textsuperscript{4}

Currently, most photoswitches are based on trans-cis isomerization. The cartoon in Figure 03 shows that the trans azo molecule on the right has an acceptor chromophore and a donor chromophore, which upon exposing to blue light undergo trans to cis isomerization to give the corresponding cis azo molecule. In the cis conformation, the accepter and donor moieties are closer to one another, which resemble a closed circuit. Therefore, it functions as an “ON” state of a molecular photoswitch. On the other hand, the trans azo molecule resembles an open circuit, therefore functions as an “OFF” state of a molecular photoswitch. Trans and cis conformations are interconvertible depending on the irradiation wavelength (or the color of the light); hence it could function as a molecular photo-switch.
Background

The photochemistry of alkyl azides has been studied previously in our group. These studies of α-azides with built-in triplet sensitizers in our group have demonstrated that these compounds undergo photocleavage to form triplet nitrene which then undergo rearrangement and dimerizations. Upon the irradiation, the ketone moiety absorbs light and excites to its first singlet excited state and then inter-system crosses (ISC) to the corresponding triplet ketone. Then it transfers its energy to the azido moiety to form triplet azide and then it undergoes cleavage of a nitrogen molecule to give the triplet nitrene (Figure 03).

Figure 5. Formation of triplet alkyl nitrene from α-azidoacetophenone

The laser flash photolysis studies show that this triplet nitrene has absorption around 300 nm. However, this system also undergoes α-cleavage in competition with triplet alkyl nitrene formation.
Sing et al. extended the carbon chain by one more carbon and synthesized β-azidopropiophenone to study the photochemistry. He was the first to observe an intra-molecular sensitized triplet alkyl nitrene. He shows from laser flash photolysis that triplet alkyl nitrene has an absorbance maximum at 330 nm and a lifetime of ~20 ms. He further showed that there is a triplet signal for nitrene at 8400 G in EPR (Figure 6).
In this thesis, I was interested in finding out the possibility of quintet alkyl di-nitrene, triplet alkyl nitrene with an electron withdrawing substituent next to it etc. In addition, another half of the thesis looks at the trans to cis isomerization. We think that this takes place through a triplet 1,2-biradical and we explored the 1,2-biradical by using laser flash photolysis, time-resolved IR and time-resolved EPR techniques.
The molecule on the left of Figure 7 has a long C=C bond. On one side of the molecule, there is a xylyl chromophore. The rotation around C-C bond attached to xylyl chromophore is hindered because of the steric hindrance of the adjacent phenyl rings. Upon irradiation, this molecule undergo cis-trans isomerization around the C=C bond to give the molecule on the right of Figure 7. This results in a molecule which is more open at xylyl chromophore. Therefore, xylyl chromophore now can rotate around C-C bond. This is like not only an “OFF” state of a molecular photo-switch, it also resembles like a molecular “Rotor”. When the molecule on right irradiate at a different wavelength of light, it goes back to the original conformer of the molecule completing a closed conformer, which is like a closed circuit. Therefore, it resembles an “ON” state of a molecular photo-switch. Further, the molecule also resembles a molecular “Break”. Hence, above system shown in Figure 7 not only function as a molecular photo-switch, but also as a molecular rotar.\textsuperscript{6}
Experimental Methods

Product Studies

As the name implies, product studies is the study of products of a reaction. The purpose of this experimental method is identifying the photo-products after irradiation of a reactant with light. Samples are usually prepared in a solvent of interest with a certain concentration. We irradiate these samples in a photo-cabinet with a filter of our choice (Eg. Pyrex, Quartz). A filter allows cutting off the wavelengths below a certain wavelength of light (For example, Pyrex filter cut off wavelengths below 300 nm). The new photo-products are identified by standard characterization methods such as $^1$H NMR, $^{13}$C NMR, FTIR, HRMS or GC-MS techniques.

Figure 9. Photo-cabinet used for product studies

Laser Flash Photolysis

Laser flash photolysis was done with an Excimer laser (308 nm, 17 ns). The system has been described in detail elsewhere.
A stock solution of the sample in a selected solvent was prepared with spectroscopic grade solvent, such that the solutions had absorption between 0.3 and 0.6 at 308 nm. Typically, ~2 mL of the stock solution was placed in a 10 mm × 10 mm wide, 48 mm long quartz cuvette and was purged with argon for 5 min or oxygen for 15 min. The rates were obtained by fitting an average of three to five kinetic traces.

Laser Flash Photolysis is a time-resolved ultraviolet/visible spectroscopic technique that is used to detect and identify short-lived intermediates. Further, it will also allow measuring the lifetime of these intermediates.
Matrix Isolation

Matrix isolation studies were performed using conventional equipment. This is a technique that can be used to trap short-lived intermediates at cryogenic temperatures and study them spectroscopically. Further, this technique will also allow studying the uni-molecular reactivity. During this technique, the substrate is mixed with large excess of unreactive host gas and is condensed on a surface that is sufficiently cold enough to solidify the materials. From this method, one ends up with a sample where each substrate molecule is immobilized with a cavity surrounded by one or more layers of inert material is thus “isolated” from other substrate molecules in a “matrix” of host gas.
Figure 12. Matrix isolation setup

Phosphorescence

Phosphorescence is the emission of light from an excited triplet state of a molecule to a ground state of the molecule. This transition is a spin-forbidden transition, and involves inter system crossing. Therefore, it is usually a slow process and also a low intense process. We studies phosphorescence of molecules find out the experimental energy from 0th vibrational level of excited triplet states to 0th vibrational level of ground state. We compared the experimentally measured triplet energy with the calculated triplet energy to get a better understanding of the triplet excited state of molecules.
EPR Spectroscopy

Time-Resolved EPR Spectroscopy was carried out with Continuous Wave Nd/YAG laser (266 nm, 355nm, 532 nm, 1 ns). A stock solution of the sample in a selected solvent was prepared with spectroscopic grade solvent, such that the solutions had absorption between 0.3 and 0.6 at 266 nm or 355 nm or 532 nm. EPR samples were prepared as follows. ~0.5 mL of the sample was added to an EPR tube. The dissolved oxygen was removed by vacuum. Then the sample was sealed from the top to prevent any oxygen getting in. The EPR measurements were obtained by fitting an average of three to ten traces.

Time-resolved EPR is a spectroscopic technique that is used to detect and identify short-lived intermediates. Further, it will also allow measuring the lifetime of these intermediates. This is sensitive to mainly paramagnetic species.

Figure 13. EPR Spectrometer in Hiroshima University, Hiroshima, Japan
Time-Resolved IR Spectroscopy

Time-Resolved IR Spectroscopy was carried out with Nd/YAG laser (266 nm, 1 ns). A stock solution of the sample in a selected solvent was prepared with spectroscopic grade solvent, such that the solutions had absorption between 0.3 and 0.6 at 266 nm. Typically, argon was purged for 5 min or oxygen for 15 min. The rates were obtained by fitting an average of three to five kinetic traces.

Time-resolved IR is a spectroscopic technique that is used to detect and identify short-lived intermediates. Further, it will also allow measuring the lifetime of these intermediates. This will give more structural information than time-resolved UV/Visible spectroscopy.

Calculations

DFT / TD DFT

Density Functional Theory (DFT) and Time Dependent DFT (TD-DFT) addresses some of the drawbacks of *ab initio* methods such as Hartree Fork. In *ab initio* method, the energy of the molecule and all of its derivatives depend on the wave function. In reality, the wave function is just a physical function and it does not have any meaning and it doesn’t exist. When the square of the wave function is taken, then it relates to the probability of finding an electron in molecule. Probability in turn relates to the energy of the molecule. Determination of electron density of a molecule allows predicting certain things about a molecule, which forms the density functional theory. One of the major differences in *ab initio* method and DFT is that the incorporation of
electron-electron correlation functions. This is actually the difference of absolute answer of Schrodinger equation and the Hartree Fork theory.

Electron Density = \( \rho (x, y, z) \)

Energy = \( F[\rho (x, y, z)] \)

The target is to find \( F \) using DFT for which one would need certain approximations to be made. It is accepted that DFT methods are better choice than \textit{ab initio} methods, and they are generally more accurate with less computational expense.

References


Chapter 02

Triplet-Sensitized Photoreactivity of a Geminal Diazidoalkane

Triplet-Sensitized Photoreactivity of a Geminal Diazidoalkane

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ABSTRACT

Photolysis of 1 in chloroform yielded 2 as the major product and a small quantity of 3. Laser flash photolysis demonstrated that upon irradiation, the first excited triplet state of the ketone (T1K) of 1 is formed and decayed to form radical 4, which has a λmax at 380 nm (τ = 2μs). Radical 4 expelled a nitrogen molecule to yield imine radical 5 (λmax at 300 nm). Density functional theory (DFT) calculations showed that the transition state barrier for the formation of 5 is approximately 4 kcal/mol. In comparison, photolysis of 1 in argon matrices resulted in triplet nitrene 6, which was further characterized with 15N and D isotope labeling and DFT calculations. Prolonged irradiation of 6 yields triplet imine nitrene 7.
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1. Introduction

Excitation of aryl azides causes them to fall apart, expel a nitrogen molecule and form singlet aryl nitrenes.\textsuperscript{1} At a cryogenic temperature, the singlet aryl nitrene intersystem crosses to its triplet configuration. Photolysis of aryl azides at low temperatures has been used to successfully form triplet aryl nitrenes and high-spin quintet aryl di-nitrenes and septet aryl tri-nitrenes from the corresponding diaryl and triaryl azides.\textsuperscript{2-6} In comparison, triplet alkyl nitrenes cannot be formed by direct irradiation of alkyl azides because they yield imine products. Kyba and Abramovitch theorized that the singlet excited state of the alkyl azides reacted in a concerted manner to form the imine products.\textsuperscript{7} However, they also hypothesized that photolysis of the alkyl azides resulted in singlet alkyl nitrenes that rearrange to form the imine products faster than they undergo intersystem crossing to the triplet state.\textsuperscript{8} In comparison, triplet-sensitized photolysis of alkyl azides has been shown to be efficient in forming triplet alkyl nitrenes, both at ambient and cryogenic temperatures.\textsuperscript{9-13}

![Scheme 1](image-url)
The photochemistry of diazide alkanes has not been studied extensively; however, Moriarty and Kliegman have shown that direct irradiation of diazidodiphenylmethane results in the formation of 1,5-diphenyltetrazole and a small amount of 2-phenylbenzimidazole (Scheme 1). This reaction presumably occurs by singlet reactivity of the excited state of the azido chromophore to form an imine that reacts further.\textsuperscript{14,15} In addition, Barash et al. have shown that photolysis of 9,9-diazido-9H-fluorenewith benzophenone as a triplet sensitizer yielded an ESR signal that can be attributed to the formation of the corresponding mononitrene (Scheme 2).\textsuperscript{16} Prolonged irradiation at 365 nm led to the formation of the triplet carbene shown in Scheme 2. The formation of the triplet carbene intermediate was verified by irradiation of the diazo precursor, which also yielded the same ESR signal.

\textbf{Scheme 2}

In this paper, we describe the triplet reactivity of diazidodervative 1. Product studies, laser flash photolysis, phosphorescence, matrix isolation, isotope labeling and density functional theory (DFT) calculations were used to elucidate the reactivity of 1. Photolysis of 1 in solution yielded primarily 2 by homolytic cleavage of one of the azido groups. In argon matrices, triplet
nitrene 6 was the major product. Prolonged irradiation of 6 yielded triplet imine nitrene 7 rather than quintet dinitrene 8 in argon matrices (Scheme 3).

\[ \text{Scheme 3} \]
2. Results

2.1 Product Studies

Photolysis of 1 in argon-saturated chloroform-d through a Pyrex filter at 196 K yielded 2 as the major product, along with a small amount of 3 (Scheme 4). Irradiation of 1 through a Pyrex filter ensured that only the ketone chromophore absorbed the light and formed the singlet excited state of the ketone ($S_{1K}$), as alkyl azides only have a weak absorption below approximately 300 nm.10,17,18 Because 1 is an acetophenone derivative, the $S_{1K}$ of 1 is expected to intersystem cross to its triplet excited state, and the first and the second excited states of the triplet ketone ($T_{1K}$ and $T_{2K}$) are within a few kcal/mol of each other.18,19,20 Energy transfer from $T_{1K}$ or $T_{2K}$ of 1 to the azido moiety formed the triplet excited state of the azide chromophore ($T_A$) in 1, which can fall apart to yield triplet nitrene 6 and a nitrogen molecule (Scheme 5). Several other intramolecular sensitizations of alkyl azides have been reported to from triplet alkyl nitrenes.9,12 Because products 2 and 3 have less than two nitrogen atoms, it is not likely that 6 react further to form di-nitrene 8. Instead, the C-N$_3$ bond in 6 cleaves to form 5 and an azido radical. It can also be theorized that a radical abstracts a hydrogen atom from 6 to form 9. Radical 9 can cleave to form 2, whereas 5 can result in both 2 and 3, as shown in Scheme 5.
It is also possible that photolysis of 1 does not form triplet nitrene 6, but the azido group cleaves to yield an azido radical and 4, which rearranges to form 5 (Scheme 6). We have previously reported that intramolecular sensitization of alkyl azides can result in cleavage of azido groups,$^{21,22}$ and that a radical adjacent to an azido group rearranges to form imine radicals.$^{23}$

Scheme 5

Scheme 6
We photolyzed 1 in argon-saturated toluene to verify whether any new products were observed in solvent with abstractable H atoms. GC-MS analysis of the reaction mixture showed the formation of 2 and 3 as the major products, in addition to 10, which can be attributed to trapping imine radical 5 with a benzyl radical (Scheme 7). Furthermore, 1,2-diphenylethane was detected and must have been derived from the solvent by dimerization of two benzyl radicals. A small amount of 11 was also formed in toluene. In oxygen-statured toluene, the major products were 2 and small amounts of 3 and 11. Product studies in toluene support that irradiation of 1 result in radical 5, and in an oxygen-saturated solution, oxygen reacts with radical 5 to form 2. Furthermore, we theorized whether 3 and 11 can be attributed to the formation of a triplet carbene intermediate.

Scheme 7
2.2 Phosphorescence

The phosphorescence of 1 was measured in ethanol glasses at 77 K (Figure 1). The (0,0) band for the phosphorescence was estimated to be approximately 407 nm; thus, the energy of the first excited triplet ketone ($T_{1K}$) of 1 was calculated to be 70 kcal/mol, which is approximately 2 and 3 kcal/mol lower than observed for the analogous $p$-methylacetophenone and $p$-trifluoromethyl acetophenone.24

2.3 Calculations

The stationary points on the triplet and quintet surface of 1 were calculated to better understand the factors governing the reactivity of 1 using Gaussian0925 at the B3LYP level of theory with the 6-31+G(d) basis set.26,27

The ground-state ($S_0$) of 1 was optimized in the gas phase and several minimal energy conformers were found (see Supporting Information) due to the azido groups. The conformer of

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Phosphorescence spectrum of 1 in ethanol at 77 K, as obtained by 300 nm irradiation.}
\end{figure}
1 was used for the calculations in which the azido groups are lined up, as shown in Figure 2. This conformer was selected for the calculations because its calculated IR spectrum contained an azido stretch at 2257 cm⁻¹ (f=109) and 2250 (f=995) due to symmetrical and anti-symmetrical stretching of the two azido groups, respectively (f is the calculated oscillator strength). The neat IR spectrum of 1 had a strong azido band at 2105 cm⁻¹. The other low energy conformers of 1 contained two azido bands with similar oscillator strengths, but their frequencies were better resolved. The S₀ geometry of 1 was used to perform TD-DFT calculations, which located the first excited triplet ketone (T₁K) of 1 at 72 kcal/mol above the ground state (S₀) in the gas phase (Scheme 8). Inspection of the molecular orbitals shows that T₁K of 1 has a (n,π*) configuration, whereas T₂K is 76 kcal/mol above S₀ and has a (π,π*) configuration. Thus, the TD-DFT calculations yielded vertical excitation energy for T₁K of 1, which is similar to the result obtained from the phosphorescence of 1.

![Figure 2. The optimized structure of 1, T₁K of 1 and Tₐ of 1.](image)

Optimization of the T₁K of 1 found that it is located 67 kcal/mol above S₀, which is considerably lower energy than the numbers obtained by TD-DFT calculations and the
phosphorescence spectrum. Inspection of the molecular orbitals and the C=O bond in T_{1K},
elongated to 1.321 Å, indicated that the optimized structure of T_{1K} of 1 had a (n,π*)
configuration. The bond lengths and bond angles of the azido moiety in T_{1K} of 1 were similar to
the corresponding bonds and angles in the S_0 of 1, demonstrating that the T_{1K} of 1 was localized
on the acetophenone moiety. It should be noted that we have previously shown that density
functional calculations underestimate the energy of triplet ketones with (n,π*)
configurations.\textsuperscript{18,22,33}

The triplet excited state of the azido group (T_A) in 1 that is located 44 kcal/mol above the S_0
was also optimized. The N-N-N bond in the T_A of 1 has a bond angle of approximately 120.4°
and a N1-N2 bond length of 1.423 Å. Additionally, the bond length and the bond angle of the
carbonyl group is similar to the corresponding bond length and bond angle in the S_0 of 1,
indicating that this triplet excited state is localized on the azido moiety. The triplet transition
state for the T_A of 1 to cleave and form 6 (T_N) and a N_2 molecule is located only 0.1 kcal/mol
above the T_A of 1. Thus, the energy of T_A in 1 and the transition state for forming a nitrene is
similar to what was reported for mono substituted alkyl azides.\textsuperscript{18,22} The triplet transition state
was located for 6 forming 7 (T_{Im}) by simultaneously expelling a nitrogen molecule and
undergoing a 1,2-Hatom shift 40 kcal/mol above 6, which was similar to what Nguyen et al.
have reported for azidomethane.\textsuperscript{34}
Scheme 8. Calculated (B3LYP/6-31+G(d)) stationary points on the triplet surface of 1 to form nitrene 6 and 7. Energies are in kcal/mol.
The triplet transition state for 1 to cleave and form an azido radical and 4 was calculated. It was determined that it was located approximately 3 kcal/mol below the $T_{1K}$ of 1 (Scheme 9). Intrinsic reaction coordinate (IRC) calculations\textsuperscript{35,36} correlated this transition state with 4 and the azido radical; and a triplet excited state that has an elongated C-N bond. However, UB3LYP calculations cannot be used to optimize the triplet excited state because it is not the lowest triplet excited state of the azido or aryl ketone chromophores.

Scheme 9. Calculated (B3LYP/6-31+G(d)) stationary points on the triplet surface of 1 for azido cleavage. Energies are in kcal/mol.
Additionally, we calculated the quintet excited state of the azido chromophore (T_A) of 6 and found that it was located 46 kcal/mol above the ground state of 6, and the transition state for the T_A of 6 to form 8 was located 0.1 kcal/mol above the T_A of 6 (Scheme 10). The energy surface for 6 to form 8 was similar to what was observed for the T_A of 1 to form 6. However, 8 was destabilized by 2 kcal/mol in comparison to 6.

Finally, the quintet transition state for 8 undergoing 1,2-H atom shift to form quintet nitrene 7 (Scheme 10) was calculated and located 48 kcal/mol above 8. The calculations indicated that quintet imine-nitrene 7 was 9 kcal/mol more stable than quintet di-nitrene 8. Triplet imine nitrene 7 was 61 kcal/mol more stable than 6 due to the release of the N_2 molecule and because the nitrene moiety was stabilized \textit{via} conjugation with the imine chromophore.
Scheme 10. Calculated (B3LYP/6-31+G(d)) stationary points on the triplet and quintet surfaces of 6 forming 8 and 7. Energies are in kcal/mol.

The triplet transition state for 6 cleaving to form 5 and an azido radical was located 9 kcal/mol above 6 (Scheme 11). Similarly, the transition state for radical 9 to cleave to form an azido radical and 2 was located 11 kcal/mol above 9. The calculations supported that 6 and 9 can be expected to undergo azido cleavage at ambient temperature. Finally, the transition state for 5 abstracting an H atom from toluene was calculated and located 15 kcal/mol above 5. Therefore 5 is anticipated to be a long lived intermediate because it is not expected to abstract H atoms from
the solvent efficiently, but rather toluene or azido radicals are more likely to abstract H-atom from 5.

Scheme 11. Calculated (B3LYP/6-31+G(d)) stationary points on the triplet surfaces of 6 for formation of 4 and 5. Energies are in kcal/mol.
The optimized structures of nitrenes 6, 7 and 8 (Scheme 12) were compared. In 6, the C-N bond for the nitrene moiety was 1.425 Å, whereas in 8, the C-N bonds increased to 1.440 Å due to the electronic repulsions between the two nitrene units (Scheme 12). Furthermore, the electron repulsion caused the N-C-N bond angle to increase to 114.1° in 8 from 109.1° in 6. In comparison, the C-N bond in 7 was shorter because the nitreno and imine moieties were conjugated. The calculations show that the spin density was localized on the nitrogen atoms in 6 and 8, whereas in 7, the conjugation delocalized the spin density over the N-nitrene and iminyl moieties.

The calculations indicated that on the triplet surface, 1 can easily both undergo azido cleavage to form radical 4 (Scheme 9) and energy transfer to form triplet alkyl nitrene 6 (Scheme 8). However, it is not likely that quintet di-nitrene 8 is formed from photolysis of 6, but rather the more stable triplet iminyl nitrene 7 (Scheme 10).

---

**Scheme 12.** C-N Bond lengths and N-C-N bond angles in 1, 6, 7 and 8.
2.4 Laser Flash Photolysis

Laser flash photolysis of 1 was performed to elucidate the triplet reactivity of 1 at ambient temperature in solution. Laser flash photolysis (Excimer laser, $\lambda = 308$ nm, 17 ns)\textsuperscript{23} of 1 in argon-saturated acetonitrile produced transient absorptions with $\lambda_{\text{max}}$ at approximately 400 and 480 nm (Figure 3). As the intensity of these bands decreased with time, a new absorption with a $\lambda_{\text{max}}$ at 330 nm was formed (Figure 3). The calculated (TD-DFT) absorption spectrum of $T_{1K}$ of 1 contained major electron transitions at 461 ($f = 0.027$), 438 ($f = 0.0087$), 376 ($f = 0.0127$), 313 ($f = 0.0276$), and 300 nm ($f = 0.0372$), where $f$ is the calculated oscillator strength (Figure 4). In addition, the calculated absorption spectrum of 4 in acetonitrile had a major electronic transition at 500 ($f = 0.1115$), 362 ($f = 0.3084$) and 353 nm ($f = 0.4529$), as shown in Figure 4. The transient spectrum obtained at shorter time scales was assigned to $T_{1K}$ of 1 and 4. In comparison, the calculated spectrum for 5 contained major electronic transitions at 286 ($f = 0.0378$) and 271 nm ($f = 0.551$) and a smaller one at 345 nm ($f = 0.0004$). Due to the intense band at 271 nm we propose that the absorption for 5 trails out to 330 nm, which fit with the transient spectrum obtained at a longer time scale (Figure 3). It should be highlighted that there are some residual absorption at 330 nm due to product formation in addition to absorption of 5.

In oxygen-saturated acetonitrile, the transient absorption was reduced and the $\lambda_{\text{max}}$ shifted to 380 nm, which was assigned to 4 (Figure 3).
Kinetic analysis of the transient absorptions in acetonitrile further supported these assignments. In argon-saturated acetonitrile, the transient absorption due to 4 (480 nm) was formed at a rate constant of $1.0 \times 10^7 \text{ s}^{-1}$ and it decayed with a rate constant of $5 \times 10^5 \text{ s}^{-1}$ (Figure 5a). Because the absorption coefficient for T$_{1K}$ of 1 was less at 480 nm than for 4, the growth of 4 was observed rather than the decay of T$_{1K}$ of 1. The rate for forming 5 was measured at 340 nm and was the same within experimental error as the decay for 4 (Figure 5b). Radical 5 was long-lived with a decomposition rate constant of $4 \times 10^2 \text{ s}^{-1}$ (Figure 6a).

In addition, a small amount of growth, with a rate constant of $3.3 \times 10^3 \text{ s}^{-1}$, was observed at 340 nm (Figure 6b). We theorized that this transient was due to radical 5 being formed from triplet nitrene 6, indicating that a small amount of 6 was formed from the photolysis of 1 in competition with radical 4.

In oxygen-saturated solution, the transient from 4 formed faster than the resolution of the laser (pulse width of 17 ns). Thus, by assuming that the concentration of oxygen in acetonitrile was $9.1 \times 10^{-3} \text{ M}$, the T$_{1K}$ of 1 must be quenched with oxygen with a rate constant of more than $6 \times 10^9 \text{ s}^{-1} \text{ M}^{-1}$, which is comparable to what has been measured for acetophenone in acetonitrile ($3.7 \times 10^9 \text{ s}^{-1} \text{ M}^{-1}$) and $p$-methylacetophenone (see Supporting Information). In oxygen-saturated acetonitrile, the decay of 4 can be fitted as a mono-exponential function to yield a rate constant.
of $1.2 \times 10^7 \text{ s}^{-1}$, and the rate of oxygen quenching 4 in acetonitrile can be estimated to be approximately $1.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, which is similar to what has been reported for other carbon-based radicals.$^{37-39}$
Figure 4. TD-DFT (B3LYP/6-31G+G(d)) calculated UV spectrum of the T\(_{1K}\) of 1, 6, 4 and 5 using TD-DFT level of theory with a 6-31G+(d) basis set.

Figure 5. Kinetic trace obtained at a) 480 nm in argon- (red trace) and oxygen-saturated (blue trace) acetonitrile, b) 340 nm in argon-saturated acetonitrile.
Figure 6. Kinetic traces obtained at 340 nm from laser flash photolysis of 1 in argon-saturated acetonitrile at different timescale.

Laser flash photolysis demonstrated that the major reactivity of 1 in solution is to form radical 4, which expels a nitrogen molecule to form iminyl radical 5. In oxygen-saturated solution, the triplet ketone becomes shorter lived than the time resolution of the laser, and radical 4 is formed in decreased yields. Furthermore, radical 4 is efficiently trapped with molecular oxygen. Because we observed a small growth at 340 nm, we theorize that a small amount of triplet nitrene 6 is formed and it slowly forms radical 5.
2.5 Matrix Isolation

We investigated the photochemistry of 1 in argon matrices at 14 K to identify its reactivity in the absence of diffusion. We deposited 1 into argon matrices in several different experiments by placing a sample of 1 in a small stainless steel side arm, connected to the deposition line by an UltraTorr tee. The vapor of the compound was entrained in flowing argon, and carried to the cold window and deposited. Irradiation of 1 in argon matrices led to the growth of new absorption bands, mostly occurring near those of the parent azide (Figure 7). This result was expected because the acetophenone moiety was not significantly affected by irradiation and the majority of the observed vibrational bands belonged to it. The infrared spectrum of 1 showed intense azido bands at 2136, 2126, 2115, and 2078 cm\(^{-1}\) (Figure 8 and Figure 9), which are all depleted upon irradiation. This multiplet of azido bands is likely due to different conformers of 1, which additionally may be trapped in different matrix sites. After irradiation, a new azido band was observed at 2137 cm\(^{-1}\). In addition, new bands were observed at 1269 and 850 cm\(^{-1}\), which we assign to the formation of 6 based on calculations.

* = \(^{15}\text{N} 25\%

\(^{15}\text{N} \) isotope substitution  \(D\) isotope substitution

Scheme 13
To further verify that the azido band at 2137 cm\(^{-1}\) was due to the formation of 6, we conducted similar experiments for deuterium-and \(^{15}\)N isotope-labeled 1 (1-d\(_5\) and 1-\(^{15}\)N, see Scheme 13). In 1-d\(_5\), five H atoms were fully replaced with deuterium atoms, whereas in 1-\(^{15}\)N, each azido moiety had either the \(\alpha\)- or the \(\gamma\)-N atom as a \(^{15}\)N atom. Therefore, IR bands due to both \(^{15}\)N and \(^{14}\)N isotopes were observed. The infrared spectrum of 1-d\(_5\) showed intense azido bands at 2122 and 2107 cm\(^{-1}\) and weaker ones at 2138 and 2069 cm\(^{-1}\) (Figure 10). The calculations indicated that deuteration of 1 interchanges the symmetric and anti-symmetric stretches of the two azido bands; therefore, the infrared spectrum of 1-d\(_5\) was different than for 1. Upon irradiation, all azido bands were depleted beside the one at 2138 cm\(^{-1}\), which grew in intensity and a new band was formed at 2119 cm\(^{-1}\). These results further supported the assignment of this band to 6. The calculations showed that upon deuteration, the azido stretch in 6 coupled with the C-D stretch and the two azido vibrational bands had different intensities. Furthermore, the infrared spectrum of 1 formed from \(^{15}\)N-labeled sodium azide showed azido bands at 2150, 2139, 2132, 2121, 2114, 2108, 2092 and 2068 cm\(^{-1}\) (Figure 11). After irradiation, the intensity of the azido bands at 2132 and 2114 cm\(^{-1}\) increased, whereas the other azido bands were depleted. The azido bands that increased upon irradiation were placed 18 cm\(^{-1}\) apart, which fits well with calculations showing how the \(^{15}\)N isotope labeling of 6 will shift the azido band 25 cm\(^{-1}\).

An additional vibrational band identified at 850 cm\(^{-1}\) was affected by \(^{15}\)N-isotope labeling and assigned to a C-N stretch in 6, which was coupled to a stretching of the aromatic ring. Upon \(^{15}\)N-labeling, this band shifted to 842 cm\(^{-1}\), which was in excellent agreement with the calculated shift of 6 cm\(^{-1}\). This band shifted to 793 cm\(^{-1}\) in 6-d\(_5\) and its intensity also decreased and fit the calculations well (Table 1).
Prolonged irradiation of 1 in matrices resulted in a significant new band 3408 cm\(^{-1}\), which was assigned to the N-H band in triplet 7, based on its positions and calculations. The reactivity of 1 was monitored as a function of irradiation time to verify that 7 was formed by secondary photolysis of 6 (Figure 9 and Figure 10). Formation of the N-H band was observed after more than 4 hours of irradiation, whereas the azido band due to the triplet nitrene 6 at 2138 cm\(^{-1}\) was formed significantly faster.

Characterization of 7 was further supported by isotope labeling. For example, deuterium isotope labeling of 7 shifted the N-H band by 874 cm\(^{-1}\), fitting well with the calculated shift of 917 cm\(^{-1}\) (Table 2). We were not able to identify any additional vibrational bands for 7 that were affected by \(^{15}\)N isotope labeling, presumably because the intensity of the imine stretches are low, as further supported by the calculations.

<table>
<thead>
<tr>
<th>Normal Isotope</th>
<th>Normal Isotope</th>
<th>(^{15})N</th>
<th>(D \times 5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_3)</td>
<td>2137</td>
<td>2132</td>
<td>2138</td>
</tr>
<tr>
<td></td>
<td>2233(442)(^a)</td>
<td>2231 (434)(^a)</td>
<td>2241 (320)(^a)</td>
</tr>
<tr>
<td>C-N</td>
<td>850</td>
<td>850</td>
<td>812</td>
</tr>
<tr>
<td></td>
<td>859 (30)(^a)</td>
<td>859 (30)(^a)</td>
<td>808 (9)(^a)</td>
</tr>
<tr>
<td></td>
<td>852 (27)(^a)</td>
<td>852 (27)(^a)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>842</td>
<td>853 (27)(^a)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) The values in parenthesis are calculated oscillator strengths.
Table 2. Selected IR bands after prolonged irradiation of 1 in argon matrices and calculated IR bands for $^7$.

<table>
<thead>
<tr>
<th>Stretch</th>
<th>Normal Isotope</th>
<th>$^{15}$N</th>
<th>D x 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=N-H</td>
<td>3411</td>
<td>3408 (5)$^a$</td>
<td>3405</td>
</tr>
</tbody>
</table>

$^a$) The values in parenthesis are calculated oscillator strengths.

Figure 7. Photolysis of 1 in argon matrices. a) Before irradiation (red) and b) after irradiation (black).
Figure 8. a) Before irradiation (red), b) after irradiation (black) of 1, and c) difference spectra (blue).
**Figure 9.** Irradiation of 1 as a function of time: a) before irradiation (pink); b) after 1 min irradiation (red); c) 11 min (purple); d) 41 min (dark blue); e) 1 hour and 41 min (light blue); f) 3 hours and 41 min (grey); g) 18 hours and 41 min (black) of irradiation.
Figure 10. Photolysis of 1-d₅ as a function of time: a) before the irradiation (pink); b) after 1 hour (red); c) 2.5 hours (purple); d) 3.5 hours (dark blue); e) 4.5 hours (light blue); f) 20 hours (black) of irradiation.
3. Discussion

We have shown that diazide 1 undergoes efficient azido cleavage in solution to form radical 4, which expels a nitrogen molecule to form radical 5. In addition to the azido cleavage, we theorized that 1 also forms a small amount of triplet alkyl nitrene 6. We have shown previously that azide 12A, 12B and 13 also undergo azido cleavage in competition with energy transfer to form triplet alkyl nitrene intermediates (Scheme 14). Radical stabilizing substituents adjacent
to the azido moiety lower the transition state barrier for the azido cleavage, which explains why 1, 12 and 13 all undergo efficient azido cleavage in solution.

![Scheme 14](image)

In comparison, photolysis of 1 in argon matrices does not lead to azido cleavage, but rather the formation of triplet alkyl nitrene intermediates. This result is similar to what we observed for azides 12A and 12B as well. It is possible that azides 1 and 12A and 12B undergo azido cleavage in matrices but the radical pair recombines because they cannot diffuse apart. However, it is also possible that the thermal population of the excited state that is the precursor to the azido cleavage is not feasible at low temperatures.

Prolonged irradiation of nitrene 6 does not lead to the formation of quintet di-nitrene 8, but rather triplet imine nitrene 7 via concurrent extrusion of a nitrogen molecule and a 1,2-H atom shift. The calculated transition state barrier for this reaction was 40kcal/mol, and thus formation of 7 from 6 is only feasible photochemically. We propose that direct absorption by triplet 6 resulted in a triplet excited state of 6 and formation of 7, and this process did not need the ketone moiety as a triplet sensitizer. Triplet sensitization of germinal diazo alkanes is not likely to yield quintet di-nitrene.
As mentioned above, Barash et al. studied triplet sensitized photolysis of 9,9-diazido-9H-fluorenewith benzophenone, which resulted in the corresponding mononitrene; prolonged irradiation produced the triplet carbene (Scheme 2).\textsuperscript{16} It can be theorized that triplet nitrene 6 can react to form diazirine 14, which upon irradiation forms triplet carbene 15. We specifically looked for IR bands due to diazirine 14 and triplet carbene 15 in argon matrices, but we could not successfully identify formation of either compound. Nonetheless, we cannot rule out that small amount of triplet carbene 15 was formed and that it is the precursor to products 3 and 11 (Scheme 15), especially since we do not eliminate oxygen in argon-saturated solutions but rather reduce the oxygen concentration.

4. Conclusion

It has been presented that photolysis of 1 in solution results in cleavage of one of the azido groups to form radical 4, which expels a nitrogen molecule to form iminyl radical 5. At cryogenic temperatures, 1 forms triplet alkyl nitrene 6; however, prolonged irradiation of 6 does not yield di-nitrene 8, but rather triplet imine nitrene 7.
5. Experimental

5.1 Calculations

All geometries were optimized at a B3LYP level of theory and with the 6-31G+(d) basis set as implemented in the Gaussian09 programs.\textsuperscript{25-27} All transition states were confirmed to have one imaginary vibrational frequency by analytical determination of the second derivatives of the energy with respect to internal coordinates. Intrinsic reaction coordinate\textsuperscript{40} calculations were used to verify that the located transition states corresponded to the attributed reactant and product.\textsuperscript{35,36} The absorption spectra were calculated using time-dependent density functional theory (TD-DFT).\textsuperscript{28-32} The effect of solvation was calculated using the self-consistent reaction field (SCRF) method with the integral equation formalism polarization continuum model (IEFPCM) with acetonitrile, methanol and dichloromethane as solvents.\textsuperscript{41-45}

5.2 Laser Flash Photolysis.

Laser flash photolysis was performed with an Excimer laser (308 nm, 17 ns).\textsuperscript{23} The system has been described in detail elsewhere.\textsuperscript{23} A stock solution of 1 in acetonitrile was prepared with spectroscopic grade acetonitrile, such that the solution had absorption between 0.3 and 0.6 at 308 nm. Typically, approximately 1 mL of the stock solution was placed in a 10 mm × 10 mm wide, 48 mm long quartz cuvette and was purged with argon for 5 minutes or oxygen for 15 minutes. The rates were obtained by fitting an average of two to five kinetic traces.

5.3 Matrix isolations

Matrix isolation studies were performed using conventional equipment.\textsuperscript{5}
5.4 Preparation of 1

5.4.1 Synthesis of 4-dibromomethylacetophenone.

p-Methylacetophenone (1.8g, 13mmol) was dissolved in CCl₄ (30 mL) and N-bromosuccinimide (5.7 g, 32mmol, 1:2.5eq.) was added. A spatulum of benzoyl peroxide was added to the mixture and the reaction was allowed to reflux while stirring for 20 hours. The solvent was removed under vacuum and the organic products were extracted with diethyl ether (50mL). The extract was washed with water and dried over anhydrous MgSO₄. The solvent was removed under vacuum and the crude p-dibromomethylacetophenone was crystallized in MeOH/Acetone at 0ºC (2.4 g, 8.3mmol, 33 % yield).

Mp.: 66 – 68ºC. ¹H NMR (CDCl₃, 400 MHz): δ 2.6 (s, 3H), 6.7 (s, 1H), 7.7 (d, J = 8.4 Hz, 2H), 8.0 (d, J = 8.4 Hz, 2H) ppm; ¹³C NMR (CDCl₃, 100 MHz):δ 26.7, 39.6, 126.9, 128.7, 138.0, 146.1, 196.9 ppm; IR (CDCl₃): 3011, 1682 (s, C=O), 1605, 1575, 1505, 1409, 1357, 1263, 1228, 1185, 1146, 1114, 1073, 1014, 958, 835, 738, 698, 634, 611, 583 cm⁻¹. HRMS: m/z calculated for C₉H₇O₇Br₂ [M+H]+, 290.9020; found, 290.9016. GC/MS (EI): m/z 290 (M⁺), 275, 247, 210 (100%), 195, 183, 168, 141, 130, 115, 103, 89, 78.

5.4.2 Synthesis of 4-diazidomethylacetophenone (1)

4-Dibromomethylacetophenone (2.4 g, 8.3mmol) was dissolved in dry acetonitrile (15 mL). Azide exchange resin, (azide on Amberlite® IRA-400, particle size 16-50 mesh, capacity 3.8 mmol/g, 8.8g, 33.4mmol, 1:4 eq.) was added to the mixture and allowed to stir for 21 days. The mixture was filtered and the solvent was removed by air suction, yielding the crude 1-(4-
diazidomethyl-phenyl)-ethanone (0.67g, 3mmol, 37% yield). $^1$H NMR data was consistent with similar reported literature for analogous alkyl diazides. $^{46}$

$^1$H NMR (CDCl$_3$, 400 MHz): δ 2.6 (s, 3H), 5.8 (s, 1H), 7.5 (d, J = 8 Hz, 2H), 8.0 (d, J = 8 Hz, 2H) ppm; $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 26.7, 78.2, 126.7, 129.0, 138.1, 139.2, 197.3ppm; IR (CDCl$_3$): 3060, 3006, 2926, 2106 (s, N 3), 1686 (s, C=O), 1610, 1576, 1508, 1412, 1360, 1339, 1304, 1290, 1266, 1247, 1185, 1116, 1075, 1017, 958, 898, 815, 767, 719, 637, 617, 596, 557 cm$^{-1}$. HRMS: $m/z$ calculated for C$_9$H$_8$ON$_6$Na [M+Na]$^+$, 239.0657; found, 239.0668.

5.4.3 Synthesis of isotope labeled 1.

5.4.3.1 Synthesis of 1-[4-(2H$_3$)methyl(2H$_4$)phenyl]ethan-1-one (C$_9$D$_7$H$_3$O)

C$_7$D$_8$ (2.5g, 25 mmol) was added to AlCl$_3$ (7.4 g, 55 mmol, 1:2.2 eq)$^{47}$ in a round bottom flask stored at 0°C. Ac$_2$O (3.1 g, 30 mmol, 1:1.2 eq) was dissolved in CH$_2$Cl$_2$ (30 mL) and added to the above mixture dropwise using a dropping funnel for 15 minutes while stirring. The reaction was allowed to proceed for 4 ½ hours. The reaction was chilled by pouring it into cold water (50 mL). One or two drops of HCl were added to the flask. The mixture was extracted using CH$_2$Cl$_2$ and water. The organic layer was dried using anhydrous MgSO$_4$ and was later filtered. The solvent was removed to obtain the crude product C$_9$D$_7$H$_3$O. (2.8g, 19.6 mmol, 83 % yield).

$^1$H NMR (CDCl$_3$, 400 MHz): δ 2.581 (s, 3H) ppm; $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 20.3 – 21.1, 26.5, 127.8 – 128.4, 128.6 – 129.1, 134.6, 143.6, 197.8 ppm; IR (CDCl$_3$): 3004, 2255, 2120, 1682 (s, C=O), 1581, 1545, 1425, 1357, 1327, 1295, 1250, 1174, 1050, 1018, 950, 848, 824,
5.4.3.2  Synthesis of 1-{4-[dibromo(2H)methyl](2H4)phenyl}ethan-1-one
(C9D5H3Br2O)

C9D7H3O (1.5 g, 11 mmol) was dissolved in benzene (30 mL) and N-bromosuccinimide (4.8 g, 26 mmol, 1:2.2 eq) was added. Two spatula of benzoyle peroxide were added to the reaction. The mixture was stirred for 20 hours while refluxing. The solvent was removed and the organic products were extracted using diethyl ether and water. The extract was dried using anhydrous MgSO4, which was later filtered off. The solvent was removed to obtain the semi-oily crude C9D5H3Br2O. The crude product was purified using a silica column (10% ethyl acetate : 90% n-hexane) (2.7 g, 9.1 mmol, 71 % yield).

1H NMR (CDCl3, 400 MHz) : δ 2.617 (s, 3H) ppm; 13C NMR (CDCl3, 100 MHz): δ 26.615, 39.3 – 39.8, 126.2 – 126.7, 128.0 – 129.1, 136.7, 142.5, 197.3 ppm; IR (CDCl3): 3065, 2928, 2203, 2139, 1786, 1715, 1683 (s, C=O), 1597, 1579, 1552, 1451, 1420, 1359, 1328, 1317, 1250, 1197, 1173, 1110, 1069, 1024, 953, 935, 851, 826, 778, 740, 712, 685, 656, 639, 627, 599, 551 cm⁻¹.

5.4.3.3  Synthesis of 1-{4-[diazido(2H)methyl](2H4)phenyl}ethan-1-one (C9D5H3N6O) (1-d5)

C9D5H3Br2O (0.4 g, 1.3 mmol) was dissolved in dry acetonitrile (25 mL) and azido exchange resin (azide on Amberlite® IRA-400, particle size 16-50 mesh, capacity 3.8 mmol/g, 1.3 g, 5.1 mmol) reagent was added. The mixture was allowed to stir for 21 days. The mixture was filtered
and the supernatant was decanted. The solvent was removed to obtain the crude \textbf{1-d$_5$} (C$_9$D$_5$H$_3$N$_6$O, 0.14g, 0.6 mmol, 50% yield).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 2.622 (s, 3H) ppm; $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 26.7, 77.5 – 78.0, 126.0 – 126.5, 128.1 – 128.5, 137.9, 139.0, 197.5 ppm; IR (CDCl$_3$): 3005, 2966, 2924, 2448, 2101 (s, N$_3$), 1686 (s, C=O), 1609, 1582, 1551, 1418, 1360, 1327, 1247, 1182, 1148, 1067, 1038, 1001, 954, 852, 825, 766, 692, 638, 620, 605, 557 cm$^{-1}$. HRMS: $m/z$ calculated for C$_9$H$_4$D$_5$N$_6$O$_5$ [M+H]$^+$, 222.1152; found, 222.1150.

5.4.3.4 Synthesis of 1-{4-[(15N$_2$)diazido)methyl]phenyl}ethan-1-one (C$_9$H$_8$N$_2$N$_4$O)$^{(1-15N)}$

4-Dibromomethylacetophenone (0.25g, 0.86 mmol) was dissolved dry acetonitrile (40 mL). $^{15}$N-NaN$_3$ (0.23 g, 3.4 mmol, 4eq.) and azido exchange resin (azide on Amberlite® IRA-400, particle size 16-50 mesh, capacity 3.8 mmol/g, 0.90 g, 3.4 mmol, 4eq) was added to the solution. The above mixture was allowed to stir for 21 days. The mixture was filtered and the solvent was removed by air suction to yield $^{15}$N-substituted \textbf{1} (0.22g, 0.8 mmol, 93% yield).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 2.63 (s, 3H), 5.80 (s, 1H), 7.54 (d, J = 8 Hz, 2H), 8.02 (d, J = 8 Hz, 2H) ppm; $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 26.7, 78.1, 78.2, 126.7, 129.0, 138.1, 139.2, 197.3 ppm; $^{15}$N NMR (CDCl$_3$, 75 MHz), external standard (H$_2$NC(O)NH$_2$): $\delta$ 93.1, 227.5, 262.1 ppm; IR (CDCl$_3$): 3281, 3060, 3006, 2923, 2345, 2087 (s, N$_3$), 1687 (s, C=O), 1610, 1577, 1508, 1412, 1359, 1338, 1304, 1290, 1266, 1239, 1179, 1115, 1075, 1017, 959, 895, 813, 764, 739, 712, 658,
637, 616, 596, 555, 500, 477 cm⁻¹. HRMS: m/z calculated for C₉H₉O¹⁴N₄¹⁵N₂ [M+H]⁺, 219.0779; found, 219.0768.

5.5 Photolysis of 1

5.5.1 Photolysis of 1 in Chloroform-d at 196 K

A solution of 1 (~5 mg, 23 μmol) in CDCl₃ (1 mL) was purged with argon and photolyzed via a Pyrex filter for 4 hours at 196 K. GC-MS analysis of the reaction mixture showed the formation of 2 and 3 in the ratio 4:1, with a small amount of remaining starting material. The products were characterized by GC-MS chromatography, ¹H-NMR, ¹³C-NMR and IR spectroscopy of the reaction mixture. ¹H-NMR and GC-MS data matched with reported literature.⁴⁸,⁴⁹

2: ¹H NMR (CDCl₃, 400 MHz): δ 2.65 (s, 3H), 7.78 (d, J = 8.4 Hz, 2H), 8.05 (d, J = 8.4 Hz, 2H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ 26.8, 116.4, 118.0, 128.8, 132.5, 139.0, 196.5; IR (CDCl₃): 2231 (CN), 1687 (C=O) cm⁻¹. GC/MS (EI): m/z 145 (M), 130 (100%), 102, 75.

3: ¹H NMR (CDCl₃, 400 MHz): δ 2.671 (s, 3H), 7.988 (d, J = 8.4 Hz, 2H), 8.200 (d, J = 8.4 Hz, 2H), 10.117 (s, 1H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ 27.0, 128.7, 130.5, 139.9, 141.2, 191.6, 197.4 ppm. IR (CDCl₃): 1720 (C=O), 1687 (C=O) cm⁻¹; GC/MS (EI): m/z 148 (M), 133 (100%), 119, 105, 77.
5.5.1 Photolysis of 1 in Toluene

5.5.1.1 Photolysis of 1 in nitrogen-saturated toluene at 298 K

A solution of 1 (~ 60 mg, 0.28 mmol) in Toluene (10 mL) was purged with nitrogen for 15 min and photolyzed via a Pyrex filter for 4 h at 298 K. GC-MS analysis of the reaction mixture showed the formation of 2 (40%), 3 (24%), 10 (30%), 11 (6%). In addition the GC-MS analysis showed formation of 1,2-diphenylethane from the solvent.

2: GC/MS (EI): m/z 145 (M\(^+\)), 130 (100%), 102, 75. 3: GC/MS (EI): m/z 148 (M\(^+\)), 133 (100%), 105, 77. 10: GC/MS (EI): m/z 237 (M\(^+\)), 194, 104, 91 (100%), 76, 65. 11: GC/MS (EI): m/z 224 (M\(^+\)), 209, 181, 133, 118, 105, 91 (100%), 77, 65. 1,2-Diphenylethane(C\(_{14}\)H\(_{14}\)): GC/MS (EI): m/z 182 (M\(^+\)), 165, 91 (100%), 65.

5.5.1.2 Photolysis of 1 in oxygen-saturated toluene at 298 K

A solution of 1 (~ 60 mg, 0.28 mmol) in toluene (10 mL) was purged with oxygen for 15 min and photolyzed via a Pyrex filter for 4 h at 298 K. GC-MS analysis of the reaction mixture showed the formation of 2 (81%), 3 (7%) and 11 (12%).

2: GC/MS (EI): m/z 145 (M), 130 (100%), 102, 75. 3: GC/MS (EI): m/z 148 (M), 133 (100%), 105, 77. 11: GC/MS (EI): m/z 224 (M), 209 (100%), 178, 165, 152, 105, 89, 77, 65.
6. Acknowledgement

This work was supported by the National Science Foundation and the Ohio Supercomputer Center. R. A. A. U. R is grateful for support from the University Research Council at the University of Cincinnati and for the Harry B. Mark fellowship.

Supporting Information Available: Cartesian coordinates, energies, vibrational frequencies of 1 through 8 and NMR spectra of 1, 1-d, 1-\textsuperscript{15}N, 2 and 3 are available free of charge via the Internet at http://pubs.acs.org

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Chapter 03

Competition between Azido Cleavage and Triplet Nitrene Formation in Azidomethylacetophenones

Competition Between Azido Cleavage and Triplet Nitrene Formation in Azidomethylacetophenones

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ABSTRACT. Photolysis of p-azidomethyl acetophenone (1a) in argon-saturated solutions yield predominantly imine 2a, whereas irradiation of 1a in oxygen-saturated solutions results in heterocycle 3a, aldehyde 4a and nitrile 5a. Density functional theory calculations place the energy of the first and second excited state of the triplet ketones (T1K and T2K) in 1a in close proximity to each other. The triplet transition state for cleaving the C-N bond in 1a to form azido and benzyl radicals 1aB is located only 3 kcal/mol above T1K, indicating that azido cleavage is feasible. The calculations place the energy of the triplet azido group (TA) in 1a ~25 kcal/mol below T1K; thus, this process is also easily accessible via energy transfer. Further, the transition state barrier for TA to expel N2 and form triplet nitrene is less than 1 kcal/mol above TA in 1a. Laser flash photolysis of 1a reveals the formation of the triplet excited ketones in 1a, which decay to form benzyl radical 1a and triplet alkynitrenes. The triplet ketones and the benzyl radicals are quenched with molecular oxygen at rates close to diffusion, whereas the triplet nitrenes react slower with oxygen (~5 x 10^5 M^-1s^-1). We conclude that the triplet alkynitrenes
intercept the benzyl radicals to form 2 in argon-saturated solution, whereas the benzyl radicals are trapped to form 4 in oxygen-saturated solution; thus, the triplet nitrenes react with oxygen to form 3.

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I. Introduction

Nitrenes are reactive intermediates that have a monovalent nitrogen atom.\textsuperscript{1-3} The nonbonding electrons on the monovalent nitrogen atom can either be paired, denoting a singlet nitrene, or unpaired, representing a triplet nitrene. Singlet nitrenes are highly reactive intermediates that insert into surrounding chemical bonds and have therefore been used in various applications, such as photo affinity labeling,\textsuperscript{4, 5} cross-linking of polymers\textsuperscript{6-9} and modification of surfaces.\textsuperscript{10-12} In contrast, triplet nitrenes are generally less reactive, and due to their high-spin characteristics, they have potential as building blocks for organic magnets.\textsuperscript{13, 14} Triplet alkynitrenes have only been investigated sporadically because direct irradiation of alkyl azides does not yield triplet alkynitrenes, but rather, imine products from a concerted rearrangement of the singlet excited state of the alkylazides.\textsuperscript{15} Formation of triplet alkynitrenes from alkylazides requires triplet sensitization.\textsuperscript{16, 17} We have reported that the irradiation of simple $\alpha$-azidopropiophenones, which have a build-in triplet sensitizer, results in selective formation of triplet alkynitrene intermediates.\textsuperscript{16} Intramolecular triplet sensitization of alkyl azides, however, does not always lead to formation of alkynitrenes. For example, photolysis of $\alpha$-azidoacetophenone derivatives results in both triplet energy transfer to form triplet alkynitrenes and $\alpha$-cleavage to form benzoyl radicals.\textsuperscript{17, 18} Furthermore, photolysis of $\beta$-azido propiophenone derivatives that have $\beta$-phenyl substituent primarily results in photo-initiated cleavage to form azido and benzyl radicals.\textsuperscript{19} Triplet alkynitrenes are highly unreactive because they do not abstract H-atom from the solvent or react with their precursor; instead, they dimerize to form azo-dimers.\textsuperscript{16, 20-22} Triplet alkynitrenes, however, react efficiently with benzoyl radicals to form amides,\textsuperscript{18, 23} and can be trapped with triplet oxygen to form nitro compounds.\textsuperscript{16}
To investigate further the ability of triplet alkynitrenes to act as radical scavengers, we investigated the photochemistry of \( p \)-azidomethyl acetophenone (1a). This molecule can be expected to both undergo energy transfer to form triplet alkynitrenes (1aN) and cleave to form azido and benzyl radicals (1aB). We used transient spectroscopy and density functional theory calculations to show that photolysis of 1a results in the formation of triplet alkynitrene and benzyl radical. The major photoproducts in argon-saturated solutions are 2a, prompting us to conclude that triplet alkynitrene 1aN trap benzyl radicals 1aB to form 2a.

II. Results

IIA. Product Studies.

Photolysis of 1a in argon-saturated methanol solutions resulted in the formation of imine 2a (Scheme 1). In comparison, photolysis of 1a in oxygen-saturated chloroform or methanol yields mainly heterocycle 3a, aldehydede 4a and acetyl benzonitriles 5a (Scheme 2).

\[ \text{Scheme 1. Photolysis of 1a in Argon-Saturated Methanol} \]
Thus, we theorize that, upon photolysis, \( \text{1a} \) forms the triplet state of the ketone, which undergoes energy transfer to form the triplet excited state of azido moiety in \( \text{1a} \) and falls apart to yield triplet alkynitrene \( \text{1aN} \) (Scheme 3). In competition with energy transfer, \( \text{1a} \) also undergoes cleavage of the azido group to form radicals \( \text{1aB} \). We propose that triplet nitrene \( \text{1aN} \) react with radical \( \text{1aB} \) to form imine \( \text{2a} \) in argon-saturated solution. We do not observe products due to dimerization of \( \text{1aB} \) because triplet nitrene \( \text{1aN} \) must trap \( \text{1aB} \) more efficiently than they dimerize. However, in oxygen-saturated methanol and chloroform, \( \text{1aB} \) is trapped with oxygen to form \( \text{4a} \), allowing nitrene \( \text{1aN} \) to react with oxygen to form \( \text{3a} \) and \( \text{5a} \). Corsaro et al. have shown that benzonitrile oxide and benzonitrile undergo cycloaddition to form 3,5-diphenyl-[1,2,4]oxadiazole\(^{23b}\). Therefore, we propose that \( \text{1aN} \) reacts with oxygen to form the corresponding nitrile oxide and oxygen abstracts hydrogen atoms from \( \text{1aN} \) to yield \( \text{5a} \), which adds to the acetylbenzonitrile oxide to form \( \text{4a} \).

We speculated whether \( \text{1aB} \) can react with \( \text{1a} \) to form \( \text{2a} \). Because photolysis of 1,3-diphenylpropan-2-one has been reported to result in the formation of benzyl radicals\(^{[23]}\), we photolyzed 1,3-diphenylpropan-2-one and adamantly azide in methanol. By irradiation through a Pyrex filter, we ensured that only 1,3-diphenylpropan-2-one absorbed the light not adamantly azide. The only product observed was 1,3-diphenylethane, and therefore we conclude that benzyl radicals do not react with alkyl azides (Scheme 4).
Scheme 3. Proposed Reaction Mechanisms for 1a

Scheme 4. Photolysis of 1,3-diphenylpropan-2-one and 1-adamantyl azide
II.B. Molecular Modeling.

All structures were optimized using Gaussian0924 at the B3LYP25, 26 level of theory and with the 6-31+G(d) basis set at the Ohio Super Computer Center. Time-dependent density functional theory (TD-DFT)27-31 calculations of 1a showed that the first and second excited states of the triplet ketone (T_{1K} and T_{2K}, respectively) were located at 73 and 76 kcal/mol above its ground state (S_0). Inspection of the molecular orbitals shows that T_{1K} and T_{2K} have (n,\pi^*) and (\pi,\pi^*) configurations, respectively (Table 1). The effect of solvation was calculated using the self-consistent reaction field (SCRF) method with the polarization continuum model (PCM) with acetonitrile as the solvent.32-35 The calculated energies of T_{1K} and T_{2K} in acetonitrile are 75 and 78 kcal/mol; thus, solvation does not change these values significantly. Furthermore, the calculated energy for T_{1K} in 1a is similar to the measured triplet state energy for the analogous m-methylacetophenone and p-methylacetophenone.36, 37

Table 1. Energies of T_{1K} and T_{2K} in 1a Using TD-DFT and UB3LYP Calculations

<table>
<thead>
<tr>
<th>1a</th>
<th>TD-DFT</th>
<th>UB3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gas phase</td>
<td>CH_3CN</td>
</tr>
<tr>
<td>(n, \pi^*)</td>
<td>73</td>
<td>78</td>
</tr>
<tr>
<td>(\pi, \pi^*)</td>
<td>76</td>
<td>75</td>
</tr>
</tbody>
</table>

We also optimized T_{1K} of 1a at the UB3LYP level of theory in the gas phase. The optimized structure of T_{1K} of 1a have carbonyl groups with a bond length of 1.32 Å, which is consistent with the triplet ketones having an (n,\pi^*) configuration;38, 39 visualization of the molecular orbitals of T_{1K} in 1a further support this assignment. The bond lengths and angles of the azido
group of T1K of 1a is similar to what was observed for the S0 of 1a, thus indicating that the triplet excited state is localized on the aryl ketone moiety. The calculated energies of the optimized T1K in 1a are 68 and 69 kcal/mol above S0, respectively, which is somewhat lower than those estimated from the TD-DFT calculations. However, we have previously shown that the B3LYP/6-31G+(d) calculation underestimates the energies of triplet ketones with the (n,π*) configuration.23, 40 In addition, solvation does not significantly change the energies of T1K in 1a.

Optimization of the triplet configuration of the azido moieties (TA) in 1a in the gas phase shows that the N1-N2 and N2-N3 bonds are lengthened to 1.45 and 1.18 Å, respectively, as compared to 1.24 and 1.14 Å in S0 of 1a. Furthermore, the azido groups are bent because the N1-N2-N3 bonds have an angle of 120° in the triplet state. The energies of TA of 1a is 44 kcal/mol above S0. Thus, the triplet energies and optimized structures of TA in 1a are similar to what has been reported previously.23a The bond length and angles of the carbonyl group in TA of 1a are similar to what we observed for the S0 of 1a, thus indicating that the triplet excited state is localized on the azido group.

We calculated the transition state for forming triplet alkylnitrene (1aN) from TA of 1a in the gas phase and found that it was located less than 1 kcal/mol above the TA of 1a. Intrinsic reaction coordinates (IRC)41 calculations were performed to correlate these transition states with TA of 1 and 1N.42-44

We calculated the triplet transition state for cleavage of the azido group in 1a in the gas phase. These triplet transitions states are located at 3 kcal/mol above T1K in 1a. IRC calculations correlate these transitions state with a triplet state that has elongated C-N-N bonds and the 1B and azido radicals instead of with the T1K of 1. This process is similar to what has been reported
for α-cleavage in triplet ketones, where the characteristic state for an α-cleavage has a \((n,\sigma^*)\) nature; in contrast, the excitation is into the triplet \((n,\pi^*)\) state of the ketone chromophore.\(^{45,46}\)

In Figure 1, stationary points on the triplet surface of \(1a\) are plotted. The transition state barrier for breaking the C-N bond in \(1a\) to form \(1aB\) is only 3 kcal/mol above \(T_{1K}\), and therefore the azido cleavage should be easily accessible at ambient temperatures. Because the energies of \(T_{1K}\) and \(T_{2K}\) are similar, we expect them to be in equilibrium and thus energy transfer and azido cleavage to be competitive, from these triplet excited states.

![Energy Surface Diagram](image)

**Figure 1.** Calculated stationary points on the energy surface of \(1a\) to form \(1N\) and \(1B\) at the UB3LYP and TD-B3LYP levels of theory. The energies are in kcal/mol.

Finally, we used TD-DFT calculations to calculate the UV-absorption spectra of \(T_{1K}\) of \(1a\), benzyl radicals \(1aB\) and triplet nitrenes \(1aN\). The calculated spectra in acetonitrile are displayed in Figure 2.
Figure 2. Calculated Major Absorption Spectral Features (above 300 nm) for $T_{1K}$ of 1a, 1aN and 1aB in acetonitrile. $f$ is the calculated oscillator strength for the electronic transitions.

IIC. Laser Flash Photolysis (LFP)

We used LFP to identify the intermediates formed upon photolysis of 1a. Laser flash photolysis (Excimer, $\lambda = 308$ nm, 17 ns) of 1a in argon-saturated acetonitrile produces a broad transient absorption with $\lambda_{\text{max}}$ between ~350 and 420 nm due to the absorption of $T_{1K}$ of 1a, which decays with a rate constant of $3.2 \times 10^6$ s$^{-1}$ (Figure 3). We assign this transient absorption to $T_{1K}$ of 1a because the triplet ketone in p-methylacetophenone has similar absorption. In oxygen-saturated acetonitrile, $T_{1K}$ of 1a becomes shorter-lived and decays with a rate constant of $1 \times 10^7$ s$^{-1}$ due to quenching by oxygen. Simultaneously with the decay of $T_{1K}$ of 1a, a new transient absorption with $\lambda_{\text{max}}$ at ~350 nm forms with the same rate constant; we assign this absorption to 1aB and 1aN (Figure 3). We base this assignment on the similarity of this transient absorption to the calculated absorption spectra of 1aB and 1aN (see Figure 2). On shorter
timescales, we observe a decay that can be fitted with mono-exponential function to yield a lifetime of ~30 μs and assign it to 1aB. On longer time scale or on millisecond timescale we observe a decay that cannot be fitted with mono-exponential function. We assign this decay to 1aN. Because 1aN decays by several different routes (Scheme 3), its decay cannot be fitted with a mono-exponential function. The assignment of the transient absorption of 1aB and 1aN is further supported by laser flash photolysis of 1a in oxygen-saturated acetonitrile. In oxygen-saturated acetonitrile we did not observe transient absorption due to 1aB, presumably because 1aN reacts with a rate on the order of diffusion with oxygen. In comparison, the triplet nitrene 1aN has a lifetime of ~200 μs in oxygen-saturated acetonitrile; by assuming the concentration of oxygen is 0.091 M, we can estimate that 1aN reacts with oxygen with a rate of 5 x 10^5 M^{-1}s^{-1}.
We have previously estimated that triplet β-nitrenopropiophenones react somewhat slower with oxygen or with a rate of $5 \times 10^4$ M$^{-1}$s$^{-1}$. In comparison, Liang and Schuster reported that triplet $p$-nitrophenylnitrene reacts with oxygen at a rate of less than $2 \times 10^5$ M$^{-1}$s$^{-1}$. However,
Gritsan and Pritchina estimated this same rate to be somewhat larger.\textsuperscript{49-51} The rates for triplet alkyl- and arylnitrenes reacting with oxygen are, however, in agreement with computational work by Liu et al., who reported that triplet alkyl nitrenes and triplet phenyl nitrenes can be expected to react similarly with oxygen.\textsuperscript{52}

Thus, laser flash photolysis of 1a gives similar results. The laser flash photolysis supports the theory that 1a form long-lived triplet nitrene (1aN) in competition with azido cleavage to form 1aB.

\textbf{III. Discussion}

The laser flash photolysis demonstrated that 1a form both triplet nitrenes 1aN and benzyl radicals 1aB upon irradiation. We propose that triplet alkynitrene 1aN trap the benzyl radicals to form 2a, because in oxygen-saturated solutions the benzyl radicals are trapped to form aldehyde and in the absence of the benzyl radicals the triplet nitrenes decay by reacting with oxygen and form 3a. Thus, triplet alkynitrenes 1aN are inert or stable intermediates that have lifetimes on the order of milliseconds, as they do not react with the solvent or their precursor, but rather intercept radicals such as oxygen and 1aB. Therefore, the reactivity of 1a is similarly to what we have previously reported for \(\alpha\)-azidoacetophenone 6 which undergoes \(\alpha\)-cleavage to form benzyol radicals and energy transfer to yield triplet alkynitrenes 6N (Scheme 5).\textsuperscript{17,18,23} Nitrene 6N did not dimerize to form azo-dimers but rather reacted with benzyol radicals to form 6P. However, the reactivity of 6N was further complicated since it was photolabile and underwent \(\alpha\)-cleavage to form benzyol radical.
Scheme 5. α-Cleavage and nitrene formation from 6 to give photoproduct 6P

We have shown previously that photolysis of azide 7 (Scheme 6) in solutions results mainly in azido cleavage to form azido radical and benzyl radical 7B.\textsuperscript{19} The major difference between 7 and 1a is that the triplet ketone in 7 also undergoes deactivation via β-phenyl quenching in competition with product formation. In more details, propiophenone derivatives with β-phenyl substituents undergo efficient deactivation of their triplet ketones. The mechanism for β-phenyl quenching has not yet been fully characterized,\textsuperscript{53-55} however, it has been proposed that the deactivation is due to a charge transfer from the β-phenyl ring to the electron deficient triplet ketone.\textsuperscript{56} Although, more recently Bucher has preformed calculations to support that the β-phenyl quenching is due to addition of the carbonyl oxygen to the ipso- or ortho-carbon atoms of the β-phenyl ring, which is followed by intersystem crossing and relaxation to the ground state.\textsuperscript{57}

The β-phenyl quenching in 7 presumably, limits the energy transfer to form the corresponding triplet alkynitrene but not azido cleavage.

Scheme 6. Photolysis of 7
IV. Conclusion

Laser flash photolysis has demonstrated that 1a form both triplet nitrenes 1aN and benzyl radicals 1aB upon irradiation. DFT calculations further support the photoreactivity of 1a. The triplet nitrenes are stable intermediates that act as radical scavengers and trap the benzyl radicals to form 2a. In the absence of benzyl radicals, the triplet nitrene react with oxygen and forming 3a.

V. Experimental and Computational Methods

Synthesis of 1a.

Azides 1a was synthesized by brominating the corresponding methyl acetophenone derivatives, followed by reaction with sodium azide, as described below.

1-(4-Bromomethyl-phenyl)-ethanone

4-Methylacetophenone (5.01 g, 37.4 mmol), N-bromosuccinimide (8.05 g, 45.2 mmol) and benzyl peroxide (0.071 g, 0.326 mmol) were dissolved in benzene (300 mL). The solution was degassed by bubbling argon through it for 20 minutes. This solution was photolyzed with a Honoiva Mercury lamp via a Pyrex sleeve. Once GC-MS spectroscopy indicated that 4-methylacetophenone was depleted the reaction mixture was filtered using glass wool, washed with distilled water and saturated aqueous sodium bicarbonate solution. The organic layer was dried with magnesium sulfate and was concentrated under vacuum to yield an oil that was
characterized to be 1-(4-bromomethylphenyl)-ethanone (6.72 g, 33.1 mmol, 88.5% yields). The characterization of the product was confirmed by obtaining IR and $^1$H-NMR spectra and the spectral data matched with those reported earlier.$^{59}$

Mp 38-40 °C. (Lit.$^{60}$ Mp 40-42 °C). IR (CH$_2$Cl$_2$): 1683 cm$^{-1}$. $\delta_H$ 2.60 (s, 3H), 4.50 (s, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H) ppm. $^{13}$C-NMR (CDCl$_3$, 100 MHz): 26.69, 32.14, 128.84, 129.25, 136.90 142.81, 197.39 ppm

1-(4-Azidomethyl-phenyl)-ethanone (1a).

1-(4-Bromomethyl-phenyl)-ethanone (5.0 g, 24.6 mmol) was dissolved in a mixture of ethanol (150 mL) and acetic acid (1.5 mL) and cooled in an ice bath. To this solution, was added dropwise sodium azide (10 g, 156 mmol) which was dissolved in minimal amounts of water. The resulting mixture was stirred in an ice bath for 2 hours and stored at 4 °C 72 hours. The reaction mixture was extracted with diethyl ether (100 mL) and the organic layer was washed with water, then dried with magnesium sulfate and concentrated under vacuum. The resulting oil was purified via a silica column using an ethyl acetate and hexane mixture as the eluent to yield 1-(4-azidomethyl-phenyl)-ethanone (505 mg, 2.89 mmol, 11.7% yield). The $^1$H-NMR spectra of 1-(4-azidomethyl-phenyl)-ethanone matched that found in the literature.$^{61}$

IR (CDCl$_3$): 3005, 2102, 1684, 1609, 1574, 1412, 1359, 1267, 1182, 1116, 1075, 1017, 956, 847, 814, 694, 660, 595 cm$^{-1}$. $^1$H-NMR (CDCl$_3$, 400 MHz): $\delta_H$ 2.63 (s, 3H), 4.44 (s, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.99 (d, J = 8.0 Hz, 2H) ppm. $^{13}$C-NMR (CDCl$_3$, 100 MHz): $\delta_C$ 26.67, 54.24, 128.15, 128.88, 136.93, 140.58, 197.53 ppm
Preparative photolysis

Preparative Photolysis of 1a in Oxygen-saturated Toluene.
1-(4-Azidomethyl-phenyl)-ethanone (0.459 g, 2.6 mmol) was dissolved in dry distilled toluene (100 mL). The solution was photolyzed for 15 hours using a Honoiva Mercury lamp via a Pyrex sleeve. The reaction was monitored HPLC chromatography and the irradiation was stopped when the HPLC showed formation of two new major products, 4a (17%) and 3a (24%) and remaining starting material (31%). HPLC chromatography yielded recovered starting material (25 mg, 0.14 mmol, 30% yield), 4-acetyl-benzaldehyde (5 mg, 0.0368 mmol, 16% yield) and 1-{4[5-(4-ccetyl-phenyl)-[1,2,4]oxadiazol-3-yl]-phenyl}-ethanone 3a (10 mg, 0.0328 mmol, 44% yield).

IR (CH2Cl2) νmax 2924, 1693, 1589, 1526, 1406, 1357, 1267, 960, 845, 760, 714, 600, 474 cm⁻¹.

1H-NMR (CDCl3, 400 MHz): δH 2.17 (s, 6H), 8.29-8.10 (dd, 8.5 and 8.5 Hz, 4H), 8.36-8.34 (dd, 8.5 and 8.5 Hz, 4H) ppm. 13C-NMR (CDCl3, 100 MHz): δC 29.45, 127.53, 128.22, 128.58, 128.73, 139.28, 139.86, 196.85, 197.20 ppm. GC/MS 306 (M⁺ 16%), 291 (100), 147 (30), 104 (30). HRMS: Calc. for C₁₈H₁₄N₂O₃: 306.1004, Found: 306.1081.

Photolysis of 1a.

GC-MS analysis of 0.06 M and 0.18 M methanol solutions of 1a after irradiation showed only formation of 2a. Similar results were obtained in argon-saturated acetonitrile and chloroform solutions.

Oxygen-saturated chloroform solutions of 1a (0.06 M) was photolyzed and the reaction mixture was analyzed with GC-MS. The conversion was kept below 30%. The major products observed were 3a, 4a and 5a.
Calculations:

All geometries were optimized as implemented in the Gaussian09 programs,\textsuperscript{24} at the B3LYP level of theory and with the 6-31G+(d) basis set.\textsuperscript{25, 26} All transition states were located at the UB3LYP level of theory, and each transition state was confirmed to have one imaginary vibrational frequency by analytical determination of the second derivatives of the energy with respect to internal coordinates. IRC calculations were used to verify that the located transition states corresponded to the attributed reactant and product.\textsuperscript{27-31} Vertical UV absorption spectra were calculated at the TD-B3LYP level with the 6-31+G(d) basis set using the optimized B3LYP/6-31+G(d) geometry for the S\textsubscript{0} state. The effect of solvation was calculated using the self-consistent reaction field (SCRF) method with the polarization continuum model (PCM) with acetonitrile as the solvent.\textsuperscript{32-35}

Laser Flash Photolysis.

Laser flash photolysis was done with excimer laser (308 nm, 17 ns). The system has been described elsewhere.\textsuperscript{62} A stock solution of azide 1\texttext{a} was prepared with spectroscopic grade acetonitrile, such that the solutions had an absorption between 0.6 and 0.8 at 308 nm. Typical ~ 1 mL of the stock solution was placed in a cm quartz cuvette and was purged with nitrogen for 5 min. The rates were obtained by fitting an average of 3 to 8 kinetic traces.

Acknowledgments

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S. M. thank the Chemistry Department at the University of Cincinnati for Harry Mark fellowship.

References


Chapter 04

Efficient Trans-Cis Isomerization via Triplet 1,2-biradical; A Study using Time-resolved UV/Visible, Time-resolved IR, Matrix isolation and DFT calculations

![Chemical Reaction Diagram]

1a, X = H
1b, X = OCH₃
1c, X = CN

2a-c
Efficient Trans-Cis Isomerization via Triplet 1,2-biradical; A Study using Time-resolved UV/Visible, Time-resolved IR, Matrix isolation and DFT calculations

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ABSTRACT. Trans-Cis isomerization of α, β unsaturated alkenes can be used to design photoswitches. We investigated the photoreactivity of trans alkenes 1a-c. We used laser flash photolysis (LFP, λ=308 nm, 17 ns; λ=266 nm, 5 ns; λ=355 nm, 5 ns), product studies, time resolved IR (TRIR, λ = 266 nm), matrix isolation studies (λ > 300 nm), phosphorescence and theoretical DFT calculations to identify the intermediates formed by irradiating 1a-c. Solutions photolysis (λ > 300 nm) of 1a-c yields TK of 1a-c which then decays to form biradicals (TBR) of 1a-c. TBR of 1a-c can rotate around C – C bond and form 2a-c or rearrange back to form 1a-c again. The lifetime of TBR of 1a-c is significantly longer than that for the TK of 1a-c.

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1. Introduction

Photoinduced trans-cis isomerization has long been known and has become increasingly of interest within the past few decades because it can be used in chemical applications such as optical data storage devices, molecular photo-switches, and photo-triggers or in biological applications such as drug delivery systems.\textsuperscript{1-3} This excitement in research is further stimulated by the success of digital optical data systems, in which recording of information is carried out by light.\textsuperscript{1} The demand to search for molecular memory elements for data processing by light that will allow for high storage capacities and high switching rates has gained great impetus in the past decade.\textsuperscript{1, 4}

Stilbene is one of the most popular models for studying trans-cis isomerization of polyenes (Scheme 1).\textsuperscript{5} Stilbene dendrimers with molecular weights over 6000 undergo a photochemical isomerization in less than 10 ns that corresponds to the lifetime of the excited singlet state, whereas photo-isomerization of stilbene usually lasts from 60 to 400 fs.\textsuperscript{5, 6} Currently, most photo-switches are based on trans-cis isomerization.\textsuperscript{7}

\begin{center}
\includegraphics[width=0.5\textwidth]{scheme1.png}
\end{center}

\textbf{Scheme 1.} Trans-Cis photo-isomerization of stilbene

Although stilbene undergoes two-way isomerization, styrylanthrecene only undergo one-way cis-trans isomerization (Scheme 2).\textsuperscript{8}
Scheme 2. One-way isomerization of cis-styrylanthrecene

The triplet potential energy surface of the one-way isomerization was first proposed in 1983\(^9\) as simply descending from the cis triplet (3c\(^*\)) to the trans triplet (3t\(^*\)), passing through the perpendicular triplet (3t\(^*\)) shown in Figure 1a.\(^8\) In this potential energy surface, the resulting 3t\(^*\) undergoes either unimolecular deactivation to the ground-state trans (1t\(^1\)), or energy transfers to the ground-state cis (1c\(^1\)) to regenerate 3c\(^*\) therefore accomplishing the quantum chain process.\(^8\) Figure 1b shows a typical potential energy surface of the two-way isomerizing olefins like stilbene, in which the deactivation takes place solely from the perpendicular conformation.\(^8\)

To explain the specific direction of the one-way isomerization from cis to trans, one could suppose that the energy minimum would be slightly shifted from just perpendicular conformation to trans side (Figure 1c).\(^8\) Hereafter, this perpendicular conformation is referred to as triplet 1,2-biradical (or triplet biradical).
In this paper, we explore the triplet-sensitized photoinduced trans – cis isomerization of \( \alpha, \beta \)-unsaturated alkenes 1a, 1b and 1c. We were able to see two way trans-cis isomerization of the alkenes 1a-c. We determined the lifetimes of the triplet ketone excited state of the alkenes 1a-c using laser flash photolysis and also were able to characterize the triplet 1,2-biradicals of 1a-c and measure their lifetimes. In addition, we observed the triplet-sensitized trans-cis isomerization in cryogenic matrices at 14 K for 1a-b, and to our knowledge, this is the first time a triplet-sensitized trans-cis isomerization at very low temperatures were reported.

**Figure 1.** Potential energy surfaces proposed for one-way (a and c) and two-way (b) isomerizing olefins (Ref. 8)
2. Results

a) Product Studies

![Chemical Reaction Diagram]

1a, X = H  
1b, X = OCH₃  
1c, X = CN

<table>
<thead>
<tr>
<th>Compound</th>
<th>% Conversion#</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>1a</td>
</tr>
<tr>
<td>Argon saturated CDCl₃</td>
<td>68 (1h)</td>
</tr>
<tr>
<td>Oxygen saturated CDCl₃</td>
<td>82 (1h)</td>
</tr>
<tr>
<td>Argon Saturated CD₃OD</td>
<td>60 (1 h)</td>
</tr>
<tr>
<td>Oxygen Saturated CD₃OD</td>
<td>56 (1 h)</td>
</tr>
</tbody>
</table>

Values in parenthesis are the irradiation time

2a, 2b and 2c are stable at room temperature for more than 7 days

#Conversion percentages are from ¹H NMR integrations of methyl peaks
Scheme 3. Product studies

Figure 2. Product studies of 1a in argon and oxygen saturated chloroform-d. The percentages shown in the plot are for the trial with the highest conversion.
**Figure 3.** Product studies of 1a in argon and oxygen saturated methanol-d₄. The percentages shown in the plot are for the trial with the highest conversion. On average the percent conversion to 2a in argon-saturated methanol-d₄ after 15 min, 30 min and 1 hour are 19% ± 5%, 24% ± 7% and 31% ± 9% respectively. The percent conversion to 2a in oxygen-saturated methanol-d₄ after 15 min, 30 min and 1 hour are 19% ± 14%, 34% ± 7% and 38% ± 6% respectively.

**Figure 4.** Product studies of 1b in argon and oxygen saturated chloroform-d. The percentages shown in the plot are for the trial with the highest conversion.
Figure 5. Product studies of 1b in argon and oxygen saturated methanol-d₄. The percentages shown in the plot are for the trial with the highest conversion. On average the percent conversion to 2b in argon-saturated methanol-d₄ after 15 min and 1 hour are 19% ± 15%, 43% ± 2% respectively. The percent conversion to 2b in oxygen-saturated methanol-d₄ after 15 min and 1 hour are 18% ± 13%, 40% ± 5% respectively.

Figure 6. Product studies of 1c in argon and oxygen saturated chloroform-d. The percentages shown in the plot are for the trial with the highest conversion. On average the percent conversion
to 2c in argon-saturated chloroform-d after 60 min is 24% ± 20%. The percent conversion to 2c in oxygen-saturated chloroform-d after 60 min and 1 hour is 25% ± 20%. The large percentage error is due to the use of different lamps with different intensities.

Figure 7. Product studies of 1c in argon and oxygen saturated methanol-d₄. The percentages shown in the plot are for the trial with the highest conversion. On average the percent conversion to 2c in argon-saturated methanol-d₄ after 330 min is 30% ± 15%. The percent conversion to 2c in oxygen-saturated methanol-d₄ after 330 min and 1 hour is 33% ± 13%. The large percentage error is due to the use of different lamps with different intensities.
Figure 8. The change of the % conversion of the cis isomers 2a, 2b and 2c with respect to time over 7 days period in dark. The % conversion at 0 hours is the conversion of the trans isomers 1a, 1b and 1c after 1 hour of irradiation with light > 300 nm.

Photolysis of 1a-c in argon-saturated chloroform-d and argon-saturated methanol-d₄ via a Pyrex filter at 298 K has yielded 2a-c as the major product (Scheme 3, Figure 2-8). Irradiation of 1a-c in oxygen-saturated chloroform-d and oxygen-saturated methanol-d₄ via a Pyrex filter at 298 K also yielded 2a-c as the major product. Irradiation via Pyrex filter ensures that only the ketone moiety absorbs the light and forms the singlet excited state of the ketone (S₁K) of 1a-c, which then inter system crosses to the triplet excited state of the ketone (T₁K) of 1a-c. The first and the second excited states of (T₁K and T₂K) are within 1 - 9 kcal/mol of each other for 1a-d. We propose that energy transfer from T₁K of 1a-c to the alkene moiety forms triplet biradical (TBR) of 1a-c, which rotates around the C – C bond to form cis alkenes 2a-c.
"Only 1a was excited at this wavelength"

Scheme 4. Proposed Mechanism for the trans - cis isomerization of 1a-c.

b) Ground State UV/VIS Spectra

The ground state UV/Vis spectra of 1a-c and 2a-c are shown below (Figure 9). Comparison of ground state UV shows that 1a and 2a have different UV/Vis spectra. Further, 1c and 2c also has different UV/Vis spectra. Alkenes 1a has an absorption band at ~ 330 nm that is stronger than for the corresponding acetophenone derivatives, which have an (n,π*) absorption band around 320 nm (ε = 50, Table 2)."
**Figure 9.** Ground State UV/Vis spectra of 0.1 mM 1a (onset: 1 μM (green), 0.01 M (blue)), 2a, 0.1 mM 1b, 2b and 0.01 mM 1c (onset: 0.01 M (red)), 2c in EtOH at 298 K.

**Table 1.** The Ground State UV absorption λ_max and ε for 1a, 2a, 1b and 1c.

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<th></th>
<th>λ_max (ε) nm (M⁻¹cm⁻¹)</th>
<th>λ_max (ε) nm (M⁻¹cm⁻¹)</th>
<th>λ_max (ε) nm (M⁻¹cm⁻¹)</th>
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<td>1a</td>
<td>329 (109)</td>
<td>279 (1.08 x 10⁴)</td>
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<td>2a</td>
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<td>1b</td>
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<td>1c</td>
<td>350 (102)</td>
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**c) Calculations**

To better understand the reactivity of 1a-c we calculated the triplet surface of 1a-c using the Gaussian03¹¹ and Gaussian09 at the B3LYP level of theory and with the 6-31+G(d) basis set.¹² ¹³ We used the calculations to support the proposed mechanism for trans – cis isomerization.

**I. Calculations of 1a → 2a**

We optimized the ground-state (S₀) of 1a, S₀ of 2a, T_K of 1a and T_BR of 1a (Figure 13). The energy of S₀ of 2a is 2 kcal/mol higher than S₀ of 1a. The TD-DFT calculations of S₁ of 1a shows that it is located at 78 kcal/mol. Analysis of molecular orbitals shows that it has a (n,π*) configuration where the major electronic excitation is from the non-bonding orbital of oxygen to anti-bonding molecular orbital (Table 2, Figure 13). TD-DFT calculations of S₁ of 1a in acetonitrile shows that the electron transitions are affected by solvation and that S₁ of 1a is
located at 82 kcal/mol above its $S_0$ in acetonitrile. Analysis of molecular orbitals shows that it has mixed electronic transition. The major electron transitions are from non-bonding orbital of oxygen to anti-bonding molecular orbital hence has a ($\pi,\pi^*$) configuration; and a ($\pi,\pi^*$) configuration with electron transition is mainly originated from phenyl ring (Table 2, Figure 11).

**Table 2.** Electronic transitions of 1a above 250 nm in gas phase

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Table 3. Electronic transitions of 1a above 250 nm in acetonitrile

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Figure 10. Molecular orbitals corresponds to electronic transitions of 1a above 250 nm
Figure 11. Molecular orbitals corresponds to electronic transitions of 1a above 250 nm in acetonitrile

We also calculated the ground state UV/Visible spectrum of acetophenone in gas phase for comparison (Table 4, Figure 12). Acetophenone shows that S1K is due to the (n,π*) configuration. This suggests that absorbing chromophore of alkene 1a behave remarkably similar to that of acetophenone.

Table 4. Electronic transitions of acetophenone above 250 nm in gas phase

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Figure 12. Molecular orbitals corresponds to electronic transitions of acetophenone
Analysis of bond lengths of $S_0$ of $1a$ and $S_0$ of $2a$ shows that they both have C=O bond length of 1.23 Å and vinyl bond of 1.34 Å. We also optimized the $T_{1K}$ of $1a$ and found that it is located 62 kcal/mol above $S_0$ of $1a$, which is considerably lower than the energy obtained by TD-DFT calculations. The optimized structure of $T_{1K}$ of $1a$ shows that C=O bond length has been increased from 1.23 Å to 1.33 Å. Further, it also shows that carbonyl carbon to α-C bond distance has been reduced from 1.49 Å to 1.42 Å whereas the C=C bond length has been increased from 1.34 Å in $S_0$ to 1.39 Å in $T_{1K}$ of $1a$. Moreover, the decrease of the carbonyl carbon to quaternary phenyl carbon bond length from 1.50 Å in $S_0$ to 1.45 Å in $T_{1K}$ of $1a$ shows that optimized structure of $T_{1K}$ of $1a$ is delocalized mainly to the C=C and the C=O chromophores and to much lesser extent to the phenyl ring. However, the bond lengths in the phenyl ring are not affected in the $T_{1K}$ of $1a$ suggesting that $T_{1K}$ of $1a$ has (n,π*) configuration.

| $S_0$ of $1a$ | $S_0$ of $2a$ |
Figure 13. Optimized $S_0$ Conformers of 1a, $T_K$ of 1a and $T_{BR}$ of 1a.

TD-DFT calculations of 1a show that the $T_{1K}$ of 1a is located 67 kcal/mol above $S_0$ of 1a and has a ($n,\pi^*$) configuration where the major electronic excitation is from the non-bonding orbital of oxygen to the anti-bonding $\pi$-molecular orbital. $T_{2K}$ of 1a was located 71 kcal/mol above its $S_0$. $T_{2K}$ of 1a and has mixed ($\pi,\pi^*$) configuration where the electron transition originate from both the C=C chromophore; and from the phenyl ring.

TD-DFT calculations of 1a in acetonitrile show that there are changes in electron transitions based on the solvation. The $T_{1K}$ of 1a is located 70 kcal/mol above $S_0$ of 1a in acetonitrile and has a mixed ($\pi,\pi^*$) and ($n,\pi^*$) configuration. This indicates that the electron excitation in $T_{1K}$ of 1a originate mainly from the non-bonding orbital of the oxygen atom with smaller contribution from the C=C, phenyl chromophores. $T_{2K}$ of 1a is 73 kcal/mol above $S_0$ of 1a is due to mixed transitions from the C=C and phenyl chromophore ($\pi,\pi^*$) into a $\pi^*$-molecular orbital.
We also optimized the $T_{1K}$ of $2a$ and found that it is located at 63 kcal/mol above $S_0$ of $1a$. The optimized structure of $T_{1K}$ of $2a$ shows that C=O bond length has been increased from 1.23 Å in the $S_0$ to 1.33 Å in the $T_{1K}$ of $2a$. Further, it also shows that carbonyl carbon to $\alpha$-C bond distance has been reduced from 1.50 Å in the $S_0$ to 1.42 Å in the $T_{1K}$ of $2a$, whereas the C=C bond length has been increased from 1.35 Å in the $S_0$ to 1.37 Å in the $T_{1K}$ of $2a$. Moreover, the decrease of the carbonyl carbon to quaternary phenyl carbon bond length from 1.50 Å in the $S_0$ to 1.46 Å in the $T_{1K}$ of $2a$, shows that optimized structure of the $T_{1K}$ of $2a$ is delocalized mainly to the C=O moiety and to lesser extent on the C=C and the phenyl chromophores. The bond
lengths in the phenyl ring are not been affected in the T$_{1K}$ of 2a suggesting that the electron transition is mainly due to (n,π*) transition.

TD-DFT calculations of 1a show that the T$_{1K}$ of 2a is located 65 kcal/mol above S$_0$ of 1a and has a (n,π*) configuration where the major electronic transfer is from the non-bonding orbital of the oxygen to the anti-bonding π-molecular orbital. T$_{2K}$ of 2a is 73 kcal/mol above S$_0$ of 1a and is due to mixed electronic transitions. The major electron transition is originates from C=C chromophore; and a minor electron transition is originated from the phenyl ring to the anti-bonding π-molecular orbital.

We calculated the transition state for the T$_{1K}$ of 1a to form the triplet biradical (T$_{BR}$) of 1a and found that it is located 1 kcal/mol above the T$_{1K}$ of 1a. Intrinsic Reaction Coordinate (IRC) calculations confirm the transition state correlate to the T$_{1K}$ of 1a and T$_{BR}$ of 1a. Optimization of T$_{BR}$ of 1a located it at 58 kcal/mol above S$_0$ of 1a. Bond length analysis shows that C=O bond length has been reduced from 1.33 Å in T$_{K}$ of 1a to 1.25 Å in T$_{BR}$ of 1a. Further, C=C bond length has been increased from 1.39 Å in T$_{K}$ of 1a to 1.46 Å in T$_{BR}$ of 1a. Moreover, H-C-C-H dihedral angle has been reduced from 179.3° in T$_{K}$ of 1a to 94.5° in T$_{BR}$ of 1a. This suggests the biradical is localized on α-carbon and β-carbon atoms. We calculated the transition state for the T$_{1K}$ of 2a to form the triplet biradical and found that it is located 3 kcal/mol above the T$_{1K}$ of 2a. IRC calculations confirm the transition state correlate to the T$_{1K}$ of 2a and T$_{BR}$ of 1a.
II. Calculations of 1b $\rightarrow$ 2b

We optimized the ground-state ($S_0$) of 1b (Figure 16). The energy of $S_0$ of 2b is 2 kcal/mol higher than $S_0$ of 1b. The TD-DFT calculations of $S_1$ of 1b shows that it is located at 80 kcal/mol. Analysis of molecular orbitals shows that it has a (n,$\pi^*$) configuration where the major electronic excitation is from the non-bonding orbital of oxygen to anti-bonding molecular orbital (Table 5, Figure 14). TD-DFT calculations of $S_1$ of 1a in acetonitrile shows that there are no significant changes in electron transitions based on the solvation and it is located at 84 kcal/mol.

Table 5. Electronic transitions of 1b above 250 nm in gas phase

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Figure 14. Molecular orbitals corresponds to electronic transitions of $S_1$ of 1b and $S_2$ of 1b
We also calculated the ground state UV/Visible spectrum of p-methoxyacetophenone in gas phase for comparison (Table 4, Figure 12). The calculations on p-methoxyacetophenone shows that its S$_{1\text K}$ has (n,$\pi^*$) configuration. This suggests that absorbing chromophore of alkene 1b is similar to that of p-methoxyacetophenone.

**Table 6.** Electronic transitions of p-Methoxyacetophenone above 250 nm in gas phase

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**Figure 15.** Molecular orbitals corresponds to electronic transitions of p-Methoxyacetophenone

Analysis of bond lengths of S$_0$ of 1b and S$_0$ of 2b shows that they both have C=O bond length of 1.23 Å and C=C bond lengths of 1.34 Å and 1.35 Å respectively. We also optimized the T$_{1\text K}$ of 1b and found that it is located 62 kcal/mol above S$_0$ of 1b, which is considerably lower than the energy obtained by TD-DFT calculations. The optimized structure of T$_{1\text K}$ of 1b
shows that C=O bond length has been increased from 1.23 Å in its S\(_0\) to 1.33 Å. Further, it also shows that carbonyl carbon to α-C bond distance has been reduced from 1.49 Å in its S\(_0\) to 1.42 Å in T\(_{1K}\) of 1b whereas the C=C bond length has been increased from 1.34 Å in its S\(_0\) to 1.38 Å in T\(_{1K}\) of 1b. Moreover, the decrease of the carbonyl carbon to quaternary phenyl carbon bond length from 1.50 Å in its S\(_0\) to 1.46 Å in T\(_{1K}\) of 1b shows that optimized structure of T\(_{1K}\) of 1b is delocalized mainly on the C=O and less to extent to the C=C phenyl and chromophores. The bond lengths in the phenyl ring has not been affected noticeably in the T\(_{1K}\) of 1b suggesting that the electron transition is mainly due to (n,π\(^*\)) transition.

<table>
<thead>
<tr>
<th>(S_0) of 1b</th>
<th>(S_0) of 2b</th>
</tr>
</thead>
</table>

\[\begin{align*}
1.39 & \quad 1.40 \\
1.36 & \quad 1.40 \\
1.39 & \quad 1.34 \\
1.40 & \quad 1.40 \\
1.50 & \quad 1.50 \\
1.23 & \quad 1.23 \\
1.41 & \quad 1.41 \\
1.40 & \quad 1.40 \\
1.50 & \quad 1.50 \\
1.42 & \quad 1.42 \\
1.40 & \quad 1.40 \\
1.39 & \quad 1.39 \\
1.40 & \quad 1.40 \\
1.50 & \quad 1.50
\end{align*}\]

<table>
<thead>
<tr>
<th>T(_K)</th>
<th>T(_{BR})</th>
</tr>
</thead>
</table>

\[\begin{align*}
1.39 & \quad 1.40 \\
1.36 & \quad 1.40 \\
1.39 & \quad 1.34 \\
1.40 & \quad 1.40 \\
1.50 & \quad 1.50 \\
1.23 & \quad 1.23 \\
1.41 & \quad 1.41 \\
1.40 & \quad 1.40 \\
1.50 & \quad 1.50 \\
1.42 & \quad 1.42 \\
1.40 & \quad 1.40 \\
1.39 & \quad 1.39 \\
1.40 & \quad 1.40 \\
1.50 & \quad 1.50
\end{align*}\]

**Figure 16.** Optimized Conformers of \(S_0\) of 1b, \(S_0\) of 2b, T\(_K\) of 1b and T\(_{BR}\) of 1b.
TD-DFT calculations of 1b show that the T₁ of 1b is located 68 kcal/mol above S₀ of 1b and has mainly (π,π*) configuration. The major electronic excitations for T₁ of 1b originate from phenyl ring, C=C chromophore; with a minor contribution from the non-bonding orbital of oxygen. Whereas the T₂ of 1b is 70 kcal/mol above S₀ of 1b and has a (n, π*) configuration, and the electronic excitation originates from the non-bonding orbital of oxygen to anti-bonding π-molecular orbital.

![Scheme 6](image)

**Scheme 6.** Energy diagram of 1b & 2b (energy is in kcal/mol)

We also optimized the T₁K of 2b and found that it is located at 63 kcal/mol above S₀ of 1b. The optimized structure of T₁K of 2b shows that C=O bond length has been increased from 1.23
Å in the S0 to 1.33 Å in T1K of 2b. Further, it also shows that carbonyl carbon to α-C bond length has been reduced from 1.49 Å to 1.42 Å whereas the C=C bond length has been increased from 1.35 Å in the S0 to 1.38 Å in T1K of 2b. Moreover, the decrease of the carbonyl carbon to quaternary phenyl carbon bond length from 1.50 Å in the S0 to 1.46 Å in T1K of 2b shows that optimized structure of T1K of 2b is delocalized mainly to the C=O chromophore and less extent to the C=C and phenyl chromophores. The bond lengths in the phenyl ring has not been affected in the T1K of 2b in comparison to the S0 of 2b, suggesting that the electron transition is mainly due to (n,π*) transition.

TD-DFT calculations of 2b show that the T1 of 2b is located 68 kcal/mol above the S0 of 1b. This state is due to mixed electronic transition where the major electronic transition is from the non-bonding molecular orbital of oxygen to anti-bonding π-molecular orbital; and the other electronic transition is from the phenyl ring to the anti-bonding π-molecular orbital. This is somewhat different to T1 of 1b because it also has contributions arising from the electronic transitions from the C=C chromophore. On the other hand T2 of 2b is 73 kcal/mol above S0 of 1b and has (π,π*) electronic configuration. This state is also due to mixed electronic transition where the major electronic transition is originating from the phenyl ring to the anti-bonding molecular orbital; and the minor electron transition is from the non-bonding molecular orbital of oxygen to anti-bonding π-molecular orbital. T2 of 2b is also somewhat different to that of T2 of 1b because T2 of 2b also has major electronic transitions from phenyl ring to the anti-bonding π-molecular orbital whereas T2 of 1b has major electronic transition from non-bonding orbital of oxygen to π-orbital.
We calculated the transition state for the T1K of 1b to form the triplet biradical (TBR) of 1b and found that it is located 2 kcal/mol above the T1K of 1b. IRC calculations confirm the transition state correlate to the T1K of 1b and TBR of 1b. The TBR of 1b is 58 kcal/mol above S0 of 1b. Bond length analysis shows that C=O bond has been reduced from 1.33 Å in T_K of 1b to 1.25 Å in TBR of 1b. Further, C=C bond length has been increased from 1.38 Å in T_K of 1b to 1.46 Å in TBR of 1b. Moreover, H-C-C-H dihedral angle has been reduced from 179.9° in T_K of 1b to 96.1° in TBR of 1b. This suggests the biradical is localized on α-carbon and β-carbon atoms. We also optimized the T1K of 2b and found that it is located 63 kcal/mol above S0 of 1b. We calculated the transition state for the T1K of 2b to form the triplet biradical and found that it is located 4 kcal/mol above the T1K of 2b. IRC calculations confirm the transition state correlate to the T1K of 2b and TBR of 1b.

### III. Calculations of 1c → 2c

We optimized the ground-state (S0) of 1c (Figure 19). The energy of S0 of 2c is 2 kcal/mol higher than S0 of 1c. The TD-DFT calculations of S1 of 1c show that it is located at 76 kcal/mol above its S0. Analysis of molecular orbitals shows that it has a (n,π*) configuration where the major electronic excitation is from the non-bonding orbital of oxygen to an antibonding π-molecular orbital (Table 7, Figure 17). TD-DFT calculations of S1 of 1b in acetonitrile do not show any changes in electron transitions based on the solvation.

**Table 7.** Electronic transitions of 1c above 250 nm in gas phase

<table>
<thead>
<tr>
<th>Excited State</th>
<th>1: Singlet-A</th>
<th>3.2822 eV</th>
<th>377.75 nm</th>
<th>f=0.0005</th>
</tr>
</thead>
<tbody>
<tr>
<td>43 -&gt; 46</td>
<td>-0.13544</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

121
44 -> 46  -0.12987
45 -> 46  0.64920

Excited State 2: Singlet-A 4.4106 eV 281.11 nm f=0.1231
42 -> 46  -0.40008
43 -> 46  0.46317
44 -> 46  -0.22393
44 -> 47  -0.10954
44 -> 48  -0.14968

Excited State 3: Singlet-A 4.4639 eV 277.75 nm f=0.4151
42 -> 46  -0.38136
44 -> 46  0.51823
44 -> 48  -0.13383

Excited State 4: Singlet-A 4.6422 eV 267.08 nm f=0.0774
42 -> 46  0.33355
43 -> 46  0.43314
44 -> 46  0.29480
44 -> 47  0.14210
45 -> 46  0.13535

Figure 17. Molecular orbitals corresponds to electronic transitions of S1 of 1c and S2 of 1c

We also calculated the ground state UV/Visible spectrum of p-cyanoacetophenone in gas phase for comparison (Table 8, Figure 18). p-cyanoacetophenone shows that its S1K has (n,π*) configuration. This suggests that absorbing chromophore of alkene 1c behave very similar to that of p-cyanoacetophenone.

Table 8. Electronic transitions of p-cyanoacetophenone above 250 nm in gas phase
Analysis of bond lengths of \( S_0 \) of \( 1c \) and \( S_0 \) of \( 2c \) shows that they both have C=O bond length of 1.23 Å and C=C bonds of 1.34 Å and 1.35 Å respectively. We also optimized the \( T_{1K} \) of \( 1c \) and found that it is located 60 kcal/mol above \( S_0 \) of \( 1c \), which is somewhat lower than the energy obtained by TD-DFT calculations. The optimized structure of \( T_{1K} \) of \( 1c \) shows that C=O bond length has been increased from 1.23 Å in the \( S_0 \) to 1.32 Å in the \( T_{1K} \) of \( 1c \). Further, it also shows that the carbonyl carbon to \( \alpha \)-C bond distance has been reduced from in the \( S_0 \) 1.48 Å to 1.43 Å in the \( T_{1K} \) of \( 1c \) whereas the C=C bond length has been increased from 1.34 Å in the \( S_0 \) to 1.38 Å in the \( T_{1K} \) of \( 1c \). Moreover, the decrease of the carbonyl carbon to quaternary phenyl carbon bond from 1.51 Å in the \( S_0 \) to 1.44 Å shows that optimized structure of \( T_{1K} \) of \( 1c \) is delocalized mainly to the C=O chromophore and to lesser extent to the C=C and phenyl moieties. However,
the bond lengths in the phenyl ring has not been affected noticeably in the $T_{1K}$ of 1c, thus also suggesting that the electron transition is mainly due to a $(n, \pi^*)$ transition.

TD-DFT calculations of 1c show that the $T_{1K}$ of 1c is located 64 kcal/mol above $S_0$ of 1c and has a $(n, \pi^*)$ configuration where the electronic excitation is from the non-bonding orbital of oxygen to the anti-bonding molecular orbital. In comparison, the $T_{2K}$ of 1c is 69 kcal/mol above the $S_0$ of 1c and has a $(\pi, \pi^*)$ configuration, where the electronic excitation is originating from the C=C chromophore to the anti-bonding molecular orbital. This is remarkably different to $T_{2K}$ of 1a and $T_{2K}$ of 1b where the major electron transitions are either from non-bonding orbital of oxygen to $\pi$–orbital or phenyl ring to $\pi$-orbital. Hence, we think the major photo-reactivity we observe come from the $T_{2K}$ of 1c which results in direct isomerization of 1c to 2c. Further, this isomerization is also wavelength dependent.
TD-DFT calculations of 1a in acetonitrile show that there are some changes in electron transitions based on the solvation. The T_{1K} of 1c has mixed (n,\pi^*) and (\pi,\pi^*) configurations. The electron excitation originates mainly from both the non-bonding orbital of the oxygen and from the C=C chromophore to the anti-bonding molecular orbital. T_{2K} of 1c in acetonitrile has a major electron transition originated from C=C chromophore.
**Scheme 7.** Energy diagram of 1c & 2c (energy is in kcal/mol)

We optimized the ground-state \(S_0\) of 2c. The optimized structure of \(T_{1K}\) of 2c shows that C=O bond length has been increased from 1.23 Å in the \(S_0\) of 2c to 1.33 Å in the \(T_{1K}\) of 2c. Further, it also shows that carbonyl carbon to \(\alpha\)-C bond distance has been reduced from 1.48 Å in the \(S_0\) of 2c to 1.43 Å in the \(T_{1K}\) of 2c, whereas the C=C bond length has been increased from 1.35 Å in the \(S_0\) of 2c to 1.37 Å in the \(T_{1K}\) of 2c. Moreover, the decrease of the carbonyl carbon to quaternary phenyl carbon bond length from 1.51 Å in the \(S_0\) of 2c to 1.45 Å in the \(T_{1K}\) of 2c, shows that optimized structure of the \(T_{1K}\) of 2c is delocalized mainly to the C=O chromophore and lesser extent to phenyl and C=C chromophore. However, the bond lengths in the phenyl ring has not been affected in the \(T_{1K}\) of 2c suggesting that it has \((n,\pi^*)\) configuration.

TD-DFT calculations of 2c show that the \(T_{1K}\) of 2c is located 65 kcal/mol above the \(S_0\) of 1c. This state has an electronic transition originating from the non-bonding molecular orbital of oxygen to anti-bonding molecular orbital. On the other hand \(T_2\) of 2c is 72 kcal/mol above the \(S_0\) of 1c and is due to mixed electronic transitions where the major electronic transition is originating from the C=C chromophore to the anti-bonding molecular orbital; and the minor electron transition is from the phenyl ring to anti-bonding molecular orbital. \(T_2\) of 2c is similar to that of \(T_2\) of 1c where both has major electronic transition from C=C chromophore to the anti-bonding molecular orbital.

We optimized the \(T_{1K}\) of 1c and found that it is located 60 kcal/mol above the \(S_0\) of 1c, which is somewhat lower than the energy obtained by TD-DFT calculations. We calculated the transition state for the \(T_{1K}\) of 1c to form the triplet biradical \((T_{BR})\) of 1c and found that it is
located 2 kcal/mol above the T\textsubscript{1K} of 1c. IRC calculations confirm the transition state correlate to the T\textsubscript{1K} of 1c and T\textsubscript{BR} of 1c. The T\textsubscript{BR} of 1c is 58 kcal/mol above S\textsubscript{0} of 1c. Bond length analysis shows that C=O bond length has been reduced from 1.32 Å in the T\textsubscript{K} of 1c to 1.23 Å in the T\textsubscript{BR} of 1c. Further, C=C bond length has been increased from 1.38 Å in the T\textsubscript{K} of 1c to 1.46 Å in the T\textsubscript{BR} of 1c. Moreover, H-C-C-H dihedral angle has been reduced from 179.5° in the T\textsubscript{K} of 1c to 93.7° in the T\textsubscript{BR} of 1c. This suggests the biradical is localized on α-carbon and β-carbon atoms. We calculated the transition state for the T\textsubscript{1K} of 2c to form the triplet biradical and found that it is located 3 kcal/mol above the T\textsubscript{1K} of 2c. IRC calculations confirm the transition state correlate to the T\textsubscript{1K} of 2c and T\textsubscript{BR} of 1c.

Table 9. Location of the absorbing chromophore for different calculated electronic states in gas phase using Gaussian03 DFT/TDDFT level of theory with 6-31G+(d) basis set

<table>
<thead>
<tr>
<th>Compound</th>
<th>Location of the absorbing chromophore for different calculated electronic states</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S\textsubscript{1}</td>
</tr>
<tr>
<td>1a</td>
<td>C=O</td>
</tr>
<tr>
<td>1b</td>
<td>C=O</td>
</tr>
<tr>
<td>1c</td>
<td>C=O</td>
</tr>
</tbody>
</table>

Table 10. Calculated bond length’s of C=O and C=C bonds of the T\textsubscript{K} and the T\textsubscript{BR} of 1a-d and 2a-d using the UB3LYP method.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond Length (Å)</th>
<th>Compound</th>
<th>Bond Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( T_K )</td>
<td>( T_{BR} )</td>
<td>( T_K )</td>
</tr>
<tr>
<td></td>
<td>C=O</td>
<td>C=C</td>
<td>C=O</td>
</tr>
<tr>
<td>1a</td>
<td>1.32706</td>
<td>1.38547</td>
<td>1.24542</td>
</tr>
<tr>
<td>1b</td>
<td>1.32795</td>
<td>1.37544</td>
<td>1.24627</td>
</tr>
<tr>
<td>1c</td>
<td>1.32395</td>
<td>1.37916</td>
<td>1.24493</td>
</tr>
</tbody>
</table>

IV. Spin Densities

<table>
<thead>
<tr>
<th>C Number</th>
<th>( \frac{\text{Spin Density}}{1a} )</th>
<th>( \frac{\text{Spin Density}}{1b} )</th>
<th>( \frac{\text{Spin Density}}{1c} )</th>
</tr>
</thead>
<tbody>
<tr>
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<td>+0.04</td>
</tr>
<tr>
<td>2</td>
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<td>-0.14</td>
<td>-0.13</td>
</tr>
<tr>
<td>3</td>
<td>+0.05</td>
<td>+0.06</td>
<td>+0.06</td>
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</tr>
<tr>
<td>5</td>
<td>+0.04</td>
<td>+0.01</td>
<td>+0.05</td>
</tr>
<tr>
<td>6</td>
<td>-0.11</td>
<td>-0.09</td>
<td>-0.11</td>
</tr>
</tbody>
</table>

\textbf{Figure 20.} Spin density of \( T_{BR} \) of 1a-c and 2a-c
We also calculated the spin density of the T_{BR} of 1a (or 2a), T_{BR} of 1b (or 2b) and T_{BR} of 1c (or 2c). We found that the spin density on α-carbon atom is around 0.72 and is significantly less than the spin density on the β-carbon atom that is 0.93. This is because the radical on α-carbon atom is in conjugation with C=O group. In comparison, radical on β-carbon atom is localized hence has spin densities close to 1. Further, we also noticed that the spin density on β-carbon atom does not change upon the substitution at para position of the phenyl ring. However, the spin density on α-carbon slightly increase when an electron donating group is at the para position of the phenyl ring and the spin density on α-carbon slightly decrease when an electron withdrawing group is attached at the para position of the phenyl ring. This is because electron donating groups push electrons towards phenyl ring and eventually to the C=O group, hence the oxygen and α-carbon has higher spin density but electron withdrawing groups pulls electrons from the phenyl ring resulting in less spin density on oxygen and α-carbon. Examination of spin
density on phenyl ring shows that the spin density is positive on 1,3,5-carbons for 1a and 1c ranging from +0.03 to +0.06 where as spin density is positive on only 3,5-carbons for 1b ranging from +0.01 to +0.06.

Spin Density calculations of triplet ketones of 1a-c does not show a significant changes upon substitution at para position of the phenyl ring (Figure 21). However, the spin density calculations clearly demonstrate that the triplet ketone is localized on the C=O and the C=C chromophores. The spin density analysis shows that there is no affect on spin density values of phenyl carbons upon substitution for both T_{1K} of 1a-1c and T_{BR} of 1a-1c. The largest spin density on phenyl ring is at C-4 with -0.13, -0.13 and -0.14 for 1a, 1b and 1c respectively.

d) Laser Flash Photolysis

(I). LFP of 1a in CH$_3$CN with $\lambda = 308$ nm laser

We performed laser flash photolysis to support the proposed reaction mechanism for 1a. Laser flash photolysis (Excimer laser, 308 nm, 17 ns)$^{14}$ of 1a in argon-saturated acetonitrile produced a transient absorption with $\lambda_{\text{max}}$ at ~360 nm and at ~500 nm (Figure 22). The intensity of the band at 360 nm and 500 nm decreases with time. We assigned the absorption at 360 nm and 500 nm to both $T_{1K}$ of 1a and $T_{BR}$ of 1a, based on the following. The calculated TD-DFT absorption spectrum of the $T_{1K}$ of 1a in acetonitrile has the major electronic transfer at 469nm ($f=0.1423$), 327 nm ($f=0.0570$), 326 ($f=0.0812$), 316 ($f=0.1618$) and 309 nm ($f=0.2403$) (Figure 24), which fits well with the observed spectra. The calculated TD-DFT absorption spectrum of
the TBR of 1a in acetonitrile has the major electronic transfer at 469 nm ($f=0.0375$), 437 nm ($f=0.0127$) and 337 nm ($f=0.0452$), which also fits well with the observed spectra.

1 μs time window in Ar, Air and O2
We also measured the transient UV/Visible spectra in air-saturated acetonitrile and in oxygen-saturated acetonitrile to further characterize the intermediates formed. Analysis of the transient UV/Visible spectra shows the reduction in transient absorption intensity indicating that oxygen quenches the $T_{1K}$ of 1a hence reduce the yield of $T_{BR}$ of 1a.

To further aid in the assignment of the intermediates, we measured the transient UV/Vis spectra in longer time interval (in 25 μs time window) (Figure 23). There are three major
absorptions with $\lambda_{\text{max}}$ at ~330-400 nm, ~440 nm and ~500 nm. The absorption at 440 nm and 500 nm completely decays to the baseline after 164 $\mu$s whereas the absorption at 360 nm is reduced but not fully decayed. This suggests that there is some ground state product absorption at 360 nm. The reduction in absorption is mainly due to the decay of $T_{1K}$ of 1a and $T_{\text{BR}}$ of 1a.

25 $\mu$s time window in Ar

![Figure 23](image.png)

**Figure 23.** Transient UV / Vis spectra in 25 $\mu$s time window (a). 1.00 – 4.20 $\mu$s (red) (b). 4.80 – 12.80 $\mu$s (blue) (c). 13.80 – 27.60 $\mu$s (black) (d). 29.80 – 164.40 $\mu$s (light green)
Figure 24. Calculated UV of the $T_{1K}$ of 1a and the $T_{BR}$ of 1a in acetonitrile using TD-DFT level of theory with UB3LYP/6-31+G(d) basis set.
Figure 25. Calculated UV of the $T_{1K}$ of $1a$ and the $T_{BR}$ of $1a$ in Gas phase using TD-DFT level of theory with UB3LYP/6-31+G(d) basis set.

Kinetic analysis of the transient absorption further supports this assignment. The transient absorption at 500 nm in argon-saturated acetonitrile can be fitted into a mono-exponential decay function. This absorption is formed with a rate constant of $9.832 \times 10^6$ s$^{-1} \pm 7.58 \times 10^5$ s$^{-1}$, $\tau = 102$ ns and decays with a rate constant of $3.082 \times 10^5$ s$^{-1} \pm 1.31 \times 10^4$ s$^{-1}$, $\tau = 3.2 \mu s$ (Figure 26). We assign this formation rate constant to the formation of $T_{BR}$ of $1a$. Since the precursor to that is $T_{1K}$ of $1a$, we theorize that $T_{1K}$ of $1a$ decays with a lifetime of 102 ns. This supports the transient absorption assignment at 500 nm to $T_{BR}$ of $1a$. The transient absorption at 360 nm can be fitted into a mono-exponential function at lower time intervals, but requires a double-exponential function for fitting at longer time. In shorter time, the transient absorption at 360 nm grows in with a rate constant of $1.195 \times 10^7$ s$^{-1} \pm 2.34 \times 10^5$ s$^{-1}$ ($\tau = 84$ ns) decays with a rate constant of $2.785 \times 10^5$ s$^{-1} \pm 1.58 \times 10^4$ s$^{-1}$ ($\tau = 3.6 \mu s$) in argon saturated-solvent. This is consistent with the lifetime of the intermediate at 500 nm. Therefore, we assign this shorter lifetime at 360 nm to $T_{BR}$ of $1a$. At longer time, the transient absorption at 360 nm decays with rate constants of $2.942 \times 10^5$ s$^{-1} \pm 5.57 \times 10^4$ s$^{-1}$ ($\tau = 3.4 \mu s$) and $3.74 \times 10^4$ s$^{-1} \pm 5.35 \times 10^3$ s$^{-1}$ ($\tau =$
26.7 μs). We assign the shorter lifetime again to T_{BR} of 1a and the longer lifetime to the residual product formation.

100 ns time window at 360nm in Ar

\[ k_1 = 1.195 \times 10^7 \text{s}^{-1} \pm 2.34 \times 10^5 \text{s}^{-1}, \tau = 84 \pm 2 \text{ ns} \]

1 μs time window at 360nm in Ar

\[ k_1 = 2.785 \times 10^5 \text{s}^{-1} \pm 1.58 \times 10^4 \text{s}^{-1}, \tau = 3.6 \pm 0.02 \text{ μs} \]
$5 \mu s$ time window at $360\text{nm}$ in Ar

\begin{align*}
    k_1 &= 2.698 \times 10^5 \text{s}^{-1} \pm 3.26 \times 10^4 \text{s}^{-1}, \quad \tau = 3.7 \pm 0.04 \mu\text{s}; \\
    k_2 &= 3.71 \times 10^4 \text{s}^{-1} \pm 1.66 \times 10^4 \text{s}^{-1}, \quad \tau = 27.0 \pm 12 \mu\text{s}.
\end{align*}

$10 \mu s$ time window at $360\text{nm}$ in Ar

\begin{align*}
    k_1 &= 2.942 \times 10^5 \text{s}^{-1} \pm 5.57 \times 10^4 \text{s}^{-1}, \quad \tau = 3.4 \pm 0.06 \mu\text{s}; \\
    k_2 &= 3.74 \times 10^4 \text{s}^{-1} \pm 5.35 \times 10^3 \text{s}^{-1}, \quad \tau = 26.7 \pm 3.8 \mu\text{s}.
\end{align*}
100 ns time window at 500nm in Ar

\[ k_1 = 9.832 \times 10^6 \text{ s}^{-1} \pm 7.58 \times 10^5 \text{ s}^{-1}, \tau = 102 \pm 8 \text{ ns}. \]

2.5 \( \mu \)s time window at 500nm in Ar

\[ k_1 = 3.082 \times 10^5 \text{ s}^{-1} \pm 1.31 \times 10^4 \text{ s}^{-1}, \tau = 3.2 \pm 0.1 \mu \text{s} \]

**Figure 26.** Kinetics of 1a in CH\(_3\)CN. (a). 100 ns time window at 360 nm in Ar (b). 1 \( \mu \)s time window at 360nm in Ar. (c). 5 \( \mu \)s time window at 360nm in Ar. (d). 10 \( \mu \)s time window at 360nm in Ar. (e). 100 ns time window at 500 nm in Ar (f). 2.5 \( \mu \)s time window at 500nm in Ar.
In oxygen-saturated solutions the intensity of the bands at ~360 nm and ~500 nm are decreased (Figure 27). Thus oxygen quenches the T\textsubscript{1K} of 1a, hence the yield of the T\textsubscript{BR} of 1a is reduced because the T\textsubscript{1K} of 1a is the precursor to the T\textsubscript{BR} of 1a. Therefore, the absorbance at 500 nm and 360 nm are completely depleted in oxygen-saturated acetonitrile solutions due to the quenching of T\textsubscript{1K} of 1a. The remaining absorbance at 360 nm could also be due to the residual product absorption.

**Quenching with O\textsubscript{2}**

![Graph showing transient UV/Vis spectra for quenching studies of 1a; the T\textsubscript{BR} of 1a (a). In argon (0.02 – 0.30 μs) (red) (b). In air (0.02 – 0.30 μs) (green) (c). In oxygen (0.02 – 0.30 μs) (blue)]

**Figure 27.** Transient UV/Vis spectra for quenching studies of 1a; the T\textsubscript{BR} of 1a (a). In argon (0.02 – 0.30 μs) (red) (b). In air (0.02 – 0.30 μs) (green) (c). In oxygen (0.02 – 0.30 μs) (blue)
Rate in Air is $6.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ if $[\text{O}_2] = 0.009 \text{ M} \times 20\%$ and rate constant $(k) = 1.10 \times 10^6 \text{ s}^{-1}$

(0.009 M x 20% is because air contains only 20% of O$_2$)

**Figure 28.** Quenching studies of 1a in Ar (red), Air (green) and Oxygen (blue) at 360 nm in 2.5 μs time window.
Rate in Air is $3.5 \times 10^8 \, \text{M}^{-1} \, \text{s}^{-1}$ if $[\text{O}_2] = 0.009 \, \text{M} \times 20\%$ and the rate constant ($k$) = $6.25 \times 10^5 \, \text{s}^{-1}$

(0.009 M x 20% is because air contains only 20% of O2);

Rate in O$_2$ is $2.5 \times 10^8 \, \text{M}^{-1} \, \text{s}^{-1}$ if $[\text{O}_2] = 0.009 \, \text{M}$ and rate constant ($k$) = $2.27 \times 10^6 \, \text{s}^{-1}$

(Note: The lifetime in argon is similar to the lifetime observed at 500 nm, refer Figure 26)

**Figure 29.** Quenching studies of 1a in Ar (red), Air (green) and Oxygen (blue) at 460 nm in 2.5 μs time window.
Quenching with Isoprene

We used isoprene quenching method to find out the lifetime of an intermediate of interest at a specific wavelength. Isoprene is a molecule which is capable of quenching an excited state of a molecule thereby isoprene excites itself. This can be representing in the form of following equation.

\[ 1a^{3^*} + \text{Iso} \rightarrow 1a + \text{Iso}^{3^*} \]

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*Table 11. Isoprene quenching data for 1a (This was only carried out once, no repeat trials).*
Absorbance vs. Time [s] for different concentrations of Q (5mM Q0, 10mM Q10, 20mM Q20, 40mM Q40, 60mM Q60, 80mM Q80, and 100mM Q100).

Plot of \( \frac{I_0}{I} \) vs. [Q] (mol/L) showing a linear relationship with gradient (b) = 2.57 and intercept (a) = 1.0.
Figure 30. Stern-Volmer plot for quenching of 1a with isoprene (a). Absorbance vs. time profiles in 1μs time window at 360 nm. (b). Stern-Volmer plot for quenching of 1a with isoprene at 360 nm in 1 μs time window. (c). Absorbance vs. time profiles in 1μs time window at 500 nm (e). Stern-Volmer plot for quenching of 1a with isoprene at 500 nm in 1 μs time window
We investigated the quenching with isoprene at ~360 nm (Table 11, Figure 30) and the lifetime of the T1K of 1a. Isoprene quenches the T1K of 1a.

Stern-Volmer equation is,

\[
\frac{I_0}{I} = 1 + k_q \tau_0 [Q]
\]

where, \(I_0\) = Intensity of the 1a without the quencher, \(I\) = Intensity of the 1a with q amount of quencher, \(k_q\) = Quencher rate co-efficient, \(\tau_0\) = Lifetime of the 1a without quencher, \([Q]\) = Concentration of the quencher.

\(\tau_0\) of the 1a is 0.257 – 2.57 ns or 0.20 – 2.00; if the \(k_q\) is \(10^9 – 10^{10}\) by assuming the energy transfer is diffusion controlled. The triplet energy of the isoprene is 60.1 kcal/mol.\(^{15, 16}\) The T1K of 1a has energy of 62 kcal/mol. This suggests that the energies of both T1K of 1a and isoprene are comparable. In order to energy transfer to occur, the triplet energy of the isoprene needs to be somewhat lower than the energy of the T1K of 1a. Hence, we hypothesize that energy transfer is slow because the energies are comparable.

If we do not assume the energy transfer is diffusion controlled, then by taking the lifetime of T1K of 1a to be 3.2 \(\mu\)s, \(k_q\) can be calculated to be between \(6.25 \times 10^5\) s\(^{-1}\) to \(8.03 \times 10^5\) s\(^{-1}\).

(II). LFP of 1a in CH\(_3\)CN with \(\lambda = 355\) nm laser

Laser flash photolysis (YAG laser, 355 nm, 10 ns) of 1a in nitrogen-saturated acetonitrile produced a transient absorption with \(\lambda_{\text{max}}\) at ~300 nm and at ~430 nm (Figure 31). The intensity of the broad band from 380 nm to 550 nm decreases with time. The calculated TD-DFT
absorption spectrum of the $T_{\text{BR}}$ of 1a and $T_{1\text{K}}$ of 1a in acetonitrile (Figure 24) fits well with the observed spectra.

400 ns time window in N$_2$

![Absorbance vs Wavelength](image)

**Figure 31.** Transient UV / Vis spectra of the 1a in acetonitrile with YAG laser $\lambda = 355$ nm in nitrogen-saturated solutions (a). 248 ns – 267 ns (red) (b). 273 ns – 310 ns (blue) (c). 325 ns – 811 ns (black) (d). 832 ns – 1493 ns (light green)

The absorption with $\lambda_{\text{max}} \sim 430$ nm (Figure 31) is assigned to the $T_{1\text{K}}$ of 1a based on the similarity of this transient spectrum with the calculated absorption spectrum of $T_{1\text{K}}$ of 1a in acetonitrile. The transient absorptions at 380 nm, 460 nm and at 500 nm decays with nearly consistent rate constants of $\sim 3.392 \times 10^6$ s$^{-1} \pm 4.14 \times 10^5$ s$^{-1}$ ($\tau = 295 \pm 36$ ns) and $\sim 1.482 \times 10^5$ s$^{-1} \pm 5.91 \times 10^3$ s$^{-1}$ ($\tau = 6.7 \pm 0.3$ μs). We assign the short-lived decay to the $T_{1\text{K}}$ of 1a where as we assign the longer decay to the $T_{\text{BR}}$ of 1a.
10 μs time window at 380nm in N2

\[ k_1 = 3.392 \times 10^6 \text{ s}^{-1} \pm 4.14 \times 10^5 \text{ s}^{-1}, \quad \tau = 295 \pm 36 \text{ ns};\]

\[ k_2 = 1.072 \times 10^5 \text{ s}^{-1} \pm 4.23 \times 10^3 \text{ s}^{-1}, \quad \tau = 9.3 \pm 0.4 \mu\text{s} \]

5 μs time window at 380nm in N2

\[ k_1 = 3.392 \times 10^6 \text{ s}^{-1} \pm 4.14 \times 10^5 \text{ s}^{-1}, \quad \tau = 295 \pm 36 \text{ ns};\]

\[ k_2 = 1.482 \times 10^5 \text{ s}^{-1} \pm 5.91 \times 10^3 \text{ s}^{-1}, \quad \tau = 6.7 \pm 0.3 \mu\text{s} \]
5 µs time window at 460nm in N2

\[ k_1 = 3.392 \times 10^6 \text{ s}^{-1} \pm 4.14 \times 10^5 \text{ s}^{-1}, \quad \tau = 295 \pm 36 \text{ ns}; \]

\[ k_2 = 1.670 \times 10^5 \text{ s}^{-1} \pm 5.39 \times 10^3 \text{ s}^{-1}, \quad \tau = 6.0 \pm 0.2 \mu\text{s} \]

100 ns time window at 500nm in N2

\[ k_1 = 3.279 \times 10^6 \text{ s}^{-1} \pm 1.57 \times 10^5 \text{ s}^{-1}, \quad \tau = 305 \pm 15 \text{ ns} \]
5 μs time window at 500nm in N2

k_1 = 3.392 \times 10^6 \text{ s}^{-1} \pm 4.14 \times 10^5 \text{ s}^{-1}, \tau = 295 \pm 36 \text{ ns};

k_2 = 1.368 \times 10^5 \text{ s}^{-1} \pm 4.14 \times 10^3 \text{ s}^{-1}, \tau = 7.3 \pm 0.2 \mu\text{s}

Figure 32

1 μs time window at 380nm in N_2

k_1 = 3.392 \times 10^6 \text{ s}^{-1} \pm 4.14 \times 10^5 \text{ s}^{-1}, \tau = 295 \pm 36 \text{ ns};

k_2 = 2.553 \times 10^5 \text{ s}^{-1} \pm 2.57 \times 10^4 \text{ s}^{-1}, \tau = 4.0 \pm 0.4 \mu\text{s}
10 μs time window at 380nm in N₂

\[ k_1 = 3.392 \times 10^6 \text{ s}^{-1} \pm 4.14 \times 10^5 \text{ s}^{-1}, \tau = 295 \pm 36 \text{ ns}; \]

\[ k_2 = 1.072 \times 10^5 \text{ s}^{-1} \pm 4.23 \times 10^3 \text{ s}^{-1}, \tau = 9.3 \pm 0.4 \mu\text{s} \]

5 μs time window at 380nm in N₂

\[ k_1 = 3.392 \times 10^6 \text{ s}^{-1} \pm 4.14 \times 10^5 \text{ s}^{-1}, \tau = 295 \pm 36 \text{ ns}; \]

\[ k_2 = 1.482 \times 10^5 \text{ s}^{-1} \pm 5.91 \times 10^3 \text{ s}^{-1}, \tau = 6.7 \pm 0.3 \mu\text{s} \]
5 μs time window at 460nm in N₂

\[ k_1 = 3.392 \times 10^6 \text{s}^{-1} \pm 4.14 \times 10^5 \text{s}^{-1}, \tau = 295 \pm 36 \text{ ns}; \]

\[ k_2 = 1.670 \times 10^5 \text{s}^{-1} \pm 5.39 \times 10^3 \text{s}^{-1}, \tau = 6.0 \pm 0.2 \mu \text{s} \]

100 ns time window at 500nm in N₂

\[ k_1 = 3.279 \times 10^6 \text{s}^{-1} \pm 1.57 \times 10^5 \text{s}^{-1}, \tau = 305 \pm 15 \text{ ns} \]
5 μs time window at 500nm in N₂

\[ k_1 = 3.392 \times 10^6 \text{ s}^{-1} \pm 4.14 \times 10^5 \text{ s}^{-1}, \tau = 295 \pm 36 \text{ ns}; \]

\[ k_2 = 1.368 \times 10^5 \text{ s}^{-1} \pm 4.14 \times 10^3 \text{ s}^{-1}, \tau = 7.3 \pm 0.2 \mu\text{s} \]

**Figure 32.** Kinetics of 1a in nitrogen-saturated acetonitrile. (a). 1 μs time window at 380nm. (b). 10 μs time window at 380nm. (c). 5 μs time window at 380 nm. (d). 5 μs time window at 460 nm. (e). 100 ns time window at 500 nm. (f). 5 μs time window at 500 nm.

**Quenching with O₂ (Transient UV/Vis in O₂)**

In oxygen-saturated solutions the intensity of the broad band from ~360–500 nm is decreased. Thus oxygen quenches the T₁K of 1a, hence the yield of the TBR of 1a is reduced because the T₁K of 1a is the precursor to the TBR of 1a (Figure 33).
Figure 33. The Transient UV/Visible spectrum of 1a with 355 nm in oxygen-saturated acetonitrile.

(III). LFP of 1a in CH$_3$CN with $\lambda$ = 266 nm laser

Laser flash photolysis (YAG laser, 266 nm, 10 ns) of 1a in nitrogen-saturated acetonitrile produced a broad transient absorption from 350 nm to 600 nm and absorption with $\lambda_{\text{max}}$ at ~300 nm (Figure 34-35). The intensity of the band at 300 nm remains nearly constant the intensity of the broad absorption decreases with time. We assign the absorption at 300 nm to mainly to formation of 2a due to the direct absorption from C=C chromophore of the molecule.
10 μs time window in N₂

Figure 34. Transient UV / Vis spectra of 1a in acetonitrile with excimer laser at \( \lambda = 266 \) nm in nitrogen-saturated solutions (a). 1 (0 ns Delay) (red) (b). 2 (blue) (c). 3 (black) (d). 4 (light green)

10 μs time window in N₂
Figure 35. Expanded transient UV / Vis spectra of 1a in acetonitrile with excimer laser at $\lambda = 266$ nm in nitrogen-saturated solutions (a). 1 (0 ns Delay) (red) (b). 2 (blue) (c). 3 (black) (d). 4 (light green)

The absorption at 300 nm decays with a rate constant of $0.3808 \text{ s}^{-1} \pm 0.0176 \text{ s}^{-1}$ with a lifetime of $2.6 \pm 0.1 \text{ s}$ in acetonitrile. We assign this long decay to the formation of 2a (Figure 36).

1 s time window at 300 nm in N$_2$

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig36}
\caption{Kinetics of 1a in nitrogen-saturated acetonitrile in 1 s time window at 300 nm.}
\end{figure}

$k_1 = 0.3808 \text{ s}^{-1} \pm 0.0176$, $\tau = 2.6 \pm 0.1 \text{ s}$
e) Laser Flash Photolysis of 1b

(IV). LFP of 1b in CH₃CN with $\lambda = 308 \text{ nm}$ laser

We performed laser flash photolysis to support the proposed reaction mechanism for 1b. Laser flash photolysis (Excimer laser, 308 nm, 17 ns) of 1b in argon-saturated acetonitrile produced a transient absorption with $\lambda_{\text{max}}$ at ~360 nm and a shoulder $\lambda_{\text{max}}$ at ~420 nm (Figure 37-38). The intensity of the band at 360 nm and 500 nm decreases with time. We assign the absorption at 360 nm and 500 nm to both the T₁K of 1b and the TBR of 1b, based on the TD-DFT calculations. The calculated TD-DFT absorption spectrum of the T₁K of 1b in acetonitrile has the major electronic transfer at 478 nm ($f=0.1351$), 447.87 nm ($f=0.0592$), 335 nm ($f=0.1856$) and 327 ($f=0.3323$) (Figure 39), which fits relatively well with the observed spectra (Figure 37). The calculated TD-DFT absorption spectrum of the TBR of 1b in acetonitrile has the major electronic transfer at 564 nm ($f=0.0640$), 347 nm ($f=0.0594$) and 300 nm ($f=0.0615$), which doesn’t fit well with the observed spectra especially the calculated peak at 564 nm is not observed in experimental UV/Visible spectrum.
Figure 37. Transient UV / Vis spectra of the T_{BR} of 1b and the T_{1K} of 1b (a). 0 ns delay (red) (b). 0.05 μs delay (blue) (c). 0.14 μs delay (black) (d). 0.24 μs delay (light green)

In longer time interval, 1b also shows a $\lambda_{\text{max}}$ at ~360 nm and 400 nm which slowly decrease in absorbance (Figure 38).
10 μs time window in Ar

**Figure 38.** Transient UV/Vis spectra of 1b in 10 μs time window (a). 0.24 – 1.52 μs (red) (b). 1.52 – 4.96 μs (blue) (c). 4.96 – 14.32 μs (black) (d). 14.32 – 72.64 μs (light green)
Figure 39. Calculated UV of the T$_{1K}$ of 1b and the T$_{BR}$ of 1b in acetonitrile using TD-DFT level of theory with the UB3LYP/6-31+G(d) basis set.

Kinetic analysis of the transient absorption further supports this assignment. The transient absorption at 360 nm in argon-saturated acetonitrile can be fitted into a mono-exponential decay function in shorter time intervals and decays with a rate constant of 1.441 x 10$^4$ s$^{-1}$ ± 9.56 x 10$^2$ s$^{-1}$ ($\tau = 69.4$ μs) (Figure 40). The transient absorption at 360 nm requires a double-exponential function for fitting at longer time. At longer time, the transient absorption at 360 nm decays with lifetimes of 4.827 x 10$^1$ s$^{-1}$ ± 4.56 x 10$^0$ s$^{-1}$ ($\tau = 20.7$ ms). We assign the longer lifetime to the residual product formation.

Kinetic studies shows that the transient absorption at 420 nm and can be fitted to a double-exponential function and decays with a rates of 2.277 x 10$^6$ s$^{-1}$ ± 3.91 x 10$^5$ s$^{-1}$ ($\tau = 439$ ns) and 2.868 x 10$^5$ s$^{-1}$ ± 6.86 x 10$^4$ s$^{-1}$ ($\tau = 3.5$ μs) in argon saturated-acetonitrile (Figure 40). We assign the shorter decay to the decay of the T$_{1K}$ of 1b. The prominent intermediate at 420 nm is that of T$_{1K}$ of 1b. Further, we assign the intermediate with the lifetime of 3.5 μs to the T$_{BR}$ of 1b.
Kinetics

360 nm, 25 μs time window in Ar

\[ k_1 = 1.441 \times 10^4 \text{ s}^{-1} \pm 9.56 \times 10^2 \text{ s}^{-1}, \tau = 69.4 \ \text{μs} \]

360 nm, 250 μs time window in Ar

\[ k_1 = 8.828 \times 10^3 \text{ s}^{-1} \pm 1.71 \times 10^3 \text{ s}^{-1}, \tau = 113.3 \ \text{μs}; \]

\[ k_2 = 1.201 \times 10^3 \text{ s}^{-1} \pm 4.48 \times 10^2 \text{ s}^{-1}, \tau = 832.0 \ \text{μs} \]
350 nm, 10 ms time window in Ar

\[ k_1 = 2.694 \times 10^2 \text{ s}^{-1} \pm 8.55 \times 10^1 \text{ s}^{-1} \], \tau = 3.7 \text{ ms};

\[ k_2 = 4.827 \times 10^1 \text{ s}^{-1} \pm 4.56 \times 10^0 \text{ s}^{-1} \], \tau = 20.7 \text{ ms}

420 nm, 1 \mu s time window in Ar
k₁ = 2.277 x 10⁶ s⁻¹ ± 3.91 x 10⁵ s⁻¹, \( \tau = 439 \text{ ns} \);

k₂ = 2.868 x 10⁵ s⁻¹ ± 6.86 x 10⁴ s⁻¹, \( \tau = 3.5 \mu \text{s} \)

**Figure 40.** Kinetics of 1b in CH₃CN in Ar (a). At 360 nm, 25 \( \mu \text{s} \) time window (b). At 360 nm, 250 \( \mu \text{s} \) time window (c). At 360 nm, 10 ms time window (d). At 420 nm, 1 \( \mu \text{s} \) time window

**Quenching Studies for 1b in CH₃CN**

In oxygen-saturated solutions, the intensity of the broad absorption band at 360 nm was reduced (Figure 41-43), and the absorption at 420 nm was quenched (Figure 43). This suggests that the TK of 1b is quenched by triplet O₂. In addition, the precursor to the formation of the TBR of 1b is TK of 1b hence the absorption of TBR of 1b is also reduced.

1 \( \mu \text{s} \) time window

**Figure 41.** Quenching studies of 1b in acetonitrile (a). In Ar with 0 ns delay (red) (b). In O₂ with 0 ns delay (blue)
360 nm, 50 μs time window in O₂

\[ k_1 = 3.53 \times 10^4 \text{ s}^{-1} \pm 1.77 \times 10^3 \text{ s}^{-1}, \tau = 28.3 \mu\text{s}; \]

\[ k_2 = 9.06 \times 10^3 \text{ s}^{-1} \pm 2.9 \times 10^3 \text{ s}^{-1}, \tau = 110.3 \mu\text{s} \]

**Figure 42.** Kinetics of 1b in CH₃CN in O₂ at 360 nm in 50 μs time window

420 nm, 1 μs time window

**Figure 43.** Quenching studies of 1b in CH₃CN (a). In Ar (red) (b). In O₂ (blue)
LFP of 1b in CH₃CN with λ = 355 nm laser

We performed laser flash photolysis to support the proposed reaction mechanism for 1b. Laser flash photolysis (YAG laser, 355 nm, 10 ns) of 1b in argon-saturated acetonitrile produced a transient absorption with λ_max at ~360 nm and a shoulder λ_max at ~450 nm (Figure 44). In addition, the transient absorption continues to 700 nm. The intensity of the band at 360 nm and 450 nm decreases with time. We assign the absorption at 360 nm to the T₁K of 1b and the TBR of 1b and the absorption at 450 nm to the T₁K of 1b, based on the calculated TD-DFT absorption spectrum of the T₁K of 1b and the TBR of 1b, which fits relatively well with the observed spectra (Figure 39).

1 μs time window in N₂
Figure 44. Transient UV / Vis spectra of 1b in acetonitrile (a). 1 (0 ns Delay) (red) (b). 2 (blue) (c). 3 (black) (d). 4 (light green)

Kinetic analysis of the transient absorption further supports this assignment. The transient absorption at 360 nm in shorter time interval can be fitted into a double exponential function. The shorter decay decays with a rate constants of $3.766 \times 10^6 \text{ s}^{-1} \pm 3.56 \times 10^5 \text{ s}^{-1}$ ($\tau = 266 \text{ ns}$) and we assigned it for the $T_K$ of 1b. The transient absorption at 360 nm and 400 nm in longer time window can also be fitted into a double exponential function. This transient grows in with a rate constant of $2.556 \times 10^5 \text{ s}^{-1} \pm 2.72 \times 10^4 \text{ s}^{-1}$ ($\tau = 3.9 \text{ μs}$) and decays with rate constants of $3.194 \times 10^5 \text{ s}^{-1} \pm 9.95 \times 10^3 \text{ s}^{-1}$ ($\tau = 3.1 \text{ μs}$) and $3.045 \times 10^4 \text{ s}^{-1}$ ($\tau = 32.8 \text{ μs}$). We assigned shorter decay with the lifetime $\sim 3.1 \text{ μs}$ for the $T_{BR}$ of 1b in nitrogen saturated-solvent (Figure 45). The long decay with 32.8 μs is assigned to the residual product formation.

330 nm, 5 μs time window in N₂

![Absorbance graph](image)

$k_1 = 2.556 \times 10^5 \text{ s}^{-1} \pm 2.72 \times 10^4 \text{ s}^{-1}$, $\tau = 3.9 \text{ μs}$
360 nm, 1 μs time window in N₂

\[ k_1 = 3.766 \times 10^6 \text{ s}^{-1} \pm 3.56 \times 10^5 \text{ s}^{-1}, \tau = 266 \text{ ns}; \]
\[ k_2 = 2.371 \times 10^5 \text{ s}^{-1} \pm 2.54 \times 10^4 \text{ s}^{-1}, \tau = 4.2 \mu\text{s} \]

380 nm, 100 ns time window in N₂

\[ k_1 = 3.719 \times 10^6 \text{ s}^{-1} \pm 3.75 \times 10^4 \text{ s}^{-1}, \tau = 269 \text{ ns}. \]
400 nm, 1 μs time window in N₂

\[ k_1 = 4.650 \times 10^6 \, \text{s}^{-1} \pm 1.83 \times 10^5 \, \text{s}^{-1}, \tau = 215 \, \text{ns}; \]

\[ k_2 = 3.194 \times 10^5 \, \text{s}^{-1} \pm 9.95 \times 10^3 \, \text{s}^{-1}, \tau = 3.1 \, \mu\text{s} \]

660 nm, 1 μs time window in N₂

\[ k_1 = 2.968 \times 10^6 \, \text{s}^{-1} \pm 4.41 \times 10^5 \, \text{s}^{-1}, \tau = 337 \, \text{ns}; \]

\[ k_2 = 4.978 \times 10^5 \, \text{s}^{-1} \pm 6.77 \times 10^4 \, \text{s}^{-1}, \tau = 2.0 \, \mu\text{s} \]
**Figure 45.** Kinetics in acetonitrile and in N₂ (a). At 330 nm, 5 µs time window (b). At 360 nm, 1 µs time window (c). At 380 nm, 100 ns time window (d). At 400 nm, 1 µs time window. (e). At 660 nm, 1 µs time window.

**Quenching Studies**

In oxygen-saturated solutions, the intensity of the bands around 360 nm and 450 nm quenched (Figure 46-47) and the intensity has been greatly reduced. This confirms that T₁K of 1b quenches with O₂.

380 nm, 100 ns time window

\[ k_{Ar} = 3.6 \times 10^6 \text{ s}^{-1} \pm 3.8 \times 10^4 \text{ s}^{-1}, \tau = 276 \text{ ns} \pm 3 \text{ ns}; \]

\[ k_{O2} = 1.4 \times 10^7 \text{ s}^{-1} \pm 1.8 \times 10^5 \text{ s}^{-1}, \tau = 74 \text{ ns} \pm 1 \text{ ns}; \]

**Figure 46.** Quenching studies of 1b in acetonitrile (a). In N₂ (red) (b). In O₂ (blue)
380 nm, 1 μs

380 nm, 2.5 μs
380 nm, 100 μs

![Absorbance vs Time Graph]

440 nm, 5 μs time window

![Absorbance vs Time Graph]

**Figure 47.** Quenching studies of 1b in acetonitrile (a). In N₂ (red) (b). In O₂ (blue)
Quenching with Isoprene

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<td>0.013 ± 0.000</td>
<td>2.154</td>
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<tr>
<td>3000</td>
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<td>3.111</td>
<td>6.665</td>
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</table>

Table 12. Isoprene Quenching Data for 1b
Figure 48. Stern-Volmer plot for quenching of 1b with isoprene at 350 nm in 100μs time window and 500 μs time window with [Q] from zero to 7 mol/L.

We also investigated the quenching with isoprene at ~350 nm (Table 12, Figure 48) and the lifetime of the T1K of 1b. The lifetime of the T1K of 1b was found by fitting the data into a linear line giving the Stern-Volmer Plot while holding the intercept at 1.0. Isoprene quenches the T1K of 1b. τ₀ of 1b is 0.037 – 0.37 ns if the kq is 10⁹ – 10¹⁰ by assuming the energy transfer is diffusion controlled. This is 3 – 4 orders of magnitude smaller than the observed value for T1K of 1b. We assume the energy transfer is diffusion controlled because the energy of isoprene and the energy of the T1K of 1b are comparable. Relatively constant A₀/A value suggest that there is minor quenching with isoprene. Further, addition of isoprene volumes higher than 500 μL results in dilution of the concentration of 1b, resulting less transient absorption.
f) Laser Flash Photolysis of 1c

(VI). LFP of 1c in CH₃CN with λ = 308 nm laser in solution

We performed laser flash photolysis to support the proposed reaction mechanism for 1c. Laser flash photolysis (Excimer laser, 308 nm, 17 ns) of 1c in argon-saturated acetonitrile produced a transient absorption with λₘₐₓ at ~360 nm (Figure 49-51). The intensity of the band at 360 nm remains nearly constant with time in 1 μs and 100 μs time interval measurements, whereas it decreases in 1 ms timescale. We assign the absorption at 360 nm to the formation of photo product based on TD-DFT calculations. The calculated TD-DFT absorption spectrum of the TₓBR of 1c in acetonitrile has the major electronic transfer at 447 nm (f=0.0438), 367 nm (f=0.0997) and 319 nm (f=0.0348) (Figure 52). The calculated TD-DFT absorption spectrum of the T₁K of 1c in acetonitrile has the major electronic transfer at 522 nm (f=0.2586), 348. nm (f=0.4477) and 335 (f=0.1494), however, we did not observe the T₁K of 1c or TₓBR of 1c in acetonitrile. We hypothesize that the major reactivity in solution comes from singlet excited state.
1 μs time window in Ar

![Graph](image1)

**Figure 49.** Transient UV / Vis spectra of 1c for 2.5 mM argon-saturated acetonitrile (a). 0.02 – 0.28 μs (red) (b). 0.28 – 0.90 μs (blue) (c). 0.90 – 2.00 μs (black) (d). 2.00 – 7.52 μs (light green)

100 μs time window in Ar

![Graph](image2)
Figure 50. Transient UV / Vis spectra of \(1c\) (a) 2.40 – 32.00 μs (red) (b) 32.00 – 81.60 μs (blue) (c) 81.60 – 181.60 μs (black) (d) 181.60 – 780.00 μs (light green)

1 ms time window in Ar

Figure 51. Transient UV / Vis spectra of \(1c\) (a) 24.00 – 320.00 μs (red) (b) 320.00 – 816.00 μs (blue) (c) 816.00 – 1816.00 μs (black) (d) 1816.00 – 7800.00 μs (light green)
Figure 52. Calculated UV of the $T_{1K}$ of 1c and the $T_{BR}$ of 1c in acetonitrile using TD-DFT level of theory with the UB3LYP/6-31+G(d) basis set.

Kinetic analysis of the transient absorption further supports this assignment. The transient absorption at 360 nm can be fitted into a mono exponential function that grows in with a rate constant of $1.669 \times 10^7 \text{ s}^{-1} \pm 7.55 \times 10^5 \text{ s}^{-1}$ ($\tau = 60 \text{ ns}$) decays with a rate constants of $61.92 \text{ s}^{-1} \pm 1.72 \text{ s}^{-1}$ ($\tau = 16.1 \text{ ms}$) (Figure 53). We assign this decay to formation of photoproduct.
Kinetics

360 nm, 5 ms time window in Ar

\[ k_1 = 61.92 \text{ s}^{-1} \pm 1.72 \text{ s}^{-1}, \tau = 16.1 \text{ ms} \]

360 nm, 100 ns time window in Ar with 10X attenuation
$k_1 = 1.669 \times 10^7 \text{ s}^{-1} \pm 7.55 \times 10^5 \text{ s}^{-1}$, $\tau = 60 \text{ ns}$ (This is not a significant growth. This may have resulted from the instrument).

**Figure 53.** Kinetics of 1c in CH$_3$CN in Ar (a). At 360nm, 5 ms time window (b). At 360 nm, 100 ns time window

**Quenching Studies for 1c in CH$_3$CN**

In oxygen-saturated solutions, the intensity of the broad absorption band at 360 nm was reduced (Figure 54-56). This is because the $T_{1K}$ of 1c is quenched by O$_2$ which results in less formation of photoproduct. This suggests that there could be minor triplet reactivity of 1c.

1 ms time window

**Figure 54.** Quenching studies of 1c in acetonitrile (a). In Ar (24.00 – 320.00 μs) (red) (b). In O$_2$ (24.00 – 320.00 μs) (blue)
360 nm, 5 ms time window in O₂

\[ k_1 = 69.097 \text{ s}^{-1} \pm 1.3 \text{ s}^{-1}, \quad \tau = 14.5 \text{ ms} \]

**Figure 55.** Kinetics of 1c in CH₃CN in O₂ at 360 nm in 5 ms time window

5 ms time window
Figure 56. Quenching studies of 1c in CH$_3$CN (a). In Ar (red) (b). In O$_2$ (blue)

Quenching with Isoprene

<table>
<thead>
<tr>
<th>$Q_V$ (µL)</th>
<th>$Q_{TOTAL}$ (mL)</th>
<th>Absorbance, A</th>
<th>$A_0/A$</th>
<th>[Q] (mol/L)</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>1.5</td>
<td>0.069 ± 0.011</td>
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<tr>
<td>10</td>
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</tr>
<tr>
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<td>4000</td>
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<td>0.035 ± 0.003</td>
<td>1.971 ± 0.169</td>
<td>7.271</td>
</tr>
</tbody>
</table>

Table 13. Isoprene Quenching Data for 1c
We also investigated the quenching with isoprene at ~360 nm (Table 13, Figure 57) and found that there is no reduction in absorbance for isoprene volumes less than 500 μL. Which suggests that the T1K of 1c is extremely short lived. There is a reduction in the absorbance with isoprene volumes higher than or equal to 500 μL because of the change in concentration of the mixture with the addition of isoprene (becomes significant). The lifetime of the T1K of 1c was found by fitting the data points to a linear line while holding the intercept at 1.00. Isoprene quenches the T1K of 1c and τ₀ of 1c is 0.01 – 0.1 ns if the kq is 10⁹ – 10¹⁰ by assuming the energy transfer is diffusion controlled.
(VII). LFP of 1c in CH$_3$CN with $\lambda = 308$ nm laser in Solid State

We performed laser flash photolysis to understand the reaction mechanism for 1c in solid state. Laser flash photolysis (Excimer laser, 308 nm, 17 ns) of 1c in crystal suspension produced a transient absorption with $\lambda_{\text{max}}$ at $\sim$320 nm (Figure 58) and absorption at 400 nm. The intensity of the band at 360 nm remains nearly constant with time in 50 μs time interval measurements. The absorption at 400 nm decays within 5 μs time window. We hypothesize that the major reactivity in solid state also comes from singlet excited state. But, we also see minor triplet reactivity in solid state, which we did not observe in solution for 1c.

1 μs time window in Ar-saturated crystal suspension

![Figure 58. Transient UV / Vis spectra of 1c in solid crystal suspension](image)

The absorption at 400 nm decays within 5 μs time window. We hypothesize that the major reactivity in solid state also comes from singlet excited state. But, we also see minor triplet reactivity in solid state, which we did not observe in solution for 1c.

Figure 58. Transient UV / Vis spectra of 1c in solid crystal suspension (a). 0.02 – 0.30 μs (red) (b). 0.30 – 1.00 μs (blue) (c). 1.00 – 2.00 μs (black) (d). 2.00 – 7.50 μs (light green)
50 μs time window in Ar-saturated crystal suspension

**Figure 59.** Transient UV/Vis spectra of 1c in solid crystal suspension (a). 0.80 – 10.40 μs (red) (b). 10.40 – 30.80 μs (blue) (c). 30.80 – 80.80 μs (black) (d). 80.80 – 390.40 μs (light green)

Kinetic analysis of the transient absorption further supports this assignment. The transient absorption at 400 nm can be fitted into a mono exponential function decays with a rate constant of $2.08 \times 10^5$ s$^{-1}$ ± $2.49 \times 10^3$ s$^{-1}$ ($\tau = 4.8$ μs) (Figure 60). We assign this decay to the decay of T$_{BR}$ of 1c.
**Kinetics**

340 nm, 2.5 ms time window in Ar

![Absorbance plot at 340 nm with absorption data](image)

\[ k_1 = 24.745 \, \text{s}^{-1} \pm 2.49 \, \text{s}^{-1}, \quad \tau = 40.4 \pm 4.1 \, \text{ms} \]

400 nm, 5 μs time window in Ar

![Absorbance plot at 400 nm with absorption data](image)

\[ k = 2.08 \times 10^5 \, \text{s}^{-1} \pm 2.49 \times 10^3 \, \text{s}^{-1}, \quad \tau = 4.8 \, \mu\text{s} \pm 0.06 \, \mu\text{s} \]
400 nm, 10 μs time window in Ar

\[ k = 1.85 \times 10^5 \, s^{-1} \pm 9.11 \times 10^3 \, s^{-1}, \tau = 5.4 \, \mu s \pm 0.3 \, \mu s \]

400 nm, 50 μs time window in Ar

\[ k = 2.55 \times 10^4 \, s^{-1} \pm 9.95 \times 10^2 \, s^{-1}, \tau = 39.2 \, \mu s \pm 1.5 \, \mu s \]
380 nm, 5 μs time window in Ar

\[ k = 2.14 \times 10^5 \text{ s}^{-1} \pm 8.36 \times 10^3 \text{ s}^{-1}, \ \tau = 4.7 \mu \text{s} \pm 0.2 \mu \text{s} \]

**Figure 60.** Kinetics in argon-saturated crystal suspension (a). At 360 nm in 50 μs time window (b). At 400 nm in 5 μs time window (c). At 400 nm in 10 μs time window (d). At 380 nm in 5 μs time window

**Quenching Studies**

1 μs time window in Oxygen-saturated crystal suspension
**Figure 61.** Transient UV / Vis spectra of 1c in solid crystal suspension (a). 0.02 – 0.30 μs (red) (b). 0.30 – 1.00 μs (blue) (c). 1.00 – 2.00 μs (black) (d). 2.00 – 7.50 μs (light green)

50 μs time window in Oxygen-saturated crystal suspension

**Figure 62.** Transient UV / Vis spectra of 1c in solid crystal suspension (a). 0.80 – 10.40 μs (red) (b). 10.40 – 30.80 μs (blue) (c). 30.80 – 80.80 μs (black) (d). 80.80 – 390.40 μs (light green)

1 μs time window in argon-saturated and oxygen-saturated crystal suspension comparison
**Figure 63.** 1 μs time window in argon-saturated and oxygen-saturated crystal suspension comparison (a). 0.02 – 0.30 μs (argon-red) (a). 0.02 – 0.30 μs (oxygen-blue)

50 μs time window in argon-saturated and oxygen-saturated crystal suspension comparison

**Figure 64.** 50 μs time window in argon-saturated and oxygen-saturated crystal suspension comparison (a). 0.80 – 10.40 μs (argon-red) (a). 0.80 – 10.40 μs (oxygen-blue)

380 nm, 5 μs time window in oxygen
$k = 1.30 \times 10^5 \text{ s}^{-1} \pm 5.28 \times 10^3 \text{ s}^{-1}$, $\tau = 7.7 \mu\text{s} \pm 0.3 \mu\text{s}$
**Figure 65.** Kinetic Traces for the comparison of argon-saturated and oxygen-saturated crystal suspension comparison at (a). 360 nm in 2.5 ms time window (b). 400 nm in 5 μs time window (c). 380 nm in 5 μs window.

The lifetimes in oxygen-saturated crystal suspension has not been affected by the oxygen saturation.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lifetimes</th>
</tr>
</thead>
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<tr>
<td></td>
<td>$T_K$</td>
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<tr>
<td></td>
<td>From LFP</td>
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<tr>
<td>1a</td>
<td>102 ± 8 ns (308 nm)</td>
</tr>
<tr>
<td></td>
<td>295 ± 30 ns (355 nm)</td>
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<tr>
<td>1b</td>
<td>439 ± 75 ns (308 nm)</td>
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<tr>
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<td>266 ± 25 ns (355 nm)</td>
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<tr>
<td>1c</td>
<td>- - (308 nm)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 14.** Summary of the lifetimes of $T_K$ of 1a-c and $T_{BR}$ of 1a-c.

The lifetime difference between 1a and 1b is mainly due to the electron donating substituent. Electron donating substituent like –OCH$_3$ group lowers the energy of (\(\pi,\pi^*\)) ketone ($T_{1K}$ of 1b) and hence undergo energy transfer. Therefore, it has a shorter lifetime. The biradical is also not stable due to the electron donation from the –OCH$_3$ group hence $T_{BR}$ of 1b also has a shorter lifetime. The lifetimes with isoprene suggests that they decrease from 1a to 1b to 1c. This
indicates that the prerequisite for diffusion controlled quenching is having comparable energies for isoprene and the $T_{1K}$ of 1a-1c.

### g) Time Resolved Infra-Red Spectroscopy (TRIR)

We carried out time resolved IR spectroscopy to further characterize the trans – cis (E to Z) isomerization of 1a in cyclohexane. We monitored the IR peaks from 1750 cm$^{-1}$ – 1500 cm$^{-1}$ in different time windows (Figure 66). Immediately after the laser pulse, we observed two negative peaks at 1685 cm$^{-1}$ and 1635 cm$^{-1}$ which we account for the depleted C=O and C=C stretches of trans (E)-1a. This assignment is based on the calculated IR peaks of C=O and C=C stretches of trans (E)-1a (Figure 67). In addition, we also observed two new peaks at 1670 cm$^{-1}$ and 1610 cm$^{-1}$ which we account for the newly formed C=O and C=C stretches of cis (Z)-1a. This assignment is also based on the calculated IR peaks of C=O and C=C stretches of cis (Z)-1a. Analysis of TRIR in different time intervals shows that these negative peaks did not decay back to the base line and also the new peaks did not decay back to the baseline meaning the trans – cis isomerization.
Figure 66. TRIR spectrum of 1a in argon-saturated cyclohexane in 100 μs time window at room temperature irradiated with λ = 266 nm laser.

Figure 67. Calculated C=O and C=C vibrations of (E)-1a and (Z)-1a using TD-DFT level of theory with B3LYP/6-31+G(d) basis set (Scaling factor = 0.97).
TRIR studies in oxygen-saturated cyclohexane showed that there is not much decrease in intensity suggesting that the reactivity is from singlet excited state (Figure 68). Irradiation with $\lambda = 266$ nm laser does not result in triplet sensitized photo-reactivity; hence E-1a directly goes to Z-1a upon irradiation through singlet pathway. This is supported by the molecular orbital diagrams which show two significant electron transitions at 274 nm and 256 nm (Figure 69). These electron transitions are attributed to an excitation of an electron from alkene moiety directly to anti-bonding molecular orbital suggesting it is not triplet sensitized at 266 nm, indicating singlet reactivity. Hence, laser flash photolysis at 266 nm hence results in these two electron transitions giving singlet reactivity.

![Figure 68. TRIR spectrum of 1a in oxygen-saturated cyclohexane in 100 $\mu$s time window at room temperature irradiated with $\lambda = 266$ nm laser.](image)
<table>
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<th>V (LUMO)</th>
<th>IV (HOMO)</th>
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</thead>
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<td>III (HOMO-1)</td>
<td>II (HOMO-2)</td>
</tr>
<tr>
<td>I (HOMO-3)</td>
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</tr>
</tbody>
</table>

358 nm (f=0.0003): IV $\rightarrow$ V

285 nm (f=0.0127): III $\rightarrow$ V

274 nm (f=0.5177): II $\rightarrow$ V

256 nm (f=0.1061): I $\rightarrow$ V

**Figure 69.** Orbitals involved in electron transitions above 250 nm in hexane on singlet surface.
h) Matrix Isolation

(I). Triplet-Sensitized photolysis of 1a in Argon Matrices

We studied the photochemistry of 1a in argon matrices at 14 K to identify its triplet sensitized photoreactivity in an inert environment. We deposited 1a into argon matrices in several different experiments, entraining the vapor pressure over a sample of pure 1a in flowing argon, and depositing the resulting sample on a 14 K cryogenic surface. Irradiation of 1a in argon matrices led to the growth of new absorption bands, mostly occurring very near those of the parent alkene (Figure 70-71), which is expected since the acetophenone moiety is not significantly affected by irradiation and the majority of the observed vibrational bands belong to it. The infrared spectrum of 1a showed a strong C=O band at 1688 cm\(^{-1}\) and a strong C=C band at 1668 cm\(^{-1}\), both of which are changed upon irradiation (Figure 70). The strong new C=O band appeared at 1678 cm\(^{-1}\) and C=C band was observed at 1661 cm\(^{-1}\), which we assign to 2a based on theoretical calculations. The calculated shift of C=O band of 1a to form 2a and the calculated shift of C=C band of 1a to form 2a closely agrees with the experimental shifts (Table 15).
Figure 70: The matrix IR of 1a from 1770 cm\(^{-1}\) to 1650 cm\(^{-1}\) (a). Before irradiation (red) (b). After irradiation (blue) (c). The difference (pink).

Further, we assigned twelve new peaks to 2a based on experimental IR band shift and calculated IR band shifts (Table 15, Figure 71-73).

Figure 71: The matrix IR of 1a from 1250 cm\(^{-1}\) to 1170 cm\(^{-1}\) (a). Before irradiation (red) (b). After irradiation (blue) (c). The difference (pink).
Figure 72: The matrix IR of 1a from 1050 cm\(^{-1}\) to 960 cm\(^{-1}\) (a). Before irradiation (red) (b). After irradiation (blue) (c). The difference (pink).

Figure 73: The matrix IR of 1a from 790 cm\(^{-1}\) to 680 cm\(^{-1}\) (a). Before irradiation (red) (b). After irradiation (blue) (c). The difference (pink).
<table>
<thead>
<tr>
<th>Calculated IR Bands / cm⁻¹</th>
<th>Experimental IR Bands / cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trans (1a)</td>
<td>Cis (2a)</td>
</tr>
<tr>
<td>1736 (156) C=O,C=C</td>
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</tr>
<tr>
<td>1678 (199) C=O,C=C</td>
<td>1670 (131) C=O,C=C</td>
</tr>
<tr>
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<td>1648 (17)</td>
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<td>751 (90)</td>
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<td>685 (9)</td>
<td>699 (17)</td>
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</table>

**Table 15**: Comparison of calculated IR bands of 1a and 2a with experimentally identified and assigned new IR bands and depleted IR bands (*- sign means a shift of peaks to lower wavenumbers, + sign means shift of peaks to higher wavenumbers).*
(II). Triplet-Sensitized photolysis of 1b in Argon Matrices

We studied the photochemistry of 1b in argon matrices at 14 K to identify its triplet sensitized photoreactivity in an inert environment. We deposited 1b into argon matrices in several different experiments, entraining the vapor pressure over a sample of pure 1b in flowing argon, and depositing the resulting sample on a 14 K cryogenic surface. Irradiation of 1b in argon matrices led to the growth of new absorption bands, mostly occurring very near those of the parent alkene (Figure 74-76), which is expected since the acetophenone moiety is not significantly affected by irradiation and the majority of the observed vibrational bands belong to it. The infrared spectrum of 1b showed a strong C=O band at 1681 cm\(^{-1}\) which was changed upon irradiation (Figure 74). The strong new C=O band appeared at 1676 cm\(^{-1}\), which we assign for 2b based on theoretical calculations. The calculated shift of C=O band of 1b to form 2b closely agrees with the experimental shifts.
**Figure 74:** The matrix IR of 1b from 1710 cm\(^{-1}\) to 1660 cm\(^{-1}\) (a). Before irradiation (red) (b). After irradiation (blue) (c). The difference (pink).

Further, we assigned eleven new peaks to 2b based on experimental IR band shift and calculated IR band shifts (Table 16, Figure 75-76).

**Figure 75:** The matrix IR of 1b from 1240 cm\(^{-1}\) to 1160 cm\(^{-1}\) (a). Before irradiation (red) (b). After irradiation (blue) (c). The difference (pink).

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201
**Figure 76:** The matrix IR of 1b from 870 cm\(^{-1}\) to 780 cm\(^{-1}\) (a). Before irradiation (red) (b). After irradiation (blue) (c). The difference (pink).

<table>
<thead>
<tr>
<th>Calculated IR Bands</th>
<th>Experimental IR Bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trans (1b) / cm(^{-1})</td>
<td>Cis (2b) / cm(^{-1})</td>
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<tr>
<td>1733 (158)</td>
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<td>1248 (250)</td>
<td>1259 (351)</td>
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<tr>
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<td>1293 (16)</td>
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Table 16: Comparison of calculated IR bands of 1b and 2b with experimentally identified and assigned new IR bands and depleted IR bands (- sign means a shift of peaks to lower wavenumbers, + sign means shift of peaks to higher wavenumbers).

| 1210 (143) | 1201 (255) | -9 | 1173 | 1171 | -2 |
| 1050 (36) | 1043 (57) | -7 | -- | 1088 | -- |
| 840 (32) | 810 (59) | -30 | 812 | 787 | -25 |
| 794 (1) | 801 (22) | +7 | 801 | 795 | -6 |

(III). Triplet-Sensitized photolysis of 1c in Argon Matrices

We studied the photochemistry of 1c in argon matrices at 14 K to identify its triplet sensitized photo-reactivity in an inert environment. We deposited 1c into argon matrices in several different experiments, entraining the vapor pressure over a sample of pure 1c in flowing argon, and depositing the resulting sample on a 14 K cryogenic surface. Irradiation of 1c in argon matrices led to the growth of new absorption bands, mostly occurring very near those of the parent alkene (Figure 77-80), which is expected since the acetophenone moiety is not significantly affected by irradiation and the majority of the observed vibrational bands belong to it. The infrared spectrum of 1c showed strong C=O band at 1688 cm⁻¹ and 1671 cm⁻¹; and a strong C=C band at 1634 cm⁻¹ which are changed upon irradiation (Figure 77). The strong new C=O band appeared at 1681 cm⁻¹ and C=C band was observed at 1624 cm⁻¹, which we assign for 2c based on theoretical calculations. The calculated shift of C=O band of 1c to form 2c and the calculated shift of C=C band of 1c to form 2c closely agrees with the experimental shifts (Table 203).
17). Further, we have identified nearly 13 new or shifted IR bands and they are listed in Table 17 along with the assigned calculated band.

**Figure 77.** The matrix IR of 1c from 1780 cm\(^{-1}\) to 1500 cm\(^{-1}\) showing the carbonyl region (a). Before irradiation (red) (b). After irradiation (blue) (c). The difference (pink).
Figure 78. The matrix IR of 1c from 1260 cm$^{-1}$ to 1190 cm$^{-1}$ (a). Before irradiation (red) (b). After irradiation (blue) (c). The difference (pink).
**Figure 79.** The matrix IR of 1c from 1060 cm\(^{-1}\) to 990 cm\(^{-1}\) (a). Before irradiation (red) (b). After irradiation (blue) (c). The difference (pink).

**Figure 80.** The matrix IR of 1c from 820 cm\(^{-1}\) to 750 cm\(^{-1}\) (a). Before irradiation (red) (b). After irradiation (blue) (c). The difference (pink).
<table>
<thead>
<tr>
<th>Calculated IR Bands / cm⁻¹</th>
<th>Experimental IR Bands / cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Trans (1c)</strong></td>
<td><strong>Cis (2c)</strong></td>
</tr>
<tr>
<td>1737 (165)</td>
<td>1730 (194)</td>
</tr>
<tr>
<td>C=O,C=C</td>
<td>C=O,C=C</td>
</tr>
<tr>
<td>1678 (235)</td>
<td>1670 (165)</td>
</tr>
<tr>
<td>C=O,C=C</td>
<td>C=O,C=C</td>
</tr>
<tr>
<td>1434 (2)</td>
<td>1423 (18)</td>
</tr>
<tr>
<td>1378</td>
<td>1368</td>
</tr>
<tr>
<td>1331 (75)</td>
<td>1294 (2)</td>
</tr>
<tr>
<td>1243 (171)</td>
<td>1245 (244)</td>
</tr>
<tr>
<td>1062 (29)</td>
<td>1047 (20)</td>
</tr>
<tr>
<td>1035 (13)</td>
<td>1030 (47)</td>
</tr>
<tr>
<td>934 (81)</td>
<td>925 (57)</td>
</tr>
<tr>
<td>831 (38)</td>
<td>808 (60)</td>
</tr>
<tr>
<td>809</td>
<td>787</td>
</tr>
<tr>
<td>774 (14)</td>
<td>784 (16)</td>
</tr>
<tr>
<td>748 (2)</td>
<td>731 (13)</td>
</tr>
<tr>
<td>559 (10)</td>
<td>564 (15)</td>
</tr>
</tbody>
</table>
Table 17. Comparison of calculated IR bands of 1c and 2c with experimentally identified and assigned, new IR bands and depleted IR bands (- sign means a shift of peaks to lower wavenumbers, + sign means shift of peaks to higher wavenumbers).

Further, we also observed secondary photoproduts during the extended photolysis of 1c in argon matrices at 14 K. We assign these secondary photoproduts to 4-cyanobenzaldehyde and propyne (Scheme 8). Irradiation of 1c for 1 hour and 20 minutes resulted in a new band at 1725 cm⁻¹ which is assigned to C=O stretch of 4-cyanobenzaldehyde (Figure 81-82). Further, we also located another new peak at 1352 cm⁻¹ which was also grew in after 1 hour and 20 min. We also assign this peak to the formation of 4-cyanobenzaldehyde. Careful examination of the IR spectra shows that after 20 min of irradiation, new peaks grew in at 3367 cm⁻¹, 663 cm⁻¹ and 655 cm⁻¹ which we assign to propyne (Figure 83-84). The intense peak at 1603 cm⁻¹ is not assigned.

Scheme 8. Secondary photoproduts in argon-matrices at 14 K.
Figure 81. The matrix IR of 4-cyanobenzaldehyde from 1780 cm$^{-1}$ to 1500 cm$^{-1}$ showing the growth of a new peak $\sim$1725 cm$^{-1}$(a). Before irradiation (red) (b). After irradiation of 5 min (blue) (c). After irradiation of 10 min (pink). (d). After irradiation of 20 min (brown). (e). After irradiation of 1 hour and 20 min (light green). (f). After irradiation of 3 hours and 20 min (light blue).
Figure 82. The matrix IR of 4-cyanobenzaldehyde from 1780 cm\(^{-1}\) to 1500 cm\(^{-1}\) showing the growth of a new peak \(~1725\) cm\(^{-1}\) (a). Before irradiation (red) (b). After irradiation of 5 min (blue) (c). After irradiation of 10 min (pink). (d). After irradiation of 20 min (brown). (e). After irradiation of 1 hour and 20 min (light green). (f). After irradiation of 3 hours and 20 min (light blue).

Figure 83. The matrix IR of propyne from 3600 cm\(^{-1}\) to 3100 cm\(^{-1}\) showing the growth of a new peak \(~3367\) cm\(^{-1}\) (a). Before irradiation (red) (b). After irradiation of 5 min (blue) (c). After
irradiation of 10 min (pink). (d). After irradiation of 20 min (brown). (e). After irradiation of 1 hour and 20 min (light green). (f). After irradiation of 3 hours and 20 min (light blue).

**Figure 84.** The matrix IR of propyne from 680 cm\(^{-1}\) to 640 cm\(^{-1}\) showing the growth of a new peak ~662 and 655 cm\(^{-1}\)(a). Before irradiation (red) (b). After irradiation of 5 min (blue) (c). After irradiation of 10 min (pink). (d). After irradiation of 20 min (brown). (e). After irradiation of 1 hour and 20 min (light green). (f). After irradiation of 3 hours and 20 min (light blue).
Table 18. The peak assignments for secondary photoproducts after 3 hours and 20 min of irradiation.

<table>
<thead>
<tr>
<th>Mode</th>
<th>4-cyanobenzaldehyde</th>
<th>propyne</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed</td>
<td>Calculated</td>
</tr>
<tr>
<td>C=O</td>
<td>1725</td>
<td>1782 (302)</td>
</tr>
<tr>
<td>H-C=O</td>
<td>1352</td>
<td>1345 (22)</td>
</tr>
<tr>
<td>H-C≡C</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>H-C≡C</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>H-C≡C</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

i) Crystal Structure of 1c

Figure 85. Crystal structure of 1c.
Figure 86. Crystal structures in a, b, c axis.

Figure 87. The shortest bond distances to form dimmers.
j) Solid State Photolysis of 1c

Solid State photolysis of 1c yielded alkene dimer (3c) (Scheme 9). FT-IR analysis of the KBr pallet of 1c showed the formation of few new IR peaks at 2230 (C≡N), 1734 (C=O), 1719 (C=O), 1701 (C=O), 1694 (C=O), 1685 (C=O), 1608, 1504, 1324, 1291, 1263, 1213, 1177, 1017, 867, 840, 770, 691, 644 and 563 cm\(^{-1}\) which could be attributed to the formation of 3c in crystals (Figure 88-90).

**Scheme 9.** Solid state photolysis in KBr.
Figure 88. Solid state photolysis of 1c in KBr, IR peaks from ~2300 – 1500 cm\(^{-1}\). (a). Before irradiation (red) (b) After 18 hours of irradiation (blue) (c) Onset is CN peak shift
**Figure 89.** Solid state photolysis of 1c in KBr, IR peaks from ~1500 – 950 cm\(^{-1}\). (a). Before irradiation (red) (b) After 18 hours of irradiation (blue)
Figure 90. Solid state photolysis of 1c in KBr, IR peaks from ~1000 – 450 cm\(^{-1}\). (a). Before irradiation (red) (b) After 18 hours of irradiation (blue)

Table 19. The comparison of the calculated IR bands of 1c and 3c with experimental IR bands of 1c before and after irradiation

<table>
<thead>
<tr>
<th>Stretch</th>
<th>Calculated IR Bands / cm(^{-1})</th>
<th>Experimental IR Bands / cm(^{-1})</th>
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</thead>
<tbody>
<tr>
<td>Trans (1c)</td>
<td>Dimer (3c)</td>
<td>Depleted bands</td>
</tr>
<tr>
<td>C=\text{N}</td>
<td>2236 (36)</td>
<td>2235</td>
</tr>
<tr>
<td></td>
<td>2237 (25), 2237 (40)</td>
<td>2230</td>
</tr>
<tr>
<td>C=O,C=C</td>
<td>1737 (165)</td>
<td>1743 (136), 1734 (143)</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>C=O,C=C</td>
<td>1678 (235)</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>1505 (57)</td>
<td>1524 (7), 1524 (9)</td>
</tr>
<tr>
<td></td>
<td>1443 (16)</td>
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<td></td>
<td>1418 (51), 1398 (26)</td>
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<td>1373 (41)</td>
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<tr>
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<td>1336 (36)</td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>1243 (171)</td>
<td>1240 (253)</td>
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<td>1206 (124)</td>
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<td>683</td>
</tr>
<tr>
<td>559</td>
<td>10</td>
<td>580</td>
</tr>
</tbody>
</table>

### k) Phosphorescence

We also measured the phosphorescence spectra of 1a and 1c, 2c in ethanol at 77 K with different wavelengths of irradiation. The phosphorescence spectra of 1 mM 1a shows that the (0, 0) transition is at 371 nm which corresponds to 77 kcal/mol with 300 nm excitation (Figure 91a). The excitation at 260 nm resulted a (0,0) transition at 346 nm which corresponds to 82 kcal/mol. (Figure 91b) The phosphorescence spectra of 1 mM 2a shows that the (0,0) transition is at 375 nm which corresponds to 76 kcal/mol. (Figure 91c-d) To gain more insight into the peak at ~520 nm in the phosphorescence spectrum of 1a, we monitored the phosphorescence intensity with respect to different concentrations of 1a (Figure 92-94). The phosphorescence spectra of 0.01 M 1b shows that the (0, 0) transition is at ~411 nm which corresponds to 70 kcal/mol, this agrees with calculated T2 (\(\pi, \pi^*\)) transition of 1b (Figure 95). Further, the phosphorescence spectra of 0.1 M 2b shows that the (0, 0) transition is at ~384 nm which corresponds to 74 kcal/mol, this agrees with calculated T2 (\(\pi, \pi^*\)) transition of 2b. The phosphorescence spectra of 0.02 M 1c shows that the (0, 0) transition is at ~ 410 nm which corresponds to 70 kcal/mol, this agrees with calculated T2 (\(\pi, \pi^*\)) transition of 1c (Figure 96-97). Further, the phosphorescence spectra of 0.02
M 2c shows that the (0, 0) transition is at ~ 394 nm which corresponds to 72 kcal/mol, this agrees with calculated T₂ (π, π*) transition of 2c.

**Phosphorescence of 1a and 2a**

Phosphorescence spectrum of 1 mM 1a in ethanol at 77 K with excitation at 300 nm.

![Phosphorescence spectrum of 1 mM 1a in ethanol at 77 K with excitation at 300 nm.](image)

Phosphorescence spectrum of 1 mM 1a in ethanol at 77 K with excitation at 260 nm.

![Phosphorescence spectrum of 1 mM 1a in ethanol at 77 K with excitation at 260 nm.](image)
Phosphorescence spectrum of 1 mM 2a in ethanol at 77 K with excitation at 300 nm.

Phosphorescence spectrum of 1 mM 2a in ethanol at 77 K with excitation at 260 nm.
Phosphorescence spectrum of 1 mM $1a$ and $2a$ in ethanol at 77 K with excitation at 300 nm and 260 nm.

**Figure 91**: Phosphorescence spectra of 1 mM $1a$ in ethanol at 77 K with (a). 300 nm excitation (b). 280 nm excitation; Phosphorescence spectra of 1 mM $2a$ in ethanol at 77 K with (c). 300 nm excitation (d). 260 nm excitation (e). Combined phosphorescence spectra at 300 nm and 260 nm excitations.

**Self Quenching Studies**

We measured the phosphorescence intensity with respect to change in concentration of $1a$. According to Favaro et al. the emitted light intensity ($I$) and the concentration ($C$) is related by the following equation:17

$$I = K \frac{1 - \exp(-2.3el[M])}{1 + k_{sq} \tau_{\infty}[M]}$$
The above equation can be rearranged to following two equations.

At high concentrations: \( \frac{1}{l} = \frac{1}{k} (1 + ksq. \tau \omega. [M]) \) and

at low Concentration: \( \frac{1}{l} = K'(\frac{1}{[M]} + ksq. \tau \omega) \)

Figure 92. Phosphorescence spectra of 1a with different concentrations
Figure 93. Plot of $I$ vs [1a]

Figure 94. Plot of $I^{-1}$ vs. $[1a]^{-1}$

Table 20. Self quenching data

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Intercept / Slope (x $10^{4}$ M$^{-1}$)</th>
<th>$\tau_\infty$ (µs)</th>
<th>$k_{sq}$ (x $10^{10}$ M$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>4.25</td>
<td>3.5</td>
<td>1.2</td>
</tr>
</tbody>
</table>
Phosphorescence of 1b and 2b

Phosphorescence spectrum of 0.01 M 1b in ethanol at 77 K with excitation at 300 nm.

Phosphorescence spectrum of 0.1 M 2b in ethanol at 77 K with excitation at 300 nm.
Phosphorescence spectrum of 0.1 M 2b in ethanol at 77 K with excitation at 260 nm.

![Phosphorescence spectrum of 0.1 M 2b in ethanol at 77 K with excitation at 260 nm.](image)

**Figure 95**: Phosphorescence spectra of 0.01 M 1b in ethanol at 77 K with (a). 300 nm excitation and 0.1 M 2b in ethanol at 77 K with (b). 300 nm excitation (c). 260 nm excitation

**Phosphorescence of 1c and 2c**

Phosphorescence spectrum of 0.1 M 1c in ethanol at 77 K with excitation at 300 nm.

![Phosphorescence spectrum of 0.1 M 1c in ethanol at 77 K with excitation at 300 nm.](image)
Phosphorescence spectrum of 0.1 M \textbf{1c} in ethanol at 77 K with excitation at 280 nm.

![Phosphorescence spectrum of 0.1 M \textbf{1c} in ethanol at 77 K with excitation at 280 nm.](image)

Phosphorescence spectrum of 0.1 M \textbf{1c} in ethanol at 77 K with excitation at 260 nm.

![Phosphorescence spectrum of 0.1 M \textbf{1c} in ethanol at 77 K with excitation at 260 nm.](image)
Phosphorescence spectrum of 0.1 M 1c in ethanol at 77 K with excitation at 260 nm, 280 nm and 300 nm.

**Figure 96**: Phosphorescence spectra of 0.1 M 1c in ethanol at 77 K with (a). 300 nm excitation (b). 280 nm excitation (c). 260 nm excitation (d). 300 nm, 280 nm and 260 nm excitations.
Phosphorescence spectrum of 0.02 M 1c in ethanol at 77 K with excitation at 300 nm.

Phosphorescence spectrum of 0.02 M 1c in ethanol at 77 K with excitation at 260 nm.
Phosphorescence spectrum of 0.02 M 2c in ethanol at 77 K with excitation at 300 nm.

Molecule = 2c; Excitation = 300 nm; (0,0) = 373 nm

Phosphorescence spectrum of 0.02 M 2c in ethanol at 77 K with excitation at 260 nm.

Molecule = 2c; Excitation = 260 nm; (0,0) = 394 nm
Phosphorescence spectrum of 0.02 M 1c and 2c in ethanol at 77 K with excitation at 260 nm and 300 nm.

**Figure 97**: Phosphorescence spectra of 0.02 M 1c in ethanol at 77 K with (a). 300 nm excitation (b). 260 nm excitation, and 0.02 M 2c in ethanol at 77 K with (c). 300 nm excitation (d). 260 nm excitation (e) Combined plot of 300 nm and 260 nm excitation.

**3. Discussion**

Irradiation of 1a-c in argon-saturated and oxygen-saturated chloroform-d, methanol-d4 solutions yielded 2a-c as the major product. LFP studies showed that there are two main intermediates both in chloroform-d and in methanol-d4 which we attributed to T1K of 1a-c and TBR of 1a-c. The lifetime of the TBR of 1a-c is higher than T1K of 1a-c. In addition, with electron
donating substituent, the lifetime of the biradical increases. Further, LFP also shows that, oxygen quenches $T_{1K}$ of 1a-c but it doesn’t quench $T_{BR}$ of 1a-c. TRIR studies of 1a shows that it quickly isomerizes to 2a and the new peaks doesn’t decay back to the zero (baseline), which means it is uni-directional isomerization. Further, this isomerization take place through a singlet intermediate, no more triplet sensitization because the laser used has a wavelength of 266 nm which promotes electronic transition directly from alkene moiety. Oxygen does not reduce the intensity of the TRIR peaks supporting the singlet pathway of forming the product 2a. Triplet sensitized photolysis of 1a-c in cryogenic argon-matrices at 14 K resulted in trans-cis isomerization of 1a-c to form 2a-c. To our knowledge, this is the first time that a triplet-sensitized trans-cis isomerization in argon matrices at 14 K was reported. Phosphorescence spectra shows that (0, 0) transitions of alkenes 1a-c mostly corresponds to emission from $T_2 \rightarrow S_0$. Solid state photolysis of 1c in KBr shows the formation of dimer 3c in crystal lattices.

4. Experimental

1) Calculations

All geometries were optimized at B3LYP level of theory and with 6-31G+(d) basis set as implemented in the Gaussian03 and Gaussian09 programs. All transition states were confirmed to have one imaginary vibrational frequency by analytical determination of the second derivatives of the energy with respect to internal coordinates. Intrinsic reaction coordinates calculations were used to verify that the located transition states corresponded to the attributed reactant and product. The absorption spectra were calculated using time-dependent density
functional theory (TD-DFT).\textsuperscript{21-25} The effect of solvation was calculated using the self-consistent reaction field (SCRF) method with the integral equation formalism polarization continuum model (IEFPCM) with acetonitrile, methanol and dichloromethane as solvents.\textsuperscript{26-30}

\textbf{m) Laser Flash Photolysis.}

Laser flash photolysis was done with an Excimer laser (308 nm, 17 ns).\textsuperscript{31} The system has been described in detail elsewhere.\textsuperscript{31} A stock solution of 1a-c in acetonitrile and methanol was prepared with spectroscopic grade acetonitrile and methanol, such that the solutions had absorption between 0.3 and 0.6 at 308 nm. Typically, \textasciitilde 1 mL of the stock solution was placed in a 10 mm \times 10 mm wide, 48 mm long quartz cuvette and was purged with argon for 5 min or oxygen for 15 min. The rates were obtained by fitting an average of three to five kinetic traces.

\textbf{n) Laser Flash Photolysis using Nanocrystalline Suspensions.}

We followed the procedure described by Garcia-Garibe and co-workers with slight modifications.\textsuperscript{32} Samples for laser flash photolysis experiment was prepared by injecting 5 \textmu L of 1c (0.1 M) solution in acetone into 3 mL of distilled water. The resulting suspension (1.7 \times 10^{-4} M) was homogenized at room temperature. The optical density of the resulting suspension was adjusted by serial dilution with distilled water to prepare a suspension with 1.7 \times 10^{-5} M concentration. The suspensions had absorption between 0.3 and 0.6 at 308 nm. Typically, \textasciitilde 2 mL of the stock solution was placed in a 10 mm \times 10 mm wide, 48 mm long quartz cuvette and was purged with argon for 5 min or oxygen for 15 min. The rates were obtained by fitting an average of three to five kinetic traces.
o) X-ray Single Crystal Structure Data

For X-ray examination and data collection, a suitable colorless, block-shaped crystal, approximate dimensions 0.25 x 0.23 x 0.16 mm, was mounted in a loop with Paratone-N oil and transferred to the goniostat bathed in a cold stream. Crystals shatter when attempts were made to cut the needle.

Intensity data were collected at 150K on a standard Bruker SMART6000 CCD diffractometer using graphite-monochromated Cu Kα radiation, λ=1.54178Å. A series of 11-s data frames measured at 0.3° increments of ω were collected to calculate a unit cell. For data collection frames were measured for a duration of 11-s at 0.3° intervals of ω with a maximum 2θ value of ~135°. The data frames were processed using the program SAINT. The data were corrected for decay, Lorentz and polarization effects as well as absorption and beam corrections based on the multi-scan technique.

The structure was solved by direct methods using SIR2004, expanded using the difference Fourier technique and refined by full-matrix least squares on F² using SHELXTL. Non-hydrogen atoms were refined with anisotropic displacement parameters. H-atoms were calculated and treated with a riding model. The H-atom isotropic displacement parameters were defined as a*Ueq of the adjacent atom (a=1.5 for methyl and 1.2 for all others). The refinement of the Flack parameter proved to be meaningless. As the complex contains only light atoms, the refinement reported is of the merged data. The refinement converged with crystallographic agreement factors of R1=4.27%, wR2=11.6% for 1275 reflections with I>2σ(I) (R1=4.87%, wR2=11.87% for all data) and 119 variable parameters.
p) Matrix isolations

Matrix isolation studies were performed using conventional equipment.\textsuperscript{33}

q) Solid State Photolysis of 1c

1c (5 mg, 0.03 mmol) was grinded with 0.245 g of KBr (1:49 w/w ratio) and a pallete was prepared. Then the KBr pallete of 1c was photolyzed via a Pyrex filter for 18 hours at 298 K. FT-IR analysis of the KBr pallete was carried out.

r) Phosphorescence

The solutions of 1a (1mM), 2a (1mM), 1b (0.02M), 2b (0.02M), 1c (0.02M) and 2c (0.02M) solutions were prepared in ethanol. The phosphorescence spectra were obtained on a phosphorimeter in ethanol glasses at 77K. The solutions were irradiated at 300 nm and 260 nm. The emission spectra recorded between 280 and 800 nm.

s) Ground State UV/Vis

The solutions of 1a (1mM), 2a (1mM), 1b (0.1mM), 2b (0.1mM), 1c (0.02M) and 2c (0.02M) solutions were prepared in ethanol. The UV/Vis spectra were obtained on a UV/Vis spectrometer in ethanol at 298K. The absorption spectra were recorded between 280 and 800 nm.
t) Preparations of 1a-c

Synthesis of 1-Phenyl-but-3-ene-1-ol

10.6 g (0.1 mol) of benzaldehyde was mixed in 25 mL of DMF. Allyl bromide 14.4 g (0.12 mol, 1.2 eq) was added to the above mixture and then 40 g of SnCl$_2$ (0.2 mol, 2 eq) was added. Then 50 mL of DMF was added to the mixture and then NaI 20g (0.134 mol, 1.3 eq) was added one spatula at a time very slowly for a period of 10 min. Then another 25mL of DMF was added to the mixture and allowed to stir for overnight (20 hours). 30g of NH$_4$F was dissolved in 100 mL of H$_2$O and added to the mixture to quench the reaction. 100 mL of ethyl ether was added to the quenched mixture and allowed to stir for further 30 min. The ether layer was extracted and washed twice with water. The ether extract was dried using anhydrous MgSO$_4$. The ether was evaporated and the crude 1-Phenyl-but-3-ene-1-ol (14.320 g, 0.097 mol) was obtained (% Yeild = 96.8 %). $^1$H NMR, $^{13}$C NMR, IR spectra were taken in CDCl$_3$. The spectroscopic data match with the reported literature.$^{34-38}$

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 2.431 (t, J = 6.8 Hz, 2H, -CH$_2$), 2.666 (br s, 1H, -OH), 4.618 (t, J = 6.8 Hz, 1H, -CH), 5.081 – 5.132 (m, 2H, =CH$_2$), 5.711 – 5.814 (m, 1H, =CH), 7.210 – 7.316 (m, 5H, Ph-H) ppm.; IR (CDCl$_3$): 3371 (br, OH), 3076, 3030, 3007, 2979, 2933, 2906, 1950, 1875, 1811, 1641, 1603, 1494, 1454, 1433, 1416, 1358, 1316, 1198, 1115, 1077, 1048, 1000, 916, 871, 830, 758, 700, 643, 609, 538 cm$^{-1}$. 

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**Synthesis of 1-Phenyl-but-3-ene-1-one**

4 g of CrO₃ (0.04 mol) was dissolved in 4 mL of H₂SO₄ (12N) acid and slurry was made. 12 mL of water was added to the slurry and mixed further to make the Jones reagent (H₂CrO₄). 14.320 g (0.097 mol) of 1-Phenyl-but-3-ene-1-ol was dissolved in 100 mL of cold acetone and then ¼ pipette of H₂CrO₄ was added to the 1-Phenyl-but-3-ene-1-ol at a time while stirring at 0 °C until the green color change to orange. Then the solution was filtered and the solvent was removed. The crude was dissolved in 100mL of ether and extracted with 100 mL of water. Then the ether layer was washed once with water (100 mL) and then with saturated NaHCO₃ (100 mL) and then with brine (100 mL). Anhydrous MgSO₄ was added to remove traces of H₂O. The solvent was removed to get 1-Phenyl-but-3-ene-1-one (11.088 g, 0.076 mol) (% Yeild = 78.5 %).

**1H NMR, 13C NMR, IR spectra were taken in CDCl₃. The spectroscopic data match with the reported literature.**

1H NMR, 13C NMR, IR spectra were taken in CDCl₃. The spectroscopic data match with the reported literature.

1H NMR (CDCl₃, 400 MHz): δ 3.711 (d, J = 6.8 Hz, 2H, -CH₂-), 5.162 – 5.208 (m, 2H =CH₂), 6.021 – 6.123 (m, 1H, =CH), 7.413 (t, J = 7.6 Hz, 2H, Ph-H), 7.515 (t, J = 7.6, Hz, 1H, Ph-H), 7.934 (d, J = 7.2 Hz, 2H, Ph-H) ppm.; IR (CDCl₃): 3081, 1683 (s, C=O), 1645, 1598, 1581, 1449, 1425, 1395, 1334, 1276, 1210, 1180, 1004, 922, 755, 690, 617, 593 cm⁻¹.

**Synthesis of 1a (1-Phenyl-but-2-ene-1-one)**

11.088 g (0.076 mol) of 1-Phenyl-but-3-ene-1-one was dissolved in 100 mL of methanol and 3 - 4 drops of triethylammine were added. The reaction mixture was allowed to stir overnight (20 hours). The solvent was removed and it was extracted with ether and H₂O. Then
the ether layer was dried with anhydrous MgSO₄. Then ¹H NMR and IR were taken. 20% Ethyl acetate: 80% Hexane flash column was ran to purify the 1a (1-Phenyl-but-2-ene-1-one) (4.530 g, 0.031 mol) (% Yeild = 31 %). Then a ¹H NMR, ¹³C NMR and IR were taken again for pure 1a. The spectroscopic data match with the reported literature.⁴⁰⁻⁴³

¹H NMR (CDCl₃, 400 MHz): δ 1.984 (d, J = 6.8 Hz, 3H, -CH₃), 6.900 (d, J = 15.2 Hz, 1H, =CH), 7.034 – 7.123 (m, 1H, =CH), 7.449 (t, J = 7.4 Hz, 2H, Ph-H), 7.537 (t, J = 7.4 Hz, 1H, Ph-H), 7.918 (d, J = 8 Hz, 2H, Ph-H) ppm.; ¹H NMR (CD3OD, 400 MHz): δ 2.002 (d, J = 5.2 Hz, 3H, -CH₃), 7.007 – 7.077 (m, 2H, =CH), 7.476 – 7.612 (m, 3H, Ph-H), 7.948 (d, J = 8.8 Hz, 2H, Ph-H) ppm.; ¹³C NMR (CDCl₃, 100 MHz): δ 18.60, 127.56, 128.51, 132.58, 137.94, 145.04, 190.78 ppm.; IR (CDCl₃): 3058, 2912, 1702, 1673 (s, C=O), 1598, 1579, 1448, 1332, 1297, 1220, 1179, 1038, 1024, 965, 918, 830, 759, 693, 664 cm⁻¹. GC/MS (EI): m/z: 146 (M⁺), 131, 117, 105 (100%), 77, 69. UV/Visible λmax (ε): 329 nm (ε = 109 M⁻¹ cm⁻¹), 279 nm (ε = 1.08 x 10⁴ M⁻¹ cm⁻¹), 279 nm (ε = 1.14 x 10⁴ M⁻¹ cm⁻¹).

**Synthesis of 1-(4-Methoxy-phenyl)-but-3-ene-1-ol**

13.50 g (0.1 mol) of anisaldehyde was mixed in 25 mL of DMF. Allyl bromide 14.4 g (0.12 mol, 1.2 eq) was added to the above mixture and then 40 g of SnCl₂ (0.2 mol, 2 eq) was added. Then 50 mL of DMF was added to the mixture and then NaI 20g (0.134 mol, 1.3 eq) was added one spatula at a time very slowly for a period of 10 min. Then another 25mL of DMF was added to the mixture and allowed to stir for overnight (20 hours). 30g of NH₄F was dissolved in 100 mL of H₂O and added to the mixture to quench the reaction. 100 mL of ethyl ether was
added to the quenched mixture and allowed to stir for further 30 min. Then the ether layer was extracted and washed twice with water. The ether extract was dried using anhydrous MgSO₄. The ether was evaporated and the crude 1-(4-Methoxy-phenyl)-but-3-ene-1-ol (15.554 g, 0.087 mol) was obtained (% Yeild = 88 %). A ¹H NMR, ¹³C NMR, IR spectra were taken in CDCl₃. The spectroscopic data match with the reported literature.³⁷,³⁸

¹H NMR (CDCl₃, 400 MHz) : δ 2.018 (d, J = 2.8 Hz, 1H, -OH), 2.496 (t, J = 6.8 Hz, 2H, -CH₂), 3.801 (s, 3H, -OCH₃), 4.683 (dt, J = 6.4 Hz, J = 2.4 Hz, 1H, -CH), 5.114 - 5.11675 (m, 2H, =CH₂), 5.744 – 5.848 (m, 1H, =CH), 6.882 (d, J = 8.8 Hz, 2H, Ph-H), 7.279 (d, J = 8.8 Hz, 2H, Ph-H) ppm.; ¹³C NMR (CDCl₃, 100 MHz): δ 43.768, 55.289, 72.989, 113.800, 118.247, 127.089, 134.634, 136.067, 159.040 ppm.; IR (CDCl₃) : 3404 (br, OH), 3075, 3002, 2934, 2836, 1640, 1612, 1586, 1514, 1464, 1442, 1302, 1248, 1175, 1106, 1036, 917, 872, 832, 768, 629, 586, 548 cm⁻¹.

**Synthesis of 1-(4-Methoxy-phenyl)-but-3-ene-1-one**

4 g of CrO₃ (0.04 mol) was dissolved in 4 mL of H₂SO₄ (12N) acid and slurry was made. 12 mL of water was added to the slurry and mixed further to make the Jones reagent (H₂CrO₄). 15.554 g (0.087 mol) of 1-(4-Methoxy-phenyl)-but-3-ene-1-ol was dissolved in 100 mL of cold acetone and then ¼ pipet of H₂CrO₄ was added to the 1-(4-Methoxy-phenyl)-but-3-ene-1-ol at a time while stirring at 0 °C until the green color change to orange. Then the solution was filtered and the solvent was removed. The crude was dissolved in 100mL of ether and extracted with 100 mL of water. Then the ether layer was washed once with water (100 mL) and then with saturated NaHCO₃ (100 mL) and then with brine (100 mL). Anhydrous MgSO₄ was added to remove
traces of H₂O. The solvent was removed to get 1-(4-Methoxy-phenyl)-but-3-ene-1-one (4.267 g, 0.024 mol) (% Yield = 27.7 %). ¹H NMR, ¹³C NMR, IR spectra were taken in CDCl₃. The spectroscopic data match with the reported literature.³⁷, ³⁹, ⁴⁴

¹H NMR (CDCl₃, 400 MHz): δ 3.708 (d, J = 6.8 Hz, 2H, -CH₂-), 3.867 (s, 3H, -OCH₃), 5.179 – 5.225 (m, 2H, =CH₂), 6.030 – 6.132 (m, 1H, =CH), 6.936 (d, J = 8.8 Hz, 2H, Ph-H), 7.950 (d, J = 8.8 Hz, 2H, Ph-H) ppm.; IR (CDCl₃): 2841, 1676 (s, C=O), 1601, 1576, 1510, 1420, 1331, 1261, 1215, 1170, 1030, 912, 834, 733, 608 cm⁻¹.

**Synthesis of 1b (1-(4-Methoxy-phenyl)-but-2-ene-1-one)**

4.267 g (0.024 mol) of 1-(4-Methoxy-phenyl)-but-3-ene-1-one was dissolved in 100 mL of methanol and 3 - 4 drops of triethylammine were added. The reaction mixture was allowed to stir overnight (20 hours). The solvent was removed and it was extracted with ether and H₂O. Then the ether layer was dried with anhydrous MgSO₄. Then ¹H NMR and IR were taken. 20% Ethyl acetate : 80% Hexane flash column was ran to purify the ⁱb (1-(4-Methoxy-phenyl)-but-2-ene-1-one) (0.808 g, 4.6 mmol) (% Yeild = 19 %). Then a ¹H NMR, ¹³C NMR and IR were taken again for pure ¹b. The spectroscopic data match with the reported literature.⁴²-⁴⁴

¹H NMR (CDCl₃, 400 MHz): δ 1.990 (d, J = 6.0 Hz, 3H, -CH₃), 3.872 (s, 3H, -OCH₃), 6.900 – 7.014 (m, 3H, =CH, Ph-H), 7.030 – 7.264 (m, 1H, =CH), 7.948 (d, J = 8.4 Hz, 2H, Ph-H) ppm.;
¹H NMR (CD₃OD, 400 MHz): δ 2.017 (d, J = 4.8 Hz, 3H, -CH₃), 3.893 (s, 3H, -OCH₃), 6.982 – 7.117 (m, 4H, 2 Ph-H, 2 =CH), 7.995 (d, J = 8.8 Hz, 2H, Ph-H) ppm.; IR (CDCl₃): 2840, 1664 (s, C=O), 1618, 1598, 1507, 1440,1335, 1299, 1259, 1224, 1170, 1024, 963, 917, 809 cm⁻¹; GC/MS
(EI): m/z: 176 (M⁺), 161, 135 (100%), 107, 92, 77, 69. UV/Visible λ max (ε): 287 nm (ε = 6.00 x 10⁴ M⁻¹ cm⁻¹), 221 nm (ε = 6.03 x 10⁴ M⁻¹ cm⁻¹).

**Synthesis of 4-(1-Hydroxybut-3-enyl)benzonitrile**

1.3162 (0.01 mol) of 4-formylbenzonitrile was mixed in 25 mL of DMF. Allyl bromide 1.4572 g (0.012 mol, 1.2 eq) was added to the above mixture and then 20.0896 g of SnCl₂ (0.1 mol, 10 eq) was added. Then 50 mL of DMF was added to the mixture and then NaI 10.04 g (0.067 mol, 6.5 eq) was added one spatula at a time very slowly for a period of 10 min. Then another 25 mL of DMF was added to the mixture and allowed to stir for overnight (20 hours). 30 g of NH₄F was dissolved in 100 mL of H₂O and added to the mixture to quench the reaction. 100 mL of ethyl ether was added to the quenched mixture and allowed to stir for further 30 min. Then the ether layer was extracted and washed twice with water. The ether extract was dried using anhydrous MgSO₄. The ether was evaporated and the crude 4-(1-Hydroxybut-3-enyl)benzonitrile (1.34 g, 7.7 mmol) was obtained (% Yeild = 77 %). A ¹H NMR, ¹³C NMR, IR spectra were taken in CDCl₃. The spectroscopic data match with the reported literature.⁴⁵,⁴⁶

¹H NMR (CDCl₃, 400 MHz): δ 2.332 (s, 1H, -OH), 2.401 – 2.475 (m, 1H, -CH₂), 2.507 – 2.589 (m, 1H, -CH₂), 4.790-4.821 (m, 1H, -CH), 5.151-5.197 (m, 2H, =CH₂), 5.726 - 5.829 (m, 1H, =CH), 7.476 (d, J = 8.4 Hz, 2H, Ph-H), 7.638 (d, J = 8.4 Hz, 2H, Ph-H) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ 43.850, 72.353, 111.171, 118.858, 119.508, 126.509, 132.247, 133.354, 149.151 ppm.; IR (CDCl₃): 3435 (br, OH), 3077, 3006, 2980, 2931, 2906, 2229 (s, C≡N), 1928, 1641, 1609, 1504, 1412, 1303, 1199, 1173, 1105, 1056, 1018, 999, 920, 873, 840, 760, 649, 630, 566 cm⁻¹.
Synthesis of 4-But-3-enoylbenzonitrile

4 g of CrO₃ (0.04 mol) was dissolved in 4 mL of H₂SO₄ (12N) acid and slurry was made. 12 mL of water was added to the slurry and mixed further to make the Jones reagent (H₂CrO₄). 1.34 g (7.7 mmol) of 4-(1-Hydroxybut-3-enyl)benzonitrile was dissolved in 100 mL of cold acetone and then ¼ pipet of H₂CrO₄ was added to the 4-(1-Hydroxybut-3-enyl)benzonitrile at a time while stirring at 0 °C until the green color change to orange. Then the solution was filtered and the solvent was removed. The crude was dissolved in 100mL of ether and extracted with 100 mL of water. Then the ether layer was washed once with water (100 mL) and then with saturated NaHCO₃ (100 mL) and then with brine (100 mL). Anhydrous MgSO₄ was added to remove traces of H₂O. The solvent was removed to get 4-But-3-enoylbenzonitrile (1.19 g, 7.0 mmol) (% Yeild = 90 %). 20% Ethyl acetate: 80% Hexane flash column was ran to purify the 4-but-3-enoylbenzonitrile. ¹H NMR, ¹³C NMR, IR spectra were taken in CDCl₃.

¹H NMR (CDCl₃, 400 MHz): δ 3.776 (d, J = 6.8 Hz, 2H, -CH₂-), 5.217 – 5.296 (m, 2H, =CH₂), 6.010 – 6.112 (m, 1H, =CH), 7.784 (d, J = 8.4 Hz, 2H, Ph-H), 8.056 (d, J = 8.4 Hz, 2H, Ph-H) ppm.; ¹³C NMR (CDCl₃, 100 MHz): δ 43.63, 116.49, 117.89, 119.57, 128.70, 129.99, 132.56, 139.45 ppm.; IR (CDCl₃): 3093, 3047, 2228 (s, C≡N), 1689 (s, C=O), 1645, 1606, 1566, 1425, 1406, 1394, 1335, 1291, 1210, 1177, 1108, 1009, 995, 936, 856, 834, 822, 769, 602, 574, 534 cm⁻¹.
Synthesis of 1c (E)-4-But-2-enoylbenzonitrile

1.19 g (7.0 mmol) of 4-But-3-enoylbenzonitrile was dissolved in 100 mL of methanol and 3 - 4 drops of triethylamine were added. The reaction mixture was allowed to stir overnight (20 hours). The solvent was removed and it was extracted with ether and H2O. Then the ether layer was dried with anhydrous MgSO4. Then 1H NMR and IR were taken. 20% Ethyl acetate: 80% Hexane flash column was ran to purify the 1c (E)-4-But-2-enoylbenzonitrile (0.92 g, 7.0 mmol) (% Yeild = 77 %). Then a 1H NMR, 13C NMR and IR were taken again for pure 1c.

1H NMR (CDCl3, 400 MHz): δ 2.035 (dd, J = 6.8 Hz, J = 1.2 Hz, 3H, -CH3), 6.860 (dd, J = 15.4 Hz, J = 1.2 Hz, 1H, =CH), 7.078 – 7.168 (m, 1H, =CH), 7.772 (d, J = 8.4 Hz, 2H, Ph-H), 7.988 (d, J = 8.4 Hz, 2H, Ph-H) ppm.; 1H NMR (CD3OD, 400 MHz): δ 2.044 (d, J = 6.4 Hz, 3H, -CH3), 7.040 (d, J = 15.6 Hz, 1H, =CH), 7.106 – 7.144 (m, 1H, =CH), 7.892 (d, J = 7.2 Hz, 2H, Ph-H), 8.090 (d, J = 6.8 Hz, 2H, Ph-H) ppm.; 13C NMR (CDCl3, 100 MHz): δ 18.79, 115.82, 118.05, 127.01, 128.88, 132.40, 141.21, 147.26, 189.36 ppm.; IR (CDCl3): 3095, 3048, 2972, 2914, 2850, 2231 (s, C≡N), 1672 (s, C=O), 1654, 1624 (s, C=C), 1560, 1442, 1405, 1375, 1332, 1293, 1220, 1177, 1107, 1073, 1040, 1017, 965 920, 864, 839, 809, 759, 663, 642, 567, 544 cm⁻¹.; GC/MS (EI): m/z : 171(M⁺), 156, 142, 130, 115, 102, 75, 69 (100%), 63, 51. UV/Visible λmax (ε): 350 nm (ε = 102 M⁻¹ cm⁻¹), 258 nm (ε = 7.5 x 10⁴ M⁻¹ cm⁻¹).
u) Photolysis of 1a-c

Product Studies of 1a in Argon-Saturated CDCl₃

A solution of 1a (~ 20 mg, 137 μmol) in CDCl₃ (2 mL) was purged with argon and photolyzed via a Pyrex filter for 1 hour at 298 K. GC analysis of the reaction mixture showed the formation of 2a (54%), with 46% of remaining starting material. The products were characterized by GC-MS chromatography and ¹H-NMR spectroscopy of the reaction mixture. The spectroscopic data match with the reported literature.⁴⁰,⁴¹

2a: ¹H NMR (CDCl₃, 400 MHz): δ 2.146 (dd, J = 7.2 Hz, J = 1.6 Hz, 3H, -CH₃), 6.399 – 6.481 (m, 1H, =CH), 6.827 (dd, J = 11.2 Hz, J = 1.6 Hz, 1H, =CH), 7.444 – 7.569 (m, 3H, Ph-H), 7.912 – 8.064 (m, 2H, Ph-H) ppm.; GC/MS (EI): m/z 145 ((M-H)+, 100%), 130, 116, 104, 77, 69, 50.

Product Studies of 1a in Oxygen-Saturated CDCl₃

A solution of 1a (~ 20 mg, 137 μmol) in CDCl₃ (2 mL) was purged with oxygen and photolyzed via a Pyrex filter for 1 hour at 298 K. GC analysis of the reaction mixture showed the formation of 2a (39%), with 61% of remaining starting material. The products were characterized by GC-MS chromatography and ¹H-NMR spectroscopy of the reaction mixture. The spectroscopic data match with the reported literature.⁴⁰,⁴¹

2a: ¹H NMR (CDCl₃, 400 MHz): δ 2.146 (dd, J = 7.2 Hz, J = 1.6 Hz, 3H, -CH₃), 6.399 – 6.481 (m, 1H, =CH), 6.827 (dd, J = 11.2 Hz, J = 1.6 Hz, 1H, =CH), 7.444 – 7.569 (m, 3H, Ph-H), 7.912 – 8.064 (m, 2H, Ph-H) ppm.; GC/MS (EI): m/z 145 ((M-H)+, 100%), 130, 127, 116, 104, 77, 69, 50.
Product Studies of 1a in Argon-Saturated CD$_3$OD

A solution of 1a (~ 20 mg, 137 μmol) in CD$_3$OD (2 mL) was purged with argon and photolyzed via a Pyrex filter for 1 hour at 298 K. GC analysis of the reaction mixture showed the formation of 2a (26%), with small amount of remaining starting material and impurities. The products were characterized by GC-MS chromatography and $^1$H-NMR spectroscopy of the reaction mixture.

2a: $^1$H NMR (CD$_3$OD, 400 MHz): $\delta$ 2.118 (d, J = 7.2 Hz, 3H, -CH$_3$), 6.475 – 6.540 (m, 1H, =CH), 6.928 (d, J = 11.6 Hz, 1H, =CH), 7.486 – 7.620 (m, 3H, Ph-H), 7.944-7.963 (m, 2H, Ph-H) ppm.; GC/MS (EI): m/z 146 (M$^+$, 100%), 131, 127, 117, 105, 77, 69, 51.

Product Studies of 1a in Oxygen-Saturated CD$_3$OD

A solution of 1a (~ 20 mg, 137 μmol) in CD$_3$OD (2 mL) was purged with oxygen and photolyzed via a Pyrex filter for 1 hour at 298 K. GC analysis of the reaction mixture showed the formation of 2a (45%), with small amount of remaining starting material and impurities. The products were characterized by GC-MS chromatography and $^1$H-NMR spectroscopy of the reaction mixture.

2a: $^1$H NMR (CD$_3$OD, 400 MHz): $\delta$ 2.118 (d, J = 5.6 Hz, 3H, -CH$_3$), 6.475 – 6.540 (m, 1H, =CH), 6.928 (d, J = 11.6 Hz, 1H, =CH), 7.486 – 7.620 (m, 3H, Ph-H), 7.944-7.963 (m, 2H, Ph-H) ppm.; GC/MS (EI): m/z 146 (M$^+$, 100%), 131, 127, 117, 105, 77, 69, 51.
Product Studies of 1b in Nitrogen-Saturated CDCl₃

A solution of 1b (~ 20 mg, 114 μmol) in CDCl₃ (2 mL) was purged with nitrogen and photolyzed via a Pyrex filter for 4 hours at 298 K. GC analysis of the reaction mixture showed the formation of 2b (38%), with small amount of remaining starting material and impurities. The products were characterized by GC-MS chromatography and ¹H-NMR spectroscopy of the reaction mixture.

2b: ¹H NMR (CDCl₃, 400 MHz): δ 2.120 (dd, J = 7.2 Hz, J= 1.6 Hz, 3H, -CH₃), 3.895 (s, 3H, -OCH₃), 6.354 – 6.401 (m, 1H, =CH), 6.794 (dd, J = 11.6 Hz, J= 1.6 Hz, 1H, =CH), 6.903 – 6.958 (m, 2H, Ph-H), 8.054 (d, J = 8.2 Hz, 2H, Ph-H) ppm.; GC/MS (EI): m/z 176 (M⁺), 161, 145, 135 (100%), 127, 115, 107, 92, 77, 69, 64.

Product Studies of 1b in Oxygen-Saturated CDCl₃

A solution of 1b (~ 20 mg, 114 μmol) in CDCl₃ (2 mL) was purged with oxygen and photolyzed via a Pyrex filter for 4 hours at 298 K. GC analysis of the reaction mixture showed the formation of 2b (26%), with small amount of remaining starting material and impurities. The products were characterized by GC-MS chromatography and ¹H-NMR spectroscopy of the reaction mixture.

2b: ¹H NMR (CDCl₃, 400 MHz): δ 2.120 (dd, J = 7.2 Hz, J= 1.6 Hz, 3H, -CH₃), 3.895 (s, 3H, -OCH₃), 6.354 – 6.401 (m, 1H, =CH), 6.794 (dd, J = 11.6 Hz, J= 1.6 Hz, 1H, =CH), 6.903 – 6.958 (m, 2H, Ph-H), 8.054 (d, J = 8.2 Hz, 2H, Ph-H) ppm.; GC/MS (EI): m/z 176 (M⁺), 161, 145, 135 (100%), 127, 115, 107, 92, 77, 69, 64.
Product Studies of 1b in Argon-Saturated CD₃OD

A solution of 1b (~ 20 mg, 114 μmol) in CD₃OD (2 mL) was purged with argon and photolyzed via a Pyrex filter for 1 hour at 298 K. GC analysis of the reaction mixture showed the formation of 2b (43%), with 1b (47%) and small amount of impurities. The products were characterized by GC-MS chromatography and ¹H-NMR spectroscopy of the reaction mixture.

2b: ¹H NMR (CD₃OD, 400 MHz): δ 2.092 (d, J = 7.2 Hz, 3H, -CH₃), 3.876 (s, 3H, -OCH₃), 6.405 – 6.488 (m, 1H, =CH), 6.904 (d, J = 11.2 Hz, 1H, =CH), 6.956 – 7.082 (m, 2H, Ph-H), 7.966 (d, J = 9.2 Hz, 2H, Ph-H) ppm.; GC/MS (EI): m/z 175 ((M-1)⁺, 100%), 159, 144, 134, 127, 115, 107, 91, 77, 63, 50.

Product Studies of 1b in Oxygen-Saturated CD₃OD

A solution of 1b (~ 20 mg, 114 μmol) in CD₃OD (2 mL) was purged with oxygen and photolyzed via a Pyrex filter for 1 hour at 298 K. GC analysis of the reaction mixture showed the formation of 2b (39%), with 1b (46%) and small amount of impurities. The products were characterized by GC-MS chromatography and ¹H-NMR spectroscopy of the reaction mixture.

2b: ¹H NMR (CD₃OD, 400 MHz): δ 2.092 (d, J = 7.2 Hz, 3H, -CH₃), 3.876 (s, 3H, -OCH₃), 6.405 – 6.488 (m, 1H, =CH), 6.904 (d, J = 11.2 Hz, 1H, =CH), 6.956 – 7.082 (m, 2H, Ph-H), 7.966 (d, J = 9.2 Hz, 2H, Ph-H) ppm.; GC/MS (EI): m/z 175 ((M-1)⁺, 100%), 159, 145, 134, 127, 115, 106, 92, 77, 68, 63, 50.
Product Studies of 1c in Argon-Saturated CDCl₃

A solution of 1c (~ 22 mg, 129 μmol) in CDCl₃ (2 mL) was purged with argon for 5 minutes and photolyzed via a Pyrex filter for 4 hours at 298 K. GC analysis of the reaction mixture showed the formation of 2c (43%), with 1c (57%) remaining starting material. The products were characterized by GC-MS chromatography and ¹H-NMR spectroscopy of the reaction mixture.

2c: ¹H NMR (CDCl₃, 400 MHz): δ 2.193 (dd, J = 7.2 Hz, J = 1.6 Hz, 3H, -CH₃), 6.523 – 6.607 (m, 1H, =CH), 6.860 (dd, J = 11.6 Hz, J = 1.6 Hz, 1H, =CH), 7.770 (d, J = 8.4 Hz, 2H, Ph-H), 8.010 (d, J = 8.4 Hz, 2H, Ph-H) ppm.; ¹³C NMR (CDCl₃, 100 MHz): δ 16.459, 115.855, 124.215, 128.669, 132.467, 132.552, 141.713, 146.683, 190.339 ppm.; GC/MS (EI): m/z 171 (M⁺, 100%), 156, 142, 130, 115, 102, 89, 75, 69, 63, 51. IR (CDCl₃): 3096, 3048, 2941, 2233 (C=N), 1665 (C=O), 1612 (C=C), 1560, 1435, 1400, 1361, 1293, 1227, 1119, 1025, 1014, 914, 866, 831, 783, 732, 708, 644, 577, 544 cm⁻¹.

Product Studies of 1c in Oxygen-Saturated CDCl₃

A solution of 1c (~ 20 mg, 117 μmol) in CDCl₃ (2 mL) was purged with oxygen for 15 minutes and photolyzed via a Pyrex filter for 4 hours at 298 K. GC analysis of the reaction mixture showed the formation of 2c (44%), with 1c (56%) remaining starting material. The products were characterized by GC-MS chromatography and ¹H-NMR spectroscopy of the reaction mixture.
Product Studies of 1c in Argon-Saturated CD$_3$OD

A solution of 1c (~ 22 mg, 129 μmol) in CD$_3$OD (2 mL) was purged with argon for 5 minutes and photolyzed via a Pyrex filter for 5.5 hours at 298 K. $^1$H NMR analysis of the reaction mixture showed the formation of 2c (45%), with 1c (55%) remaining starting material. The products were characterized by GC-MS chromatography and $^1$H-NMR spectroscopy of the reaction mixture.

Product Studies of 1c in Oxygen-Saturated CD$_3$OD

A solution of 1c (~ 22 mg, 129 μmol) in CD$_3$OD (2 mL) was purged with oxygen for 15 minutes and photolyzed via a Pyrex filter for 5.5 hours at 298 K. GC-MS analysis of the reaction mixture showed the formation of 2c (29%), with 1c (71%) remaining starting material. The
products were characterized by GC-MS chromatography and $^1$H-NMR spectroscopy of the reaction mixture.

2c: $^1$H NMR (CD$_3$OD, 400 MHz): $\delta$ 2.170 (d, J = 7.2 Hz, 3H, -CH$_3$), 6.572 – 6.661 (m, 1H, =CH), 6.972 (d, J = 11.6 Hz, 1H, =CH), 7.882 – 7.902 (m, 2H, Ph-H), 8.038 – 8.164 (m, 2H, Ph-H) ppm.; GC/MS (EI): m/z 172 ((M+1)$^+$), 130, 102 (100%), 75, 70, 51.

5. Conclusions
We have found that irradiation of 1a-c gives 2a-c. We have demonstrated from LFP that 1a-b forms 1,2-triplet biradical intermediate before forming 2a-b or 1a-b. We predict from TRIR that direct singlet reactivity of C=C chromophore of 1a form 2a at shorter wavelengths. We have demonstrated that triplet sensitized irradiation of 1a-c gives 2a-c in argon-matrices.

6. Acknowledgement
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(3) SMART v5.634 and SAINT v7.66A data collection and data processing programs, respectively. Bruker Analytical X-ray Instruments, Inc., Madison, WI; SADABS v2008/1 for the

7. References


Chapter 05

Corannulene Derivatives as a Singlet Sensitizer
ABSTRACT.

Corannulene derivatives have potential use as sensitizers. We investigated the photoreactivity of corannulene (1a) and its derivatives 2a and 3a. We used laser flash photolysis, product studies, phosphorescence and computational calculations to identify the products and intermediates formed by irradiating 1a, 2a and 3a. The Photolysis of 2a and 3a results in the formation of aldehyde derivatives. The mechanism for the formation of the aldehyde will be presented.
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**Introduction**

Corannulene is one third of fullerene, and yet there are only a limited number of studies on corannulene derivatives as a singlet sensitizer. Fullerene is a remarkable electron and energy acceptor hence they are very attractive for participating in photo-induced electron and energy transfer processes. Since, corannulene is one third of fullerene, we theorize corannulene also has very good electron and energy acceptor properties.\(^1,2\)

In this paper, we explore the potential of corannulene derivatives 2a and 3a as a singlet sensitizer or singlet oxygen generator in polar aprotic and non-polar solvents.

**Results**

**Product Studies**

Scheme 1

\[
\begin{align*}
\text{2a} & \xrightarrow{hv (>300\text{nm})} \text{4a} + \text{4a} \\
\text{CDCl}_3 & \text{4 hours, 298 K} \\
\text{Ar} & \\
\text{4a} & \xrightarrow{hv (>300\text{nm})} \text{4a} + \text{4a} \\
\text{CDCl}_3 & \text{1 hour, 298 K} \\
\text{O}_2 & \\
\end{align*}
\]

*Note: This product study was carried out once due to the harsh synthesis and purification*
Photolysis of 2a in argon-saturated chloroform-d via a Pyrex filter at 298 K yielded 4a as the major product (Scheme 1). Irradiation of 2a in oxygen-saturated chloroform-d via a Pyrex filter at 298 K also yielded 4a as the major product; however, the conversion is much faster compared to argon-saturated chloroform-d. Irradiation via Pyrex filter ensures that only the corannulene alkene absorbs the light and forms the singlet excited state of the corannulene (S\textsubscript{1C}) which then inter system crosses to the triplet excited state of the corannulene (T\textsubscript{1C}) in 2a, as corannulene alone has only a weak absorption below \(\sim\)300 nm. Although 2a is an aromatic derivative, its first and the second excited states of (T\textsubscript{1C} and T\textsubscript{2C}) are 7 – 14 kcal/mol of each other. Energy transfer from T\textsubscript{1C} to triplet O\textsubscript{2} forms the 2a and \(^1\)O\textsubscript{2}. Then 2a and \(^1\)O\textsubscript{2} reacts to give 4a.

Scheme 2

Note: This product study was carried out only once due to the harsh synthesis and purification

Photolysis of 3a in argon-saturated chloroform-d via a Pyrex filter at 298 K yielded 4a as the major product (Scheme 2) and small amounts of 5 and 6. Photolysis of 3a in oxygen-saturated
chloroform-d via a Pyrex filter at 298 K yielded 4a as the major product (Scheme 2) and small amounts of 5. Irradiation via Pyrex filter ensures that only the corannulene alkene absorbs the light and forms the singlet excited state of the corannulene \( S_{1C} \) which then inter system crosses to the triplet excited state of the corannulene \( T_{1C} \) of 3a. Although, 3a is an aromatic derivative, its first and the second excited states of \( T_{1C} \) and \( T_{2C} \) are 12 – 17 kcal/mol of each other. Energy transfer from \( T_{1C} \) to triplet \( O_2 \) forms the 3a and \( ^1O_2 \). Then 3a and \( ^1O_2 \) reacts to give 4a (Scheme 7). In addition, the photolysis also gives products due to the cleavage at \( \alpha \)-carbon to the ketone moiety which then either reacts with \( O_2 \) to give benzoic acid (5) or abstract a H to give benzaldehyde (6).

**Calculations**

To better understand the reactivity of 2a, 3a we calculated the triplet surface of 2a, 3a using the Gaussian03\(^3\) and Gaussian09 at the B3LYP level of theory and with the 6-31+G(d) basis set.\(^4,5\) We used the calculations to find identify the most favorable reaction on the triplet surface of 2a, 3a to understand the factors that control that govern the reactivity of on the triplet surface of 2a and 3a.

**Calculations of 2a**

We optimized the ground-state \( S_0 \) of 2a (Figure 1). TD-DFT calculations of 2a show that \( T_{1C} \) of 2a is located 54 kcal/mol above \( S_0 \) and has a \( (\pi,\pi^*) \) configuration where the electronic excitation is from the conjugated corannulene alkene (HOMO) moiety to corannulene moiety (LUMO) (Figure 2). Whereas \( T_{2C} \) is 61 kcal/mol above and also has a \( (\pi,\pi^*) \) configuration, where the electronic excitation is from the corannulene moiety (HOMO – 2) to itself (LUMO).
We optimized $T_{1C}$ of $2a$ and found that it is located 47 kcal/mol above $S_0$, which is considerably lower than the energy obtained by TD-DFT calculations. Inspection of the molecular orbitals in gas phase indicate that $T_{1C}$ of $2a$ has ($\pi,\pi^*$) configuration. We calculated the transition state for $T_{1C}$ of $2a$ cleaving to form biradical and found that it is located 4 kcal/mol above $T_{1C}$ of $2a$. The $T_{BR}$ of $2a$ is 51 kcal/mol above $S_0$. 

Figure 1: Optimized $S_0$ of $2a$, $T_{1C}$ of $2a$, $T_{BR}$ of $2a$ and $4a$. 
Figure 2: Molecular orbitals of 2a in gas phase calculated from $S_0$ of 2a

We also calculated the triplet energy surface for addition of two triplet oxygen (Scheme 3) and for addition of one triplet oxygen (Scheme 4) to determine the more feasible pathway of oxygen addition. Further, we also calculated the singlet energy surface for addition of two singlet oxygen (Scheme 5) and for addition of one singlet oxygen (Scheme 6).
Scheme 3 (On Triplet Surface)

Scheme 4 (On Triplet Surface)
Scheme 5 (On Singlet Surface)

Scheme 6 (On Singlet Surface)
Calculations of 3a

We optimized the ground-state ($S_0$) of $3a$ (Figure 3). TD-DFT calculations of $3a$ show that $T_{1C}$ of $3a$ is located 47 kcal/mol above $S_0$ and has a ($\pi,\pi^*$) configuration where the electronic excitation is from the conjugated sensitized corannulene alkene moiety (HOMO) to itself (LUMO) (Figure 4). Whereas $T_{2C}$ is 59 kcal/mol above and also has a ($\pi,\pi^*$) configuration, where the electronic excitation is from the corannulene moiety (HOMO – 1) to conjugated sensitized corannulene alkene moiety (LUMO).

![Figure 3: Optimized $S_0$ of $3a$.]
Figure 4: Molecular orbitals of 3a in gas phase calculated from $S_0$ of 3a

We optimized $T_{1C}$ of 3a and found that it is located 42 kcal/mol above $S_0$, which is considerably lower than the energy obtained by TD-DFT calculations. Inspection of the molecular orbitals indicate that $T_{1C}$ of 3a has $(\pi, \pi^*)$ configuration. We calculated the transition state for $T_{1C}$ of 3a cleaving to form biradical of 3a and found that it is located 4 kcal/mol above $T_{1C}$ of 3a. The $T_{BR}$ of 3a is 47 kcal/mol above $S_0$.

We propose the following mechanism for to account the formation of corannulene aldehyde (4a) (Scheme 7).
Laser Flash Photolysis of 2a

(I). In CHCl₃

We performed laser flash photolysis to support the proposed reaction mechanism for 2a. Laser flash photolysis (Excimer laser, 308 nm, 17 ns) of 2a in argon-saturated chloroform produced a transient absorption with $\lambda_{\text{max}}$ at ~360 nm (Figure 5-7). As the intensity of the band at 360 nm decrease with time, a new absorption with $\lambda_{\text{max}}$ at 480 nm was formed. We assign the absorption at 360 nm to T$_{1C}$ of 2a based on the TD-DFT calculations and kinetics. The calculated TD-DFT absorption spectrum of T$_{1C}$ of 2a in chloroform has the major electronic transfer at 489 nm ($f$=0.2303), 465 nm ($f$=0.2646) and 317 nm ($f$=0.2889) (Figure 8). The peak at 317 nm in calculated spectrum closely fits with the observed spectra. Kinetic analysis of the transient absorption further supports this assignment. The transient absorption at 360 nm in shorter time scale can be fitted into a mono-exponential function and decays with a rate constant of 4.97 x 10$^5$ s$^{-1}$ ($\tau$ = 2 μs) in argon saturated-solvent (Figure 10). We assign this absorption to the T$_{1C}$ of 2a.
In longer time scale, the transient absorption at 360 nm can be fitted into a double exponential decay with a rate constant of $5.764 \times 10^4 \text{ s}^{-1}$ ($\tau = 17.3 \mu\text{s}$). The transient absorption at 480 nm in shorter time scale can be fitted into a mono-exponential decay with a rate constant of $7.359 \times 10^4 \text{ s}^{-1}$ ($\tau = 13.6 \mu\text{s}$). We assign these transients at 360 nm and 480 nm with lifetimes of ~ 14-17 $\mu\text{s}$ to residual product formation. In longer time scale, the transient absorption at 480 nm can be fitted into a double exponential function and this absorption decays with a rate constant of $7.9 \times 10^3 \text{ s}^{-1}$ ($\tau = 126 \mu\text{s}$). We also assign this transient to the residual product formation.

1 $\mu\text{s}$ time window in Ar

**Figure 5**: Transient UV / Vis spectra of 2a (a). 0.02 – 0.30 $\mu\text{s}$ (red) (b). 0.30 – 0.94 $\mu\text{s}$ (blue) (c). 0.94 – 2.02 $\mu\text{s}$ (black) (d). 2.02 – 6.82 $\mu\text{s}$ (light green)
Figure 6: Transient UV / Vis spectra of 2a (a). 0.12 – 0.96 μs (red) (b). 0.96 – 3.44 μs (blue) (c). 3.44 – 8.52 μs (black) (d). 8.52 – 35.04 μs (light green)
Figure 7: Transient UV / Vis spectra of 2a (a). 0.12 – 0.96 μs (red) (b). 0.96 – 3.44 μs (blue) (c). 3.44 – 8.52 μs (black) (d). 8.52 – 35.04 μs (light green)

Figure 8: Calculated UV of T$_{1C}$ of 2a (red) and T$_{BR}$ of 2a (blue) in chloroform using TD-DFT level of theory with UB3LYP/6-31+G(d) basis set.
Figure 9: Calculated UV/Vis of Corannulene peroxide-radicals of 2a in chloroform using TD-DFT level of theory with UB3LYP/6-31+G(d) basis set.

1 μs time window at 360 nm in Ar

\[ k_1 = 4.967 \times 10^5 \text{ s}^{-1} \pm 1.16 \times 10^4 \text{ s}^{-1}, \tau = 2.0 \pm 0.1 \text{ μs} \]
10 µs time window at 360nm in Ar

\[
k_1 = 4.417 \times 10^5 \text{ s}^{-1} \pm 4.24 \times 10^4 \text{ s}^{-1}, \quad \tau = 2.3 \pm 0.2 \mu\text{s}
\]

\[
k_2 = 5.764 \times 10^4 \text{ s}^{-1} \pm 5.72 \times 10^3 \text{ s}^{-1}, \quad \tau = 17.3 \pm 1.7 \mu\text{s}
\]

10 µs time window at 480nm in Ar

\[
k_1 = 7.359 \times 10^4 \text{ s}^{-1} \pm 4.44 \times 10^3 \text{ s}^{-1}, \quad \tau = 13.6 \pm 0.8 \mu\text{s}
\]
25 μs time window at 480nm in Ar

Figure 10: Kinetics of 2a in CHCl₃. (a). 1 μs time window at 360nm in Ar. (b). 10 μs time window at 360nm in Ar. (c). 10 μs time window at 480nm in Ar. (d). 25 μs time window at 480nm in Ar.

In oxygen-saturated solutions the intensity of the band around ~360 nm is decreased and the rate constant for the decay is increased to 2.620 × 10⁵ s⁻¹ (Figure 13). Thus oxygen quenches T₁C of 2a. Furthermore, the intensity at 480 nm for O₂ saturated solutions of 2a showed a higher absorption. We hypothesize that this is due to higher amount of formation of 2a-O₂ complexes (Figure 11-13). This means that the precursor to the formation of 2a-O₂ complexes could also be that of T₁C of 2a.
Quenching with $O_2$

**Figure 11:** Transient UV / Vis spectra for quenching studies of $2a$ (a). 0.02 – 0.30 $\mu$s (red) (b).

0.02 – 0.30 $\mu$s (blue)

**Figure 12:** Transient UV / Vis spectra for quenching studies of $2a$ (a). 0.02 – 0.30 $\mu$s (red) (b).

0.02 – 0.30 $\mu$s (blue)
Rates in O₂ are;

\[ k_1 = 2.620 \times 10^5 \, \text{s}^{-1}, \tau = 3.8 \, \mu\text{s} \]

\[ k_2 = 2.663 \times 10^4 \, \text{s}^{-1}, \tau = 37.6 \, \mu\text{s} \]

Figure 13: Quenching kinetics of 2a in CHCl₃. (a). 10 μs time window at 360nm in Ar (red) & O₂ (blue). (b). 25 μs time window at 480nm in Ar (red) & O₂ (blue).
(II). In Hexane

To find out the affect from the solvent, we further performed laser flash photolysis in hexane to support the proposed reaction mechanism for 2a. Laser flash photolysis (Excimer laser, 308 nm, 17 ns) of 2a in argon-saturated hexane produced a transient absorption with $\lambda_{\text{max}}$ at ~ 340 nm, 410 nm, 480 nm and 520 nm (Figure 14-15). We assign the absorption at 340 nm, 410 nm, 480 nm and 520 nm to $T_{1C}$ of 2a, based on the TD-DFT calculations and kinetics. The calculated TD-DFT absorption spectrum of $T_{1C}$ of 2a in cyclohexane (Note: cyclohexane was used for the solvent for calculations as there was no solvent by the name “hexane” in Gaussian03 or Gaussian09, and cyclohexane is also a non-polar solvent bearing much closer properties to hexane) has the major electronic transfer at 487 nm ($f$=0.2540), 466 nm ($f$=0.2358), 373 nm ($f$=0.0371), 344 nm ($f$=0.0347), 340 nm ($f$=0.0459), 331 nm ($f$=0.0637) and 317 nm ($f$=0.2100) (Figure 16). Nearly all the calculated absorptions fit well with the observed peaks except for the calculated peak of 317 nm; this is because the electronic transition takes place from HOMO to a Rydberg state (see supporting information).
1 μs time window in Ar

![Graph showing transient UV/Vis spectra](image)

**Figure 14:** Transient UV/Vis spectra of 2a in hexane (a). 0.02 – 0.30 μs (red) (b). 0.30 – 0.94 μs (blue) (c). 0.94 – 2.02 μs (black) (d). 2.02 – 6.82 μs (light green)

5 μs time window in Ar

![Graph showing transient UV/Vis spectra](image)

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Figure 15: Transient UV/Vis spectra of 2a in hexane (a). 0.12 – 0.96 μs (red) (b). 0.96 – 3.44 μs (blue) (c). 3.44 – 8.52 μs (black) (d). 8.52 – 35.04 μs (light green)

Figure 16: Calculated UV/Vis of T_{1C} of 2a (red) and T_{BR} of 2a (blue) in cyclohexane using TD-DFT level of theory with UB3LYP/6-31+G(d) basis set.

The transient absorptions at 350 nm and at 400 nm grow with rate constants of $1.305 \times 10^7$ s$^{-1}$ ($\tau = 77$ ns) and $1.674 \times 10^7$ (\tau = 60 ns) respectively in argon saturated-solvent, nearly with same growth times (Figure 17). This is due to the formation of T_{1C} of 2a from S_{1C} of 2a. The absorbance at 350 nm decays with a rate constant of $9.567 \times 10^4$ s$^{-1}$ ($\tau = 10.4$ μs) and this is due to the residual product formation. The absorbance at 400 nm decays bi-exponentially with rate
constants of $5.631 \times 10^5$ s$^{-1}$ ($\tau = 1.8 \mu$s) and $1.051 \times 10^5$ s$^{-1}$ ($\tau = 9.5 \mu$s) respectively. The faster decay is T$_{1C}$ of 2a and the slower decay is due to the residual product formation. This assignment is also based on the comparison with calculated TD-DFT. Furthermore, the absorbance at 500 nm decays with a rate constant of $9.292 \times 10^4$ s$^{-1}$ ($\tau = 10.8 \mu$s) and this is the also due to the residual product formation. The similar lifetimes at 350 nm, 400 nm and 500 nm confirms that all these absorptions are due to T$_{1C}$ of 2a, which is also comparable with the calculated UV/Vis.

In oxygen-saturated solutions, the intensity of the bands around 350 nm, 400nm and 500nm quenched completely (Figure 18-19), and this confirms that precursor to the products is T$_{1C}$ of 2a in non-polar hexane solutions.

100 ns time window at 350nm in Ar

$k_1 = 1.305 \times 10^7$ s$^{-1}$ $\pm$ $3.73 \times 10^5$ s$^{-1}$, $\tau = 77 \pm 2$ ns
10 µs time window at 350nm in Ar

\[ k_1 = 9.567 \times 10^4 \text{ s}^{-1} \pm 7.90 \times 10^2 \text{ s}^{-1}, \quad \tau = 10.4 \pm 0.1 \text{ µs} \]

50 ns time window at 400nm in Ar

\[ k_1 = 1.674 \times 10^7 \text{ s}^{-1} \pm 3.01 \times 10^5 \text{ s}^{-1}, \quad \tau = 60 \pm 1 \text{ ns} \]
$1 \mu s$ time window at 400nm in Ar

$k_1 = 4.338 \times 10^5 \text{ s}^{-1} \pm 7.59 \times 10^3 \text{ s}^{-1}, \tau = 2.3 \pm 0.04 \mu s$

$5 \mu s$ time window at 400nm in Ar

$k_1 = 5.631 \times 10^5 \text{ s}^{-1} \pm 2.33 \times 10^4 \text{ s}^{-1}, \tau = 1.8 \pm 0.1 \mu s$

$k_2 = 1.051 \times 10^5 \text{ s}^{-1} \pm 3.49 \times 10^3 \text{ s}^{-1}, \tau = 9.5 \pm 0.3 \mu s$
10 μs time window at 500nm in Ar

$k_1 = 9.292 \times 10^4 \text{ s}^{-1} \pm 1.09 \times 10^3 \text{ s}^{-1}$, $\tau = 10.8 \pm 0.1 \mu\text{s}$

**Figure 17:** Kinetics of 2a in hexane. (a) 100 ns time window at 350nm in Ar. (b) 10 μs time window at 350nm in Ar. (c) 50 ns time window at 400 nm in Ar. (d) 1 μs time window at 400 nm in Ar. (e) 5 μs time window at 400 nm in Ar. (f) 10 μs time window at 500 nm in Ar.

**Quenching with O$_2$**
Figure 18: Transient UV / Vis spectra of 2a for quenching studies of T$_{1C}$ of 2a (a). In Ar (red) (b). In O$_2$μs (blue)

![Graph showing transient UV/Vis spectra](image)

Figure 19: Quenching kinetics of 2a in Hexane. (a). 5 μs time window at 400nm in Ar (red). (b). 5 μs time window at 400nm in O$_2$ (blue).

![Graph showing quenching kinetics](image)

Laser Flash Photolysis of 3a

(i). In CHCl$_3$

We performed laser flash photolysis to support the proposed reaction mechanism for 3a. Laser flash photolysis (Excimer laser, 308 nm, 17 ns) of 3a in argon-saturated chloroform produced a transient absorption with $\lambda_{\text{max}}$ at $\sim$360 nm (Figure 20-21). The absorption at 360nm was only visible at very low time window. As the intensity of the band at 360 nm decrease with time, a new absorption with $\lambda_{\text{max}}$ at 540 nm was formed (Figure 22). We assign the absorption at 540 nm to T$_{1C}$ of 3a, based on the TD-DFT calculations and kinetics. The calculated TD-DFT
absorption spectrum of $T_{1C}$ of 3a in chloroform has the major electronic transfer at 590 nm ($f=0.0372$), 544 nm ($f=0.9310$), 398 nm ($f=0.0330$), 388 nm ($f=0.0869$), 334 nm ($f=0.0551$) and 319 nm ($f=0.2359$) (Figure 24), which fits well with the observed peak at 540 nm, 420 nm and 360 nm.

100 ns time window in Ar

Figure 20: Transient UV / Vis spectra of 3a in CHCl$_3$ (a). 0.00 – 0.06 $\mu$s (red) (b). 0.06 – 0.16 $\mu$s (blue) (c). 0.16 – 0.29 $\mu$s (black) (d). 0.29 – 0.65 $\mu$s (light green)
Figure 21: Expanded Transient UV / Vis spectra of 3a in CHCl₃ from 350 nm to 400 nm (a). 0.00 – 0.06 μs (red) (b). 0.06 – 0.16 μs (blue) (c). 0.16 – 0.29 μs (black) (d). 0.29 – 0.65 μs (light green)

1 μs time window in Ar
Figure 22: Transient UV / Vis spectra of 3a in CHCl₃ (a). 0.02 – 0.28 μs (red) (b). 0.28 – 0.82 μs (blue) (c). 0.82 – 1.73 μs (black) (d). 1.73 – 7.24 μs (light green)

1 μs time window in Ar

![Graph showing absorbance vs. wavelength for different time windows]

Figure 23: Transient UV / Vis spectra of 3a in CHCl₃ (a). 0.02 – 0.28 μs (red) (b). 0.28 – 0.82 μs (blue) (c). 0.82 – 1.73 μs (black) (d). 1.73 – 7.24 μs (light green)

![Graph showing dwell time vs. wavelength for different wavelengths]
**Figure 24:** Calculated UV of T$_{1C}$ of 3a (red) in CHCl$_3$ using TD-DFT level of theory with UB3LYP/6-31+G(d) basis set.

The transient UV/Vis of 3a showed also showed a broad absorption from 380 nm to 600 nm (Figure 22). Kinetic studies shows that the transient absorption at 540 nm decays with a rate constants of $6.67 \times 10^6$ s$^{-1}$ ($\tau = 150$ ns) and $4.661 \times 10^5$ s$^{-1}$ ($\tau = 2.1$ μs) in argon saturated-chloroform (Figure 25). We hypothesize the faster decay is the decay of T$_{1K}$ of 3a and the slower decay is the decay of T$_{1C}$ of 3a. Kinetics in longer time periods shows that the absorption at 540 nm has a bi-exponential nature. The faster decay has a rate constant of $9.229 \times 10^4$ s$^{-1}$ ($\tau = 13.1$ μs) and we assign this decay to the residual product formation. The slower decay has a rate constant of $7.725 \times 10^3$ s$^{-1}$ ($\tau = 129$ μs) and this decay is also attributed to the formation of photoproducts.

In oxygen-saturated solutions and in shorter time interval, the intensity of the peaks at 360 nm and 540 nm has been quenched whereas the absorptions from 400 nm – 480 nm was unaffected. In longer time intervals, the broad absorption band from 380 nm to 600 nm is mostly quenched (Figure 26-28), and this confirms that we mainly see T$_{1C}$ of 3a in chloroform solutions. Kinetics in oxygen saturated solutions at 540 nm further shows that there is a long decay although the intensity is reduced. The intensity reduction is due to the quenching of T$_{1C}$ of 3a and T$_{1K}$ of 3a.

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540 nm, 500 ns time window in Ar

\[ k_1 = 6.667 \times 10^6 \text{ s}^{-1} \pm 6.1 \times 10^5 \text{ s}^{-1}, \tau = 150 \pm 14 \text{ ns} \]

\[ k_2 = 6.715 \times 10^5 \text{ s}^{-1} \pm 1.32 \times 10^5 \text{ s}^{-1}, \tau = 1.5 \pm 0.3 \mu\text{s} \]

540 nm, 1 \mu s time window in Ar

\[ k_1 = 4.661 \times 10^5 \text{ s}^{-1} \pm 6.28 \times 10^3 \text{ s}^{-1}, \tau = 2.1 \pm 0.3 \mu\text{s} \]
540 nm, 50 μs time window in Ar

\[ k_1 = 7.577 \times 10^4 \text{ s}^{-1} \pm 7.41 \times 10^3 \text{ s}^{-1}, \tau = 13.1 \pm 1.3 \mu s \]

\[ k_2 = 4.028 \times 10^3 \text{ s}^{-1} \pm 9.47 \times 10^2 \text{ s}^{-1}, \tau = 248.3 \pm 58.4 \mu s \]

**Figure 25**: Kinetics of 3a at 540 nm in CHCl₃ and in Ar (a). In 500 ns time window (b). 1 μs time window (c). 50 μs time window
Quenching Studies for 3a in CHCl₃

100 ns time window

**Figure 26**: Quenching studies of 3a in CHCl₃ (a). In Ar from 0.00 – 0.06 μs (red) (b). In O₂ from 0.00 – 0.06 μs (blue)

1 μs time window

**Figure 27**: Quenching studies of 3a in CHCl₃ (a). In Ar from 0.02 – 0.28 μs (red) (b). In O₂ from 0.02 – 0.27 μs (blue)
540 nm, 50 ns time window in O₂

\[ k_1 = 2.826 \times 10^7 \text{ s}^{-1} \pm 5.06 \times 10^5 \text{ s}^{-1}, \ \tau = 35.4 \pm 0.6 \text{ ns} \]

**Figure 28:** Kinetics of 3a at 540 nm, 50 ns time window in CHCl₃ and in O₂

540 nm, 10 μs time window

**Figure 29:** Quenching kinetics of 3a in CHCl₃. (a). 10 μs time window at 540 nm in Ar (red).
(b). 10 μs time window at 540 nm in O₂ (blue).
(II). In Hexane

To find out the solvent effect on the photochemistry of 3a, we further performed laser flash photolysis in hexane to support the proposed reaction mechanism for 3a. Laser flash photolysis (Excimer laser, 308 nm, 17 ns) of 3a in argon-saturated hexane produced a transient absorption with \( \lambda_{\text{max}} \) at ~520 nm (Figure 30-33). The other major absorptions were at \( \lambda_{\text{max}} \) at 450 nm and 360.

100 ns time window in Ar

![Graph showing transient UV/Vis spectra of 3a in Hexane](image)

**Figure 30**: Transient UV/Vis spectra of 3a in Hexane (a). 0.00 – 0.04 μs (red) (b). 0.04– 0.10 μs (blue) (c). 0.10 – 0.21 μs (black) (d). 0.21 – 0.60 μs (light green)
1 μs time window in Ar

Figure 31: Transient UV / Vis spectra of 3a in hexane (a). 0.02 – 0.22 μs (red) (b). 0.22 – 0.70 μs (blue) (c). 0.70 – 1.70 μs (black) (d). 1.70 – 7.34 μs (light green)

1 μs time window in Ar
**Figure 32**: Expanded transient UV / Vis spectra of 3a in hexane (a). 0.02 – 0.22 μs (red) (b). 0.22 – 0.70 μs (blue) (c). 0.70 – 1.70 μs (black) (d). 1.70 – 7.34 μs (light green) 5 μs time window in Ar

**Figure 33**: Transient UV / Vis spectra of 3a in hexane (a). 0.12 – 0.56 μs (red) (b). 0.56 – 2.04 μs (blue) (c). 2.04 – 5.68 μs (black) (d). 5.68 – 37.48 μs (light green)
Figure 34: Calculated UV of T$_{1C}$ of 3a (red) in Cyclohexane using TD-DFT level of theory with UB3LYP/6-31+G(d) basis set.

The transient UV/Vis of 3a showed the major $\lambda_{max}$ ~ 520nm. We assign this absorption to the T$_{1C}$ of 3a based on the similarity of this transient spectrum with the calculated absorption spectrum of 3a in cyclohexane. The calculated TD-DFT absorption spectrum of T$_{1C}$ of 3a in cyclohexane has the major electronic transfer at 586 nm ($f=0.0293$), 534 nm ($f=0.9218$), 398 nm ($f=0.0363$), 385 nm ($f=0.0962$), 342 nm ($f=0.0438$), 334 nm ($f=0.0433$) and 318 nm ($f=0.2529$), which fits well with the observed spectra.

The transient absorptions at 520 nm grow with rate constant of $1.305 \times 10^7$ s$^{-1}$ ($\tau = 77$ ns) in argon saturated-hexane (Figure 35). This is due to the formation of T$_{1C}$ of 3a from S$_{1C}$ of 3a. The absorbance at 520 nm decays with a rate constant of $6.421 \times 10^5$ s$^{-1}$ ($\tau = 1.6 \mu$s) and this is the decay of T$_{1C}$ of 3a. This assignment is based on the comparison with calculated TD-DFT.

520 nm, 50 ns time window in Ar
\[ k_1 = 1.305 \times 10^7 \text{ s}^{-1} \pm 3.5 \times 10^5 \text{ s}^{-1}, \tau = 77 \pm 2 \text{ ns} \]

520 nm, 1 \( \mu \text{s} \) time window in Ar

\[ k_1 = 6.421 \times 10^5 \text{ s}^{-1} \pm 6.81 \times 10^3 \text{ s}^{-1}, \tau = 1.6 \pm 0.02 \mu \text{s} \]

540 nm, 1 \( \mu \text{s} \) time window in Ar

\[ k_1 = 5.272 \times 10^5 \text{ s}^{-1} \pm 5.46 \times 10^3 \text{ s}^{-1}, \tau = 1.9 \pm 0.02 \mu \text{s} \]
**Figure 35:** Kinetics of 3a at in hexane and in Ar (a). At 360 nm, 25 μs time window (b). At 520 nm, 50 ns time window (c). At 520 nm, 1 μs time window (d). At 540 nm, 1 μs time window.

**Quenching Studies**

In oxygen-saturated solutions, the intensity of the band around 520 nm quenched completely (Figure 36-40), and this confirms that we observe T\textsubscript{1C} of 3a at 520 nm. Further, we also observed the quenching at 360 nm. This is due to the quenching of T\textsubscript{1C} of 3a, which is the precursor to the photoproduct formation.

100 ns time window

**Figure 36:** Quenching studies of T\textsubscript{1C} of 3a in hexane (a). In Ar from 0.00 – 0.04 μs (red) (b). In O\textsubscript{2} from 0.00 – 0.04 μs (blue)
1 μs time window

**Figure 37:** Quenching studies of $T_{1C}$ of 3a in hexane (a). In Ar from 0.02 – 0.22 μs (red) (b). In O$_2$ from 0.02 – 0.21 μs (blue)

5 μs time window

**Figure 38:** Quenching studies of $T_{1C}$ of 3a in hexane (a). In Ar from 0.12 – 0.56 μs (red) (b). In O$_2$ from 0.12 – 0.64 μs (blue)
520 nm, 50 ns time window

![Graph](image)

**Figure 39:** Quenching kinetics of $T_{1C}$ of 3a in Hexane. (a). 50 ns time window at 520nm in Ar (red). (b). 50 ns time window at 520nm in O$_2$ (blue).

520 nm, 1 μs time window

![Graph](image)

**Figure 40:** Quenching kinetics of $T_{1C}$ of 3a in Hexane. (a). 1 μs time window at 520nm in Ar (red). (b). 1 μs time window at 520nm in O$_2$ (blue).
Fluorescence and Phosphorescence

We measured the fluorescence spectrum of $2a$ at 298 K (Figure 41). It shows a broad absorption from 420 nm to 580 nm with the onset $\sim$402 nm, which attributes for 71 kcal/mol. This is the energy of $S_{1C}$ of $2a$ where the calculated energy of $S_{1C}$ of $2a$ using TD-DFT is 76 kcal/mol.

![Fluorescence spectrum of 2a at 298 K in CH$_2$Cl$_2$](image)

**Figure 41**: Fluorescence spectrum of $2a$ at 298 K in CH$_2$Cl$_2$

We also measured the phosphorescence spectrum of $2a$ at 77 K in an ethanol matrix with a time delay of 5 ms over a time window of 50 ms (Figure 42). The phosphorescence spectra of 1.8 mM $2a$ shows that the (0,0) transition is at 484 nm which corresponds to 59 kcal/mol with 300 nm excitation (Figure 42a). The excitation at 260 nm resulted a (0,0) transition at 494 nm which corresponds to 58 kcal/mol. (Figure 42b) The calculated energy of $T_{1C}$ of $2a$ using TD-DFT is 54 kcal/mol which is in close agreement with the experimental value of $T_{1C}$ of $2a$. We theorize the broad shoulder at $\sim$450 nm is due to delayed fluorescence.
Phosphorescence spectrum of 2a in ethanol matrix at 77 K excited at 300 nm

(0,0) = 484 nm = 59 kcal/mol

Phosphorescence spectrum of 2a in ethanol matrix at 77 K excited at 260 nm

(0,0) = 494 nm = 58 kcal/mol
The phosphorescence spectra of 1.8 mM 3a shows that the (0,0) transition is at 486 nm which corresponds to 59 kcal/mol with 300 nm excitation (Figure 43a). The excitation at 260 nm resulted in two (0,0) transitions. One electronic transition is at 376 nm which corresponds to 76 kcal/mol (Figure 43b). We think this is due to the electron transition from acetophenone chromophore. The other transition is at 494 nm which corresponds to 58 kcal/mol. We think this electron transition is from the Corannulene alkene chromophore. The calculated energy of T$_{1C}$ of 3a using TD-DFT is 47 kcal/mol where as the calculated energy of T$_{2C}$ of 3a using TD-DFT is 61 kcal/mol. T$_{2C}$ of 3a is in close agreement with the second experimental (0,0) band of 3a. Further, this broad absorption shoulder at 450 nm could also be due to the delayed fluorescence.
Phosphorescence spectrum of 3a in ethanol matrix at 77 K excited at 260 nm

![Phosphorescence spectrum of 3a in ethanol matrix at 77 K excited at 260 nm](image)

**Figure 43**: Phosphorescence spectrum of 3a in ethanol matrix at 77 K (a) Excited at 300 nm (b) Excited at 260 nm

**Discussion**

Irradiation of 2a and 3a in chloroform-d in Ar saturated solutions yielded corannulene aldehyde, whereas irradiation of 2a and 3a in chloroform-d in O₂ saturated solutions yielded corannulene aldehyde as the major product and benzoic acid and benzaldehyde as the minor products.

LFP studies showed that there are two main intermediates both in chloroform and in hexane which we attributed to T₁C of 2a and 3a; and to TBR of 2a and 3a. In argon saturated-CHCl₃, 2a showed the formation of T₁C of 2a, TBR of 2a and also 2a-O₂ complexes. Only T₁C of 2a was quenched in oxygen saturated-chloroform solutions. However, in non-polar hexane...
solutions, we only observe T\textsubscript{1C} of 2a. This was completely quenched by triplet O\textsubscript{2}. In argon saturated-CHCl\textsubscript{3} solutions, 3a showed the formation of T\textsubscript{1C} of 3a and T\textsubscript{BR} of 3a. In oxygen saturated CHCl\textsubscript{3}, T\textsubscript{1C} of 3a was completely quenched where as the yield of T\textsubscript{BR} of 3a has reduced. In non polar hexane solutions we observed the formation of T\textsubscript{1C} of 3a from S\textsubscript{1C} of 3a and then the decay of T\textsubscript{1C} of 3a. We also observed the simultaneous growth of T\textsubscript{BR} of 3a and the decay of T\textsubscript{BR} of 3a.

We hypothesize 2a and 3a excites to its S\textsubscript{1C} of 2a-3a and then undergo ISC to form T\textsubscript{1C} of 2a and 3a. Then T\textsubscript{1C} of 2a-3a rearrange to form T\textsubscript{BR} of 2a-3a. This will react with triplet oxygen to form 2a-3a and singlet oxygen. Singlet oxygen reacts back with 2a-3a to form perox radicals of 2a and 3a. This will undergo auto-oxidation to form 4a.

Fluorescence and phosphorescence spectra of 2a and 3a were used to locate the experimental energies for S\textsubscript{1C} of 2a, T\textsubscript{1C} of 2a, T\textsubscript{1C} of 3a and T\textsubscript{1K} of 3a. The experimental energies seemed to have a good agreement with the calculated values using TD-DFT method.

**Experimental Calculations**

All geometries were optimized at B3LYP level of theory and with 6-31G+(d) basis set as implemented in the Gaussian03 and Gaussian09 programs.\textsuperscript{4, 5} All transition states were confirmed to have one imaginary vibrational frequency by analytical determination of the second derivatives of the energy with respect to internal coordinates. Intrinsic reaction coordinates\textsuperscript{6} calculations were used to verify that the located transition states corresponded to the attributed reactant and product.\textsuperscript{7, 8} The absorption spectra were calculated using time-dependent density
functional theory (TD-DFT). The effect of solvation was calculated using the self-consistent reaction field (SCRF) method with the integral equation formalism polarization continuum model (IEFPCM) with acetonitrile, methanol and dichloromethane as solvents.

**Laser Flash Photolysis.**

Laser flash photolysis was done with an Excimer laser (308 nm, 17 ns). The system has been described in detail elsewhere. A stock solution of 2a, 3a in CHCl₃ and hexane were prepared with spectroscopic grade CHCl₃ and hexane, such that the solutions had absorption between 0.3 and 0.6 at 308 nm. Typically, ~1 mL of the stock solution was placed in a 10 mm x 10 mm wide, 48 mm long quartz cuvette and was purged with argon for 5 min or oxygen for 15 min. The rates were obtained by fitting an average of three to five kinetic traces.

**Fluorescence and Phosphorescence**

The solutions of 2a (1.8 mM) and 3a (1.8 mM) solutions were prepared in ethanol. The fluorescence spectrum of 2a was obtained on a fluorimeter in CH₂Cl₂ at 298 K. The phosphorescence spectra of 2a and 3a were obtained on a phosphorimeter in ethanol glasses at 77K. The solutions were irradiated at 300 nm and 260 nm. The emission spectra recorded between 280 and 800 nm.
Preparation of 2a, 3a and 4a

Corannulene Aldehyde (4a)

To a solution of corannulene (0.10 g, 0.4 mmol) in anhydrous methylene chloride (20 mL) under a blanket of nitrogen was added \(\alpha,\alpha\)-dichloromethyl methyl ether (0.46 g, 3.2 mmol) and titanium tetrachloride (0.41 g, 2.0 mmol). The mixture was stirred at room temperature for a period of 2 h. Ice was then added and allowed to stir for an additional 20 min. The crude mixture was extracted with methylene chloride, dried with MgSO₄, filtered, evaporated under reduced pressure and purified by column chromatography using a gradient cyclohexane–CH₂Cl₂ eluent to provide a yellow solid (0.10 g, 90%).

\(^1\)H NMR (400 MHz, CDCl₃) \(\delta = 7.81-7.93\) (m, 7H), 8.39 (s, 1H), 8.69 (d, \(J=8.0\) Hz, 1H), 10.39 (s, 1H) \(^13\)C NMR (CDCl₃) \(\delta = 193.3, 139.1, 138.1, 136.5, 136.0, 135.2, 135.1, 134.9, 132.4, 131.2, 130.8, 128.9, 128.9, 128.8, 128.7, 127.8, 127.6, 127.6, 127.3, 127.2, 127.0

Corannulene Alkene (2a)

To a stirred solution of ethyltriphenylphosphonium bromide (1.46 g, 3.9 mmol) in anhydrous THF (30 mL) under a flow of argon was added n-butyl lithium (0.20 g, 3.1 mmol). The solution was allowed to stir for 30 min at room temperature. Corannulene aldehyde (0.11 g, 0.39 mmol) in anhydrous THF (30 mL) was then added. The solution was then allowed to stir for an additional 24 h at room temperature. The crude mixture was extracted with methylene chloride, dried with MgSO₄, filtered, evaporated under reduced pressure and purified by column
chromatography using a gradient cyclohexane–CH$_2$Cl$_2$ eluent to provide a yellow solid (0.04 g, 35%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 2.14 (dd, J = 6.8 Hz, 1.2 Hz, 3H), 6.59-6.64 (m, 1H) 7.03 (d, J = 15.6 Hz, 1H), 7.72-7.83 (m, 7H), 8.05 (d, J = 8.8 Hz, 1H) $^{13}$C NMR (CDCl$_3$) $\delta$ = 138.1, 136.2, 135.9, 135.7, 135.6, 135.0, 131.1, 130.9, 130.6, 130.5, 130.4, 129.1, 128.9, 127.2, 127.2, 127.2, 127.1, 127.0, 127.0, 126.8, 126.8, 125.8, 123.3, 19.2

**Corannulene Alkene with Acetophenone sensitizer (3a)**

To a stirred solution of phenacyltriphenylphosphonium bromide (0.82 g, 1.8 mmol) in anhydrous THF (30 mL) under a flow of argon was added n-butyl lithium (0.09 g, 1.4 mmol). The solution was allowed to stir for 30 min at room temperature. Corannulene aldehyde (0.05 g, 0.18 mmol) in anhydrous THF (30 mL) was then added. The solution was then allowed to stir for an additional 24 h at room temperature. The crude mixture was extracted with methylene chloride, dried with MgSO$_4$, filtered, evaporated under reduced pressure and purified by column chromatography using a gradient cyclohexane–CH$_2$Cl$_2$ eluent to provide a yellow solid (0.021 g, 30%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.56 (t, J = 7.2 Hz, 2H), 7.63 (t, J = 7.2 Hz, 1H), 7.80-7.83 (m, 6H), 7.87 (d, J = 8.8 Hz, 1H), 7.98 (d, J = 15.6 Hz, 1H) 8.13-8.17 (m, 4H), 8.44 (d, J = 15.6 Hz, 1H) $^{13}$C NMR (CDCl$_3$) $\delta$ = 190.2, 142.7, 138.3, 136.6, 136.5, 135.9, 135.7, 135.3, 134.9, 133.0, 131.5, 131.1, 131.0, 130.2, 128.9, 128.8, 128.7, 128.2, 128.0, 127.7, 127.7, 127.6, 127.3, 127.1, 127.1, 125.3, 125.3
Photolysis of 2a and 3a

Product Studies of 2a in Ar
A solution of 2a (~ 10 mg, 34 μmol) in CDCl₃ (2 mL) was purged with argon and photolyzed via a Pyrex filter for 4 hours at 298 K. GC analysis of the reaction mixture showed the formation of 4a (52%), with small amount of remaining starting material and impurities. The products were characterized by GC-MS chromatography and ¹H-NMRspectroscopy of the reaction mixture.

4a: GC/MS (EI): m/z 278 (M⁺, 100%), 250, 222, 207, 193, 133, 124, 111, 91, 73, 60.

Product Studies of 2a in O₂
A solution of 2a (~ 10 mg, 34 μmol) in CDCl₃ (2 mL) was purged with oxygen and photolyzed via a Pyrex filter for 1 hour at 298 K. GC analysis of the reaction mixture showed the formation of 4a (34%), with small amount of remaining starting material and impurities. The products were characterized by GC-MS chromatography and ¹H-NMRspectroscopy of the reaction mixture.

4a: GC/MS (EI): m/z 278 (M⁺, 100%), 250, 222, 207, 198, 191, 139, 124, 73.

Product Studies of 3a in Ar
A solution of 3a (~ 10 mg, 26 μmol) in CDCl₃ (2 mL) was purged with argon and photolyzed via a Pyrex filter for 30 min at 298 K. GC analysis of the reaction mixture showed the formation of 4a (<5%), with small amount of remaining starting material. The products were characterized by GC-MS chromatography and ¹H-NMRspectroscopy of the reaction mixture.

4a: GC/MS (EI): m/z 278 (M⁺, 100%), 249, 222, 207, 191, 179, 147, 139, 125, 98, 69.
3: GC/MS (EI): m/z 122 (M⁺, 100%), 105, 86, 77, 65, 51.

4: GC/MS (EI): m/z 105 (M-H⁺, 100%), 91, 77, 71, 51.

Product Studies of 3a in O₂
A solution of 3a (~ 10 mg, 26 µmol) in CDCl₃ (2 mL) was purged with argon and photolyzed via a Pyrex filter for 30 min at 298 K. GC analysis of the reaction mixture showed the formation of 4a (15%), with small amount of remaining starting material. The products were characterized by GC-MS chromatography and ¹H-NMR spectroscopy of the reaction mixture.

4a: GC/MS (EI): m/z 278 (M⁺, 100%), 249, 222, 207, 191, 179, 147, 139, 125, 98, 69.

5: GC/MS (EI): m/z 122 (M⁺, 100%), 105, 86, 77, 65, 51.

Conclusions
We have shown that 2a and 3a are good singlet sensitizer as shown in the proposed mechanism. We observe the T1C of 2a and 3a from LFP with lifetimes ~2 µs which then react with triplet oxygen to generate singlet oxygen. Singlet oxygen reacts with 2a and 3a to give 4a.
Acknowledgement

This work was supported by NSF and the Ohio Supercomputer Center. Acknowledgement also goes to Dr. Derek Jones for the initial synthesis of $2a$ and $3a$ and to Mr. Kelley McKissic who synthesized $2a$ during the later stage of the project.

References


Chapter 06

Reactivity of Vinyl Azides in Solution and Matrix

Isolation Studies
Reactivity of Vinyl Azides in Solution and Matrix Isolation Studies

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ABSTRACT.

We investigated the photoreactivity of vinyl azides 5a and 5b. We used product studies, laser flash photolysis (LFP, λ=308 nm, 17 ns), matrix isolation, phosphorescence and theoretical calculations and identified the products, excited states and intermediates formed by irradiating 5a and 5b. Solutions photolysis of 5a and 5b in argon-saturated chloroform-d yielded 6a-6b, 7a-b and 8a-b. Solution photolysis of 5a in oxygen-saturated chloroform-d also yields 6a, 7a and 8a whereas 5b yields 6b, 7b, 8b and 9b. We propose that upon irradiation of 5a-5b in argon-saturated solvent, they first form S_{1K} of 5a-5b which inter system crosses (ISC) to from T_{1K} of 5a-5b. T_{1K} of 5a-5b then rearrange to form T_{BR} of 5a-5b. T_{BR} of 5a-5b extrudes a N_{2} molecule to form triplet nitrene (T_{N}) of 5a, 5b. T_{N} of 5a, 5b; undergo (a). 1,2 H shift from β-carbon to α-carbon and ISC resulting 6a, 6b; (b). rotation around H-C=C-N; and ISC to form 7a, 7b; (c). ISC and cyclize to form 8a, 8b. In oxygen saturated solutions, 5b forms 6b, 7b and 8b and a small
amount of 9b. Compound 9b can be from the α-cleavage of 5b or 6b. The lifetime of T_{BR} of 5b is significantly longer than that for 5a. Matrix isolation studies of 5a resulted in the formation of 6a and 17a simultaneously, suggesting both come from a triplet excited state of 5a. Matrix isolation studies of 5b resulted in trans-cis isomerization of 5b.

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Introduction

Alkyl nitrenes are reactive intermediates which have high spin properties and long lived hence could be used in applications like potential organic magnets. Azides are a major precursor to the formation of nitrenes and in this chapter; we explored the photoreactivity of vinyl azides 5a and 5b.

Miorana showed that the thermolysis of β-azidomethacrylophenone (1A) gave 4-methyl-5-phenylisoxazole (4A) and 2-benzoylpropionitrile (3A) (Scheme 1). However, Nesmeyanov and co-workers reports that the major cyclic product is 4-methyl-5-phenyloxadazole (5A) which was formed through 2-benzoyl-2-methyl-2H-azirine (2A). The authors proposed that all the photoproducts were formed from a vinylnitrene intermediate, preferably a singlet vinyl nitrene intermediate.

Scheme 1. Thermolysis of β-azidomethacrylophenone

Isomura et al. studied the formation of 2-acyl-2H-azirines from β-acylvinyl azides. Thermolysis of 0.020 M solution of vinyl azide (1A) in toluene for 8 hours under refluxing conditions, yielded 37% of 3A, 23% of 4A and 40% of 5A. Further, when Isomura and co-
workers thermolyzed 1A in chlorobenzene solutions at 95 °C, they observed the formation of 2A [with \(^1\)H NMR signals at \(\delta\) 1.44 (3H, d J 1.5 Hz) and 9.75 (1H, q, J=1.5 Hz)] and 3A. 2A is not stable enough to be isolated; it rearranged into 4A and 5A. The percent conversion of the products formation versus the time of irradiation for 1A is shown in Figure 1.

![Figure 1. Thermolysis of 1A in chlorobenzene (From reference 1)](image)

Nesmeyanov et al. studied the effect of stereochemical and electronic factors on the thermal activation of 2-azidovinyl ketones and showed that they form the corresponding isoxazoles.\(^4\) Further, thermal activation of trans-3-azidoacrylophenones showed that it gave benzoylacetonylitrile as the major product (Scheme 2). However, thermolysis of trans-3-azido-2-methylacrylophenone yielded 4-methyl-5-phenyloxazole as the major product and smaller amount of 2-benzyolpropionitrile and traces of 4-methyl-5-phenylisoxazole.\(^4\) Further, they suggested that 2-benzyolpropionitrile is not stable, and it will partially decompose to yielded benzoic acid and hydrocyanic acid.\(^4\) In addition, they also noted that these oxidation products could also come from partial oxidation of the 4-methyl-5-phenylisoxazole.
In addition, they also suggested that in the case of non-substituted trans-2-azidovinyl ketone, it might undergo trans-cis isomerization and then yield phenylisoxazole. Thermolysis of azidovinylketones is believed to form singlet nitrene intermediate to from the products. However, it is also possible that the thermal products are formed in a concerted manner from the singlet excited state of the vinyl azides. We were interested in studying the photoreactivity of azidovinylketones using a built in triplet sensitizer and characterize the intermediates formed upon excitation. We are also interested in determining whether azidovinylketone undergo cis trans isomerization and whether they expel nitrogen to from triplet vinylnitrenes. Sato has carried out photolysis of 5a in benzene and observed the formation of benzoylacetonitrile (3-oxo-3-phenyl-propionitrile) instead of benzoylazirine (Scheme 3). Further, Sato suggested that treatment of the residual solution with sodium methoxide resulted in another crop of

**Scheme 2.** Thermal activation of trans-2-azidovinyl ketones (From Reference 4)
benzoylacetonitrile possibly through phenyl isoxazole. The ring opening of isoxazoles upon treatment with sodium methoxide has been reported previously.

**Scheme 3**: Photolysis of 3-azido-1-phenyl-propenone

Scheme 4. Product studies of 5b in argon-saturated, oxygen saturated and air-saturated chloroform-d solutions

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<th>Trial</th>
<th>Irradiation time</th>
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<th>O₂</th>
<th>Ar</th>
<th>O₂</th>
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<tr>
<td></td>
<td>6.0 hrs (GC-MS)</td>
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<td>56%</td>
<td>19%</td>
<td>22%</td>
<td>12%</td>
<td>31%</td>
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<tr>
<td>Trial 02</td>
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<td>57%</td>
<td>20%</td>
<td>19%</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>23%</td>
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<tr>
<td>Trial 03</td>
<td>0.5 hrs</td>
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<td>28%</td>
<td>33%</td>
<td>33%</td>
<td>39%</td>
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<tr>
<td></td>
<td>0.5 hrs+16 hrs Dark</td>
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<td>34%</td>
<td>38%</td>
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<tr>
<td>Trial 04</td>
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<td>50%</td>
<td>38%</td>
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Scheme 5. Product studies of 5a in argon-saturated, air-saturated and oxygen-saturated chloroform-d solutions

![Diagram](image)

<table>
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<tr>
<th></th>
<th>Irradiation time</th>
<th>Ar</th>
<th>O₂</th>
<th>Air</th>
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<td>24%</td>
<td>28%</td>
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<tr>
<td></td>
<td>2.5 hrs</td>
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<td>--</td>
<td>17%</td>
<td>--</td>
<td>18%</td>
<td>--</td>
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<tr>
<td></td>
<td>6.0 hrs</td>
<td>85%</td>
<td>90%</td>
<td>8%</td>
<td>10%</td>
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<tr>
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<td>10%</td>
<td>38%</td>
<td>27%</td>
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Note: For trial 03, there is 58% of 5a remaining after 0.25 hrs of irradiation and 25% of 5a is remaining after 0.5 hrs of irradiation

Photolysis of 5a, 5b in argon-saturated chloroform-d via Pyrex filter at 298 K yielded 6a-6b, 7a-7b and 8a-8b (Scheme 4, Figure 2-3). Further irradiation of the reaction mixture diminished the yield of products 7a, 7b and 8a, 8b whereas the amount of 6a-6b increased (Figure 2-3). We monitored the products ratio as a function of irradiation time and found that the yield of 7a, 7b and 8a, 8b decreased while the yield of 6a, 6b increased (Figure 4-6). Irradiation of 5a in oxygen-saturated chloroform-d via a Pyrex filter at 298 K also yielded 6a, 7a and 8a (Scheme 5). Irradiation of 5b in oxygen-saturated chloroform-d via a Pyrex filter at 298 K yielded 6b, 7b, 8b and 9b (Scheme 4). We also monitored the product ratio as a function of irradiation time in argon- and oxygen-saturated chloroform solution for 5a and found as before that the yield of 7a
and 8a decreased as the yields of 6a increased (Figure 2-6). Similar analysis of the product ratio as a function of irradiation time in argon-saturated chloroform solution for 5b shows that the yield of 7a and 8a decreased as the yields of 6b increased where as such a comparison of 5b in oxygen saturated solutions is complex due to the overlapping of ¹H NMR peaks.

Figure 2. ¹H NMR spectra of 5a before and after irradiation in argon-saturated chloroform-d solutions. (o-azirine-8a, □-isoxazole-7a, Δ-nitrile-6a)
Figure 3. $^1$H NMR spectra of 5b before and after irradiation with respect to time in argon-saturated chloroform-d solutions (a). Full spectra (o-azirine-8b, □-isoxazole-7b, Δ-nitrile-6b) (b). Expanded aromatic region

However, photolysis of 5a by Sato\textsuperscript{5} in benzene yielded only 6a (Scheme 3). Sato further states that upon addition of NaOMe, additional amount of 6a was formed suggesting the presence of 7a before the addition of NaOMe. Presence of 6a and 7a is consistent with our studies whereas we also observed 8a in chloroform. Based on the product studies we propose that upon irradiation via Pyrex filter, the aryl ketone moiety and the C=C chromophore absorbs the light and forms the singlet excited state ($S_1$) of 5a, 5b which then intersystem crosses to the triplet excited state ($T_1$) of 5a, 5b. It is also possible that C=C chromophore directly absorb light and forms its singlet excited state that intersystem crosses to $T_{BR}$ of 5a, 5b. Presumably, $T_{BR}$ of 5a, 5b forms triplet nitrene ($T_N$) of 5a, 5b by extruding N$_2$ molecule. $T_N$ of 5a, 5b must decay by (a). undergoing 1,2 H shift from β-carbon to α-carbon and ISC to yield 6a, 6b; (b). rotation around the H-C=C-N: and cyclize and ISC to form 7a, 7b; (c). cyclization and ISC to form 8a, 8b. In oxygen saturated solutions, 5b forms 6b, 7b and 8b and a small amount of 9b. Presumably, 6b undergo α-cleavage to form 9b. It is consistent with Nesmenayov’s work.\textsuperscript{4}
Figure 4. Product ratio (6b, 7b and 8b) as a function of irradiation of 5b in argon-saturated solutions. The product ratio and conversion were calculated from the $^1$H NMR spectra by integrating the peaks at 8.051 ppm for 8b, 7.738 ppm for 7b, 7.898 ppm for 6b and 6.764 ppm for 5b.

Figure 5. Product ratio (6a, 7a, 8a) as a function of irradiation of 5a in argon-saturated solutions. The product ratio and conversion were calculated from the $^1$H NMR spectra by integrating the
peaks at 8.060 ppm for 8a, 7.806 ppm for 7a, 7.930 ppm for 6a and 6.772 ppm for 5a of the reaction mixture.

**Figure 6.** Product ratio (6a, 7a, 8a) as a function of irradiation of 5a in oxygen-saturated solutions. The product ratio and conversion were calculated from the $^1$H NMR spectra by integrating the peaks at 8.060 ppm for 8a, 7.806 ppm for 7a, 7.930 ppm for 6a and 6.772 ppm for 5a of the reaction mixture.
2. Ground State UV

The ground state UV/Vis spectra of 5a and 5b are shown below (Figure 7). Vinyl azide 5a has a strong absorption band at 292 nm that trails out to 300 nm. Further, 5a also has a shoulder at 257 nm. 5b has a very strong absorption band at 307 nm which is stronger than for the corresponding acetophenone derivatives, which have an \((n,\pi^*)\) absorption band around 320 nm \((\varepsilon = 50, \text{Table 1})\).\(^6\)

![Figure 7](image-url)
Table 1. The Ground State UV absorption $\lambda_{\text{max}}$ and $\varepsilon$ for acetophenone, 5a and 5b.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{max}}$ (nm) (M$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{max}}$ (nm) (M$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{max}}$ (nm) (M$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetophenone$^6$</td>
<td>320 (50)</td>
<td>278 (1110)</td>
<td>240 (1.3 x 10$^4$)</td>
</tr>
<tr>
<td>5a</td>
<td>292 (1.74 x 10$^4$)</td>
<td>257 (7.56 x 10$^3$)</td>
<td></td>
</tr>
<tr>
<td>5b</td>
<td>307 (2.11 x 10$^4$)</td>
<td>230 (9.07 x 10$^3$)</td>
<td></td>
</tr>
</tbody>
</table>

3. Calculations

To better understand the reactivity of 5a, 5b we calculated the triplet surface of 5a, 5b using the Gaussian03$^7$ and Gaussian09 at the B3LYP level of theory and with the 6-31+G(d) basis set.$^8, 9$ We used the calculations to identify the most favorable reaction on the triplet surface of 5a, 5b and to understand the factors that control and govern the reactivity of on the triplet surface of 5a and 5b.

(a). Calculations of 5a

We optimized the ground-state ($S_0$) of 5a (Figure 9). The TD-DFT calculation of $S_1$ of 5a shows that it is located at 76 kcal/mol above its $S_0$. Analysis of molecular orbitals shows that $S_1$ of 5a has (n,$\pi^*$) configuration where the major electronic excitation is from the non-bonding orbital of oxygen to anti-bonding molecular orbital (Table 2, Figure 8). In comparison, the TD-DFT calculations also shows that the major electronic transitions above 295 nm are due to electron transitions from ($\pi,\pi^*$) from phenyl ring and from C=C chromophore.

Table 2. Electronic transitions of 5a above 295 nm in gas phase

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<th>374.59 nm</th>
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<td>45 -&gt; 46</td>
<td>-0.22978</td>
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</table>

**Figure 8.** Molecular orbitals corresponds to electronic transitions of 5a above 295 nm
Figure 9. Optimized $S_0$ Conformers of 5a (values below the figures are the relative energy in kcal/mol with respect to the most stable conformer).

Figure 10. Optimized conformers of $T_K$ of 5a and $T_{BR}$ of 5a.

TD-DFT calculations of 5a in gas phase show that $T_1$ of 5a is located 58 kcal/mol above $S_0$ of 5a and has ($\pi,\pi^*$) configuration where the major electron transition is taking place from C=C chromophore to $\pi^*$ orbital (Scheme 7). In addition, there is very minute electron transition from non-bonding orbital of oxygen to $\pi^*$ orbital. $T_2$ is 67 kcal/mol above $S_0$ of 5a and has (n,π*) configuration where the electron transition is taking place from the non-bonding orbital of the oxygen to $\pi^*$ orbital (Table 3). TD-DFT calculations of 5a in acetonitrile show that $T_1$ of 5a is located 59 kcal/mol above $S_0$ of 5a and $T_2$ of 5a is located 72 kcal/mol above $S_0$ of 5a. However, molecular orbital examinations show that the electronic transitions are similar to the gas phase.
We also optimized the T₁ of 5a and found that it is located 54 kcal/mol above S₀ of 5a, which is somewhat lower than the energy obtained by TD-DFT calculations. Analysis of bond lengths of S₀ of 5a shows C=O bond length of 1.23 Å. The optimized structure of T₁ of 5a shows that C=O bond length has been increased from 1.23 Å in 5a to 1.27 Å in T₁ of 5a. Further, it also shows that carbonyl carbon to α-C bond distance has reduced from 1.48 Å in 5a to 1.42 Å in T₁ of 5a whereas the C=C bond length has increased from 1.35 Å in 5a to 1.46 Å in T₁ of 5a. In addition the distance between the β-carbon to N has been decreased from 1.40 Å in 5a to 1.35 Å in T₁ of 5a. The analysis of bond lengths and dihedral angles in azide chromophore of 5a and T₁ of 5a does not show any changes. The analysis of bond lengths in the phenyl ring shows that there is no change of bond lengths at all. These analysis shows that optimized structure of T₁ of 5a is delocalized mainly to the C=C chromophore not to azide chromophore or to the phenyl ring.

Table 3. Energies of T₁ and T₂ of 5a using optimization and TD-DFT Calculations

<table>
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<tr>
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<th>Optimized (UB3LYP)</th>
<th>TD-DFT</th>
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<tr>
<td></td>
<td>T₁</td>
<td>T₂</td>
</tr>
<tr>
<td>Gas Phase</td>
<td>54</td>
<td>58</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>54</td>
<td>59</td>
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We calculated the transition state for the T₁ of 5a to form the triplet biradical (T_BR) of 5a and found that it is located 1.0 kcal/mol above the T₁ of 5a and 0.2 kcal/mol above T_BR of 5a. Intrinsic Reaction Coordinate (IRC) calculations confirm the transition state correlate to the T₁ of 5a and T_BR of 5a. Optimization of T_BR of 5a located it at 55 kcal/mol above S₀ of 5a. Bond length analysis shows that C=O bond length has increased from 1.23 Å in S₀ of 5a to 1.24 Å in T_BR of 5a. Further, C=C bond length has been increased from 1.35 Å in 5a to 1.47 Å in T_BR of
Moreover, H-C-C-H dihedral angle has been reduced from 180.0° in 5a to 89.2° in TBR of 5a. This suggests the biradical is localized on α-carbon and β-carbon atoms. We calculated the transition state for the TBR of 5a to form the TN of 5a and found that it is located less than 1 kcal/mol (0.4 kcal/mol) above the TBR of 5a. IRC calculations confirm the transition state correlate to the TBR of 5a and TN of 5a.

We also optimized the structure of triplet vinyl nitrene of 5a and N₂ molecule in gas phase and located it at -3 kcal/mol with respect to S₀ of 5a. Bond length analysis shows that C=O bond length has not affected from S₀ of 5a to TN of 5a. Cₐ-Cₜ bond length has been decreased from 1.35 Å in S₀ of 5a to 1.42 Å in TN of 5a. Cₜ-N bond distance has been reduced from 1.40 Å in S₀ of 5a to 1.29 Å in TN of 5a. Moreover, H-C-C-H dihedral angle is nearly the same in S₀ of 5a and in TN of 5a. This suggests that the unpaired electrons in TN of 5a are delocalized between N- Cₜ- Cₐ. Hence, TN of 5a resembles a triplet 1,3-biradical system (Scheme 6).

Figure 11. Optimized Conformers of TN of 5a (values below the figures are the relative energy in kcal/mol with respect to the most stable conformer).
Scheme 6. C-N$_3$ and C-N bond distances of 5a, 5b; $T_N$ of 5a, 5b with spin density values on nitrene atoms. (Calculations were carried out using Gaussian 03 DFT B3LYP 6-31G+(d) basis set)

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<tr>
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<th>5b</th>
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<td>C-N bond length (Å)</td>
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<tr>
<td>C=C bond length (Å)</td>
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<td>1.347</td>
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<th></th>
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Scan calculation along the H-C=C-N: showed that the isomerization of trans configuration of triplet nitrene (Tₙ⁢(Tₐₜₚₜₚ) to cis configuration of triplet nitrene (Tₙ⁢(Cⁱᵣᵣᵣ)) goes through a 14 kcal/mol energy barrier (Figure 12). The optimized energy of the Tₙ⁢(Cⁱᵣᵣᵣ) is found to be 4 kcal/mol above the energy of Tₙ⁢(Tₐₜₚₜₚ) of 5α.
Figure 12. The rotational energy barrier of 5a along H1-C2-C3-N4 dihedral angle with 15° increments.

We calculated the energy surface for the products 6a, 7a and 8a formed from the product studies to investigate the feasibility of the product formation. The optimization of 6a shows that it is located -51 kcal/mol below the energy of T_N of 5a (Scheme 9). However, the transition state for forming 6a by 1,2-H shift to α-carbon was found to be 80 kcal/mol above T_N of 5a. This suggests that T_N of 5a undergo ISC to form 6a rather than going through a transition state. We also calculated the energy of the azirine 8a and located its energy at -12 kcal/mol below the
energy of $T_{N(\text{Trans})}$ of 5a. The transition state in forming 8a was located 56 kcal/mol above $T_{N(\text{Trans})}$ of 5a. This also suggests that $T_N$ of 5a undergo ISC to form 8a rather than going through a transition state. We further optimized the imine 17a and found that it is located at -35 kcal/mol below the $T_N$ of 5a. The transition state for forming the 17a by 1,2-H shift from $\beta$-carbon to N atom was located at 56 kcal/mol above the $T_N$ of 5a. This further suggests that $T_N$ of 5a undergo ISC to form 17a rather than rearrangement on the triplet energy surface followed by ISC. We observed the formation of intermediate 17a in argon-matrices at 20 K which is consistent with proposed intermediate by Sato\textsuperscript{5} in his work.

Scheme 8
We also optimized the isoxazole 7a, and located its energy -36 kcal/mol below the $T_{N(Cis)}$ of 5a (-32 kcal/mol below $T_{N(Trans)}$ of 5a) (Scheme 9). The transition state in forming 7a was located at 39 kcal/mol above $T_{N(Cis)}$ of 5a. This further suggests that $T_{N(Cis)}$ of 5a undergoes ISC to form 7a rather than rearrangement on the triplet energy surface followed by ISC.

Scheme 9

(b). Calculations of 5b

We optimized the ground-state ($S_0$) of 5b (Figure 14). The most stable conformer is consistent with the crystal structure of 5b. The TD-DFT calculations of $S_1$ of 5a shows that it is located at 76 kcal/mol. Analysis of molecular orbitals shows that $S_1$ of 5b has $(n,\pi^*)$ configuration where the major electronic excitation is from the non-bonding orbital of oxygen to
anti-bonding molecular orbital (Table 4, Figure 13). However, TD-DFT calculations also shows that the major electronic transitions above 290 nm are due to \( (\pi , \pi^* ) \) transitions from phenyl ring and from C=C chromophore.

**Table 4.** Electronic transitions of 5b above 290 nm in gas phase

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<th>Excited State</th>
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<td></td>
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<td>-0.28237</td>
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<td>52 -&gt; 54</td>
<td>0.56449</td>
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</table>

**Figure 13.** Molecular orbitals corresponds to electronic transitions of 5b above 290 nm
Figure 14. Optimized S_0 Conformers of 5b (values below the figures are the relative energy in kcal/mol with respect to the most stable conformer).

Figure 15. Optimized conformers of T_K of 5b and T_BR of 5b.

TD-DFT calculations of 5b in gas phase show that T_1 of 5b is located 58 kcal/mol above S_0 of 5b and has a (π,π*) configuration where the electron transition is taking place from C=C chromophore, whereas T_2K is 67 kcal/mol above S_0 and also has a (π,π*) configuration (Scheme 10). T_2 of 5b is 67 kcal/mol above S_0 of 5b and has (π,π*) configuration where the electron
transition is taking place from the phenyl ring (Table 5). TD-DFT calculations of 5b in acetonitrile show that T1 of b is located 59 kcal/mol above S0 of 5a and T2 of 5a is located 59 kcal/mol above S0 of 5b. However, molecular orbital examinations show that the electronic transitions are similar to the gas phase.

We also optimized the T1 of 5b and found that it is located 55 kcal/mol above S0 of 5b, which is somewhat lower than the energy obtained by TD-DFT calculations. Analysis of bond lengths of S0 of 5b shows C=O bond length of 1.24 Å. The optimized structure of T1 of 5b shows that C=O bond length has increased from 1.24 Å in 5b to 1.27 Å. Further, it also shows that carbonyl carbon to α-C bond distance has been reduced from 1.48 Å in S0 of 5b to 1.43 Å T1 of 5b, whereas the C=C bond length has been increased from 1.35 Å in S0 of 5b to 1.47 Å T1 of 5b. In addition the distance between the β-carbon to N has been decreased from 1.40 Å in S0 of 5b to 1.34 Å in T1 of 5b. The analysis of bond lengths in the phenyl ring shows that there is no change of bond lengths at all. These analysis shows that optimized structure of T1 of 5b is delocalized mainly to the C=C chromophore and not to the azide chromophore or to the phenyl ring. This resembles a planar triplet 1,2-biradical.

Table 5. Energies of T1 and T2 of 5b using optimization and TD-DFT Calculations

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<td>TD-DFT</td>
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<td>T1</td>
<td>T2</td>
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<tr>
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<td>55</td>
<td>58</td>
<td>67</td>
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<tr>
<td>CH3CN</td>
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<td>59</td>
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We calculated the transition state for the T1 of 5b to form the triplet biradical (TBR) of 5b and found that it is located less than 1 kcal/mol (0.54 kcal/mol) above the T1 of 5b and 0.52
kcal/mol above T_{BR} of 5b. Intrinsic Reaction Coordinate (IRC) calculations confirm the transition state correlate to the T_{1} of 5b and T_{BR} of 5b.

Optimization of T_{BR} of 5b located it at 55 kcal/mol above S_{0} of 5b. Bond length analysis shows that C=O bond length has not been changed in S_{0} of 5b and T_{BR} of 5b. Further, C=C bond length has increased from 1.35 Å in S_{0} of 5b to 1.47 Å in T_{BR} of 5b. Moreover, H-C-C-H dihedral angle has been reduced from 180.0° in S_{0} of 5b to 88.2° in T_{BR} of 5b. This suggests the biradical is localized on α-carbon and β-carbon atoms. We calculated the transition state for the T_{BR} of 5b to form the T_{N} of 5b and found that it is located less than 1 kcal/mol (0.62 kcal/mol) above the T_{BR} of 5b. IRC calculations confirm the transition state correlate to the T_{BR} of 5b and T_{N} of 5b.

We also optimized the structure of triplet vinyl nitrene of 5b in gas phase and located it at -3 kcal/mol with respect to S_{0} of 5b. Bond length analysis shows that C=O bond length has not been affected from S_{0} of 5b to T_{N} of 5b. C_{α}-C_{β} bond length has increased from 1.35 Å in T_{BR} of 5b to 1.42 Å in T_{N} of 5b. C_{β}-N bond distance has been reduced from 1.40 Å in S_{0} of 5b to 1.29 Å in T_{N} of 5b. Moreover, H-C-C-H dihedral angle has not changed in S_{0} of 5b and in T_{N} of 5b. This suggests that the unpaired electrons in T_{N} of 5b are delocalized between N- C_{β}- C_{α}. Hence, T_{N} of 5b resembles a triplet 1,3-biradical system (Scheme 6).
Figure 16. Optimized Conformers of $T_N$ of 5b (values below the figures are the relative energy in kcal/mol with respect to the most stable conformer).

Scheme 10

Further, scan calculation along the H-C=C-N: showed that the isomerization of trans configuration of triplet nitrene ($T_{N(Trans)}$) to cis configuration of triplet nitrene ($T_{N(Cis)}$) goes through a 14 kcal/mol energy barrier (Figure 17). The optimized energy of the $T_{N(Cis)}$ of 5b is found to be 2 kcal/mol above the energy of ground state $S_0$ of 5b and 5 kcal/mol above the energy of $T_{N(Trans)}$ of 5b.
We calculated the energy surface for the products 6b, 7b and 8b to elucidate the pathway for product formation. The optimization of 6b located at -50 kcal/mol below the energy of triplet nitrene $T_{N(\text{Trans})}$ of 5b (Scheme 11). However, the transition state for forming 6b by 1,2-H shift to $\alpha$-carbon was found to be 81 kcal/mol above $T_{N(\text{Trans})}$ of 5b. This suggests that $T_N$ of 5b undergo
ISC to form 6b rather than undergoing rearrangement on triplet surface followed by ISC. We also calculated the energy of the azirine 8b and its energy was located at -12 kcal/mol with respect to T_{N(Trans))} of 5b. The transition state in forming 8b was located 56 kcal/mol above T_{N(Trans))} of 5b. This suggests that T_{N} of 5b undergoes ISC to form 8b rather than undergoing rearrangement on the triplet surface followed by ISC. We further optimized the imine 17b and found that it is located at -36 kcal/mol below the T_{N} of 5b. The transition state for forming the 17b by 1,2-H shift from β-carbon to N atom was located at 55 kcal/mol above the T_{N} of 5b. This suggests that T_{N} of 5b undergoes ISC to form 17b rather than undergoing rearrangement on the triplet surface followed by ISC.

Scheme 11
We also optimized the isoxazole 7b, and located its energy -37 kcal/mol below the T\textsubscript{N(Cis)} of 5b (-32 kcal/mol below T\textsubscript{N(Trans)} of 5b) (Scheme 12). The transition state in forming 7b was located at 38 kcal/mol above T\textsubscript{N(Cis)} of 5b. This further suggests that T\textsubscript{N(Cis)} of 5b undergo ISC to form the ground state of 7b rather than undergoing rearrangement on the triplet surface followed by ISC.

Scheme 12

We optimized the ground-state (S\textsubscript{0-cis}) of 5b and found that it is located 4 kcal/mol above the S\textsubscript{0} of 5b. We also calculated the energy surface for trans-cis isomerization of 5b (Scheme 13). Upon irradiation, 5b excites to its S\textsubscript{1K} of 5b and undergoes intersystem crossing to form T\textsubscript{1} of 5b. T\textsubscript{1} of 5b rearranges to T\textsubscript{BR} of 5b which either intersystem cross to form cis-5b or it forms T\textsubscript{1} of cis-5b. T\textsubscript{1} of cis-5b could also intersystem cross to form cis-5b.
Scheme 13. Trans-cis isomerization of 5b through triplet 1,2-biradical

The proposed mechanism for photoproducts, excited states and intermediates are shown in Scheme 14.
Scheme 14. Proposed Mechanism
We compared the optimized structure of nitrenes $T_N$ of 5a, 5b (Scheme 6). In $T_N$ of 5a, 5b the C-N bond for the nitrene moiety was 1.288 Å and it has been reduced from 1.396 Å in 5a and 1.398 Å in 5b. Spin density calculations of $T_N$ of 5a and $T_N$ of 5b shows that the majority of spin density is delocalized and are on C$_{302}$ and N$_1$ atoms. This indicates that vinyl nitrenes of 5a and 5b are more like triplet 1,3-biradicals rather than vinyl nitrene.

**Scheme 15.** C-N$_3$ bond distances and H-C-C-N dihedral angles for $T_1$ of 5a, $T_1$ of 5b; $T_{BR}$ of 5a, $T_{BR}$ of 5b with spin density values (Calculations were carried out using Gaussian 03 DFT B3LYP 6-31G+(d) basis set).
We compared the spin density of T\textsubscript{1} of 5a, T\textsubscript{1} of 5b, T\textsubscript{BR} of 5a and T\textsubscript{BR} of 5b (Scheme 15). In T\textsubscript{1} of 5a, 5b the C-N bond length is 1.346 \text\AA{} and 1.345 \text\AA{}, respectively, and it is 1.365 \text\AA{} in T\textsubscript{BR} of 5a and 5b. It also shows that most of the spin density is on carbonyl oxygen, C\textsubscript{a} and C\textsubscript{b} for T\textsubscript{1} of 5a and T\textsubscript{1} of 5b showing that these T\textsubscript{1} states are mostly conjugated from C=C chromophore to C=O chromophore. Spin density calculations of T\textsubscript{BR} of 5a and T\textsubscript{BR} of 5b shows that the majority of spin density is mainly on C\textsubscript{a} and C\textsubscript{b} atoms. Further, it also shows that the spin density has been increased on C\textsubscript{a} and C\textsubscript{b} atoms of T\textsubscript{BR} of 5a and T\textsubscript{BR} of 5b than T\textsubscript{1} of 5a and T\textsubscript{1} of 5b respectively. This indicates that T\textsubscript{1} and T\textsubscript{BR} states are similar structures. Further,
analysis of spin density on aromatic ring shows that there is no considerable spin density on carbon atoms of aromatic ring.

4. Laser Flash Photolysis (LFP)

(I). LFP of 5a in CH$_3$CN

We performed laser flash photolysis to support the proposed reaction mechanism for 5a. Laser flash photolysis (Excimer laser, 308 nm, 17 ns) of 5a in argon-saturated acetonitrile produced a transient absorption with $\lambda_{max}$ at ~360 nm (Figure 18). We assign the absorption at ~360 nm to T$_{N(\text{Trans})}$ and T$_{N(\text{Cis})}$ of 5a based on the TD-DFT UCAM-B3LYP calculations, kinetics and quenching studies. The calculated TD-DFT UCAM-B3LYP absorption spectrum of T$_{N(\text{Trans})}$ of 5a in acetonitrile has the major electronic transitions at 433.89 nm ($f$=0.0186), 352.48 nm ($f$=0.0132), 337.38 nm ($f$=0.0344) and 306.26 ($f$=0.0369); whereas the calculated TD-DFT UCAM-B3LYP absorption spectrum of T$_{N(\text{Cis})}$ of 5a in acetonitrile has the major electronic transitions at 435.57 nm ($f$=0.0185), 354.64 nm ($f$=0.0116), 340.52 nm ($f$=0.0191) and 314.15 nm ($f$=0.0568) (Figure 19-20) which fits well with the observed spectra around ~340 nm – 360 nm region.
2.5 μs time window in Ar

Figure 18. Transient UV/Vis spectra of 5a (a). 0.04 – 0.52 μs (red) (b). 0.52 – 2.02 μs (blue) (c). 2.02 – 5.00 μs (black) (d). 5.00 – 18.52 μs (green)
Figure 19. Calculated UV of (a). $T_K$ of 5a (purple), (b). $T_N$ (trans) of 5a (red), (c). $T_N$ (cis) of 5a (blue), (d). $T_{BR}$ of 5a (green); in gas phase optimized using UB3LYP level of theory and then with TD-DFT UCAM-B3LYP 6-31+G(d) basis set.
Figure 20. Calculated UV of (a) T_K of 5a (purple), (b) T_N (trans) of 5a (red), (c) T_N (cis) of 5a (blue), (d) T_BR of 5a (green); in acetonitrile using UB3LYP level of theory and then with TD-DFT UCAM-B3LYP 6-31+G(d) basis set.

The transient absorption at 360 nm can be fitted into a mono-exponential function and decays with a rate constant of $3.2 \times 10^5 \text{ s}^{-1} \pm 1.3 \times 10^4 \text{ s}^{-1}$ ($\tau = 3.1 \pm 0.1 \mu\text{s}$) in argon saturated-solvent (Figure 21). We assign this decay to the decay of T_N of 5a based on quenching studies with oxygen and based on the similarity of the lifetime of reported triplet vinyl nitrene. The
transient absorption at 440 can be fitted into a double exponential function and decays with rate constants of $2.9 \times 10^5 \text{ s}^{-1} \pm 5.3 \times 10^3 \text{ s}^{-1}$ ($\tau = 3.4 \pm 0.6 \mu s$) which we assign for $T_N$ of 5a and $2.6 \times 10^4 \text{ s}^{-1} \pm 3.0 \times 10^3 \text{ s}^{-1}$ ($\tau = 38.7 \pm 4.5 \mu s$) which we assign for the formation of the photo-products.

1 $\mu s$ time window at 360nm in Ar

\[ k = 3.2 \times 10^5 \text{ s}^{-1} \pm 1.3 \times 10^4 \text{ s}^{-1}, \tau = 3.1 \pm 0.1 \mu s \]

2.5 $\mu s$ time window at 360nm in Ar

\[ k = 3.3 \times 10^5 \text{ s}^{-1} \pm 6.4 \times 10^3 \text{ s}^{-1}, \tau = 3.0 \pm 0.1 \mu s \]
25 μs time window at 440nm in Ar

\[ k_1 = 2.9 \times 10^5 \text{ s}^{-1} \pm 5.3 \times 10^3 \text{ s}^{-1}, \tau = 3.4 \pm 0.6 \mu \text{s} \]

\[ k_2 = 2.6 \times 10^4 \text{ s}^{-1} \pm 3.0 \times 10^3 \text{ s}^{-1}, \tau = 38.7 \pm 4.5 \mu \text{s} \]

**Figure 21.** Kinetics of 5a in CH₃CN. (a). 1 μs time window at 360nm in Ar. (b). 2.5 μs time window at 360nm in Ar. (b). 25 μs time window at 360nm in Ar.

**Quenching Studies with O₂**

In oxygen-saturated acetonitrile solutions the intensity of the band around 360 nm is completely quenched (Figure 22-23). Thus oxygen quenches both \( T_N \) of 5a and \( T_K \) of 5a.
2.5 μs time window in Ar

Figure 22. Transient UV/Vis spectra for quenching studies of 5a (a). Ar (0.04 – 0.52 μs) (red)
(b). O₂ (0.04 – 0.52 μs) (blue)

2.5 μs time window at 360nm in Ar & O₂
We also calculated the UV/Vis spectra of potential intermediates that could form upon the reaction of T_N of 5a with triplet O_2 (Figure 24). It shows that most of the absorptions shift towards 300 nm upon reacting with triplet O_2 which is in agreement with the experimental data (see Figure 22). Calculations show that, there is still a strong absorption for 10a, 11a at 340 nm which we didn’t observe due to negative absorption below 330 nm in experimental transient UV/Visible. We also calculated the UV/Visible spectra of the C_o of T_N of 5a reacting with triplet O_2, resulting 12a and found that most of the electronic transitions for 12a have lower intensity than for T_N of 5a, which is why we did not observe any absorption above 300 nm in oxygen-saturated acetonitrile solutions.

Figure 23. Quenching kinetics of 5a in CH_3CN. (a). 2.5 μs time window at 360nm in Ar (red) & O_2 (blue). (b). 100 ns time window at 360nm in Ar (red) & O_2 (blue).
Figure 24. Calculated UV/Vis of (a) T\textsubscript{N} (trans) + \textsuperscript{3}\text{O}_2 of 5a (10a). (red) (b) T\textsubscript{N} (cis) + \textsuperscript{3}\text{O}_2 of 5a (11a). (blue) (c) T\textsubscript{N} + \textsuperscript{3}\text{O}_2 connected to \textalpha-carbon. (12a) (green) in acetonitrile optimized using UB3LYP level of theory and then CAM-B3LYP TD-DFT level of theory with 6-31+G(d) basis set.
**Figure 25.** Calculated UV/Vis of (a). T<sub>BR</sub> (trans) of 5a + ^3^O_2 attached to α-carbon of 5a (13a) (red), (b). T<sub>BR</sub> (trans) of 5a + ^3^O_2 attached to β-carbon of 5a (14a) (blue), (c). T<sub>BR</sub> (cis) of 5a + ^3^O_2 attached to α-carbon of 5a (15a) (green) (d). T<sub>BR</sub> (cis) of 5a + ^3^O_2 attached to β-carbon of 5a (16a) (purple) in acetonitrile optimized using UB3LYP and then CAM-B3LYP TD-DFT level of theory with 6-31+G(d) basis set.

We further calculated the reactivity of T<sub>BR</sub> of 5a with triplet O<sub>2</sub> (Figure 25). The calculations show that the resulting diradicals 13a-16a has very low absorptions from 300 nm-600 nm. However, we didn’t observe any peaks in oxygen saturated solutions hence, we rule out the possibility of formation of 13a-16a.

**Scheme 16.** Reactivity of T<sub>N</sub> of 5a with ^3^O_2 on triplet surface (Energies are in kcal/mol)
We further performed calculations to find out the energetic of Tₙ of 5a reacting with triplet oxygen (Scheme 17). Calculations show that on triplet surface, the reaction of N atom of nitrene with triplet oxygen is not desirable. However, reaction of triplet oxygen with the α-carbon atom leads to 11a which is 6.4 kcal/mol more stable than Tₙ of 5a and O₂. Further, reaction of two triplet oxygen molecules with triplet nitrene is 9 kcal/mol more stable.

We also calculated energetics of the reactivity of triplet nitrene with triplet oxygen followed by ISC (Scheme 17). These calculations show that they form more stable products.

**Scheme 17.** Reactivity of Tₙ of 5a with ³O₂ on singlet surface (Energies are in kcal/mol)
(II). LFP of 5b in CH$_3$CN

We performed laser flash photolysis to support the proposed reaction mechanism for 5b. Laser flash photolysis (Excimer laser, 308 nm, 17 ns) of 5b in argon-saturated acetonitrile produced a transient absorption with $\lambda_{\text{max}}$ at ~410 nm (Figure 26-17). We assign the absorption at ~410 nm to T$_N$(Trans) and T$_N$(Cis) of 5b based on the TD-DFT calculations, kinetics and quenching studies. The calculated TD-DFT absorption spectrum of T$_N$(Trans) of 5b in acetonitrile has the major electronic transition at 469.59 nm ($f=0.0088$), 367.48 nm ($f=0.0500$), whereas the calculated TD-DFT absorption spectrum of T$_N$(Cis) of 5b in acetonitrile has the major electronic transition at 478.84 nm ($f=0.0086$), 366.40 nm ($f=0.0432$), and 336.82 nm ($f=0.0138$) (Figure 28) which fits well with the observed spectra from 370 nm – 460 nm region. We didn’t observe the calculated electronic transitions below 340 nm because of the negative absorption due to the singlet ground state. CAM-B3LYP calculations of 5b did not improve the fit between the calculated and observed transient UV spectra further.

1 $\mu$s time window in Ar
Figure 26. Transient UV/Vis spectra of 5b (a). 0.02 – 0.30 μs (red) (b). 0.30 – 0.94 μs (blue) (c). 0.94 – 2.06 μs (black) (d). 2.06 – 7.60 μs (light green)

5 μs time window in Ar

Figure 27. Transient UV/Vis spectra of 5b (a). 0.02 – 0.30 μs (red) (b). 0.30 – 0.94 μs (blue) (c). 0.94 – 2.06 μs (black) (d). 2.06 – 7.60 μs (light green)
Figure 28. Calculated UV of (a). $T_K$ (trans) of 5b (purple) (b). $T_N$ (trans) of 5b (red), (b). $T_N$ (cis) of 5b (blue), (c). $T_{BR}$ of 5b (green) in gas phase using TD-DFT CAM-B3LYP level of theory with 6-31+G(d) basis set.
Figure 29. Calculated UV of (a). $T_K$ (trans) of 5b (purple) (b). $T_N$ (trans) of 5b (red), (b). $T_N$ (cis) of 5b (blue), (c). $T_{BR}$ of 5b (green) in acetonitrile using TD-DFT CAM-B3LYP level of theory with 6-31+G(d) basis set.
We assign the transient with $\lambda_{\text{max}} \sim 410$ nm to the $T_{\text{BR}}$ of 5b, based on the TD-DFT calculations and kinetics, which show that the major electron transitions are located at 352.37 nm ($f=0.0395$), 346.10 nm ($f=0.0352$) and 301.82 nm ($f=0.0186$) (Figure 28) although we didn’t clearly observe the electronic transition above ~480 nm. Kinetic analysis of the transient absorption further supports this assignment. The transient absorption at 420 nm decays bi-exponentially with rate constants of $2.3 \times 10^5$ s$^{-1}$ ($\tau = 4.3 \pm 0.8 \mu$s) which we assign for $T_N$ of 5b; and $8.2 \times 10^4$ s$^{-1}$ ($\tau = 12.2 \pm 1.5 \mu$s) which we assign both residual product formation from 5b in argon saturated-solvent (Figure 30). In addition, the kinetic analysis at 320 nm decays mono-exponentially with a rate constant of $1.9 \times 10^5$ s$^{-1}$ ($\tau = 5.3 \pm 0.2 \mu$s) which fits well with the rate constant of $T_N$ (Trans) and $T_N$ (Cis) of 5b at 420 nm.

1μs time window at 440nm in Ar

$$k = 1.8 \times 10^5 \text{ s}^{-1} \pm 8.7 \times 10^3 \text{ s}^{-1}, \tau = 5.6 \pm 0.3 \mu\text{s}$$
2.5 μs time window at 440nm in Ar

\[ k = 2.2 \times 10^5 \text{ s}^{-1} \pm 6.0 \times 10^3 \text{ s}^{-1}, \tau = 4.5 \pm 0.1 \text{ μs} \]

1 μs time window at 420nm in Ar

\[ k = 1.8 \times 10^5 \text{ s}^{-1} \pm 2.9 \times 10^3 \text{ s}^{-1}, \tau = 5.6 \pm 0.1 \text{ μs} \]
2.5μs time window at 420nm in Ar

$$k = 2.0 \times 10^5 \text{ s}^{-1} \pm 2.9 \times 10^3 \text{ s}^{-1}, \tau = 5.0 \pm 0.1 \mu\text{s}$$

5μs time window at 420nm in Ar

$$k_1 = 2.3 \times 10^5 \text{ s}^{-1} \pm 4.2 \times 10^4 \text{ s}^{-1}, \tau = 4.3 \pm 0.8 \mu\text{s}$$

$$k_2 = 8.2 \times 10^4 \text{ s}^{-1} \pm 1.0 \times 10^4 \text{ s}^{-1}, \tau = 12.2 \pm 1.5 \mu\text{s}$$
10 μs time window at 410 nm in Ar

\[ k_1 = 1.5 \times 10^5 \text{ s}^{-1} \pm 1.0 \times 10^4 \text{ s}^{-1}, \tau = 6.7 \pm 0.4 \mu s \]

\[ k_2 = 5.5 \times 10^4 \text{ s}^{-1} \pm 8.7 \times 10^3 \text{ s}^{-1}, \tau = 18.2 \pm 2.9 \mu s \]

2.5 μs time window at 320 nm in Ar

\[ k = 1.9 \times 10^5 \text{ s}^{-1} \pm 6.7 \times 10^3 \text{ s}^{-1}, \tau = 5.3 \pm 0.2 \mu s \]
Figure 30. Kinetics of 5b in CH$_3$CN. (a). 1 μs time window at 440nm in Ar, (b). 2.5 μs time window at 440nm in Ar, (c). 1 μs time window at 420nm in Ar, (d). 2.5 μs time window at 420nm in Ar, (e). 5 μs time window at 420nm in Ar, (f). 10 μs time window at 410nm in Ar, (g). 2.5 μs time window at 320nm in Ar.

Quenching Studies with O$_2$

In oxygen-saturated acetonitrile solutions the intensity of the band around 420 nm is completely quenched (Figure 31-32). Thus oxygen quenches T$_N$ of 5b and T$_K$ of 5b.

1 μs time window in Ar

Figure 31. Transient UV/Vis spectra for quenching studies of 5b (a). Ar (0.02 – 0.30 μs) (red) (b). O$_2$ (0.02 – 0.30 μs) (blue)
2.5 μs time window at 420nm in Ar & O₂

![Absorbance vs Time Graph](image)

5 μs time window at 420nm in Ar & O₂

![Absorbance vs Time Graph](image)

**Figure 32.** Quenching kinetics of 5b in CH₃CN. (a). 2.5 μs time window at 420 nm in Ar (red) & O₂ (blue). (b). 5 μs time window at 420 nm in Ar (red) & O₂ (blue).

We also calculated the UV/Vis spectra of potential intermediates that could form upon reacting T_N of 5b with triplet O₂ (10b-12b) (Figure 33). It shows that most of the absorptions
shift towards 300 nm upon reacting with triplet O$_2$ which is in agreement with the experimental data (see Figure 31). We also calculated the UV/Vis spectra of T$_{BR}$ of 5b reacting with triplet O$_2$ (13b-16b) (Figure 34) and found that for 13b, 15b; the absorptions shift towards 300 nm which also supports why we did not observe any absorption above 300 nm in oxygen-saturated acetonitrile solutions. However, 14b and 16b has absorptions in entire 300 nm-600 nm range, but their absorbance values have been decreased significantly. Therefore, both 14b and 16b may not form in oxygen saturated solutions or it could also possible that we may not be seeing 14b and 16b if they exist due to low molar absorptivity coefficient.
Figure 33. Calculated UV/Vis of (a). \(T_N\) (trans) + \(^3\)O\(_2\) of 5b (10b) (red), (b). \(T_N\) (cis) + \(^3\)O\(_2\) of 5b (11b) (green) (c). \(T_N\) + \(^3\)O\(_2\) connected to \(\alpha\)-carbon (12b) (blue); in acetonitrile using TD-DFT level of theory with 6-31+G(d) basis set.
Figure 34. Calculated UV/Vis of (a). T_{BR} (trans) of 5b + ^3O_2 attached to $\alpha$-carbon of 5b (13b) (red), (b). T_{BR} (trans) of 5b + ^3O_2 attached to $\beta$-carbon of 5b (14b) (blue), (c). T_{BR} (cis) of 5b + ^3O_2 attached to $\alpha$-carbon of 5b (15b) (green), (d). T_{BR} (cis) of 5b + ^3O_2 attached to $\beta$-carbon of 5b (16b) (purple); in acetonitrile using TD-DFT level of theory with 6-31+G(d) basis set.

Scheme 18. Reactivity of T_N of 5b with ^3O_2 on triplet surface (Energies are in kcal/mol)

We further performed calculations to find out the energetics of T_N of 5b reacting with triplet oxygen (Scheme 18). Calculations show that on triplet surface, the reaction of N atom of nitrene with triplet oxygen is not desired. However, reaction of triplet oxygen with the $\alpha$-carbon atom is 6.9 kcal/mol more stable. Further, reaction of two triplet oxygen molecules with triplet
nitrene is 9.6 kcal/mol more stable. But, since attaching the first oxygen is not desirable, this may also not favorable.

We also calculated energetic of the reactivity of triplet nitrene with triplet oxygen followed by ISC (Scheme 19). These calculations show that they form more stable products.

**Scheme 19.** Reactivity of T₇ of 5b with ³O₂ on singlet surface (Energies are in kcal/mol)
5. X – Ray Crystal structure of 5a and 5b

Figure 35. Crystal structure of 5a and 5b
6. Phosphorescence

We measured the phosphorescence spectra of 5a and 5b in ethanol at 77 K with different wavelengths of irradiation. The excitation at 260 nm resulted a (0,0) transition at 395 nm which also corresponds to 72 kcal/mol (Figure 36). The experimental value is higher than the calculated values; hence we hypothesize that we observe phosphorescence when a higher level triplet excited state relax to its ground state. We think we observe T2→S0 phosphorescence.

Phosphorescence spectrum of 0.01 M 5a in ethanol at 77 K, irradiated at 260 nm

![Phosphorescence spectrum of 0.01 M 5a in ethanol at 77 K, irradiated at 260 nm](image)

**Figure 36.** Phosphorescence spectra of 5a in ethanol at 77 K excited at 260 nm.

The phosphorescence spectra of 0.01 M 5b shows that the (0,0) transition is at 412 nm which corresponds to 69 kcal/mol with 300 nm excitation (Figure 37a). The excitation at 260 nm resulted a (0,0) transition at 412 nm which also corresponds to 69 kcal/mol (Figure 37b).
experimental value is higher than the calculated values; hence we hypothesize that we are observe phosphorescence when a higher level triplet excited state relax to its ground state.

Phosphorescence spectrum of $5b$ in ethanol at 77 K, irradiated at 300 nm

Phosphorescence spectrum of $5b$ in ethanol at 77 K, irradiated at 260 nm
Matrix Isolation of 5a

We investigated the photochemistry of 5a in argon matrices at 14 K to identify its reactivity in the absence of diffusion. We deposited 5a into argon matrices in several different experiments, entraining the vapor pressure over a sample of pure 5a in flowing argon, and depositing the resulting sample on a 14 K cryogenic surface. Irradiation of 5a in argon matrices led to the growth of new absorption bands, mostly occurring very near those of the parent azide (Figure 38), which is expected since the acetophenone moiety is not significantly affected by irradiation and the majority of the observed vibrational bands belong to it. The infrared spectrum of 5a showed intensive azido bands at 2130, 2127 and 2111 cm$^{-1}$. We also observed weak azido bands at 2187 and 2074 cm$^{-1}$ (Figure 40), which are all depleted upon irradiation. The various azido bands are presumably due to different conformers of 5a, which are also entrapped in different matrix sites. After the irradiation, new bands were observed at 2216 cm$^{-1}$, 1745 cm$^{-1}$ and 763 cm$^{-1}$ which we assign for 6a based on calculations (Figure 41, Figure 43 and Figure 45, Table 6). We also observed new strong intense bands at 3548, 3541, 2048, 1630, 1623, 728, 723, 487, 467, 464 and 455 cm$^{-1}$ which we assign all to the formation of 17a based on calculations (Figure 42-43, Table 6). Upon irradiation of 5a, it forms $T_N$ of 5a which undergo 1,2-H shift to give the intermediate imine 17a which rearrange to give 6a (Scheme 14). In different matrix sites, both 17a and 6a trap to give IR peaks corresponds to both. This is consistent with the proposed intermediate of Sato.$^5$ We also attempted to study the IR peak formation as a function
of time with respect to time in order to determine whether 17a is the precursor to 6a. However, we observed simultaneously formation of both 17a and 6a upon irradiation although Sato\textsuperscript{5} proposed 17a forms before 6a. We hypothesize that T\textsubscript{N} of 5a can undergo 1,2-H shift to adjacent N or adjacent C to give 17a and 6a. 17a and 6a are -35 kcal/mol and -51 kcal/mol respectively stable than T\textsubscript{N} of 5a.
Figure 38. Matrix isolation FTIR spectra (a). Before irradiation (red) (b). After irradiation of 15 min (blue) (c). The difference spectrum showing the depleted bands and new bands.

Figure 39. Calculated IR stretches for (a). Vinyl azide 5a (red; negative direction) (b). Nitrile 6a (c). Imine 17a; using Gaussian 09 with DFT B3LYP 6-31G+(d) basis set showing the depleted azido stretches and new nitrile and imine stretches.
**Figure 40.** Depletion of azido bands; growth of C=N stretch around 2200 cm$^{-1}$ region and growth of C=C=N stretch around 2047 cm$^{-1}$. (a). Before irradiation (blue) (b). After irradiation of 30 seconds (red) (c). After irradiation of 1 minute (green)

**Figure 41.** IR bands for imine stretch of 17a (a). Before irradiation (blue) (b). After 15 min irradiation (red) (c). Difference spectrum (pink).
Figure 42. New IR bands from 1700 – 1500 cm$^{-1}$ region. (a). Before irradiation (blue) (b). After 15 min irradiation (red) (c). Difference spectrum (pink).
**Figure 43.** IR bands in lower fingerprint region. (a). Before irradiation (blue) (b). After 15 min irradiation (red) (c). Difference spectrum (pink).
Figure 44. Depleted IR bands in carbonyl and aromatic regions and newly grown peaks with the increase in irradiation time show the formation of 17a (a). Before irradiation (blue) (b). After 30 seconds of irradiation (red) (c). After 1 minute of irradiation (green).
**Figure 45.** Most intense IR peaks in the finger print region showing the growth of new peaks attributed for both 17a and 6a. (a). Before irradiation (blue) (b). After 30 seconds of irradiation (red) (c). After 1 minute of irradiation (green).
Table 6. Calculated IR bands and experimental IR bands for 5a, 6a and 17a correlating the depleted experimental bands of 5a with newly formed IR bands of 6a and 17a.

<table>
<thead>
<tr>
<th>Calculated IR Bands / cm⁻¹</th>
<th>Experimental IR Bands / cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Trans (5a)</strong></td>
<td><strong>Imine (17a)</strong></td>
</tr>
<tr>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>3497 (59)</td>
<td>C=N-H</td>
</tr>
<tr>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2258 (1175)</td>
<td>--</td>
</tr>
<tr>
<td>--</td>
<td>2127 (947)</td>
</tr>
<tr>
<td>1720 (298)</td>
<td>1698 (166)</td>
</tr>
<tr>
<td>1652 (225)</td>
<td>1649 (20)</td>
</tr>
<tr>
<td>1639 (428)</td>
<td>--</td>
</tr>
<tr>
<td>1624 (114)</td>
<td>1628 (15)</td>
</tr>
<tr>
<td>Value</td>
<td>Count</td>
</tr>
<tr>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>1391</td>
<td>2</td>
</tr>
<tr>
<td>1359</td>
<td>44</td>
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<td>1238</td>
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<td>1213</td>
<td>43</td>
</tr>
<tr>
<td>1036</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>983</td>
<td>34</td>
</tr>
<tr>
<td>800</td>
<td>26</td>
</tr>
<tr>
<td>706</td>
<td>70</td>
</tr>
<tr>
<td>651</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td></td>
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</tbody>
</table>

Note: Values agrees reasonably well are shown in bold.
**Matrix Isolation of 5b**

We investigated the photochemistry of 5b in argon matrices at 14 K to identify its reactivity at in the absence of diffusion. We deposited 5b into argon matrices in several different experiments, entraining the vapor pressure over a sample of pure 5b in flowing argon, and depositing the resulting sample on a 14 K cryogenic surface. Irradiation of 5b in argon matrices led to the growth of new absorption bands, mostly occurring very near those of the parent azide (Figure 46-48), which is expected since the acetophenone moiety is not significantly affected by irradiation and the majority of the observed vibrational bands belong to it. The infrared spectrum of 5b showed intense azido bands 2135, 2126, and 2105 cm\(^{-1}\) (Figure 47), which are all depleted upon irradiation. The various azido bands are presumably due to different conformers of 5b, which are also entrapped in different matrix sites. After the irradiation new bands were observed at 2143, 1625, 1259 and 1183 cm\(^{-1}\) which we assign to the Cis-5b based on calculations (Table 7, Figure 47-48). We also analyzed the formation of 2143 cm\(^{-1}\) peak with respect to time and observed that it reaches a photo-stationary state after ~20 min of irradiation (Figure 49). Further, we also observed very weak band at 2279 cm\(^{-1}\). We assign the 2279 cm\(^{-1}\) peak to the formation of small amount of 6b based on calculations (Table 8, Figure 50).
Figure 46. Matrix Isolation FTIR spectra (a). Before irradiation (red) (b). After irradiation (blue) (c). Difference Spectrum.
Figure 47: Azido bands in 2100 cm$^{-1}$ region (a). Before irradiation (red) (b). After irradiation of 19.5 hours of irradiation (blue) (c). Difference spectrum (pink)
Figure 48. 1300 – 1100 cm⁻¹ region
Figure 49. Azido bands in 2100 cm\(^{-1}\) region showing the Cis-5b formation is the primary product. (a). Before irradiation (red); After irradiation of (b). 1 min (blue) (c). 6 min (pink) (d). 21 min (purple) (e). 81 min (Light Green) (f). 292 min (Cyan) (g). 19.5 hours (black).

![Figure 49](image)

Figure 50. New peak at 2279 cm\(^{-1}\)

Table 7. Calculated and Experimental IR bands for Trans-5b and Cis-5b

<table>
<thead>
<tr>
<th>Calculated IR Bands / cm(^{-1})</th>
<th>Experimental IR Bands / cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Trans (5b)</strong></td>
<td><strong>Cis (5b)</strong></td>
</tr>
<tr>
<td>2257 (1258) -N(_3)</td>
<td>2271 (484) -N(_3)</td>
</tr>
<tr>
<td></td>
<td>2137, 2135, 2126, 2105</td>
</tr>
<tr>
<td></td>
<td>2143, 2134</td>
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<tr>
<td>1247 (314)</td>
<td>1263 (347)</td>
</tr>
<tr>
<td></td>
<td>1169</td>
</tr>
<tr>
<td></td>
<td>1178</td>
</tr>
<tr>
<td>1365 (179)</td>
<td>1408 (163)</td>
</tr>
<tr>
<td></td>
<td>1252, 1248</td>
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<tr>
<td></td>
<td>1259</td>
</tr>
</tbody>
</table>
Table 8. Calculated and Experimental IR bands for Trans-5b and 6b

<table>
<thead>
<tr>
<th>Calculated IR Bands / cm&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>Experimental IR Bands / cm&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trans (5b)</td>
<td>Nitrile (6b)</td>
</tr>
<tr>
<td>2257 (1258) -N&lt;sub&gt;3&lt;/sub&gt;</td>
<td>--</td>
</tr>
<tr>
<td>--</td>
<td>2370 (13) C≡N</td>
</tr>
</tbody>
</table>

Discussion

Irradiation of 5a-b resulted in 6a-b, 7a-b and 8a-b in argon and oxygen-saturated chloroform-d solutions. In addition, 5b was also resulted in 9b in oxygen-saturated chloroform-d solutions. Observation of 6a and 7a is similar to Sato et al. work.<sup>5</sup> However, Sato et al. reports they did not observe 8a, but we did observe it (λ ≥ 300 nm). Calculated energies of nitrene intermediate are -3 kcal/mol for T<sub>N</sub> (trans) of 5a and 5b. T<sub>N</sub> (trans) → T<sub>N</sub> (cis) by rotation which has a rotational energy barrier of 14 kcal/mol which is easily accessible. The laser flash photolysis studies of 5a and 5b showed that, 5a and 5b both forms T<sub>N</sub> of 5a and T<sub>N</sub> of 5b. The lifetime of the T<sub>N</sub> of 5a was ~ 3 μs where as the lifetime of T<sub>N</sub> of 5b was ~ 12 μs. We also observed T<sub>BR</sub> of 5b which has a lifetime ~ 5 μs. T<sub>K</sub> of 5a and 5b was not observed, we hypothesize they form within the time resolution of the instrument. Phosphorescence spectra of 5a and 5b shows phosphorescence from higher level excited states to ground state. Matrix isolation studies of 5a shows that it readily forms imine 17a and nitrile 6a. On the other hand, matrix isolation of 5b shows the formation of small amounts of nitrile 6b in addition to Cis-5b.
Conclusions

Irradiation of 5a-b resulted in 6a-b, 7a-b and 8a-b in argon and oxygen-saturated chloroform-d solutions which come through a triplet nitrene intermediate as suggested by LFP. In addition, 5b was also resulted in 9b in oxygen-saturated chloroform-d solutions which may come from either 5b or from 6b.

Experimental

X – Ray Crystal Structure

For X-ray examination and data collection, a suitable colorless, rectangular block-like crystal, approximate dimensions 0.11 x 0.05 x 0.03 mm, was mounted in a loop with Paratone-N oil and transferred to the goniostat bathed in a cold stream.

Intensity data were collected at 150K on a standard Bruker SMART6000 CCD diffractometer using graphite-monochromated Cu Kα radiation, λ=1.54178Å. The detector was set at a distance of 5.165 cm from the crystal. A series of 15-s data frames measured at 0.3° increments of ω were collected to calculate a unit cell. For data collection frames were measured for a duration of 15-s at 0.3° intervals of ω with a maximum 2θ value of ~135°. The data frames were processed using the program SAINT. The data were corrected for decay, Lorentz and polarization effects as well as absorption and beam corrections based on the multi-scan technique.

The structure was solved by a combination of direct methods in SHELXTL and the difference Fourier technique and refined by full-matrix least squares on F². Non-hydrogen atoms
were refined with anisotropic displacement parameters. The H-atoms were calculated and treated with a riding model. The H-atom isotropic displacement parameters were defined as \(a^*U_{eq}\) of the adjacent atom (\(a=1.5\) for methyl and 1.2 for all others). The refinement converged with crystallographic agreement factors of \(R1=3.80\%\), \(wR2=9.59\%\) for 1268 reflections with \(I>2\sigma(I)\) \((R1=5.64\%, wR2=10.79\%\) for all data) and 137 variable parameters.

**Calculations**

All geometries were optimized at B3LYP level of theory and with 6-31G+(d) basis set as implemented in the Gaussian03 and Gaussian09 programs. All transition states were confirmed to have one imaginary vibrational frequency by analytical determination of the second derivatives of the energy with respect to internal coordinates. Intrinsic reaction coordinates calculations were used to verify that the located transition states corresponded to the attributed reactant and product. The absorption spectra were calculated using time-dependent density functional theory (TD-DFT). The effect of solvation was calculated using the self-consistent reaction field (SCRF) method with the integral equation formalism polarization continuum model (IEFPCM) with acetonitrile, methanol and dichloromethane as solvents.

**Laser Flash Photolysis.**

Laser flash photolysis was done with an Excimer laser (308 nm, 17 ns). The system has been described in detail elsewhere. A stock solution of 5a, 5b in CH₃CN was prepared with spectroscopic grade CH₃CN, such that the solutions had absorption between 0.3 and 0.6 at 308 nm. Typically, ~2 mL of the stock solution was placed in a 10 mm × 10 mm wide, 48 mm long
quartz cuvette and was purged with argon for 5 min or oxygen for 15 min. The rates were obtained by fitting an average of three to five kinetic traces.

**Phosphorescence**

The solutions of 5a (0.01 M) and 5b (0.01 M) solutions were prepared in ethanol. The phosphorescence spectra were obtained on a phosphorimeter in ethanol glasses at 77K. The solutions were irradiated at 300 nm and 260 nm. The emission spectra recorded between 280 and 800 nm.

**Matrix isolations**

Matrix isolation studies were performed using conventional equipment.25

**Synthesis**

Scheme 20

![Synthesis Scheme 20](image-url)
Synthesis of 1-Phenyl-prop-2-yn-1-ol (2a)

We followed the procedure reported in the literature with some modifications.\textsuperscript{26} 2.052 g (18.9 mmol) of benzaldehyde (1a) was dissolved in 25 mL of anhydrous THF at 0 °C. 48 mL (24 mmol, 1.2 eq) of HC≡CMgBr was dissolved in 15 mL of anhydrous THF and mixed with 1a at 0 °C. The mixture was allowed to stir for overnight (20 hours) at 0 °C. Saturated NH₄Cl (30 g of NH₄Cl dissolved in 100 mL of H₂O) was added to the mixture after 5 hours and allowed to stir further for 1 hour. The mixture was rotovapoured to remove THF. 100 mL of ethyl ether was added to the mixture. The ether layer was extracted and washed twice with water. The ether extract was washed with brine (saturated NaCl). The ether extract was dried using anhydrous MgSO₄. The ether was evaporated and the crude 1-Phenyl-prop-2-yn-1-ol (2a) (2.0 g, 15.2 mmol) was obtained. (% Yield = 78%). A $^1$H NMR, $^{13}$C NMR and IR spectra were taken in CDCl₃ and matches with literature.\textsuperscript{26}

$^1$H NMR (CDCl₃, 400 MHz): δ 2.379 (d, J = 4 Hz, 1H, -OH), 2.666 (d, J = 2.4 Hz, 1H, -CH), 5.460 (d, J = 2.8 Hz, 1H, =CH), 7.320 – 7.407 (m, 3H, -CH), 7.550 (d, J = 7.2 Hz, 2H, -CH) ppm; $^{13}$C NMR (CDCl₃, 100 MHz): δ 64.438, 74.860, 83.507, 126.625, 128.584, 128.703, 140.041 ppm.; IR (CDCl₃): 3354 (br, OH), 3291 (C≡C-H), 3064, 3033, 2881, 2118 (C≡C), 1957, 1603, 1493, 1455, 1393, 1276, 1192, 1080, 1022, 902, 947, 916, 821, 762, 739, 698, 650, 573, 528 cm$^{-1}$. 

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Synthesis of 1-(4-Methoxy-phenyl)-prop-2-yn-1-ol (2b)

We followed the procedure reported in the literature with some modifications. \(^{26,27}\) \(2.65 \text{ g (19.5 mmol)}\) of p-methoxybenzaldehyde (1b) was dissolved in 25 mL of anhydrous THF at 0 \(^{\circ}\)C. \(48 \text{ mL (24 mmol, 1.2 eq)}\) of HC=CMgBr was dissolved in 15 mL of anhydrous THF and mixed with 1b at 0 \(^{\circ}\)C. The mixture was allowed to stir for overnight (20 hours) at 0 \(^{\circ}\)C. Saturated NH\(_4\)Cl (30g of NH\(_4\)Cl dissolved in 100 mL of H\(_2\)O) was added to the mixture and allowed to stir further for 1 hour. The mixture was rotovapoured to remove THF. 100 mL of ethyl ether was added to the mixture. The ether layer was extracted and washed twice with water. The ether extract was washed with brine (saturated NaCl). The ether extract was dried using anhydrous MgSO\(_4\). The ether was evaporated and the crude 1-(4-Methoxy-phenyl)-prop-2-yn-1-ol (2b) (2.73 g, 16.8 mmol) was obtained. (% Yield = 86%) A \(^1\text{H NMR, \(^{13}\)C NMR and IR spectra were taken in CDCl}_3.\)

\(^1\text{H NMR (CDCl}_3, \text{ 400 MHz)}: \delta 2.486 (d, J = 4 \text{ Hz}, 1\text{H, -OH}), 2.656 (d, J = 2 \text{ Hz}, 1\text{H, -CH-}), 3.801 (s, 3\text{H, -OCH}_3), 5.398 (d, J = 4 \text{ Hz}, 1\text{H, \equivCH}), 6.896 (d, J = 8.8 \text{ Hz}, 2\text{H, -CH}), 7.462 (d, J = 8.4 \text{ Hz}, 2\text{H, -CH}) \text{ ppm.}; \(^{13}\text{C NMR (CDCl}_3, \text{ 100 MHz)}: \delta 55.351, 63.994, 74.625, 83.751, 114.018, 128.093, 132.427, 159.762 \text{ ppm}.; \text{ IR (CDCl}_3): 3397 (br, OH), 3288 (C≡C-H), 3005, 2959, 2838, 2116 (C≡C), 1611, 1588, 1512, 1464, 1442, 1422, 1305, 1250, 1175, 1112, 1031, 948, 913, 833, 767, 733, 650, 605, 566, 538 \text{ cm}^{-1}.\)
**Synthesis of 1-Phenyl-propynone (3a)**

2a (2.0 g, 15.2 mmol) was dissolved in 25 mL of acetone at 0 °C. The Jones reagent was prepared. (4 g of CrO₃ (0.04 mol) was mixed with 4 mL of conc. H₂SO₄ and a slurry was made. 12 mL (4 mL x 3) of H₂O was added to it) The Jones reagent was added dropwise to 2a over a period of 10 min until the color of the solution changes to green and then to orange. The mixture was allowed to stir for 30 min and acetone was removed. An extraction was performed with 100 mL of diethyl ether and 100 mL of H₂O. Ether layer was separated and it was washed twice with H₂O, once with 100 mL of saturated NaHCO₃ and once with 100 mL of brine (saturated NaCl). The ether extract was dried using anhydrous MgSO₄. The ether was evaporated and the crude 1-Phenyl-propynone (3a) (1.38 g, 10.6 mmol) was obtained. (% Yield = 70 %) A ¹H NMR, ¹³C NMR and IR spectra were taken in CDCl₃ and matches with literature.

¹H NMR (CDCl₃, 400 MHz): δ 3.448 (s, 1H, HC-), 7.504 (t, J = 7.8 Hz, 2H, -CH), 7.658 (t, J = 7.4 Hz, 1H, -CH), 8.184 (d, J = 8.4 Hz, 2H, -CH) ppm.; ¹³C NMR (CDCl₃, 100 MHz): δ 80.280, 80.787, 128.706, 129.719, 134.544, 136.151, 177.411 ppm.; IR (CDCl₃): 3237 (C=C-H), 2094 (C=O), 1638 (C=C), 1596, 1581, 1452, 1411, 1316, 1264, 1176, 1072, 1031, 938, 913, 737, 718, 696, 679, 627, 477 cm⁻¹.

**Synthesis of 1-(4-Methoxy-phenyl)-propynone (3b)**

2b (2.74 g, 16.8 mmol) was dissolved in 25 mL of acetone at 0 °C. The Jones reagent was prepared. (4 g of CrO₃ (0.04 mol) was mixed with 4 mL of conc. H₂SO₄ and a slurry was made. 12 mL (4 mL x 3) of H₂O was added to it) The Jones reagent was added dropwise to 2b over a
period of 10 min until the color of the solution changes to green and then to orange. The mixture was allowed to stir for 30 min and acetone was removed. An extraction was performed with 100 mL of diethyl ether and 100 mL of H₂O. Ether layer was separated and it was washed twice with H₂O, once with 100 mL of saturated NaHCO₃ and once with 100 mL of brine (saturated NaCl). The ether extract was dried using anhydrous MgSO₄. The ether was evaporated and the crude 1-(4-Methoxy-phenyl)-propynone (3b) (2.01 g, 12.5 mmol) was obtained. (% Yield = 74%) A H NMR, C NMR and IR spectra were taken in CDCl₃.

1H NMR (CDCl₃, 400 MHz): δ 3.338 (s, 1H, =CH), 3.898 (s, 3H, -OCH₃), 6.967 (d, J = 8.8 Hz, 2H, -CH), 8.136 (d, J = 8.8 Hz, 2H, -CH) ppm.; 13C NMR (CDCl₃, 100 MHz): δ55.638, 79.999, 80.419, 113.965, 129.620, 132.173, 164.80, 175.965 ppm.; IR (CDCl₃): 3251 (C-C-H), 2991, 2093 (C=O), 1599, 1573, 1511, 1460, 1424, 1307, 1258, 1189, 1171, 1117, 1024, 1009, 912, 840, 758, 718, 686, 664, 627, 600, 505, 456 cm⁻¹.

Synthesis of 3,3-Dibromo-1-phenyl-propan-1-one (4a)

We followed the procedure reported in the literature with some modifications. 3a (1.38 g, 10.6 mmol) was dissolved in 25 mL of CH₂Cl₂ and kept at -8 °C. SiO₂ (6.36 g, 106 mmol, 10 eq) was added to 3a. PBr₃ (1.924 g, 7.1 mmol, 0.66 eq) in 10mL of CH₂Cl₂ was added dropwise to 3a using a dropping funnel for a period of 10 min. The mixture was allowed to stir overnight (20 hours). SiO₂ was filtered and CH₂Cl₂ was dried. CH₂Cl₂ was removed and the crude 3,3-Dibromo-1-phenyl-propan-1-one (4a) (2.82 g, 9.6 mmol) was obtained. (% Yield = 91%) A H NMR, C NMR and IR spectra were taken in CDCl₃.
Synthesis of 3,3-Dibromo-1-(4-methoxy-phenyl)-propan-1-one (4b)

We followed the procedure reported in the literature with some modifications. 29 3b (2.01 g, 12.5 mmol) was dissolved in 25 mL of CH$_2$Cl$_2$ and kept at -8 °C. SiO$_2$ (7.40 g, 123 mmol, 10eq) was added to 3b. PBr$_3$ (2.228 g, 8.2 mmol, 0.66 eq) in 10 mL of CH$_2$Cl$_2$ was added dropwise to 3b using a dropping funnel for a period of 10 min. The mixture was allowed to stir overnight (20 hours). SiO$_2$ was filtered and CH$_2$Cl$_2$ was dried. CH$_2$Cl$_2$ was removed and the crude 3,3-Dibromo-1-(4-methoxy-phenyl)-propan-1-one (4b) (3.54 g, 11.0 mmol) was obtained. (% Yield = 88%) A $^1$H NMR, $^{13}$C NMR and IR spectra were taken in CDCl$_3$. 

$^1$H NMR (CDCl$_3$, 400 MHz): δ 3.890 (s, 3H, -OCH$_3$), 4.127 (d, J = 6.4 Hz, 2H, -CH$_2$-), 6.193 (t, J = 6.4 Hz, 1H, -CH-), 6.968 (d, J = 8.8 Hz, 2H, -CH), 7.941 (d, J = 8.8 Hz, 2H, -CH) ppm.; $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 37.32, 52.94, 55.59, 114.06, 128.79, 130.65, 164.24, 192.79 ppm.; IR (CDCl$_3$): 1673 (C=O), 1599, 1574, 1511, 1463, 1421, 1398, 1346, 1318, 1311, 1258, 1223.
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1173, 1156, 1141, 1115, 1067, 1027, 981, 921, 833, 816, 785, 655, 632 cm⁻¹; HRMS: m/z calculated for C₁₀H₁₀O₂Br₂Na⁺ [M+Na]⁺, 344.89193; found, 344.89206.

**Synthesis of 3-Azido-1-phenyl-propenone (5a)**

4a (1.69 g, 5.8 mmol) was dissolved in 20 mL of methanol and 20 mL of acetone at 0 °C. NaN₃ (1.01 g, 15.5 mmol, 5eq) was dissolved in just enough amount of H₂O (~5 mL) and added to 4a. The mixture was allowed to stir ~1 hour. Methanol/Acetone mixture was removed and an extraction was performed with diethyl ether (50 mL) and H₂O (50 mL). Ether layer was separated and it was washed twice with H₂O and once with 100 mL of brine (saturated NaCl). The ether extract was dried using anhydrous MgSO₄. The ether was evaporated and the crude 3-Azido-1-phenyl-propenone (5a) (0.710 g, 4.1 mmol) was obtained. (% Yield = 71%) The crude was recrystallized from CH₂Cl₂ and pale yellow crystals (0.150 g, % Yield = 15%) were obtained. ¹H NMR, ¹³C NMR and IR spectra were taken in CDCl₃.

M. p. (observed): 78 – 84 °C; ¹H NMR (CDCl₃, 400 MHz): δ 6.772 (d, J = 13.2Hz, 1H, -CH=), 7.481 (t, J = 7.6Hz, 2H, -CH), 7.504 (d, J = 13.2Hz, 1H, -CH=), 7.576 (t, J = 7.4 Hz, 1H, -CH), 7.917 (d, J = 7.2 Hz, 2H, -CH) ppm.; ¹³C NMR (CDCl₃, 100 MHz): δ 113.16, 128.23, 128.68, 133.02, 137.68, 144.87, 188.76 ppm.; IR (CDCl₃) : 3064, 3044, 2143 (-N₃), 1697, 1662 (C=O), 1608, 1577, 1449, 1319, 1258, 1222, 1165, 1072, 1048, 1030, 1021, 1002, 951, 910, 841, 834, 773, 732, 684, 648, 530 cm⁻¹. HRMS: m/z calculated for C₉H₇N₃ONa⁺ [M+Na]⁺, 196.04813; found, 196.04816. UV/Visible λmax (ε): 292 nm (ε = 1.74 x 10⁴ M⁻¹ cm⁻¹), 257 nm (ε = 7.56 x 10³ M⁻¹ cm⁻¹).
Synthesis of 3-Azido-1-(4-methoxy-phenyl)-propenone (5b)

4b (1.43 g, 4.4 mmol) was dissolved in 20 mL of methanol and 20 mL of acetone at 0 °C. NaN₃ (1.443 g, 22 mmol, 5eq) was dissolved in just enough amount of H₂O (~5 mL) and added to 4b. The mixture was allowed to stir 1 hour. Methanol/acetone mixture was removed and an extraction was performed with diethyl ether (50 mL) and H₂O (50 mL). Ether layer was separated and it was washed twice with H₂O and once with 100 mL of brine (saturated NaCl). The ether extract was dried using anhydrous MgSO₄. The ether was evaporated and the crude 3-Azido-1-(4-methoxy-phenyl)-propenone (5b) (0.790 g, 3.9 mmol) was obtained. (% Yield = 88%) The crude was recrystallized from CH₂Cl₂ and pale yellow crystals (0.27g, 1.3 mmol) were obtained. (% Yield of crystals = 30%) A ¹H NMR, ¹³C NMR and IR spectra were taken in CDCl₃.

M. p. (observed): 105 – 108 °C; ¹H NMR (CDCl₃, 400 MHz) : δ 3.876 (s, 3H, -OCH₃), 6.764 (d, J = 13.2 Hz, 1H, =CH), 6.950 (d, J = 8.8 Hz, 2H, -CH), 7.477 (d, J = 12.8 Hz, 1H, =CH), 7.918 (d, J = 8.8 Hz, 2H, -CH) ppm.; ¹³C NMR (CDCl₃, 100 MHz): δ 55.516, 112.990, 113.891, 130.558, 144.007, 163.593, 187.070 ppm.; IR (CDCl₃): 3044, 3024, 2976, 2844, 2141 (-N₃), 2112 (-N₃), 1658 (C=O), 1606, 1575, 1517, 1469, 1451, 1441, 1419, 1350, 1318, 1307, 1296, 1273, 1263, 1231, 1176, 1125, 1049, 1028, 1010, 954, 940, 846, 780, 743, 680, 664, 632, 601, 526, 504, 472, 457 cm⁻¹. HRMS: m/z calculated for C₁₀H₉N₃O₂Na⁺ [M+Na]⁺, 226.05870; found, 226.05873. UV/Visible λ_max (ε): 307 nm (ε = 2.11 x 10⁴ M⁻¹ cm⁻¹), 230 nm (ε = 9.07 x 10³ M⁻¹ cm⁻¹).
Photolysis of 5a in Ar

A solution of 5a (14 mg, 0.08 mmol) in CDCl$_3$ (1 mL) was purged with argon for 5 min and photolyzed via a Pyrex filter for 6 hours at 298 K. $^1$H NMR and GC analysis of the reaction mixture showed the formation of 3-Oxo-3-phenyl-propionitrile (6a), 5-Phenyl-isoxazole (7a) and (2H-Azirin-2-yl)-phenyl-methanone (8a) after 1.5 hours of photolysis and then converted to 6a upon further irradiation. The products were characterized by GC-MS chromatography, $^1$H-NMR, $^{13}$C-NMR and IR spectroscopy of the reaction mixture. The spectral data of 6a and 7a match with the reported literature.$^{1, 30, 31}$

3-Oxo-3-phenyl-propionitrile (6a): $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 4.095 (s, 2H, -CH$_2$-), 7.534 (t, $J$ = 8.0 Hz, 2H, -CH), 7.673 (t, $J$ = 7.2 Hz, 1H, -CH), 7.930 (d, $J$ = 7.2 Hz, 2H, -CH) ppm; $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 29.399, 113.755, 128.483, 129.175, 134.278, 134.760, 187.071 ppm. IR (CDCl$_3$): 2263 (CN), 1689 (C=O) cm$^{-1}$; GC/MS (EI): m/z 145 (M), 105 (100%), 77, 51.

5-Phenyl-isoxazole (7a): $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 6.530 (d, $J$ = 1.6 Hz, 1H), 7.441 – 7.553 (m, 2H), 7.609 – 7.694 (m, 1H), 7.793 – 7.817 (m, 2H), 8.295 (d, $J$ = 1.6 Hz, 1H) ppm.; $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 98.687, 125.887, 127.270, 129.034, 130.236, 150.879, 169.377 ppm. GC/MS (EI): m/z 145 (M), 105 (100%), 90, 77, 68, 63, 51.

(2H-Azirin-2-yl)-phenyl-methanone (8a): $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 3.470 (d, $J$ = 2.0 Hz, 1H), 7.441 – 7.553 (m, 3H), 8.058 (d, $J$ = 8.4 Hz, 2H), 9.569 (d, $J$ = 2.4 Hz, 1H) ppm.; $^{13}$C NMR
(CDCl$_3$, 100 MHz): $\delta$ 28.414, 128.303, 128.803, 133.588, 136.874, 152.447, 197.408 ppm.

GC/MS (EI): m/z 145 (M, 100%), 117, 105, 90, 77, 63, 51.

\(^a\)This assignment is mainly based on the $^1$H NMR peak at 9.573 ppm which compares to the $^1$H NMR peaks of 2-benzoyl-2-methyl-2H-azirine at 9.75 (q, $J = 1.5$ Hz, 1H) and also compares with the $^1$H NMR peaks of 2-methyl-2phenyl-2H-azirine at 9.80 (q, $J = 1.5$ Hz, 1H).\(^1\) In addition, the assignment of the other hydrogen on the $^1$H NMR at 3.470 ppm is based on the $^1$H NMR peak at 3.50 ppm of 2-benzoyl-3-methyl-2H-azirine.\(^10\) Further, comparison was made to the published calculated NMR for 8\(^a\) by Advanced Chemistry Development Inc. Software v 11.01 (CAS Registry Number: 68289-79-2)

**Photolysis of 5a in O\(_2\)**

A solution of 5a (14 mg, 0.08 mmol) in CDCl$_3$ (1 mL) was purged with oxygen for 10 min and photolyzed via a Pyrex filter for 6 hours at 298 K. $^1$H NMR and GC analysis of the reaction mixture showed the formation of 6a, 7a and 8a and then converted to 6a upon further irradiation. The products were characterized by GC-MS chromatography, $^1$H-NMR, $^{13}$C-NMR and IR spectroscopy of the reaction mixture. The spectral data match with the reported literature.\(^1, 30, 31\)

**Photolysis of 5b in Ar**

A solution of 5b (20 mg, 0.1 mmol) in CDCl$_3$ (1 mL) was purged with argon for 5 min and photolyzed via a Pyrex filter for 6 hours at 298 K. GC analysis of the reaction mixture showed
the formation of 3-(4-Methoxy-phenyl)-3-oxo-propionitrile (6b), 5-(4-Methoxy-phenyl)-isoxazole (7b) and (2H-Azirin-2-yl)-(4-methoxy-phenyl)-methanone (8b); and then converted to 6b upon further irradiation. The products were characterized by GC-MS chromatography, 1H-NMR, 13C-NMR and IR spectroscopy of the reaction mixture. The spectral data for 6b and 7b match with the reported literature. 1, 30-32

3-(4-Methoxy-phenyl)-3-oxo-propionitrile (6b): 1H NMR (CDCl3, 400 MHz): δ 3.896 (s, 3H, -OCH3), 4.027 (s, 2H, -CH2-), 6.980 (d, J = 8.8 Hz, 2H, -CH), 7.899 (d, J = 8.8 Hz, 2H, -CH) ppm; 13C NMR (CDCl3, 100 MHz): δ 29.048, 55.674, 114.106, 114.344, 127.474, 130.943, 164.748, 185.444 ppm. IR (CDCl3): 2260 (CN), 1682 (C=O) cm⁻¹; GC/MS (EI): m/z 175 (M), 135 (100%), 107, 92, 77, 63, 50.

5-(4-Methoxy-phenyl)-isoxazole (7b): 1H NMR (CDCl3, 400 MHz): δ 3.863 (s, 3H, -OCH3), 6.399 (d, J = 1.6 Hz, 1H, =CH), 6.966 - 6.999 (m, 2H, -CH), 7.735 (d, J = 8.8 Hz, 2H, -CH), 8.253 (d, J = 2.0 Hz, 1H, =CH) ppm; 13C NMR (CDCl3, 100 MHz): δ 55.403, 97.295, 114.410, 120.154, 127.472, 150.821, 161.108, 169.344 ppm.; IR (CDCl3): 3014, 2946, 2840, 1599, 1462, 826 cm⁻¹; GC/MS (EI): m/z 175 (M, 100%), 160, 135, 120, 107, 92, 77, 63, 51.

(2H-Azirin-2-yl)-(4-methoxy-phenyl)-methanone (8b): 1H NMR (CDCl3, 400 MHz): δ 3.426 (d, J = 2.0 Hz, 1H, -CH), 3.863 – 3.891 (m, 3H, -OCH3), 6.966 – 6.999 (m, 2H, -CH), 8.057 (d, J
= 8.8 Hz, 2H, -CH), 9.573 (d, J = 2.0 Hz, 1H, =CH) ppm; $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$
28.041, 55.539, 113.972, 130.047, 130.624, 152.865, 163.926, 195.579 ppm. IR (CDCl$_3$): 1663
(C=O) cm$^{-1}$; GC/MS (EI): m/z 175 (M, 100%), 160, 132, 120, 104, 92, 77, 63, 51.

$^a$See 8a above

**Photolysis of 5b in O$_2$**

A solution of 5b (20 mg, 0.1 mmol) in CDCl$_3$ (1 mL) was purged with oxygen and photolyzed
via a Pyrex filter for 6 hours at 298 K. GC analysis of the reaction mixture showed the formation
of 6b, 7b, 8b and 4-Methoxy-benzoic acid (9b); and then converted to 6b upon further
irradiation. The products were characterized by GC-MS chromatography, $^1$H-NMR, $^{13}$C-NMR
and IR spectroscopy of the reaction mixture. The spectral data match with the reported literature.

4-Methoxy-benzoic acid (9b): GC/MS (EI): m/z 152 (M), 135 (100%), 107, 92, 81, 77, 63, 53.

**Acknowledgement**

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Chapter 07

Reactivity of Vinyl Azides in Solid State
Reactivity of Vinyl Azides in Solid State

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ABSTRACT.

We investigated the photoreactivity of vinyl azides 1a and 1b. We used solid state crystal photolysis studies, micro/nano crystal laser flash photolysis (LFP, λ=308 nm, 17 ns), solid state photolysis in KBr pallete and theoretical calculations and identified the intermediates formed by irradiating 1a and 1b.

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**Introduction**

Solid state synthesis has been used as a greener way of making stereo and region specific molecules.\(^1\) The understanding of the bulk solid materials are essentially employs the necessity of minimum atomic movement in environments with restricted freedom to associate the occurrence of a solid-state and its come with structural details in the reacting crystal.\(^2\) Furthermore, unstable products formed during photoreactions are more readily studied due to the rigidity and lack of diffusion inherent to crystals.\(^3\)

Nitrenes are reactive intermediates which have high spin properties hence could be used in applications like potential organic magnets. Azide group is a major precursor to the formation of nitrenes. Previously, Sankaranarayanan *et al.* have reported the selective dimerization of triplet alkyl nitrenes to form cis-azo dimmers (Scheme 1).\(^4\) In his work, X-ray crystal studies shows that molecules adopt an extended structure and as such the crystal packing arrangement consists of planar, \(\pi\)-stacked molecules.\(^4\) Sankaranarayanan *et al.* further propose that the molecular orbital alignment of the adjacent nitrenes controls the solid state reactivity rather than the N-N bond distances of nitrenes.\(^4\)

Scheme 1

\[
\begin{align*}
\text{Ar} & \text{O} \quad \text{N}_3 \\
\text{hv} & \rightarrow \\
\text{Ar} & \text{O} \quad \text{N} = \text{N} \quad \text{O} \\
\text{Ar:} & \text{p-ClPh,} \\
& \text{p-BrPh}
\end{align*}
\]
The solid state photo reactivity of vinyl azides have not been studied extensively. In this paper; we describe how the crystal packing affects the selective photo-reactivity of vinyl azides 1a and 1b in crystal lattices. We performed crystal photolysis, KBr studies, solid state time micro/nano crystal time resolved laser flash photolysis to understand the photo-reactivity of vinyl azides 1a and 1b.

Results

1. Product Studies

Scheme 2

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<th>Trial 01</th>
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<td>10%</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>21 hrs</td>
<td>10%</td>
<td>7%</td>
<td>10%</td>
</tr>
<tr>
<td>Trial 02</td>
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<td>1%</td>
<td>2%</td>
</tr>
<tr>
<td>Trial 03</td>
<td>45 hrs</td>
<td>8%</td>
<td>12%</td>
<td>12%</td>
</tr>
</tbody>
</table>

Photolysis of 1a in crystals via a Pyrex filter at 298 K yielded selectively formed 2a (Scheme 2) for low conversion and for low times of irradiation. Upon further irradiation of the crystals in addition to 2a, we have also observed 3a and 4a (Scheme 2). Irradiation via Pyrex filter ensures that only the ketone moiety absorbs the light and forms the singlet excited state of the ketone (S_{1K}) which then inter system crosses to the triplet excited state (T_1) of 1a. The first and the second excited states of T_1 and T_2 of 1a are 9 kcal/mol from each other. 1a rearrange to form T_{BR}. 423
of 1a. T_{BR} of 1a then rearrange to triplet nitrene by cleaving a N\textsubscript{2} molecule. T\textsubscript{N} of 1a cyclize to give 2a selectively. Upon further irradiation, T\textsubscript{N} of 1a rotate around its C=C bond to give the cis form of T\textsubscript{N} which then cyclize and intersystem cross to form 3a. Further, 4a comes from the C-C bond fission of 2a through singlet reactivity of 2a.

Scheme 3

Note: This product studies was carried out for atleast 3 times. However, sometimes the crystals melts while irradiation due to many factors. This could be due to the crystal lattice reorganization, or either due to moisture in crystals or in the surrounding, or due to the less cooling of the lamp resulting thermally heating crystals etc. Therefore, the results of trials which resulted crystal melting is not shown.

Photolysis of 1b in crystals via a Pyrex filter at 298 K yielded selectively formed 3b (Scheme 3) for low conversion and for low times of irradiation. Irradiation via Pyrex filter ensures that only the ketone moiety absorbs the light and forms the singlet excited state of the ketone (S\textsubscript{1K}) which then inter system crosses to the triplet excited state of the ketone (T\textsubscript{1K}) of 1b. The first and the second excited states of T\textsubscript{1K} and T\textsubscript{2K} of 1b are 9 kcal/mol from each other. 1b rearrange to form T_{BR} of 1b. T_{BR} of 1b then rearrange to triplet nitrene by cleaving a N\textsubscript{2} molecule. T\textsubscript{N} of 1b
rotate around its C=C bond to give the cis form of T\textsubscript{N} which then cyclize and intersystem cross to form 3b. Isoxazole 3b can also be formed directly from T\textsubscript{BR} of 1b by C-C bond rotation followed by the expulsion of N\textsubscript{2} molecule and cyclisation simultaneously.

2. Calculations

To better understand the reactivity of 1a we calculated the triplet surface of 1a using the Gaussian03\textsuperscript{5} and Gaussian09 at the B3LYP level of theory and with the 6-31+G(d) basis set.\textsuperscript{6,7} We used the calculations to identify the most favorable reaction on the triplet surface of 1a to understand the factors that control and govern the reactivity of on the triplet surface of 1a.
3. Laser Flash Photolysis

(I). 1a in nanocrystalline suspension in Acetone / H₂O

We performed laser flash photolysis to support the proposed reaction mechanism for 1a. Laser flash photolysis (Excimer laser, 308 nm, 17 ns) of 1a in argon-saturated acetonitrile produced a transient absorption with λ_max at ~400 nm (Figure 7-2). We assign the absorption at ~400 nm and ~500 nm to T_{N(Trans)} of 1a based on the TD-DFT calculations. The calculated TD-
DFT absorption spectrum of $T_{N(Trans)}$ of 1a in gas phase has the major electronic transfer at 473.48 nm ($f=0.025$), 349.88 nm ($f=0.0496$) and 310.22 ($f=0.0228$) (Figure 09) which fits well with the observed spectra around ~360-400 nm and 500 nm region. We further assign the absorption at 400 nm and 500 nm to the $T_{BR}$ of 1a based on TD-DFT calculations and quenching studies. The calculated TD-DFT absorption spectrum of $T_{BR}$ of 1a in gas phase has the major electronic transfer at 484.55 (0.03) nm, 355.51 nm ($f=0.0317$), and 336.89 nm ($f=0.0329$).

$1 \mu s$ time window in Ar

![Figure 1](image-url)  
**Figure 1.** Transient UV / Vis spectra of 1a in 1 $\mu s$ time window (a). 0.02 – 0.32 $\mu s$ (red) (b). 0.32 – 1.00 $\mu s$ (blue) (c). 1.00 – 2.00 $\mu s$ (green) (d). 2.00 – 7.51 $\mu s$ (purple)
5 μs time window in Ar

**Figure 2.** Transient UV / Vis spectra of 1b in 5 μs time window (a). 0.12 – 0.96 μs (red) (b). 0.96 – 2.56 μs (blue) (c). 2.56 – 7.68 μs (green) (d). 7.68 – 38.64 μs (purple)
Figure 3. Calculated UV of (a). $T_K$ of 1a (purple), (b). $T_N$ (trans) of 1a (red), (c). $T_N$ (cis) of 1a (blue), (d). $T_{BR}$ of 1a (green) in gas phase optimized using UB3LYP level of theory and then CAM-B3LYP TD-DFT level of theory with 6-31+G(d) basis set.
Kinetic analysis of the transient absorption further supports this assignment. The transient absorption at 310 nm decays mono-exponentially in the shorter time scale with a rate constant of $1.0 \times 10^6 \text{ s}^{-1}$ ($\tau = 1 \mu\text{s}$). This peak is due to the instrument error from the reflection from the sample cuvette. In longer time scale, the absorption at 310 nm decays bi-exponentially with rate constants of $5.7 \times 10^5 \text{ s}^{-1}$ ($\tau = 1.7 \mu\text{s}$) and $1.4 \times 10^5 \text{ s}^{-1}$ ($\tau = 7.4 \mu\text{s}$). We assign the longer decay to $T_N$ of 1a in argon saturated-solvent (Figure 4) whereas the shorter decay is due to the reflection from the sample cuvette due to the fact that the wavelength of irradiation is at 308 nm.

The kinetic analysis in 2.5 $\mu$s and 5 $\mu$s time scales at 420 nm decays bi-exponentially with a rate constants of $1.8 \times 10^6 \text{ s}^{-1}$ ($\tau = 550 \text{ ns}$) and $1.2 \times 10^5 \text{ s}^{-1}$ ($\tau = 8.2 \mu\text{s}$) which fits well with the rate constant of $T_{BR}$ of 1a and $T_N$ of 1a respectively. In addition, kinetics at 500 nm decays mono-exponentially in shorter time scales with a rate constant $1.0 \times 10^7 \text{ s}^{-1}$ ($\tau = 100 \text{ ns}$) which we assign for $T_{BR}$ of 1a. Analysis of kinetics at much larger time scales at 500 nm shows the absorption decays bi-exponentially with the faster rate constant is consistent with the rate constant at shorter time scales and the slower rate constant is consistent with the slower rate constant at 420 nm. Hence, we assign the shorter lived intermediate to $T_{BR}$ of 1a and the longer lived intermediate to $T_N$ of 1a.
310 nm 500 ns time window in Ar

\[ k_1 = 1.01 \times 10^6 \pm 5.42 \times 10^3 \text{ s}^{-1}, \tau = 989 \text{ ns} \pm 5 \text{ ns} \]

310 nm 1 \mu s time window in Ar

\[ k_1 = 1.01 \times 10^6 \pm 5.41 \times 10^3 \text{ s}^{-1}, \tau = 990 \text{ ns} \pm 5 \text{ ns} \]
310 nm 5 μs time window in Ar

\[ k_1 = 5.72 \times 10^5 \pm 1.11 \times 10^4 \text{s}^{-1}, \tau_1 = 1.7 \mu\text{s} \pm 0.03 \mu\text{s} \]

\[ k_2 = 1.36 \times 10^5 \pm 5.75 \times 10^3 \text{s}^{-1}, \tau_2 = 7.4 \mu\text{s} \pm 0.3 \mu\text{s} \]

420 nm 2.5 μs time window in Ar

\[ k_1 = 1.8249 \times 10^6 \text{s}^{-1}, \tau_1 = 548 \text{ns} \]

\[ k_2 = 1.2251 \times 10^5 \text{s}^{-1}, \tau_2 = 8.2 \mu\text{s} \]
420 nm 5 μs time window in Ar

420 nm 10 μs time window 0.017 mM in Ar
500 nm 50 ns time window 0.17 mM in Ar

\[ k = 1.01 \times 10^7 \pm 9.2 \times 10^4 \text{ s}^{-1}, \tau = 99 \text{ ns} \pm 1 \text{ ns} \]

500 nm 1 μs time window 0.17 mM in Ar

\[ k_1 = 6.88 \times 10^6, \tau_1 = 145 \text{ ns} \]
\[ k_2 = 2.06 \times 10^5, \tau_2 = 4.9 \mu\text{s} \]
500 nm 2.5 μs time window 0.17 mM in Ar

Figure 4. Kinetics of 1a in nanocrystalline 1.7 x 10^{-4} M suspension in Acetone / H_{2}O. (a). 500 ns time window at 310 nm in Ar. (b). 1 μs time window at 310 nm in Ar. (c). 5 μs time window at 310 nm in Ar. (d). 1 μs time window at 420 nm in Ar. (e). 2.5 μs time window at 420 nm in Ar. (f). 5 μs time window at 420 nm in Ar. (g). 10 μs time window at 420 nm in Ar with 1.7 x 10^{-5} M nanocrystalline suspension. (h). 50 ns time window at 500 nm in Ar. (e). 2.5 μs time window at 520 nm in Ar.

Quenching Studies with O_{2}

In oxygen-saturated nanocrystalline suspension the intensity of the band ~ around 420 nm and 500 nm are quenched to near zero where as the absorption at 310 nm has not been quenched (Figure 5-6). Thus oxygen quenches T_{K} of 1a and T_{N} of 1a.
1 μs time window 0.17 mM in Ar & in O₂

Figure 5. Transient UV/Vis spectra showing absorption in argon and oxygen
310 nm 1μs time window 0.17 mM in Ar

420 nm 5μs time window 0.17 mM in Ar
Figure 6. Kinetics showing absorptions in argon and oxygen
(II). 1b in nanocrystalline suspension in Acetone / H₂O

We performed laser flash photolysis to support the proposed reaction mechanism for 1b. Laser flash photolysis (Excimer laser, 308 nm, 17 ns) of 1b in argon-saturated acetonitrile produced a transient absorption with λ_{max} at ~350 nm (Figure 7-8). We assign the absorption at ~350 nm to Tₐ of 1b and Tₐ of 1b based on TD-DFT UCAM-B3LYP calculations, kinetics and quenching studies. The calculated TD-DFT absorption spectrum of Tₐ of 1b in gas phase has the major electronic transfer at 425.71 nm (f=0.01), 338.44 nm (f=0.024), and 304.39 (f=0.0375), whereas the calculated TD-DFT absorption spectrum of Tₐ of 1b in gas phase has the major electronic transfer at 427.56 nm (f=0.0083), 343.03 nm (f=0.0098), and 309.94 nm (f=0.0461) (Figure 9) which fits well with the observed spectra around ~300 nm – 420 nm region. We further assign the absorption at 320 nm and 380 nm to the Tₐ of 1b based on TD-DFT UCAM-B3LYP calculations and quenching studies. The calculated TD-DFT absorption spectrum of Tₐ of 1b in gas phase has the major electronic transfer at 428.78 (0.0166) nm, 346.2 nm (f=0.0276), 339.62 nm (f=0.0181) and 334.10 nm (f=0.0138). Further, as the time increases, the λ_{max} of the transient UV/Vis shifts towards 300 nm. We did not observe the Tₐ of 1b and we think it forms within the time resolution of the instrument.
1 μs time window in Ar

Figure 7. Transient UV / Vis spectra of 1b in 1 μs time window (a). 0.02 – 0.30 μs (red) (b). 0.30 – 1.00 μs (blue) (c). 1.00 – 2.00 μs (green) (d). 2.00 – 7.20 μs (purple)

5 μs time window in Ar
Figure 8. Transient UV / Vis spectra of 1b 5 μs time window (a). 0.12 – 1.08 μs (red) (b). 1.08 – 3.08 μs (blue) (c). 3.08 – 7.56 μs (green) (d). 7.56 – 38.00 μs (purple)
Figure 9. Calculated UV of (a). \( T_K \) of 1b (purple), (b). \( T_N \) (trans) of 1b (red), (c). \( T_N \) (cis) of 1b (blue), (d). \( T_{BR} \) of 1b (green); in gas phase optimized using UB3LYP and then TD-DFT level of theory with UCAM-B3LYP 6-31+G(d) basis set.

Kinetic analysis of the transient absorption further supports this assignment. The transient absorption at 320 nm decays mono-exponentially in the longer time scale with a rate constant of \( 5.9 \times 10^4 \text{ s}^{-1} \) (\( \tau = 17 \mu s \)). We assign this decay to the decay of \( T_N \) of 1b. The transient absorption at 340 nm decays mono-exponentially with rate constants between \( 1.95 \times 10^5 \pm 3.6 \times 10^3 \text{ s}^{-1} \) (\( \tau = 5.1 \mu s \pm 0.1 \mu s \)) and of \( 1.03 \times 10^5 \pm 1.87 \times 10^3 \text{ s}^{-1} \) (\( \tau = 9.7 \mu s \pm 0.2 \mu s \)) which we assign for \( T_N \) of 1b in argon saturated-solvent (Figure 4). The transient at 340 nm grows in with a rate constant of \( 1.04 \times 10^7 \pm 7.59 \times 10^5 \text{ s}^{-1} \) (\( \tau = 96 \text{ ns} \pm 7 \text{ ns} \)). Therefore, we assign the lifetime of the \( T_{BR} \) of 1b to be ~96 ns since it is the precursor to the \( T_N \) of 1b.
320 nm 10 μs time window in Ar

\[ k_1 = 5.92 \times 10^4 \pm 1.18 \times 10^3 \text{ s}^{-1}; \quad \tau = 16.9 \pm 0.3 \mu\text{s} \]

320 nm 1 μs time window in Ar

\[ k_1 = 5.47 \times 10^5 \pm 1.33 \times 10^5 \text{ s}^{-1}; \quad \tau = 1.8 \pm 0.4 \mu\text{s} \]
340 nm 100 ns time window in Ar

\[ k_1 = 1.04 \times 10^7 \pm 7.59 \times 10^5 \text{ s}^{-1}; \quad \tau = 96 \text{ ns} \pm 7 \text{ ns} \]

340 nm 2.5 μs time window in Ar

\[ k_1 = 1.58 \times 10^5 \pm 2.94 \times 10^3 \text{ s}^{-1}; \quad \tau = 6.3 \mu\text{s} \pm 0.1 \mu\text{s} \]
340 nm 5 μs time window in Ar

\[ k_1 = 1.03 \times 10^5 \pm 1.87 \times 10^3 \text{ s}^{-1}; \quad \tau = 9.7 \mu\text{s} \pm 0.2 \mu\text{s} \]

360 nm 5 μs time window in Ar

\[ k_1 = 1.95 \times 10^5 \pm 3.6 \times 10^3 \text{ s}^{-1}; \quad \tau = 5.1 \mu\text{s} \pm 0.1 \mu\text{s} \]
400 nm 5 μs time window in Ar

\[ k_1 = 1.45 \times 10^5 \pm 8.0 \times 10^3 \text{ s}^{-1}; \quad \tau = 6.9 \mu s \pm 0.4 \mu s \]

**Figure 10.** Kinetics of 1b in nanocrystalline 1.7 x 10^{-4} M suspension in Acetone / H2O. (a). 10 μs time window at 320 nm in Ar. (b). 1 μs time window at 320 nm in Ar. (c). 100 ns time window at 340 nm in Ar. (d). 2.5 μs time window at 340 nm in Ar. (e). 5 μs time window at 340 nm in Ar. (f). 5 μs time window at 360 nm in Ar. (g). 5 μs time window at 360 nm in Ar.

**Quenching Studies with O2**

In oxygen-saturated nanocrystalline suspension the intensity of the band ~ around 360 nm is quenched to near zero (Figure 11-12). Thus oxygen quenches T_N of 1a.
1 μs time window in Ar & O₂

Wavelength [nm]

Absorbance

Ar (0.02 - 0.30 μs)

O₂ (0.02 - 0.30 μs)

Absorbance

Wavelength [nm]

Ar (2.00 - 7.20 μs)

O₂ (2.00 - 7.20 μs)
5 μs time window in Ar & O₂

![Graph showing transient UV/Vis spectra in Ar and O₂](image)

5 μs time window in Ar & O₂

![Graph showing transient UV/Vis spectra in Ar and O₂](image)

**Figure 11.** Transient UV/Vis spectra in Argon and in Oxygen
340 nm 100 ns time window in Ar & O₂

Figure 12. Kinetics of 1b in Argon and in Oxygen
4. X – Ray Crystal structure of 1a

Figure 13. Crystal structure of 1a

Crystal structure of 1a shows that it has E-configuration (Figure 13) N – N bond distances for adjacent molecules in the same layer to form a cis dimer is 3.803 Å (Figure 14). N - N bond distance for two adjacent molecules in two adjacent layers to form a trans dimer is 4.562 Å. Crystal structure analysis also shows that there are inter molecular H bonding between carbonyl oxygen and β-H atom of azide molecules in two adjacent layers. We propose that the the inter system crossing rate in crystal lattices are much faster than the rate of dimerization regardless of the N-N bond distance of two adjacent molecules. Hence we observe selective formation of 2a in crystal lattices.
Figure 14. (a). N-N bond distances of adjacent molecules in order to form cis and trans azo dimers (b). b-c planar view of inter-molecular H bonding between carbonyl oxygen and β-H atom of 1a in adjacent layers.
5. X – Ray Crystal structure of 1b

Crystal structure of 1b shows that it has E-configuration (Figure 15) N – N bond distances for adjacent molecules in the same layer to form a cis dimer is 3.784 Å (Figure 16). N - N bond distance for two adjacent molecules in two adjacent layers to form a trans dimer is 5.229 Å. We propose that the the inter system crossing rate in crystal lattices are much faster than the rate of dimerization regardless of the N-N bond distance of two adjacent molecules. Hence we observe selective formation of 3b in crystal lattices.

Figure 15. Crystal structure of 1b.
Figure 16. N1-N1 bond distances
Figure 17. Crystal packing from different planes
6. Solid State Photolysis

Solid State Photolysis of 1a

FT-IR analysis of the KBr pallet of 1a showed the formation of few new IR peaks which could be attributed to the formation of 2a in crystals. (Figure 18-20, Table 1)
Figure 18. KBr photolysis of 1a (a). Before irradiation (red) and after 10 min of irradiation (blue), (b). Before irradiation (red) and after 1 hour of irradiation (blue)
Figure 19. KBr photolysis of 1a in 2200-1400 cm\(^{-1}\) (a). Before irradiation (red) and after 10 min of irradiation (blue), (b). Before irradiation (red) and after 1 hour of irradiation (brown)
Figure 20. KBr photolysis of 1a in 1000-740 cm\(^{-1}\) (a). Before irradiation (red) (b). After 2 min of irradiation (blue) (c). After 5 min of irradiation (d). After 10 min of irradiation (e). After 20 min of irradiation (f). After 30 min of irradiation (g). After 1 hour of irradiation.

Table 1. Experimental and Calculated IR comparison of 1a and 2a

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<tr>
<th>IR Bands / cm(^{-1})</th>
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<th>New Bands</th>
<th>Calculated bands for 1a</th>
<th>Calculated bands for 2a</th>
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<tr>
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<tr>
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<td>1682 (C=O)</td>
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Solid State Photolysis of 1b

FT-IR analysis of the KBr pallete of 1b showed the formation of few new IR peaks which could be attributed to the formation of 3b in crystals (Figure 21-24, Table 2).

Figure 21. KBr photolysis of 1a (a). Before irradiation (blue) (b). After 30 min of irradiation (red).
Figure 22. KBr photolysis of 1b, 2100 cm$^{-1}$ region (a). Before irradiation (blue), (b). After 2 min of irradiation (red), (c). After 5 min of irradiation (pink) (d). After 10 min of irradiation (brown)

Figure 23. KBr photolysis of 1b, 1750-1400 cm$^{-1}$ region (a). Before irradiation (blue), (b). After 2 min of irradiation (red), (c). After 5 min of irradiation (pink) (d). After 10 min of irradiation (brown)
**Figure 24.** FTIR spectra of 1b (a). From 1300-1000 cm\(^{-1}\); Before irradiation (blue), After irradiation (red) (b) From 1000-500 cm\(^{-1}\); Before irradiation (blue), After irradiation (red)

**Table 2.** The comparison of FTIR peaks of 1b and 3b. (The bolded values are in stronger agreement with the calculated shift and experimental shift)

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<th>IR Bands / cm(^{-1})</th>
<th>Depleted bands</th>
<th>New Bands</th>
<th>Calculated bands for 1b</th>
<th>Calculated bands for 3b</th>
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<td>1720 (298) (C=O)</td>
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<td><strong>1021</strong></td>
<td>1036 (125)</td>
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Experimental

X – Ray Crystal Structure

For X-ray examination and data collection, a suitable colorless, rectangular block-like crystal, approximate dimensions 0.11 x 0.05 x 0.03 mm, was mounted in a loop with Paratone-N oil and transferred to the goniostat bathed in a cold stream.

Intensity data were collected at 150K on a standard Bruker SMART6000 CCD diffractometer using graphite-monochromated Cu Kα radiation, λ=1.54178Å. The detector was set at a distance of 5.165 cm from the crystal. A series of 15-s data frames measured at 0.3°
increments of \( \omega \) were collected to calculate a unit cell. For data collection frames were measured for a duration of 15-s at 0.3\(^{\circ}\) intervals of \( \omega \) with a maximum 2\( \theta \) value of \( \sim135^{\circ} \). The data frames were processed using the program SAINT. The data were corrected for decay, Lorentz and polarization effects as well as absorption and beam corrections based on the multi-scan technique.

The structure was solved by a combination of direct methods in SHELXTL and the difference Fourier technique and refined by full-matrix least squares on \( F^2 \). Non-hydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were calculated and treated with a riding model. The H-atom isotropic displacement parameters were defined as \( a^*U_{eq} \) of the adjacent atom (\( a=1.5 \) for methyl and 1.2 for all others). The refinement converged with crystallographic agreement factors of \( R_1=3.80\% \), \( wR_2=9.59\% \) for 1268 reflections with \( I>2\sigma(I) \) (\( R_1=5.64\% \), \( wR_2=10.79\% \) for all data) and 137 variable parameters.

Calculations

All geometries were optimized at B3LYP level of theory and with 6-31G+(d) basis set as implemented in the Gaussian03 and Gaussian09 programs.\(^6\) All transition states were confirmed to have one imaginary vibrational frequency by analytical determination of the second derivatives of the energy with respect to internal coordinates. Intrinsic reaction coordinates\(^8\) calculations were used to verify that the located transition states corresponded to the attributed reactant and product.\(^9\)\(^,\)\(^10\) The absorption spectra were calculated using time-dependent density functional theory (TD-DFT).\(^11\)\(^-\)\(^15\) The effect of solvation was calculated using the self-consistent reaction field (SCRF) method with the integral equation formalism polarization continuum model (IEFPCM) with acetonitrile, methanol and dichloromethane as solvents.\(^16\)\(^-\)\(^20\)
Laser Flash Photolysis using Nanocrystalline Suspensions.

Laser flash photolysis was done with an Excimer laser (308 nm, 17 ns).\textsuperscript{21} The system has been described in detail elsewhere.\textsuperscript{21} For the sample preparation, we followed the procedure described by Garcia-Garibe and co-workers with slight modifications.\textsuperscript{22} Samples for laser flash photolysis experiment was prepared by injecting 5 μL of 1a, 1b (0.1 M) solution in acetone into 3 mL of distilled water. The resulting suspension (1.7 x 10^{-4} M) was homogenized at room temperature. The optical density of the resulting suspension was adjusted by serial dilution with distilled water to prepare a suspension with 1.7 x 10^{-5} M concentration. The suspensions had absorption between 0.3 and 0.6 at 308 nm. Typically, ~2 mL of the stock solution was placed in a 10 mm × 10 mm wide, 48 mm long quartz cuvette and was purged with argon for 5 min or oxygen for 15 min. The rates were obtained by fitting an average of three to five kinetic traces.

Solid State Photolysis

1a (20 mg, 0.11 mmol) was grinded with 1.0 g of KBr and a pallete was prepared. Then the KBr pallete of 1a was photolyzed via a Pyrex filter for 20 hours at 298 K. FT-IR analysis of the KBr pallete was carried out.
Synthesis

Scheme 5

Conclusions

We have demonstrated from LFP that 1a and 1b forms 1,2-triplet biradical and triplet vinyl nitrene intermediates in solid state. We have further shown that 1a has selectively forms 2a in crystal lattices whereas 1b forms 3b in crystal lattices. However, 1a and 1b shows somewhat different photochemistry in solution (see Chapter 6). This unique difference could be due to the rigidity of the crystal lattices.
Acknowledgement

This work was supported by NSF and the Ohio Supercomputer Center. R. A. A. U. R. would like to thank Ann P. Villalobos Fellowship from the Department of Chemistry, University of Cincinnati. We would also like to thank,

(1) Funding for the SMART6000 diffractometer was through NSF-MRI grant CHE-0215950.

(2) SMART v5.632 and SAINT v7.46A data collection and data processing programs, respectively. Bruker Analytical X-ray Instruments, Inc., Madison, WI; SADABS v2008/1 for the application of semi-empirical absorption and beam corrections. G.M. Sheldrick, University of Göttingen, Germany; SHELXTL v6.14 for structure solution, figures and tables, neutral-atom scattering factors as stored in this package. G.M. Sheldrick, University of Göttingen, Germany and Bruker Analytical X-ray Instruments, Inc., Madison, WI.

References


Chapter 08

Studies on Photogenerated 1,3 Biradicals of Cyclopropanes using Laser Flash Photolysis
Studies on Photogenerated 1,3 Biradicals of Cyclopropanes using Laser Flash Photolysis

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ABSTRACT.

The 1,3 bi-radicals could be potentially used as antioxidants. We investigated the photoreactivity of cyclopropanes 1a&1b. We used laser flash photolysis (LFP, λ=308 nm), product studies and theoretical calculations and identified the intermediates formed by irradiating 1a&1b. Solutions photolysis of 1a yields 2a in CD3OD where as it doesn’t give any product in CDCl3. 2a forms first by forming T1K of 1a and then by forming a ketyl radical which dimerizes to give 2a. Solution photolysis of 1bgives a mixture of 1b, 2b and 2c. The laser flash photolysis (LFP, λ = 308 nm) shows the formation of T1K of 1a, ketyl radical of 1a, TBR of 1a and ketyl radical of 1b and TBR of 1b. The lifetime of biradical of 1b is significantly longer than that for 1a due to the stabilization from phenyl ring.
**Introduction**

Common organic materials, such as oil, rubber, food, and plastics undergo the process of oxidation in air, or autoxidation, which causes the materials to degrade. The autoxidation of hydrocarbons is caused by a radical chain mechanism with oxygen. However, antioxidants are able to terminate these radical chain reactions, thus stopping the process of oxidation. Some very un-reactive radicals have the ability to scavenge the radicals that are formed from the reaction with oxygen, and can be used as antioxidants. If these radicals do not have stable reactions with oxygen and hydrogen atom abstraction, then they will only add to the radical chain in the autoxidation process.

Mizuno et al. have studied the photolysis of trans-1,2-bis(4-acetyl-phenyl)cyclopropane (m) using transient spectroscopy (mode-locked Nd-YAG laser, fourth harmonic, 266 nm) and observed the first direct observation of unconstrained 1,3-biradicals in fluid solution with lifetimes of 14.7 ± 1 ns in heptane and 13.4 ± 1 ns in methanol (Scheme 1). Similar lifetimes were also observed for trans-1-(4-acetylphenyl)-2-phenylecyclopropane. Mizuno et al. investigated the effect of the number of aryl groups at biradical termini by increasing the number of aryl groups and also the effect by increasing the distance between the biradicals and found there is only a small effect on the lifetime by increasing the number of aryl groups at biradical termini. Mizuno et al. further states that the inter-terminal distance on ISC rate has two-fold contribution, one is as the distance increases, the lifetime shortens by diminishing exchange integral, but lengthened by diminishing spin-orbit coupling. Their trans-cis isomerization of trans-1,2-bis(4-acetyl-phenyl)cyclopropane is similar to our observed results for 1b and involves a triplet 1,3-biradical intermediate.
Dowd and co-workers have studied the photolytic decomposition of (1R,4R)-5-methylene-2,3-diazabicyclo[2.2.1]hept-2-ene (p) and observed the formation of 1,3 semi localized diradical (q) in electron spin resonance spectrum (ESR) at 77 K in matrix, whereas at 15 K in ethanol or glycerol glass matrix they mainly observed 1,3 delocalized diradical (r) and a weak signal for q (Scheme 2).² Further, Dowd and co-workers have demonstrated that irradiation of p in chloroform, isopentane or methylcyclohexane matrices yield more semilocalized diradical q as the major product, hence the first direct observation of a semilocalized homotrimethylenemethane 1,3-diradical.

Karti et al. reports the irradiation of 3,3’,4,4’-benzophenonetetracarboxylic dianhydride (BTDA) (313 nm) in the presence of cis- or trans-1,2-diphenylcyclopropane (cis- or trans-DPC) lead to an efficient isomerization.³ The picoseconds transient absorption spectroscopy of BTDA and trans-DPC shows a transient species that decays with a lifetime < 100 ps. They assigned this intermediate to BTDA⁻/trans-DPC⁺ radical ion pair. The product of this fast decaying radical
ion pair was investigated by time resolved photo-acoustic calorimetry (TRPAC). TRPAC shows that upon the decay of radical ion pair, an intermediate was formed with energy of $29 \pm 1$ kcal/mol above the ground state reactants (BTDA and trans-DPC) with a lifetime of $14 \pm 2$ ns. The energy and the lifetime of this intermediate is in good agreement with the expected triplet 1,3-diphenyltrimethylene biradical. This was further characterized by nano second transient absorption spectroscopy which shows an absorption maximum at 320 nm.

Muller et al. reports the first direct observation of a 2,3-hydrogen shift in a 1,3 biradical by using ESR spectroscopy. For example, arylcyclopropane forms, 1,3 biradical, and then forms arylcyclopropene through 2,3-H shift. They mention that the products formed after 2,3-H shift are stable for hours. Shaw et al. reports an ESR study of a biradical of type 1,3-cyclopentadiyl (II) upon the irradiation of 2,3-diazabicyclo-[2.2.1]heptene-2 (I) at 5.5 K (Scheme 3). Their assignment of the ESR bands to the structure II is based on the zero-field splitting parameters and the change of the hyperfine structure with deuteration of I. Further, the zero-field parameters were calculated for an idealized planar structure of II with a bond angle of 110° at the carbon separating the two trivalent carbon atoms and a C-C bond length of 1.52 Å in order to see whether the experimental parameters for II agrees with calculated ones.

Scheme 3

Adam et al. reports oxygen trapping of triplet diradicals, generated through benzophenone-sensitized laser flash photolysis of azo alkane precursors and estimated the lifetime of cycloalka-1,3-diyls (A), especially those with localized radical centers such as
cycloalka-1,3-diyls (Scheme 4). They estimated lifetimes of cyclopenta-1,3-diyl (Aa) to be 100 ± 30 ns.

Scheme 4

However, Adam et al. also reports that the time-resolved photo acoustic calorimetry (PAC) studies for I (Scheme 3) resulted a triplet lifetime value of 258 ± 14 ns for parent 1,3-cyclopentadiyl radical of I (i.e. II) which is significantly higher than the oxygen trapping method. However, the discrepancy between the lifetimes obtained by PAC and laser flash photolysis is because a too low value for the rate constant for oxygen trapping (kO2) was used to estimate the lifetime of the biradical from the competition kinetics in oxygen trapping. Adam et al. further states that by using kO2 = 5.3 x 10^9 M^-1 s^-1 (which was determined directly from PAC), oxygen trapping method leads to a triplet biradical lifetime 354 ± 57 ns for II. Moreover, 1,3-diphenyl substitution increases the triplet lifetimes (100-fold) in acetonitrile to 16 000 ns ± 2000 ns. Adam et al. have also investigated the triplet biradical trapping efficiencies and lifetimes of II. Engel et al. reports the thermolysis of cis-a-phenyl-2-(methylazo)cyclopropane and trans-a-phenyl-2-(methylazo)cyclopropane proceed through a presumed 1,3-biradical by cyclopropane
ring opening. This intermediate is also similar to the proposed 1,3-biradicals of 1a and 1b that we have investigated herein.

Caldwell et al. have also observed an acyclic 1,3-biradical ($\tau = 7–18$ ns) of $\alpha$-cyclopropylstyrenes. In this paper, we explore the photogenerated 1,3 biradicals in cyclopropane systems 1a and 1b using laser flash photolysis to find out the lifetimes. We have found that 1a undergo dimerization by forming a ketyl radical of 1a whereas, 1b forms 2b through a triplet 1,3-biradical. The lifetimes of TBR of 1a is $\sim 2.3$ μs in acetonitrile and $\sim 2.1$ μs in methanol whereas, lifetime of TBR of 1b is $\sim 1.2$ μs in acetonitrile.

**Results**

1. **Product Studies**

**Scheme 5**

<table>
<thead>
<tr>
<th>Trial</th>
<th>In Ar-94hrs</th>
<th>In Ar-65hrs</th>
<th>In O2-65hrs</th>
</tr>
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<tr>
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<td>08 %</td>
<td>15 %</td>
</tr>
<tr>
<td>Trial-2</td>
<td>57 %</td>
<td>87 %</td>
<td>77 %</td>
</tr>
</tbody>
</table>
Photolysis of 1a in argon-saturated chloroform-d via a Pyrex filter at 298 K did not yield any product (Scheme 5). Irradiation of 1a in oxygen-saturated chloroform-d via a Pyrex filter at 298 K also did not yield any product. However, photolysis of 1a in argon- and oxygen-saturated methanol-d₄ through a Pyrex filter at 298 K yielded a dimer (2a) which is presumably formed through a ketyl radical dimerization (Scheme 5). Irradiation via Pyrex filter ensures that only the ketone absorbs the light and forms the singlet excited state of the ketone (S₁K) which intersystem crosses to the triplet excited state of the ketone (T₁K) of 1a. Although 1a is an aromatic derivative, its first and the second excited state of the ketone chromophore (T₁K and T₂K) are expected to be within 2 – 7 kcal/mol of each other.¹¹ Instead of undergoing energy transfer from T₁K of 1a to the cyclopropane moiety to form triplet 1,3 biradical (T_BR) of 1a, T₁K of 1a abstract a D atom from the solvent and dimerize to form 2a.

**Scheme 6**¹²

<table>
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<tr>
<th></th>
<th>Ar</th>
<th>52%</th>
<th>trace</th>
<th>3%</th>
<th>--</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td></td>
<td>42%</td>
<td>&lt;1%</td>
<td>2%</td>
<td>3%</td>
</tr>
</tbody>
</table>

Note: 40% and 52% of 1b remained in argon and oxygen saturated methanol-d₄ after 18 hours. Only one trial of product study was carried out.

Photolysis of 1b in argon-saturated and oxygen-saturated methanol-d₄ via a Pyrex filter at 298 K yielded an isomerized product (2b) which was formed through an inversion around the
chiral centers through 1,3 biradical formation (Scheme 5). Irradiation via Pyrex filter ensures that only the ketone absorbs the light and forms the singlet excited state of the ketone (S\textsubscript{1K}) which intersystem crosses to the triplet excited state of the ketone (T\textsubscript{1K}) of 1b. The first and the second excited triplet states of the ketone in 1b (T\textsubscript{1K} and T\textsubscript{2K}) are expected to be within 3 – 8 kcal/mol of each other according to UB3LYP and TD-DFT calculations, similarly to T\textsubscript{1K} and T\textsubscript{2K} of 1a. Energy transfer from T\textsubscript{1K} of 1b to the cyclopropane moiety to form triplet 1,3 biradical (T\textsubscript{BR}) of 1b results in photoproduct 2b. There are two possible ways to form 2c by cyclopropyl ring opening to form a 1,3-triplet biradical followed by (a). 2,1-H shift or (b). Hydrogen abstraction from methanol and again followed by another hydrogen abstraction by methanol radical. We hypothesize; second pathway is more feasible in triplet manifold. 2d could be formed by dimerization of two 1,3-triplet biradical followed by ISC. α-Cleavage results the formation of 2e in argon saturated methanol whereas it results in 2f in oxygen saturated methanol.

2. Calculations

To better understand the reactivity of 1a, 1b we calculated the triplet surface of 1a, 1b using the Gaussian03\textsuperscript{13} and Gaussian09 at the B3LYP level of theory and with the 6-31+G(d) basis set.\textsuperscript{14,15} We used the calculations to identify the most favorable reaction on the triplet surface of 1a, 1b and to understand the factors that govern the reactivity on the triplet surface of 1a and 1b.

(a). Calculations of 1a

We optimized the ground-state (S\textsubscript{0}) of 1a (Figure 1). The TD-DFT calculations locate S\textsubscript{1K} of 1a at 88 kcal/mol above its S\textsubscript{0}. Analysis of molecular orbitals shows that S\textsubscript{1K} of 1a has (n,π*)
configuration where the major electronic excitation is from the non-bonding electrons of oxygen into the $\pi^*$ orbital (Table 1, Figure 2).

![Figure 1](image1.png)

**Figure 1.** Optimized $S_0$ Conformers of 1a.

<table>
<thead>
<tr>
<th>Table 1. Electronic transitions of 1a above 260 nm in gas phase</th>
</tr>
</thead>
<tbody>
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<tr>
<td>38 -&gt; 40</td>
</tr>
<tr>
<td>38 -&gt; 41</td>
</tr>
</tbody>
</table>

![Figure 2](image2.png)

**Figure 2.** Molecular orbitals corresponds to electronic transitions of $S_{1K}$ of 1a above 260 nm
TD-DFT calculations of 1a in gas phase show that T_{1K} of 5a is located 76 kcal/mol above S_0 of 1a and has (n,π*) configuration, whereas T_{2K} is 78 kcal/mol above S_0 of 1a and has (π,π*) configuration (Scheme 7).

We also optimized the T_{1K} of 1a and found that it is located 71 kcal/mol above the S_0 of 1a, which is considerably lower than the energy obtained by TD-DFT calculations (Figure 3). Analysis of bond lengths of S_0 of 1a shows C=O bond length of 1.23 Å. The optimized structure of T_{1K} of 1a shows that C=O bond length has been increased from 1.23 Å to 1.33 Å. Further, it also shows that carbonyl carbon to quaternary phenyl carbon bond length is 1.42 Å which is somewhat shorter than the corresponding bond length, 1.50 Å in the S_0 of 1a. In addition the dihedral angle of O-C_{carbonyl}-C_{ortho}-H has been reduced from 174.9° in the S_0 of 1a to 147.2° in the T_{1K} of 1a. The analysis of bond lengths in the phenyl ring shows that only the C_{carbonyl}-C_{ortho} bond lengths have been increased from 1.40 Å in the S_0 of 1a to 1.43 Å in the T_{1K} of 1a. These analysis shows that in optimized structure of T_{1K} of 1a the triplet state is delocalized mainly to the C=O chromophore.

Figure 3. Optimized conformers of T_{1K} of 1a and T_{BR} of 1a.
We calculated the transition state for the \( T_{1K} \) of \( 1a \) to form the triplet biradical (\( T_{BR} \)) of \( 1a \) and found that it is located 11 kcal/mol above the \( T_{1K} \) of \( 1a \) and 31 kcal/mol above \( T_{BR} \) of \( 1a \). Intrinsic Reaction Coordinate (IRC) calculations confirm the transition state correlate to the \( T_{1K} \) (\( n,\pi^* \)) of \( 1a \) and \( T_{BR} \) of \( 1a \).

Optimization of \( T_{BR} \) of \( 1a \) located it at 51 kcal/mol above \( S_0 \) of \( 1a \) (Figure 3). The C=O bond in \( T_{BR} \) of \( 1 \) is 1.25 Å and comparable to the C=O bond in the \( S_0 \) of \( 1a \) that is 1.23 Å. C-C bond distances of phenyl group of \( S_0 \) of \( 1a \) and \( T_{BR} \) of \( 1a \) has not been changed. Further, C\(_{carbonyl}\)-C\(_a\) bond length has been reduced from 1.49 Å in \( S_0 \) of \( 1a \) to 1.44 Å in \( T_{BR} \) of \( 1a \) and Moreover, O- C\(_{carbonyl}\)-C\(_a\)-H dihedral angle has not been changed in \( S_0 \) of \( 1a \) and in \( T_{BR} \) of \( 1a \). In addition, C-C-C angle in the cyclopropyl ring has also been increased from 60.0° in \( S_0 \) of \( 1a \) to 113.7° in \( T_{BR} \) of \( 1a \). The bond distances of cyclopropyl ring of the \( S_0 \) of \( 1a \) are 1.53 Å (C\(_a\)-C\(_{\beta1}\)), 1.53 Å (C\(_a\)-C\(_{\beta2}\)) and 1.49 Å (C\(_{\beta1}\)-C\(_{\beta2}\)). The same bond distances of \( T_{BR} \) of \( 1a \) are 1.49 Å (C\(_a\)-C\(_{\beta1}\)), 2.50 Å (C\(_a\)-C\(_{\beta2}\)) and 1.50 Å (C\(_{\beta1}\)-C\(_{\beta2}\)). The distance between two radical carbons has also been increased from 1.53 Å in \( S_0 \) of \( 1a \) to 2.50 Å in \( T_{BR} \) of \( 1a \). The optimized structure shows the two radical centers are not orthogonal to one-another. Thus, the optimized structure of \( T_{BR} \) of \( 1a \) shows that the biradical is localized on the carbon atoms.

We calculated the transition state for the \( T_{1K} \) of \( 1a \) to form the ketyl radical of \( 1a \) by hydrogen-abstraction from a solvent methanol molecule and found that it is located 4 kcal/mol above the \( T_{1K} \) of \( 1a \) and 9 kcal/mol above ketyl radical of \( 1a \) (Scheme 8). Intrinsic Reaction Coordinate (IRC) calculations confirm the transition state correlate to the \( T_{1K} \) of \( 1a \) and ketyl radical of \( 1a \).
Thus, the calculations show that $T_{1K}$ of 1a has less of a barrier to undergo hydrogen atom abstraction than cleavage to form $T_{BR}$ of 1a. These results fit with the observation that product studies yield mainly product due to hydrogen atom abstraction.

Scheme 7
Scheme 8

$$\text{S}_1 \quad 88$$

$$\text{T}_2 (\pi, \pi^*) \quad 78$$

$$\text{T}_1 (n, \pi^*) \quad 71-76$$

$$\text{TS - 2} \quad 75$$

$$\text{TS} - 2 \quad 66$$

$$\begin{align*}
\text{Ph} & \quad \text{H} \\
\text{CH}_3\text{OH} & \\
\text{Ketyl Radical of 1a}
\end{align*}$$

$$\text{O} \quad 0$$

$$\begin{align*}
\text{Ph} & \quad \text{H} \\
\text{CH}_3\text{OH}
\end{align*}$$
(b). Calculations of 1b

We optimized the ground-state ($S_0$) of 1b (Figure 4). The TD-DFT calculations locate $S_{1K}$ of 1b at 86 kcal/mol above its $S_0$. Analysis of molecular orbitals shows that $S_{1K}$ of 1b has a ($n,\pi^*$) configuration that is mixed with ($\pi,\pi^*$) configuration from both phenyl groups. (Table 1, Figure 5).

![Figure 4. Optimized $S_0$ Conformers of 1b.](image)

<table>
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<tr>
<td>4.2730</td>
<td>290.16</td>
<td>0.1701</td>
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</table>

**Table 2.** Electronic transitions of $S_{1K}$ of 1b above 270 nm in gas phase
Figure 5. Molecular orbitals of $S_{1K}$ of $1b$ in the gas phase from TD-DFT calculations on the $S_0$ of $1b$.

TD-DFT calculations of the $S_0$ of $1b$ in gas phase show that $T_{1K}$ of $1b$ is located 75 kcal/mol above the $S_0$ of $1b$ which has a $(\pi, \pi^*)$ configuration (Scheme 9). $T_{2K}$ is 78 kcal/mol above $S_0$ of $1b$ and has $(\pi, \pi^*)$ configuration.

We also optimized the $T_{1K}$ of $1b$ and found that it is located 70 kcal/mol above the $S_0$ of $1b$, which is somewhat lower than the energy obtained by TD-DFT calculations (Scheme 9, Figure 6). Analysis of bond lengths of $S_0$ of $1b$ shows C=O bond length of 1.23 Å. The optimized structure of $T_{1K}$ of $1b$ shows that C=O bond length has been increased from 1.23 Å in the $S_0$ of $1b$ to 1.32 Å. Further, it also shows that bond between the carbonyl carbon and the quaternary phenyl carbon is from 1.50 Å in the $S_0$ of $1b$ to 1.42 Å. In addition the dihedral angle of O-C$_{\text{carbonyl}}$-C$_{\alpha}$-H angle has been reduced from $154.4^\circ$ in the $S_0$ of $1b$ to $97.7^\circ$ in $T_{1K}$ of $1b$. The bond
lengths in the phenyl ring shows that only the $C_{\text{quaternary}}{-}C_{\text{ortho}}$ bond lengths have been increased from 1.40 Å to 1.42 Å and 1.41 Å to 1.43 Å. These analysis shows the triplet state of $T_{1\text{K}}$ of $1b$ is delocalized mainly to the C=O chromophore as expected for a triplet ketone with a $(n,\pi^*)$ configuration.

![Figure 6. Optimized conformers of $T_{1\text{K}}$ of $1b$ and $T_{\text{BR}}$ of $1b$.](image)

Optimization of $T_{\text{BR}}$ of $1a$ located it at 51 kcal/mol above $S_0$ of $1a$ (Figure 6). We calculated the transition state for the $T_{1\text{K}}$ of $1b$ to form the triplet biradical ($T_{\text{BR}}$) of $1b$ and found that it is located 3 kcal/mol above the $T_{1\text{K}}$ of $1b$ (73 kcal/mol above the $S_0$ of $1b$) and 34 kcal/mol above $T_{\text{BR}}$ of $1b$. Intrinsic Reaction Coordinate (IRC) calculations confirm the transition state correlate to the $T_{1\text{K}}$ of $1b$ and $T_{\text{BR}}$ of $1b$. Optimization of $T_{\text{BR}}$ of $1b$ located it at 39 kcal/mol above $S_0$ of $1b$. The C=O bond length has been increased from 1.23 Å in $S_0$ of $1b$ to 1.25 Å in $T_{\text{BR}}$ of $1b$. Further, $C_{\text{carbonyl}}-C_\alpha$ bond length has been reduced from 1.49 Å in $S_0$ of $1b$ to 1.44 Å in $T_{\text{BR}}$ of $1b$. In addition, $C_\alpha-C_{\beta1}-C_{\beta2}$ angle in the cyclopropyl ring has also been increased from 61.9° in $S_0$ of $1b$ to 114.4° in $T_{\text{BR}}$ of $1b$. The bond distances of cyclopropyl ring of the $S_0$ of $1b$ are 1.51 Å ($C_\alpha-C_{\beta1}$), 1.55 Å ($C_\alpha-C_{\beta2}$) and 1.50 Å ($C_{\beta1}-C_{\beta2}$). The same bond distances of $T_{\text{BR}}$ of $1b$ are 1.50 Å ($C_\alpha-C_{\beta1}$), 2.52 Å ($C_\alpha-C_{\beta2}$) and 1.50 Å ($C_{\beta1}-C_{\beta2}$). The distance between two radical carbons has
also been increased from 1.55 Å in S₀ of 1b to 2.52 Å in TBR of 1b. The optimized structure shows the two radical centers are nearly orthogonal to one-another. Thus, the optimized structure of TBR of 1b shows that the biradical is localized on the carbon atoms. The two radical centers are orthogonal to one-another in TBR of 1b unlike in TBR of 1a. TBR of 1a is nearly a planar molecule whereas TBR of 1b is not because of the orthogonality of two radical carbons.

We calculated the transition state for the T₁K of 1b to form the ketyl radical of 1b by hydrogen-abstraction from a solvent methanol molecule and found that it is located 7 kcal/mol above the T₁K of 1b and 10 kcal/mol above ketyl radical of 1b (Scheme 10). Intrinsic Reaction Coordinate (IRC) calculations confirm the transition state correlate to the T₁K of 1b and ketyl radical of 1b. However, the comparison of transition state energies of 1a and 1b shows that the ketyl radical formation is unfavorable in 1b whereas the triplet 1,2-biradical formation is less favorable in 1a.
The proposed mechanisms for the formation of the T\textsubscript{BR} of 1\texttextit{a}, T\textsubscript{BR} of 1\texttextit{b} and ketyl radicals of 1\texttextit{a} and 1\texttextit{b} from T\textsubscript{1K} of 1\texttextit{a} and 1\texttextit{b} are shown below (Scheme 11-12).
We also calculated the spin densities for $T_{1K}$ of 1a, $T_{1K}$ of 1b, $T_{BR}$ of 1a and $T_{BR}$ of 1b. Analysis of spin density of $T_{1K}$ of 1a and $T_{1K}$ of 1b shows that the spin density on carbonyl carbon is delocalized to some degree on the phenyl ring. Spin density calculation of $T_{BR}$ of 1a shows that the spin density on $C_\alpha$ is delocalized to C=O chromophore whereas the spin density on $C_\beta$ is not affected. In comparison, the spin density of $T_{BR}$ of 1b is somewhat different. Spin density on $C_\beta$ has been reduced to -0.70 and the spin density has delocalized to the adjacent
phenyl ring. The spin density on alternating carbons of the adjacent phenyl ring carries significant negative charge. Comparison of the spin density on C$_\alpha$ of T$_{BR}$ of 1b shows that it has also delocalized to C=O chromophore which is similar to the calculated spin density on C$_\alpha$ of T$_{BR}$ of 1a. It is clear that the radical on $\alpha$-carbon is stabilized by the adjacent acetyl moiety for both 1a and 1b. Further, radical on $\gamma$-carbon is highly stabilized in 1b due to the adjacent phenyl ring. Spin density calculations of ketyl radical of 1a and 1b shows that the spin density of the radical center has been delocalized into the adjacent phenyl ring.
Figure 7. Calculated Spin Densities of $T_{1K}$ of $1a$, $T_{1K}$ of $1b$, $T_{BR}$ of $1a$, $T_{BR}$ of $1b$, Ketyl radical of $1a$ and Ketyl radical of $1b$.

Figure 8. The reactivity of $T_{BR}$ of $1a$ and $T_{BR}$ of $1b$ with triplet Oxygen to give peroxy radicals.

Calculation of the enthalpy for formation of peroxy radicals shows that they are stable radicals than $T_{BR}$ of $1a$ or $T_{BR}$ of $1b$.

3. Laser Flash Photolysis

(1). $1a$ in CH$_3$CN

We performed laser flash photolysis to support the proposed reaction mechanism for $1a$. Laser flash photolysis (Excimer laser 308 nm) of $1a$ in argon-saturated acetonitrile produced a transient absorption with $\lambda_{max}$ at ~360 nm (Figure 9-9). We assign the absorption at 360 nm to $T_{1K}$ of $1a$, and ketyl radical of $1a$ based on the TD-DFT calculations, kinetics and quenching studies. The calculated TD-DFT absorption spectrum of $T_{1K}$ of $1a$ in acetonitrile has the major
electronic transfer at 383 nm ($f=0.0604$), 305 nm ($f=0.0263$) and 303 nm ($f=0.0376$) (Figure 11), which fits well with the observed spectra.

1 μs time window in Ar

**Figure 9.** Transient UV / Vis spectra of 1a (a). 0.02 – 0.26 μs (red) (b). 0.26 – 0.85 μs (blue) (c). 0.85 – 2.04 μs (green) (d). 2.04 – 7.62 μs (purple)
100 ns time window in Ar

Figure 10. Transient UV / Vis spectra of 1a (a). 0.00 – 0.02 μs (red) (b). 0.02 – 0.07 μs (blue) (c). 0.07 – 0.16 μs (green) (d). 0.16 – 0.53 μs (purple)
Figure 11. Calculated UV of T$_{1K}$ of 1a (red), T$_{BR}$ of 1a (blue) and ketyl radical of 1a (green) in acetonitrile using TD-DFT level of theory with UB3LYP/6-31+G(d) basis set.

We assign the transient with $\lambda_{max} \sim 360$ nm also to the ketyl radical of 1a, based on the TD-DFT calculations, which show that the major electron transitions are located at 377 nm ($f=0.0194$), and 315 nm ($f=0.0306$) (Figure 11). Kinetic analysis of the transient absorption further supports this assignment. The transient absorption at 320 nm in shorter time interval can be fitted into a mono-exponential function. It decays with a rate constant (k) of $5.72 \times 10^5$ s$^{-1} \pm 2.11 \times 10^4$ s$^{-1}$ ($\tau = 1.1 \pm 0.06$ μs) in argon saturated-acetonitrile (Figure 12). We assign this transient to the T$_{1K}$ of 1a. The transient absorption at 360 nm can be fitted into a mono-exponential function. It decays with a rate constant of $4.26 \times 10^5$ s$^{-1} \pm 3.73 \times 10^3$ s$^{-1}$ ($\tau = 2.3 \pm 0.02$ μs). We also assign the transient at 360 nm to T$_{1K}$ of 1a.
320 nm, 500 ns time window in Ar

\[ k_1 = 8.4 \times 10^5 \text{ s}^{-1} \pm 7.6 \times 10^3 \text{ s}^{-1}, \tau = 1.2 \pm 0.01 \mu\text{s} \]

320 nm, 1 \mu s time window in Ar

\[ k_1 = 5.72 \times 10^5 \text{ s}^{-1} \pm 2.11 \times 10^4 \text{ s}^{-1}, \tau = 1.1 \pm 0.06 \mu\text{s}; \]
360 nm, 500 ns time window in Ar

\[ k_1 = 5.10 \times 10^5 \pm 1.17 \times 10^4 \text{ s}^{-1}, \tau = 2.0 \pm 0.04 \mu\text{s}; \]

360 nm, 1 \mu s time window in Ar

\[ k_1 = 4.26 \times 10^5 \text{ s}^{-1} \pm 3.73 \times 10^3 \text{ s}^{-1}, \tau = 2.3 \pm 0.02 \mu\text{s}; \]
Figure 12. Kinetics of 1a in CH₃CN. (a) 500 ns time window at 320nm in Ar. (b) 1 μs time window at 320nm in Ar. (c) 500 ns time window at 360nm in Ar. (d) 1 μs time window at 360nm in Ar.

Quenching Studies with O₂

In oxygen-saturated acetonitrile solutions the intensity of the band around ~320 nm and 360 nm are completely quenched (Figure 13-14). Thus oxygen quenches T₁K of 1a.

1 μs time window in Ar

![Graph showing transient UV/Vis spectra for quenching studies of 1a (a) Ar, 0.02 – 0.26 μs (red) (b) O₂, 0.02 – 0.26 μs (blue)]

Figure 13. Transient UV / Vis spectra for quenching studies of 1a (a) Ar, 0.02 – 0.26 μs (red) (b) O₂, 0.02 – 0.26 μs (blue)
320nm, 1 μs time window in Ar & O₂

![320nm 1us Ar and O₂](image)

360nm, 1 μs time window in Ar & O₂

![360nm 1us Ar and O₂](image)

**Figure 14.** Quenching kinetics of 1a in CH₃CN. (a). 1 μs time window at 320nm in Ar (red) & O₂ (blue). (b). 1 μs time window at 360nm in Ar (red) & O₂ (blue).
Laser flash photolysis (Excimer laser 308 nm) of 1a in argon-saturated methanol produced a transient absorption with $\lambda_{\text{max}}$ at ~320 nm and at ~360 nm (Figure 15). We assign the absorption at 320 nm to $T_{1K}$ of 1a, ketyl radical of 1a and formation of photo-product based on the TD-DFT calculations, kinetics and quenching studies. The calculated TD-DFT absorption spectrum of $T_{1K}$ of 1a in methanol has the major electronic transfer at 383 nm ($f=0.0596$), 305 nm ($f=0.0232$) and 303 nm ($f=0.0418$) (Figure 16), which fits well with the observed spectra. We assign the transient with $\lambda_{\text{max}}$ ~320 nm also to the ketyl radical of 1a, based on the TD-DFT calculations, which show that the major electron transitions are located at 377 nm ($f=0.0193$), and 315 nm ($f=0.0302$).

1 μs time window in Ar

**Figure 15.** Transient UV/Vis spectra of 1a in methanol (a). 0.02 – 0.30 μs (red) (b). 0.30 – 0.94 μs (blue) (c). 0.94 – 2.02 μs (green) (d). 2.02 – 6.82 μs (purple)
Figure 16. Calculated UV of $T_{1K}$ of 1a (red), $T_{BR}$ of 1a (blue) and ketyl radical of 1a (green) in methanol using TD-DFT level of theory with UB3LYP/6-31+G(d) basis set.
Figure 17. Calculated UV of $T_{1K}$ of 1a (red), $T_{BR}$ of 1a (blue) and ketyl radical of 1a (green) in methanol using TD-DFT level of theory with UCAM-B3LYP/6-31+G(d) basis set.

The TD-DFT calculations of $T_{BR}$ of 1a show that the major electron transitions are located at 465 nm ($f=0.0389$), 351 nm ($f=0.0549$) and 328 ($f=0.0087$) (Figure 16). We did not observe the $T_{BR}$ of 1a. We also calculated UV spectra using CAM-B3LYP method (Figure 17).
CAM-B3LYP calculations show a different UV spectrum than UB3LYP for $T_{1K}$ of $1a$ whereas for $T_{BR}$ of $1a$ and Ketyl radical of $1a$, both methods give similar UV spectra. Calculated UV using UB3LYP method agrees well with the observed spectrum for $T_{1K}$ of $1a$. Kinetic analysis of the transient absorption further supports this assignment. The transient absorption at 320 nm can be fitted as a double exponential function and decays with a rate constant ($k$) of $4.8 \times 10^4$ s$^{-1}$ ($\tau = 21$ $\mu$s) in shorter time interval which we assign for the decay of ketyl radical of $1a$. This gives more time for ketyl radical of $1a$ to dimerize in methanol compared to acetonitrile where we do not observe any photoproduct. To measure the slower rate constant accurately, we measured the transient absorption in 1 ms time window and it shows a decay with a rate constant $3.5 \times 10^2$ s$^{-1}$ ($\tau = 2.9$ ms) which we assign for the formation of photoproduct $2b$ in argon saturated-methanol solvent (Figure 18). We also measured the transient absorption at 360 nm and can be fitted to a double exponential function. The faster rate constant of this decay is $1.2 \times 10^6$ s$^{-1}$ ($\tau = 830$ ns). We assign this absorption primarily to the $T_{1K}$ of $1a$.

320 nm, 100 ns time window in Ar

\[ k_1 = 1.6 \times 10^7 \text{ s}^{-1} \pm 2.4 \times 10^5 \text{ s}^{-1}, \tau = 60 \pm 0.94 \text{ ns} \]
320 nm, 2.5 μs time window in Ar

\[ k_1 = 3.7 \times 10^5 \text{ s}^{-1} \pm 7.2 \times 10^5 \text{ s}^{-1}, \tau = 2.7 \pm 5.2 \mu\text{s}; \]
\[ k_2 = 1.4 \times 10^5 \text{ s}^{-1} \pm 9.3 \times 10^4 \text{ s}^{-1}, \tau = 7.1 \pm 4.7 \mu\text{s}. \]

320 nm, 100 μs time window in Ar

\[ k_1 = 4.8 \times 10^4 \text{ s}^{-1} \pm 4.0 \times 10^3 \text{ s}^{-1}, \tau = 21 \pm 1.7 \mu\text{s}; \]
\[ k_2 = 4.7 \times 10^3 \text{ s}^{-1} \pm 2.6 \times 10^2 \text{ s}^{-1}, \tau = 213 \pm 12 \mu\text{s}. \]
320 nm, 1 ms time window in Ar

\[ k_1 = 4.0 \times 10^3 \, s^{-1} \pm 4.7 \times 10^2 \, s^{-1}, \tau = 247 \pm 29 \, \mu s; \]
\[ k_2 = 3.5 \times 10^2 \, s^{-1} \pm 3.0 \times 10^1 \, s^{-1}, \tau = 2.9 \pm 0.24 \, ms \]

360 nm, 1 µs time window in Ar

\[ k_1 = 1.2 \times 10^6 \, s^{-1} \pm 1.2 \times 10^5 \, s^{-1}, \tau = 830 \pm 83 \, ns; \]
\[ k_2 = 4.8 \times 10^5 \, s^{-1} \pm 4.8 \times 10^4 \, s^{-1}, \tau = 2.1 \pm 0.21 \, \mu s \]
**Figure 18.** Kinetics of 1a in CH$_3$OH. (a). 100 ns time window at 320nm in Ar. (b). 2.5 μs time window at 320nm in Ar. (c). 100 μs time window at 320nm in Ar. (d). 1 ms time window at 320nm in Ar. (e). 1 μs time window at 360nm in Ar.

**Quenching Studies with O$_2$**

In oxygen-saturated solutions the intensity of the band around ~360 nm is completely quenched whereas the intensity of the band around ~320 nm decreased (Figure 19). Disappearance of absorbance at 360 nm shows that T$_{1K}$ of 1a completely quenched in oxygen-saturated methanol. Further, reduction absorption at 320 nm shows that precursor to T$_{BR}$ of 1a and ketyl radical of 1a is T$_{1K}$ of 1a. Further, ketyl radical of 1a is also quenched with oxygen; hence we observed only the absorbance due to the formation of traces of photo-product in oxygen-saturated methanol solutions. The rate constant for the decay of at 320 nm in oxygen-saturated methanol is 4.2 x 10$^2$ s$^{-1}$ (τ = 2.4 ms) which is essentially remained relatively constant (Figure 19). Thus oxygen quenches T$_{1K}$ of 1a and ketyl radical of 1a.
1 μs time window in Ar & O₂ Combined

**Figure 19.** Transient UV / Vis spectra for quenching studies of 1a (a). 0.02 – 0.26 μs (red) (b). 0.02 – 0.26 μs (blue)

320 nm, 100 ns time window in Ar & O₂ Combined
320 nm, 2.5 μs time window in Ar & O₂ Combined

Rate of O₂ quenching is,

\[ k_1 = 5.0 \times 10^3 \text{ s}^{-1} \pm 7.3 \times 10^2 \text{ s}^{-1}, \tau = 200 \pm 29 \mu \text{s}. \]
320 nm, 500 μs time window in Ar & O₂ Combined

Rates of O₂ quenching are,

\[ k_1 = 3.1 \times 10^3 \text{ s}^{-1} \pm 7.4 \times 10^2 \text{ s}^{-1}, \tau = 322 \pm 77 \mu\text{s}; \]
\[ k_2 = 4.2 \times 10^2 \text{ s}^{-1} \pm 2.0 \times 10^4 \text{ s}^{-1}, \tau = 2.4 \pm 0.11 \text{ ms} \]

360 nm, 1 μs time window in Ar & O₂ Combined

**Figure 20.** Quenching kinetics of 1a in CH₃OH.  (a). 100 ns time window at 320 nm in Ar (red) & O₂ (blue). (b). 2.5 μs time window at 320 nm in Ar (red) & O₂ (blue). (c). 100 μs time window
at 320 nm in Ar (red) & O₂ (blue).(d) 500 μs time window at 320 nm in Ar (red) & O₂ (blue).(e).

1 μs time window at 360 nm in Ar (red) & O₂ (blue).

(III). 1b in CH₃CN

Laser flash photolysis (Excimer laser 308 nm) of 1b in argon-saturated acetonitrile produced a transient absorption with λ_max at ~370 nm (Figure 21). Although, the calculated TD-DFT absorption spectrum of T₁K of 1b in acetonitrile has the major electronic transfer at 511 nm (f=0.0198), 417 nm (f=0.0486), 375 nm (f=0.0160), 317nm (f=0.0195) and 304 nm (f=0.0333) (Figure 23), we did not observe T₁K of 1b under our experimental conditions. We think the lifetime of the T₁K of 1b is less than the time resolution of the instrument which is 17 ns.

1 μs window in Ar

Figure 21. Transient UV / Vis spectra of 1b in acetonitrile (a). 0.02 – 0.30 μs (red) (b). 0.30 – 1.00 μs (blue) (c). 1.00 – 2.00 μs (green) (d). 2.00 – 7.01 μs (purple)
100 ns window in Ar

**Figure 22.** Transient UV / Vis spectra of 1b in acetonitrile (a). 0.00 – 0.04 μs (red) (b). 0.04 – 0.10 μs (blue) (c). 0.10 – 0.24 μs (green) (d). 0.24 – 0.45 μs (purple)
Figure 23. Calculated UV of $T_{1K}$ of 1b (red) and $T_{BR}$ of 1b (blue) in acetonitrile using TD-DFT level of theory with UB3LYP/6-31+G(d) basis set.

We assign the absorption at 420 nm to the $T_{BR}$ of 1b, based on the TD-DFT calculations, which show that the major electron transitions are located at 466 nm ($f=0.0405$), 414 nm ($f=0.0368$), 336 nm ($f=0.0491$) and 326 ($f=0.0330$). Kinetic analysis of the transient absorption further supports this assignment. The transient absorption at 420 nm can be fitted into a mono-exponential function and has a rate constant ($k$) of $7.60 \times 10^5 \text{s}^{-1} \pm 5.92 \times 10^4 \text{s}^{-1}$ ($\tau = 1.3 \mu\text{s} \pm 0.1 \mu\text{s}$) (Figure 24). The lifetime of this transient decay has not been changed in air saturated and oxygen saturated solutions. This supports the assignment of the transient absorption at 420 nm to the $T_{BR}$ of 1b.
We assign the transient with $\lambda_{\text{max}} \sim 370$ nm to the absorption of product based on kinetics and quenching studies (Figure 25-26). We hypothesize that the phenyl ring attached to the cyclopropyl ring could directly absorb light and form photo-products through a singlet. The
transient absorption at 370 nm decays with rate constants (k) of 150 ± 34 s\(^{-1}\) (τ = 6.7 ± 1.5 ms) which we assign for the product formation in argon saturated-acetonitrile solvent (Figure 25).

370nm, 250 μs time window in Ar

\[k_1 = 1.1 \times 10^4 \text{ s}^{-1} \pm 1.8 \times 10^3 \text{ s}^{-1}, \tau = 91 \pm 15 \mu\text{s};\]

\[k_2 = 1.0 \times 10^3 \text{ s}^{-1} \pm 3.2 \times 10^2 \text{ s}^{-1}, \tau = 1.0 \pm 0.3 \text{ ms}\]

370 nm, 2.5 ms time window in Ar
\[ k_1 = 1.5 \times 10^2 \text{s}^{-1} \pm 3.4 \times 10^1 \text{s}^{-1}, \tau = 6.7 \pm 1.5 \text{ms} \]

**Figure 25.** Kinetics of 1b in CH$_3$CN. (a). 250 μs time window at 370nm in Ar. (b). 2.5ms time window at 370nm in Ar.

**Quenching Studies of 1b with O$_2$**

In oxygen-saturated solutions the intensity of the band around 370 nm is somewhat decreased (Figure 26). However, the lifetimes in the longer time scales has not been affected significantly. This further supports that the absorption we observe at 370 nm is mainly due to the photo-product formation. However, we observe that the intensity of the absorption at 370 nm has been decreased. This could be due to the quenching of T$_{1K}$ of 1b, which is the precursor to the formation of the photoprodut. We also hypothesize that the phenyl ring attached to the cyclopropyl ring could directly absorb light and form photo-products through a singlet. Absence of quenching at 420 nm suggests that the T$_{BR}$ of 1b is not quenched with oxygen.

1 μs time window in Ar & in O$_2$
Figure 26. Transient UV / Vis spectra for quenching studies of 1b (I). (a). Ar (0.02 – 0.32 μs) (red) (b). O₂ (0.02 – 0.32 μs) (blue) (II). (a). Ar (0.02 – 0.30 μs) (b). Air (0.02 – 0.30 μs) (c). O₂ (0.02 – 0.32 μs).

370 nm, 250 μs time window in O₂

Quenching rates with O₂ are;

\[ k_1 = 1.1 \times 10^4 \text{ s}^{-1} \pm 2.3 \times 10^3 \text{ s}^{-1}, \tau = 91 \pm 19 \text{ μs}; \]

\[ k_2 = 1.5 \times 10^3 \text{ s}^{-1} \pm 5.4 \times 10^2 \text{ s}^{-1}, \tau = 670 \pm 240 \text{ μs} \]

Figure 27. Kinetics of 1b in CH₃CN & in 250 μs time window at 370 nm with O₂.
370 nm, 1 μs time window in Ar & in O₂

370 nm, 250 μs time window in Ar & in O₂
Isoprene Quenching Studies of 1b

We used isoprene quenching method to find out the lifetime of an intermediate of interest at a specific wavelength. Isoprene is a molecule which is capable of quenching an excited state of a molecule thereby isoprene excites itself. This can be representing in the form of following equation.

**Figure 28.** Quenching kinetics of 1b in CH$_3$CN. (a). 1 μs time window at 370nm in Ar (red) & O$_2$ (blue). (b). 250 μs time window at 370nm in Ar (red) & O$_2$ (blue). (c). 420 nm, 500 ns time window in Ar (red), Air (green) & O$_2$ (blue). (d). 420 nm, 5 μs time window in Ar (red), Air (green) & O$_2$ (blue).
\[ \text{1a}^{3*} + \text{Iso} \rightarrow \text{1a} + \text{Iso}^{3*} \]

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Table 3. Isoprene quenching data for 1b
We investigated the quenching with isoprene at ~360 nm (Table 3, Figure 29) and the lifetime of the T_{1K} of 1b. Isoprene quenches the T_{1K} of 1b.

Stern-Volmer equation is,

\[
\frac{I_0}{I} = 1 + k_q \tau_0 [Q]
\]
where, \( A_0 \) = Intensity of the 1b without the quencher, \( A \) = Intensity of the 1b with q amount of quencher, \( k_q \) = Quencher rate co-efficient, \( \tau_0 \) = Lifetime of the 1b without quencher, \([Q]\) = Concentration of the quencher. We hold the intercept at 1 and found the gradient of the plot.

\[
\tau_0 \text{ of the } 1b \text{ is } 0.012 - 0.12 \text{ ns if the } k_q \text{ is } 10^9 - 10^{10} \text{ mol}^{-1} \text{ s}^{-1} \text{ L by assuming the energy transfer is diffusion controlled. The triplet energy of the isoprene is 60.1 kcal/mol.}^{16, 17} \text{ The } T_{1K} \text{ of } 1b \text{ has energy of 72 kcal/mol. This suggests that the energy of } 1b \text{ is higher than isoprene. In order to energy transfer to occur, the triplet energy of the isoprene needs to be somewhat lower than the energy of the } T_{1K} \text{ of } 1b. \text{ Hence, we hypothesize that energy transfer is feasible; hence we observe quenching from isoprene.}
\]

4. Fluorescence

We measured the phosphorescence of 1a and located the (0,0) transition at 319 nm. This corresponds to energy of 90 kcal/mol. This is in very good agreement with the calculated value of 88 kcal/mol using TD-DFT method. The excitation at 360 nm, 300 nm and 260 nm shows different fine structural pattern in fluorescence spectra.
Figure 30. Fluorescence spectrum of 0.05 M solution of 1a in ethanol with (a). 360 nm excitation (b). 300 nm excitation (c). 260 nm excitation.

5. Phosphorescence

We measured the phosphorescence of 1a and located the (0,0) transition at 385 nm. This corresponds to energy of 74 kcal/mol. This is in very good agreement with the calculated value of 76 kcal/mol using TD-DFT method. We also measured the phosphorescence of 1b and located the (0,0) transition at 397 nm. This corresponds to energy of 72 kcal/mol. This is in very good agreement with the calculated value of 75 kcal/mol.
Figure 31. Phosphorescence spectra in ethanol with 300 nm excitation for (a). 0.05 M solution of 1a with 50 ms integration; (b). 5 mM solution of 1b with 100 ms integration.

**Experimental Calculations**

All geometries were optimized at B3LYP level of theory and with 6-31G+(d) basis set as implemented in the Gaussian03 and Gaussian09 programs. All transition states were confirmed to have one imaginary vibrational frequency by analytical determination of the second derivatives of the energy with respect to internal coordinates. Intrinsic reaction coordinates calculations were used to verify that the located transition states corresponded to the attributed reactant and product. The absorption spectra were calculated using time-dependent density functional theory (TD-DFT). The effect of solvation was calculated using the self-consistent reaction field (SCRF) method with the integral equation formalism polarization continuum model (IEFPCM) with acetonitrile, methanol and dichloromethane as solvents.
Laser Flash Photolysis.

Laser flash photolysis was done with an Excimer laser (308 nm, 17 ns).\textsuperscript{31} The system has been described in detail elsewhere.\textsuperscript{31} A stock solution of 1a, 1b in CH\textsubscript{3}CN and CH\textsubscript{3}OH was prepared with spectroscopic grade CH\textsubscript{3}CN and CH\textsubscript{3}OH, such that the solutions had absorption between 0.3 and 0.6 at 308 nm. Typically, ~2 mL of the stock solution was placed in a 10 mm × 10 mm wide, 48 mm long quartz cuvette and was purged with argon for 5 min or oxygen for 15 min. The rates were obtained by fitting an average of three to five kinetic traces.

Phosphorescence

4 mg (~20 μmol) of 1b was dissolved in 4 mL of ethanol. The phosphorescence measurements were carried out at 77 K with 300 nm irradiation.

Photolysis of 1a and 1b

1a and 1b was purchased from Aldrich and Otawa chemicals respectively.

1a: \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): δ 1.018 – 1.064 (m, 2H), 1.226 – 1.264 (m, 2H), 2.649 – 2.711 (m, 1H), 7.472 (t, J = 7.2 Hz, 2H), 7.561 (t, J = 7.2 Hz, 1H), 8.018 (d, J = 7.2 Hz, 2H) ppm.; GC/MS (EI): m/z 146 (M\textsuperscript{+}), 131, 127, 119, 115, 105 (100%), 98, 91, 87, 77, 73, 69, 63, 59, 55, 51.
$1b$: $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 1.529 – 1.575 (m, 1H), 1.901 – 1.946 (m, 1H), 2.674 – 2.723 (m, 1H), 2.877, 2.920 (m, 1H), 7.173 (d, $J$ = 7.2 Hz, 2H), 7.223 (t, $J$ = 7.2 Hz, 1H), 7.306 (t, $J$ = 7.2 Hz, 2H), 7.449 (d, $J$ = 7.6 Hz, 2H), 7.548 (t, $J$ = 7.6 Hz, 1H), 7.988 (d, $J$ = 7.6 Hz, 2H) ppm.;
GC/MS (EI): m/z 222 (M$^+$), 207, 200, 193, 178, 165, 152, 144, 131, 115, 105 (100%), 97, 91, 85, 77, 63, 57, 51.

**Product Studies of $1a$ in Ar-saturated CDCl$_3$**

A solution of $1a$ (~50 mg, 0.3 mmol) in CDCl$_3$ (2 mL) was purged with argon and photolyzed via a Pyrex filter for 17 hours at 298 K. $^1$H NMR and GC-MS analysis of the reaction mixture showed no formation of new products.

**Product Studies of $1a$ in O$_2$-saturated CDCl$_3$**

A solution of $1a$ (~50 mg, 0.3 mmol) in CDCl$_3$ (2 mL) was purged with oxygen and photolyzed via a Pyrex filter for 17 hours at 298 K. $^1$H NMR and GC-MS analysis of the reaction mixture showed no formation of new products.

**Product Studies of $1a$ in argon-saturated CD$_3$OD**

A solution of $1a$ (~50 mg, 0.3 mmol) in CD$_3$OD (2 mL) was purged with argon and photolyzed via a Pyrex filter for 94 hours at 298 K. $^1$H NMR and GC-MS analysis of the reaction mixture showed the formation of $2a$ (37%), with remaining starting material (57%). The products were characterized by GC-MS chromatography of the reaction mixture.

**Product Studies of 1a in O₂-saturated CH₃OH**

A solution of 1a (~50 mg, 0.3 mmol) in CH₃OH (2 mL) was purged with oxygen and photolyzed via a Pyrex filter for 94 hours at 298 K. ¹H NMR and GC-MS analysis of the reaction mixture showed the formation of 2a (15%), with remaining starting material (77%). The products were characterized by GC-MS chromatography of the reaction mixture.

2a: GC/MS (EI): m/z 147 (M⁺/2, 100%), 133, 128, 120, 115, 105 (100%), 91, 77, 69, 65, 55, 51.

**Product Studies of 1b in Ar-saturated CDCl₃**

A solution of 1b (~50 mg, 0.2 mmol) in CD₃OD (2 mL) was purged with argon and photolyzed via a Pyrex filter for 34 hours at 298 K. ¹H NMR and GC-MS analysis of the reaction mixture showed the formation of 2b (52%) with remaining starting material (40%). The products were characterized by GC-MS chromatography and ¹H-NMR spectroscopy of the reaction mixture.

2b: ¹H NMR (CDCl₃, 400 MHz): δ 1.428 – 1.480 (m, 1H), 2.092 – 2.137 (m, 1H), 2.852 – 2.924 (m, 1H), 3.062 – 3.132 (m, 1H), 7.090 – 7.127 (m, 1H), 7.156 – 7.192 (m, 3H), 7.359 – 7.510 (m, 4H), 7.901 (d, J = 8.0 Hz, 2H) ppm.; GC/MS (EI): m/z 222 (M⁺), 207, 200, 193, 178, 165, 152, 144, 131, 115, 105 (100%), 97, 91, 83, 77, 63, 57, 51.

2c: GC/MS (EI): m/z 222 (M⁺), 165, 115, 105 (100%), 91, 77, 63, 51

2e: GC/MS (EI): m/z 105 (M⁺-H, 100%), 91, 77, 74, 63, 51
Product Studies of 1b in O₂-saturated CDCl₃

A solution of 1b (~50 mg, 0.2 mmol) in CD₃OD (2 mL) was purged with argon and photolyzed via a Pyrex filter for 34 hours at 298 K. ¹H NMR and GC-MS analysis of the reaction mixture showed the formation of 2b (42%) with remaining starting material (52%). The products were characterized by GC-MS chromatography and ¹H-NMR spectroscopy of the reaction mixture.

2b: ¹H NMR (CDCl₃, 400 MHz): δ 1.427 – 1.479 (m, 1H), 2.093 – 2.157 (m, 1H), 2.852 – 2.923 (m, 1H), 3.061 – 3.117 (m, 1H), 7.088 – 7.120 (m, 1H), 7.166 – 7.206 (m, 3H), 7.354 – 7.508 (m, 4H), 7.902 (d, J = 8.0 Hz, 2H) ppm.; GC/MS (EI): m/z 222 (M⁺), 207, 200, 193, 178, 165, 152, 144, 131, 115, 105 (100%), 97, 91, 85, 77, 63, 57, 51.

2c: GC/MS (EI): m/z 222 (M⁺), 207, 193, 178, 165, 145, 127, 115, 105 (100%), 91, 77, 65, 63, 51.

2d: GC/MS (EI): m/z 222 (2M⁺/2), 206, 191, 168, 150, 131, 120, 105 (100%), 91, 77, 63, 51

2f: GC/MS (EI): m/z 122 (M⁺), 105 (100%), 94, 77, 74, 65, 51

Conclusions

We have demonstrated that 1a do not give any photoproduct in acetonitrile whereas in hydrogen abstractable solvents, 1a forms both a ketyl radical which dimerize to give the photoproduct 2a. We have demonstrated that 1b undergo trans-cis isomerization to mainly give 2b and other products. We propose the formation of 2b goes through a triplet 1,3-biradical and we measured the lifetime of this intermediate from LFP to be ~1 μs.
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Chapter 09

The Photo-reactivity of β-Keto Esters; By Means of Photorelease via Trans-Cis Isomerization
The Photo-reactivity of β-Keto Esters; By Means of Photorelease via Trans-Cis Isomerization

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ABSTRACT

We investigated the photoreactivity of $1a$-$c$ for potential applications in photo-switches. We used product studies, laser flash photolysis (LFP, $\lambda =$308 nm), matrix isolation, phosphorescence and theoretical calculations and identified the intermediates formed by irradiating $1a$-$c$. Solutions photolysis of $1a$-$b$ yields $2a$-$b$ in CDCl$_3$. $2a$-$b$ forms first by forming T$_{1K}$ of $1a$-$b$ and then by forming a 1,2-biradical of $1a$-$b$ which either forms $2a$-$b$ or goes back to form $1a$-$b$. 

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Introduction

Trans-cis isomerization has long been known and has become increasingly of interest within the past few decades. This is mainly because trans→cis isomerization can be used in chemical applications such as optical data storage devices, molecular photoswitches, and phototriggers or in biological applications such as drug delivery systems\textsuperscript{1-3} and vision. This has also been employed in photo-induced photorelease systems to release molecules such as methanol\textsuperscript{4}.

It has been reported that molecules like 1a-b could undergo both trans-cis isomerization followed by hydrolysis by lactonization to give methanol under alkaline conditions\textsuperscript{5}. We were curious to see whether 1a-b undergo trans-cis isomerization upon irradiation of light above 300 nm.

In this paper, we explore the trans – cis isomerization of (E)-methyl 4-(4-methoxyphenyl)-4-oxobut-2-enoate (1a) and (E)-methyl 4-phenyl-4-oxobut-2-enoate (1b)
Results

1. Product Studies

Scheme 1. Product studies of 1a in CDCl$_3$

\[
\begin{array}{c}
\text{hv (}>300 \text{ nm)} \quad \text{CDCl}_3 \\
\text{298 K} \\
\text{Ar, O}_2
\end{array}
\]

\[
\begin{array}{c}
\text{1a} \\
\text{hv (}>300 \text{ nm)} \\
\text{CH}_2\text{Cl}_2 \\
\text{298 K} \\
\text{Ar}
\end{array}
\]

\[
\begin{array}{c}
\text{1a} \\
\text{2a}
\end{array}
\]

\[
\begin{array}{c|c|c|c|c}
\% \text{ Conversion} & \text{Ar} & \text{O}_2 & \text{Ar} & \text{O}_2 \\
\hline
0 \text{ h} & 100 & 100 & 0 & 0 \\
2 \text{ h} & 85 & 74 & 15 & 25 \\
4 \text{ h} & 43 & 54 & 57 & 46 \\
7 \text{ h} & 0 & 0^* & 100 & 100^*
\end{array}
\]

*Denotes only 6 hours of irradiation in oxygen

Scheme 2. Product studies of 1a in CH$_2$Cl$_2$

\[
\begin{array}{c}
\text{hv (}>300 \text{ nm)} \quad \text{CH}_2\text{Cl}_2 \\
\text{298 K} \\
\text{O}_2
\end{array}
\]

\[
\begin{array}{c}
\text{1a} \\
\text{hv (}>300 \text{ nm)} \\
\text{CH}_2\text{Cl}_2 \\
\text{298 K} \\
\text{Ar}
\end{array}
\]

\[
\begin{array}{c}
\text{1a} \\
\text{2a}
\end{array}
\]

\[
\begin{array}{c|c|c}
\% \text{ Conversion} & \text{O}_2 & \text{Ar} \\
\hline
0 \text{ h} & 100 & 0 \\
15 \text{ h} & 78 & 22 \\
16 \text{ h} & 100 & 0
\end{array}
\]
Photolysis of 1a in argon-saturated chloroform-d via a Pyrex filter at 298 K produced 2a (100%) (Scheme 1). Irradiation of 1a in oxygen-saturated chloroform-d via a Pyrex filter at 298 K also yields 2a (100%). Whereas, photolysis of 1a in argon-saturated CH₂Cl₂ for 16 hours via a Pyrex filter resulted in 2a (100%), and irradiation of 1a in oxygen-saturated CH₂Cl₂ for 16 hours via a Pyrex filter resulted in 1a (78%) and 2a (22%) (Scheme 2). Irradiation via Pyrex filter ensures that only the ketone absorbs the light and forms the singlet excited state of the ketone (S₁K) of 1a which then intersystem crosses (ISC) to the triplet excited state of the ketone (T₁K) of 1a. Although 1a is an aromatic derivative, its first and the second excited states of (T₁K and T₂K) are 2 – 8 kcal/mol of each other. Rearrangement of T₁K of 1a will form triplet 1,2 biradical (TBR) of 1a. TBR of 1a will either undergo ISC to form 2a or 1a back.

Photolysis of 1b in argon-saturated chloroform-d via a Pyrex filter at 298 K produced 2b (100%) (Scheme 3). Irradiation of 1b in oxygen-saturated chloroform-d via a Pyrex filter at 298 K also yields 2b (100%). Irradiation via Pyrex filter ensures that only the ketone absorbs the light and forms the singlet excited state of the ketone (S₁K) of 1b which then intersystem crosses
(ISC) to the triplet excited state of the ketone (T$_{1K}$) of 1b. Rearrangement of T$_{1K}$ of 1b will form triplet 1,2 biradical (T$_{BR}$) of 1b. T$_{BR}$ of 1b will either undergo ISC to form 2b or 1b back.

2. Calculations

To better understand the reactivity of 1a-b we calculated the triplet surface of 1a-b using the Gaussian03 and Gaussian09 at the B3LYP level of theory and with the 6-31+G(d) basis set. We used the calculations to find identify the most favorable reaction on the triplet surface of 1a-b to understand the factors that control and govern the reactivity of on the triplet surface of 1a-b.

(I). Calculations of 1a

We optimized the ground-state (S$_0$) of 1a, S$_0$ of 2a, T$_K$ of 1a and T$_{BR}$ of 1a (Figure 2). The energy of S$_0$ of 2a is 5 kcal/mol higher than S$_0$ of 1a. The TD-DFT calculations of S$_1$ of 1a shows that it is located at 72 kcal/mol. Analysis of molecular orbitals shows that it has a (n,π*) configuration where the major electronic excitation is from the non-bonding orbital of oxygen to anti-bonding molecular orbital (Figure 01, Table 01).

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Table 1. Electronic transitions of 1a above 300 nm in gas phase on singlet surface
Excited State 4: Singlet-A

<table>
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</table>

Figure 1. Molecular orbitals corresponds to electronic transitions of 1a above 300 nm.

TD-DFT calculations of 1a in gas phase show that T1K of 1a is located 61 kcal/mol above S0 of 1a and has ($\pi,\pi^*$) configuration with the major electron transition being from the phenyl chromophore with minor contribution from the non bonding electrons on oxygen. In comparison, T2K of 1a is 63 kcal/mol above S0 of 1a and has (n,\pi*) configuration with the major electron transition being from the nonbonding electrons on the oxygen with minor contribution from the phenyl chromophore.

Figure 2. Optimized S0 Conformers of 1a.
We also optimized the T$_{1K}$ of 1a and found that T$_{1K}$ of 1a is located at 55 kcal/mol above S$_0$ of 1a, which is considerably lower than the energy obtained by TD-DFT calculations (Scheme 4). Analysis of bond lengths of S$_0$ of 1a shows C=O bond length of 1.23 Å. The optimized structure of T$_{1K}$ of 1a show that C=O bond length has been increased from 1.23 Å to 1.31 Å. Further, the C-C bond between the carbonyl carbon atom and the quaternary phenyl carbon atom has been reduced from 1.49 Å to 1.47 Å, in T$_{1K}$ of 1a in comparison to its ground state. In addition the dihedral angle of O-C$_{carbonyl}$-C$_{\alpha}$-H angle has not been changed from ground state to T$_{1K}$ of 1a. Further, C$_{carbonyl}$-C$_{\alpha}$ bond length has been reduced from 1.50 Å in S$_0$ of 1a to 1.40 Å in T$_{1K}$ of 1a. The analysis of bond lengths in the phenyl ring shows that there is no change in the ground state to T$_{1K}$ of 1. These analysis shows that optimized structure of T$_{1K}$ of 1a is delocalized mainly to the C=O chromophore, hence has (n,\pi*) configuration.

![Figure 3](image)

**Figure 3.** Optimized Conformers of T$_{1K}$ of 1a and T$_{BR}$ of 1a.

We calculated the transition state for the T$_{1K}$ of 1a to form the triplet biradical (T$_{BR}$) of 1a and found that it is located 3 kcal/mol above the T$_{1K}$ of 1a. Intrinsic Reaction Coordinate (IRC) calculations confirm the transition state correlate to the T$_{1K}$ of 1a and T$_{BR}$ of 1a. Optimization of T$_{BR}$ of 1a located it at 54 kcal/mol above S$_0$ of 1a. Bond length analysis shows that C=C bond length has been increased from 1.34 Å in T$_{1K}$ of 1a to 1.46 Å in T$_{BR}$ of 1a. Moreover, H-C-C-H
dihedral angle has been reduced from 179.9° in T_{1K} of 1a to 95.3° in T_{BR} of 1a. This suggests the biradical is localized on α-carbon and β-carbon atoms and orthogonal to one another.

The TD-DFT calculations of S\textsubscript{1} of 2a show that it is located at 92 kcal/mol above S\textsubscript{0} of 1b. Analysis of molecular orbitals shows that it has a (n, π*) configuration where the major electronic excitation is from the non-bonding orbital of oxygen to anti-bonding π*-molecular orbital. TD-DFT calculations of 2a in gas phase show that T\textsubscript{1K} of 2a is located 75 kcal/mol above S\textsubscript{0} of 1b and has (π, π*) configuration with the major electron transition being from the phenyl ring. In comparison, T\textsubscript{2K} of 2a is 80 kcal/mol above S\textsubscript{0} of 1a and has (n, π*) configuration with the major electron transition being from the non bonding orbital of oxygen.

We also optimized the T\textsubscript{1K} of 2a and found that T\textsubscript{1K} of 2a is located at 60 kcal/mol above S\textsubscript{0} of 2a, which is considerably lower than the energy obtained by TD-DFT calculations (Scheme 4). Analysis of bond lengths of S\textsubscript{0} of 2a shows C=O bond length of 1.23 Å. The optimized structure of T\textsubscript{1K} of 2a show that C=O bond length has been increased from 1.23 Å to 1.31 Å. Further, the C-C bond between the carbonyl carbon atom and the quaternary phenyl carbon atom has not been affected. Further, C\textsubscript{carbonyl}-C\textsubscript{α} bond length has been reduced from 1.51 Å in S\textsubscript{0} of 2a to 1.40 Å in T\textsubscript{1K} of 2a. C\textsubscript{α}-C\textsubscript{β} bond length has been increased from 1.34 Å in S\textsubscript{0} of 2a to 1.40 Å in T\textsubscript{1K} of 2a. C\textsubscript{β}-C\textsubscript{γ} bond length has been reduced from 1.48 Å in S\textsubscript{0} of 2a to 1.45 Å in T\textsubscript{1K} of 2a. The analysis of bond lengths in the phenyl ring shows that there is no change in T\textsubscript{1K} of 2a in comparison to S\textsubscript{0} of 2a. These analysis shows that optimized structure of T\textsubscript{1K} of 2a is delocalized mainly to the -C(O)C=C-C chromophore, hence has (n, π*) configuration.
We calculated the transition state for the T_{1K} of 2a to form the triplet biradical, T_{BR} of 1a and found that it is located 3 kcal/mol above the T_{1K} of 2a. IRC calculations confirm the transition state correlate to the T_{1K} of 2a and T_{BR} of 1a.

**Scheme 4.** Energy diagram for 1a & 2a (energy is in kcal/mol)
(II). Calculations of 1b

We optimized the ground-state (S₀) of 1b, S₀ of 2b, Tᵦ of 1b and Tᵦᵦ of 1b (Figure 5-6). The energy of S₀ of 2b is 5 kcal/mol higher than S₀ of 1b. The TD-DFT calculations of S₁ of 1b show that it is located at 71 kcal/mol above S₀ of 1b. Analysis of molecular orbitals shows that it has a \((\pi, \pi^*)\) configuration where the major electronic excitation is from the non-bonding orbital of oxygen to anti-bonding \(\pi^*\)-molecular orbital (Table 2, Figure 4).

**Table 2.** Electronic transitions of 1b above 300 nm in gas phase on singlet surface

<table>
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<tr>
<th>Excited State</th>
<th>Singlet-A</th>
<th>Energy (eV)</th>
<th>Wavelength (nm)</th>
<th>f</th>
<th>&lt;S**2&gt;</th>
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<td>50 -&gt; 51</td>
<td>-0.38681</td>
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</tbody>
</table>
Excited State 3: Singlet-A 4.0304 eV 307.62 nm f=0.0002 <S**2>=0.000
47 -> 51  0.68173
47 -> 52  -0.13551

<table>
<thead>
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<th>51</th>
<th>50</th>
<th>49</th>
<th>48</th>
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Figure 4. Molecular orbitals corresponds to electronic transitions of 1b above 300 nm on singlet surface

TD-DFT calculations of 1b in gas phase show that T1K of 1b is located 61 kcal/mol above S0 of 1b and has (n,π*) configuration with the major electron transition being from the non bonding electrons of the oxygen with minor contribution from the π- orbitals of the phenyl ring. In comparison, T2K of 1b is 64 kcal/mol above S0 of 1b and has (π,π*) configuration with the major electron transition being from the phenyl ring with minor contribution from the non bonding electrons of oxygen and π- electrons of C=C chromophore.

Figure 5. Optimized S0 Conformers of 1b.

We also optimized the T1K of 1b and found that T1K of 1b is located at 55 kcal/mol above S0 of 1b, which is considerably lower than the energy obtained by TD-DFT calculations (Scheme
6). Analysis of bond lengths of $S_0$ of 1b shows C=O bond length of 1.23 Å. The optimized structure of $T_{1K}$ of 1b show that C=O bond length has been increased from 1.23 Å to 1.32 Å. Further, the C-C bond between the carbonyl carbon atom and the quaternary phenyl carbon atom has been reduced from 1.50 Å to 1.47 Å, in $T_{1K}$ of 1b in comparison to its ground state. Further, $C_{\text{carbonyl}}-C_{\alpha}$ bond length has been reduced from 1.50 Å in $S_0$ of 1b to 1.40 Å in $T_{1K}$ of 1b. The analysis of bond lengths in the phenyl ring shows that there is no change in $T_{1K}$ of 1b in comparison to $S_0$ of 1b. These analysis shows that optimized structure of $T_{1K}$ of 1b is delocalized mainly to the C=O chromophore, hence has (n,$\pi^*$) configuration.

![Figure 6. Optimized Conformers of $T_{1K}$ of 1b and $T_{BR}$ of 1b.](image)

We calculated the transition state for the $T_{1K}$ of 1b to form the triplet biradical ($T_{BR}$) of 1b and found that it is located 2 kcal/mol above the $T_{1K}$ of 1b. Intrinsic Reaction Coordinate (IRC) calculations confirm the transition state correlate to the $T_{1K}$ of 1b and $T_{BR}$ of 1b. Optimization of $T_{BR}$ of 1b located it at 53 kcal/mol above $S_0$ of 1b. Bond length analysis shows that C=C bond length has been increased from 1.34 Å in $S_0$ of 1b to 1.46 Å in $T_{BR}$ of 1b. Moreover, $H_{\alpha}-C_{\alpha}-C_{\beta}-H_{\beta}$ dihedral angle has been reduced from 179.8° in $S_0$ of 1b to 95.2° in $T_{BR}$ of 1b. This suggests the biradical is localized on $\alpha$-carbon and $\beta$-carbon atoms.
The TD-DFT calculations of $S_1$ of $2b$ show that it is located at 91 kcal/mol above $S_0$ of $1b$. Analysis of molecular orbitals shows that it has a $(n, \pi^*)$ configuration where the major electronic excitation is from the non-bonding orbital of oxygen to anti-bonding $\pi^*$–molecular orbital. TD-DFT calculations of $2b$ in gas phase show that $T_{1K}$ of $2b$ is located 78 kcal/mol above $S_0$ of $1b$ and has $(n, \pi^*)$ configuration with the major electron transition being from the non-bonding electrons of the oxygen. In comparison, $T_{2K}$ of $2b$ is 80 kcal/mol above $S_0$ of $1b$ and has $(\pi, \pi^*)$ configuration with the major electron transition being from the phenyl ring.

We also optimized the $T_{1K}$ of $2b$ and found that $T_{1K}$ of $2b$ is located at 53 kcal/mol above $S_0$ of $2b$, which is considerably lower than the energy obtained by TD-DFT calculations (Scheme 6). Analysis of bond lengths of $S_0$ of $2b$ shows C=O bond length of 1.22 Å. The optimized structure of $T_{1K}$ of $2b$ show that C=O bond length has been increased from 1.22 Å to 1.30 Å. Further, the C-C bond between the carbonyl carbon atom and the quaternary phenyl carbon atom has not been affected. Further, $C_{\text{carbonyl}}$-$C_{\alpha}$ bond length has been reduced from 1.51 Å in $S_0$ of $2b$ to 1.41 Å in $T_{1K}$ of $2b$. $C_{\alpha}$-$C_{\beta}$ bond length has been increased from 1.34 Å in $S_0$ of $2b$ to 1.39 Å in $T_{1K}$ of $2b$. $C_{\beta}$-$C_{\gamma}$ bond length has been reduced from 1.48 Å in $S_0$ of $2b$ to 1.43 Å in $T_{1K}$ of $2b$. The analysis of bond lengths in the phenyl ring shows that there is no change in $T_{1K}$ of $2b$ in comparison to $S_0$ of $2b$. These analysis shows that optimized structure of $T_{1K}$ of $2b$ is delocalized mainly to the -C(O)C=C-C chromophore, hence has $(n,\pi^*)$ configuration.

We calculated the transition state for the $T_{1K}$ of $2b$ to form the triplet biradical and found that it is located 8 kcal/mol above the $T_{1K}$ of $2b$. IRC calculations confirm the transition state correlate to the $T_{1K}$ of $2b$ and $T_{BR}$ of $1b$. 
Scheme 6. Energy diagram for 1b & 2b (energy is in kcal/mol)

Scheme 7
3. Laser Flash Photolysis

(I). 1a in CH₃CN

We performed laser flash photolysis to support the proposed reaction mechanism for 1a. Laser flash photolysis (Excimer laser 308 nm) of 1a in argon-saturated acetonitrile produced a transient absorption with ~\( \lambda_{\text{max}} \) at ~400 nm (Figure 7). We hypothesize the triplet ketone decays within the time resolution of the instrument. The calculated TD-DFT absorption spectrum of \( T_{1K} \) of 1a in acetonitrile has the major electronic transfer at 475 nm (\( f=0.1591 \)), 427 (\( f=0.0714 \)), 380 nm (\( f=0.3841 \)) and 351 nm (\( f=0.1319 \)) (Figure 9).

1 μs time window in Ar

![Figure 7. Transient UV / Vis spectra of 1a (a). 0.02 – 0.30 μs (red) (b). 0.30 – 1.05 μs (blue) (c). 1.05 – 2.02 μs (black) (d). 2.02 – 7.52 μs (light green)
25 μs time window in Ar

**Figure 8.** Transient UV / Vis spectra of 1a (a). 0.40 – 2.00 μs (red) (b). 2.00 – 10.00 μs (blue) (c). 10.00 – 30.40 μs (black) (d). 30.40 – 195.40 μs (light green)
We assign the transient with $\lambda_{\text{max}} \approx 400$ nm to the $T_{\text{BR}}$ of 1, based on the TD-DFT calculations, which show that the major electron transitions are located at 349 nm ($f=0.0448$), and 332 nm ($f=0.0176$) (Figure 9) although we didn’t observe the electronic transition at 332 nm because of the interference from fluorescence. Kinetic analysis of the transient absorption further supports this assignment. The transient absorption at 400 nm can be fitted into a mono-exponential function and decays with a rate constant of $9.450 \times 10^3$ s$^{-1}$ ($\tau = 106$ μs) in argon saturated-solvent (Figure 10 (a)).
50 μs time window at 400 nm in Ar

\[ k_1 = 9.450 \times 10^3 \text{ s}^{-1} \pm 2.47 \times 10^2 \text{ s}^{-1}, \tau = 106 \pm 3 \mu\text{s} \]

250 μs time window at 400 nm in Ar

\[ k_1 = 1.403 \times 10^4 \text{ s}^{-1}, \tau = 71.3 \mu\text{s} \]
\[ k_2 = 2.021 \times 10^3 \text{ s}^{-1}, \tau = 495 \mu\text{s} \]
500 μs time window at 400 nm in Ar

\[ k_1 = 9498.7 \pm 519 \times 10^3 \text{ s}^{-1}, \tau = 115 \mu\text{s} \]

\[ k_2 = 1402.8 \pm 79.5 \times 10^3 \text{ s}^{-1}, \tau = 769 \mu\text{s} \]

**Figure 10.** Kinetics of 1a in CH3CN. (a). 50 μs time window at 400nm in Ar. (b). 250 μs time window at 400nm in Ar. (c). 500 μs time window at 400nm in Ar.

**Quenching Studies with Oxygen**

In oxygen-saturated acetonitrile solutions the intensity of the band ~ around 400 nm is not quenched (Figure 11-13). Slight reduction of intensity is due to the quenching of T_K of 1a. Hence, the precursor to the T_{BR} of 1a is T_K of 1a. Thus oxygen does not quench T_{BR} of 1a but quench T_K of 1a.
1 μs time window in Ar & O₂ Combined

**Figure 11.** Transient UV / Vis spectra for quenching studies of 1a (a). Ar, 0.02 – 0.30 μs (red) (b). O₂, 0.02 – 0.26 μs (blue)

25 μs time window in Ar & Combined

**Figure 12.** Transient UV / Vis spectra for quenching studies of 1a in 25 μs time window (a). Ar, 0.02 – 0.30 μs (red) (b). O₂, 0.02 – 0.26 μs (blue)
Quenching Kinetics

50 μs time window at 400 nm in Ar

The rate of quenching with O₂ is,

\[ k_1 = 9.057 \times 10^3 \text{ s}^{-1}, \tau = 110 \mu\text{s} \]

250 μs time window at 400 nm in Ar

The rate of quenching with O₂ is,

\[ k_1 = 2.052 \times 10^4 \text{ s}^{-1}, \tau = 49 \mu\text{s} \]

\[ k_2 = 3.563 \times 10^3 \text{ s}^{-1}, \tau = 281 \mu\text{s} \]
Figure 13. Quenching kinetics of 1a in CH$_3$CN. (a). 1 μs time window at 400nm in Ar (red) & O$_2$ (blue). (b). 25 μs time window at 400nm in Ar (red) & O$_2$ (blue).

(II). 1b in CH$_3$CN

We performed laser flash photolysis to support the proposed reaction mechanism for 1b. Laser flash photolysis (Excimer laser 308 nm) of 1b in argon-saturated acetonitrile produced a transient absorption with $\lambda_{\text{max}}$ at ~300 nm and 360 nm (Figure 14). The calculated TD-DFT absorption spectrum of T$_{1K}$ of 1b in acetonitrile has the major electronic transfer at 453 nm ($f=0.1088$), 349 nm ($f=0.1817$) and 346 ($f=0.4764$) (Figure 14).
Figure 15. Calculated UV of (a). \( T_{1K} \) of 1b (red) and (b). \( T_{BR} \) of 1b (blue) in acetonitrile using TD-DFT level of theory with UB3LYP/6-31+G(d) basis set. We assign the transient with \( \lambda_{\text{max}} \sim 460 \text{ nm} \) to the \( T_{1K} \) of 1b, based on the TD-DFT calculations, which show that the major electron transitions are located at 501 nm \( (f=0.0333) \), 340 nm \( (f=0.0186) \) and 337 nm \( (f=0.0244) \) (Figure 15). Kinetic analysis of the transient absorption further supports this assignment. The transient absorption at 360 nm can be fitted into a mono-exponential function and decays with a rate constant of \( 4.978 \times 10^5 \text{ s}^{-1} \pm 9.36 \times 10^3 \text{ s}^{-1} \) \( (\tau = 2.0 \mu\text{s} \pm 0.04) \mu\text{s} \) in argon saturated-acetonitrile (Figure 16). Further, the transient absorption at 320 nm can be fitted into a mono-exponential function and decays with a rate constant of \( 3.688 \times 10^5 \text{ s}^{-1} \pm 1.2 \times 10^4 \text{ s}^{-1} \) \( (\tau = 2.7 \mu\text{s} \pm 0.1 \mu\text{s}) \) in argon saturated-acetonitrile.
1 \mu s time window at 320 nm in Ar

\[ k_1 = 3.688 \times 10^5 \text{ s}^{-1} \pm 1.2 \times 10^4 \text{ s}^{-1}, \tau = 2.7 \mu s \pm 0.1 \mu s \]

1 \mu s time window at 360 nm in Ar

\[ k_1 = 4.978 \times 10^5 \text{ s}^{-1} \pm 9.36 \times 10^3 \text{ s}^{-1}, \tau = 2.0 \mu s \pm 0.04 \mu s \]

**Figure 16.** Kinetics of 1b in CH$_3$CN. (a). 1 \mu s time window at 320nm in Ar. (b). 1 \mu s time window at 360nm in Ar.
Quenching Studies with Oxygen

In oxygen-saturated acetonitrile solutions the intensities of the bands around 320 nm and 360 nm are quenched (Figure 17). Reduction of intensity is due to the quenching of T\textsubscript{1K} of 1b. Hence, the precursor to the T\textsubscript{BR} of 1b is T\textsubscript{1K} of 1b. Thus oxygen does not quench T\textsubscript{BR} of 1b but quench T\textsubscript{1K} of 1b.

1 μs time window in Ar & O\textsubscript{2} Combined

Figure 17. Transient UV / Vis spectra for quenching studies of 1a (a). Ar, 0.02 – 0.30 μs (red) (b). O\textsubscript{2}, 0.02 – 0.26 μs (blue)
Quenching Kinetics

100 μs time window at 360 nm in Ar

Figure 18. Quenching kinetics of 1b in CH3CN. (a). 100 μs time window at 360 nm in Ar (red) & O2 (blue). (b). 25 μs time window at 360 nm in Ar (red) & O2 (blue).
4. Phosphorescence

We also measured the phosphorescence spectra of 11 in ethanol at 77 K with different wavelengths of irradiation and compared that with the similar ester without any substitution at para position (1b).

The phosphorescence spectra of 0.01 M 1a shows that the (0,0) transition is at 396 nm which corresponds to 72 kcal/mol with 300 nm excitation (Figure 19). The excitation at 260 nm also resulted a (0,0) transition at 396 nm which also corresponds to 72 kcal/mol. This is not in good agreement with the calculated energy of T_{1K} of 1a. Hence, we hypothesize this is due to higher excited triplet state phosphorescence.

Phosphorescence spectrum of 0.01 M solution of 1a in ethanol at 77 K, irradiated at 300 nm
Phosphorescence spectrum of 0.01M solution of 1a in ethanol at 77 K, irradiated at 260 nm

![Phosphorescence spectrum](image)

**Figure 19**: Phosphorescence spectra of 0.01M solutions of 1a in ethanol at 77 K (a) Excited at 300 nm (b) Excited at 260 nm.

The phosphorescence spectra of 0.01 M 1b shows that the (0,0) transition is at 407 nm which corresponds to 70 kcal/mol with 300 nm excitation (Figure 20). The excitation at 260 nm resulted a (0,0) transition at 403 nm which also corresponds to 71 kcal/mol. This is not in good agreement with the calculated energy of T_{1K} of 1b. Calculations suggests that there is no significant energy difference between T_{1K} of 1a and 1b, which agrees with experimentally measured energies for 1a and 1b although experimental energies are much higher than calculated energies.
Phosphorescence spectrum of 0.01M solution of 1b in ethanol at 77 K, irradiated at 300 nm

Figure 20: Phosphorescence spectra of 0.01M solutions of 1b in ethanol at 77 K (a) Excited at 300 nm (b) Excited at 260 nm.
5. Matrix Isolation

(I). Triplet-Sensitized photolysis of 1a in Argon Matrices

We studied the photochemistry of 1a in argon matrices at 14 K to identify its triplet sensitized photoreactivity in an inert environment. We deposited 1a into argon matrices with flowing argon at 15 K onto a cryogenic surface. Irradiation of 1a in argon matrices led to the growth of new absorption bands, mostly occurring very near those of the parent alkene (Figure 24), which is expected since the acetophenone moiety is not significantly affected by irradiation and the majority of the observed vibrational bands belong to it. The infrared spectrum of 1a showed a strong -C(O)O band at 1713 cm\(^{-1}\) and a strong C=O band at 1663 cm\(^{-1}\) which are shifted to 1719 cm\(^{-1}\) and 1656 cm\(^{-1}\) respectively upon irradiation (Figure 22). This is in excellent agreement with the calculated IR shifts (Table 3). Calculations shows that –C(O)O stretch shifts to higher wave number by 6 cm\(^{-1}\) which is in excellent agreement with the experimental shift of 6 cm\(^{-1}\). Calculations shows that C=O stretch of 1a shifts 7 cm\(^{-1}\) to lower wave numbers upon forming 2a, which is also in excellent agreement with the experimental shift of 7 cm\(^{-1}\). Calculations shows that C=C stretch of 1a shifts 13 cm\(^{-1}\) to higher wave numbers upon forming 2a. However, we observe the experimental C=C stretch of 1a at 1622 cm\(^{-1}\) disappear upon irradiation, but we didn’t observe a resolved C=C stretch for 2a. We theorize that C=C stretch of 2a is buried inside the C=O stretch of 2a since C=O stretch of 2a is broad. Calculations shows that ring scissoring vibrations shifts 3 cm\(^{-1}\) to higher wave numbers upon forming 2a from 1a, which is in excellent agreement with the observed experimental shift (which is also 3 cm\(^{-1}\) to higher wavenumbers). Irradiation of 1a resulted in a new peak at 1391 cm\(^{-1}\) which was shifted from 1338 cm\(^{-1}\) by 53 cm\(^{-1}\). This is in excellent agreement with the calculated shift of 51 cm\(^{-1}\). Analysis of IR spectra of before irradiation shows a strong peak for 1a at 1318 cm\(^{-1}\) which was
depleted upon irradiation and a new peak was formed at 1263 cm$^{-1}$ which we assign for the same stretch in 2a. Calculations shows that the 1334 cm$^{-1}$ peak of 1a shifts to 1285 cm$^{-1}$ peak of 2a, a shift of 49 cm$^{-1}$, which is in very good agreement with the experimental shift of 55 cm$^{-1}$. Calculations also show that the IR peak of 1a at 1205 cm$^{-1}$ shifts to 1190 cm$^{-1}$ in 2a, a total of 15 cm$^{-1}$ shift. The corresponding experimental IR peak at 1266 cm$^{-1}$ shift to 1237 cm$^{-1}$, is also in very good agreement with the calculations. Furthermore, the experimental IR peak at 1201 cm$^{-1}$ of 1a shifts to 1220 cm$^{-1}$ upon irradiation, a shift of 19 cm$^{-1}$ to higher wave number. The calculations shows that the corresponding peak at 1194 cm$^{-1}$ shifts to 1209 cm$^{-1}$, a shift of 15 cm$^{-1}$, which is a very good agreement with the experimental shift. Comparison of the above mentioned IR peaks shows that triplet sensitized irradiation of 1a in argon matrices at 15 K yields 2a.
Figure 21. The matrix IR of 1a (a). Before irradiation (blue) (b). After irradiation (red) (c). The difference (pink).

Figure 22. The matrix IR of 1a from 1800 cm$^{-1}$ to 1100 cm$^{-1}$ (a). Before irradiation (blue) (b). After irradiation (red) (c). The difference (pink).

Furthermore, we assigned seven new peaks to 2a based on experimental IR band shift and calculated IR band shifts (Table 3, Figure 23).
Figure 23: The matrix IR of 1a from 1750 cm\(^{-1}\) to 950 cm\(^{-1}\) (a). Before irradiation (blue) (b). After 15 min irradiation (red) (c). After 30 min irradiation (black).

<table>
<thead>
<tr>
<th>Calcd IR Bands / cm(^{-1})</th>
<th>Exp IR Bands / cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>Depleted</td>
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<tr>
<td>Shift bands</td>
<td>bands</td>
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<tr>
<td>Trans (1a)</td>
<td>Cis (2a)</td>
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<td>1780 (197)</td>
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<td>1723 (210)</td>
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<td>1696 (42)</td>
</tr>
<tr>
<td>IR bands</td>
<td>Experimentally identified IR bands</td>
</tr>
<tr>
<td>------------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>1647 (433)</td>
<td>1650 (377)</td>
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<tr>
<td>1611 (5)</td>
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<td>1334 (546)</td>
<td>1285 (253)</td>
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<td>1306 (451)</td>
<td>1302 (233)</td>
</tr>
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<td>1205 (90)</td>
<td>1190 (416)</td>
</tr>
<tr>
<td>1194 (550)</td>
<td>1209 (73)</td>
</tr>
<tr>
<td>960 (13)</td>
<td>942 (48)</td>
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<tr>
<td>783 (43)</td>
<td>860 (23)</td>
</tr>
</tbody>
</table>

**Table 3:** Comparison of calculated IR bands of 1a and 2a with experimentally identified and assigned new IR bands and depleted IR bands (− sign means a shift of peaks to lower wavenumbers, + sign means shift of peaks to higher wavenumbers, bolded numbers are in very good agreement with experimental and calculated values).
(II). Triplet-Sensitized photolysis of 1b in Argon Matrices

We studied the photochemistry of 1b in argon matrices at 14 K to identify its triplet sensitized photoreactivity in an inert environment. We deposited 1b into argon matrices with flowing argon at 15 K onto a cryogenic surface. Irradiation of 1b in argon matrices led to the growth of new absorption bands, mostly occurring very near those of the parent alkene (Figure 24), which is expected since the acetophenone moiety is not significantly affected by irradiation and the majority of the observed vibrational bands belong to it. The infrared spectrum of 1b showed a strong -C(O)O bands at 1745 cm\(^{-1}\), 1739 cm\(^{-1}\) and a strong C=O band at 1689 cm\(^{-1}\), 1683 cm\(^{-1}\), 1674 cm\(^{-1}\) all of which are changed upon irradiation (Table 4). Upon irradiation, The strong new C(O)O band appeared at 1753 cm\(^{-1}\) and C=O band was observed at 1694 cm\(^{-1}\), which we assign to 2b based on theoretical calculations. The calculated shift of C(O)O band of 1b to form 2b and the calculated shift of C(O)O band of 1b to form 2b closely agrees with the experimental shifts (Figure 25). Analysis of experimental IR shifts and calculated IR shifts as stated in Table 04 shows that the triplet sensitized irradiation of 1b in argon matrices at 15 K resulted in 2b.
Figure 24. The matrix IR of 1b (a). Before irradiation (blue) (b). After irradiation (red) (c). The difference (pink)
Figure 25. The matrix IR of 1b from 1800 cm\(^{-1}\) to 1650 cm\(^{-1}\) (a). Before irradiation (blue) (b). After irradiation (red) (c). The difference (pink).

Furthermore, we assigned six new peaks to 2b based on experimental IR band shift and calculated IR band shifts (Table 4, Figure 26-28).
Figure 26: The matrix IR of 1b from 1400 cm\(^{-1}\) to 1150 cm\(^{-1}\) (a). Before irradiation (blue) (b). After irradiation (red) (c). The difference (pink).
Figure 27: The matrix IR of 1b from 1050 cm\(^{-1}\) to 900 cm\(^{-1}\) (a). Before irradiation (blue) (b). After irradiation (red) (c). The difference (pink).
Figure 28: The matrix IR of 1b from 840 cm⁻¹ to 600 cm⁻¹ (a). Before irradiation (blue) (b). After irradiation (red) (c). The difference (pink).

<table>
<thead>
<tr>
<th>Calculated IR Bands / cm⁻¹</th>
<th>Experimental IR Bands / cm⁻¹</th>
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<tr>
<td><strong>Trans (1b)</strong></td>
<td><strong>Cis (2b)</strong></td>
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<td>1775 (156) C=O</td>
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<tr>
<td>1736 (157) C=O,C=C</td>
<td>1733 (228) C=O</td>
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</tr>
<tr>
<td>1686 (45)</td>
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<tr>
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<td>1426 (111)</td>
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<td>1335 (252)</td>
<td>1275 (131)</td>
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<td>744 (75)</td>
<td>767 (46)</td>
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<td>532 (7)</td>
<td>545 (30)</td>
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</table>

**Table 4:** Comparison of calculated IR bands of 1b and 2b with experimentally identified and assigned new IR bands (- sign means a shift of peaks to lower wavenumbers, + sign means shift of peaks to higher wavenumbers, bolded numbers are in very good agreement with experimental and calculated values).
Discussion

Irradiation of 1a-1b in chloroform-d in Ar saturated solutions and O2 saturated solutions yielded 2a-2b as the major product. Therefore, 1a-2b undergoes trans – cis isomerization as we theorized.

LFP studies of 1a showed that there is mainly one intermediate in acetonitrile with a lifetime ~73 μs which we attribute to T_{BR} of 1a. We assign the other lifetimes to the residual product formation. Quenching studies of 1a with oxygen shows reduction in intensity, but there is no significant change in the lifetime of T_{BR} of 1a indicating that oxygen quenches the precursor to T_{BR} of 1a. LFP studies of 1b showed that there is mainly one intermediate in acetonitrile with a lifetime ~2 μs which we attribute to T_{1K} of 1b. Quenching studies of 1b with oxygen show complete depletion of the UV/Visible absorption. This suggests the in oxygen quenches T_{1K} of 1b. Calculated UV/Visible spectra of T_{1K} of 1b and T_{BR} of 1b shows that T_{BR} of 1b has very low oscillator strength. Therefore, we theorize that we do not observe the T_{BR} of 1b in LFP.

Phosphorescence spectra of 1a shows that it has a triplet energy of 72 kcal/mol and (n,π*) nature. The phosphorescence spectra of 1b shows that it has a triplet energy of 70 kcal/mol and has mixed (n,π*) and (π,π*) nature.

Triplet sensitized irradiation of 1a and 1b in argon matrices at 15 K shows the formation of 2a and 2b. DFT/B3LYP or UB3LYP/6-31+G(d) calculations were used to support the experimental results.
Experimental

Calculations

All geometries were optimized at B3LYP level of theory and with 6-31G+(d) basis set as implemented in the Gaussian03 and Gaussian09 programs. All transition states were confirmed to have one imaginary vibrational frequency by analytical determination of the second derivatives of the energy with respect to internal coordinates. Intrinsic reaction coordinates calculations were used to verify that the located transition states corresponded to the attributed reactant and product. The absorption spectra were calculated using time-dependent density functional theory (TD-DFT). The effect of solvation was calculated using the self-consistent reaction field (SCRF) method with the integral equation formalism polarization continuum model (IEFPCM) with acetonitrile, methanol and dichloromethane as solvents.

Laser Flash Photolysis.

Laser flash photolysis was done with an Excimer laser (308 nm, 17 ns). The system has been described in detail elsewhere. A stock solution of 1 in CH$_3$CN was prepared with spectroscopic grade CH$_3$CN, such that the solutions had absorption between 0.3 and 0.6 at 308 nm. Typically, ~2 mL of the stock solution was placed in a 10 mm × 10 mm wide, 48 mm long quartz cuvette and was purged with argon for 5 min or oxygen for 15 min. The rates were obtained by fitting an average of three to five kinetic traces.

Phosphorescence

The solutions of 1 (0.01 M) and 3 (0.01 M) solutions were prepared in ethanol. The phosphorescence spectra were obtained on a phosphorimeter in ethanol glasses at 77K. The
solutions were irradiated at 300 nm and 260 nm. The emission spectra recorded between 280 and 800 nm.

**Matrix isolations**

Matrix isolation studies were performed using conventional equipment.\textsuperscript{23}

**Synthesis of 1a**

*4-(4-Methoxy-phenyl)-4-oxo-but-2-enoic acid:*

5.461 g (50 mmol) of anisole was dissolved in 30 mL of CH\textsubscript{2}Cl\textsubscript{2}. 7.505 g (75 mmol, 1.5 eq) of maleic anhydride and 9.900 g (75 mmol, 1.5 eq) of AlCl\textsubscript{3} was added to the mixture. The reaction was allowed to stir for 20 hours at room temperature. An extraction was performed with CH\textsubscript{2}Cl\textsubscript{2} (50 mL) and H\textsubscript{2}O (50 mL). CH\textsubscript{2}Cl\textsubscript{2} was separated and it was washed twice with H\textsubscript{2}O and once with 100 mL of brine (saturated NaCl). The CH\textsubscript{2}Cl\textsubscript{2} extract was dried using anhydrous MgSO\textsubscript{4}. The CH\textsubscript{2}Cl\textsubscript{2} was evaporated and a yellow crude of 4-(4-Methoxy-phenyl)-4-oxo-but-2-enoic acid (5.09 g, 25 mmol) was obtained (% Yeild = 50%). 1H NMR was obtained for the reaction mixture and we moved to the next step of the synthesis without further characterizations.

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): δ 3.904 (s, 3H, -OCH\textsubscript{3}), 6.874 (d, J = 15.6 Hz, 1H, -CH=), 6.901-7.040 (m, 2H, -CH), 7.264-7.294 (m, 1H, -CH=), 7.968-8.052 (m, 2H, -CH);
4-(4-Methoxy-phenyl)-4-oxo-but-2-enoic acid methyl ester (1a):

5.09 g (25 mmol) of 4-(4-Methoxy-phenyl)-4-oxo-but-2-enoic acid was dissolved in 30 mL of methanol. A spatula of (a catalytic amount of) para-Toluene sulfonic acid was added to the mixture. The reaction was allowed to stir for 20 hours while refluxing. An extraction was performed with diethyl ether (50 mL) and H₂O (50 mL). Diethyl ether was separated and it was washed twice with H₂O and once with 100 mL of brine (saturated NaCl). The diethyl ether extract was dried using anhydrous MgSO₄. The diethyl ether was evaporated and a yellow crude of (1.56 g, 7 mmol) was obtained (% Yeild = 28%). ¹H NMR, ¹³C NMR and IR spectra were taken in CDCl₃.

¹H NMR (CDCl₃, 400 MHz): δ 3.848 (s, 3H, -OCH₃), 3.898 (s, 3H, -OCH₃), 6.884 (d, J = 15.6 Hz, 1H, -CH=), 6.985 (d, J = 8.8 Hz, 2H, -CH), 7.938 (d, J = 15.6 Hz, 1H, -CH=), 8.012 (d, J = 8.8 Hz, 2H, -CH); ¹³C NMR (CDCl₃, 100 MHz): δ 52.297 (-OCH₃), 55.589 (-OCH₃), 114.150 (2 –CH), 129.687 (1 C), 131.331 (2 –CH, 1 –CH=), 136.766 (1 –CH=), 164.262 (1 C), 166.227 (-C(O)O), 187.548 (-C=O); IR (CDCl₃): 3064, 3029, 2954, 2844, 1716 (C(O)O), 1668 (C=O), 1626, 1593, 1512, 1458, 1445, 1420, 1337, 1305, 1265, 1198, 1164, 1116, 1027, 984, 942, 832, 766, 714, 689, 632, 596 cm⁻¹; GC/MS (EI): m/z 220 (M⁺), 205, 189, 177, 161, 146, 135 (100%), 129, 118, 107, 101, 92, 85, 77, 64, 54.

Synthesis of (E)-4-oxo-4-phenylbut-2-enoic acid

7.80 g (0.099 mol) of benzene was dissolved in 30 mL of CH₂Cl₂. 15.00 g (0.153 mol, 1.5 eq) of maleic anhydride and 19.80 g (0.148 mol, 1.5 eq) of AlCl₃ was added to the mixture. The reaction was allowed to stir for 20 hours at room temperature. An extraction was performed with CH₂Cl₂ (50 mL) and H₂O (50 mL). CH₂Cl₂ was separated and it was washed twice with H₂O and
once with 100 mL of brine (saturated NaCl). The CH$_2$Cl$_2$ extract was dried using anhydrous
MgSO$_4$. The CH$_2$Cl$_2$ was evaporated and a yellow crude of (E)-4-oxo-4-phenylbut-2-enoic acid
(9.81 g, 0.0557 mol) was obtained (% Yield = 56%). $^1$H NMR, $^{13}$C NMR and IR spectra were
taken in CDCl$_3$.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 6.919 (d, J= 15.6 Hz, 1H, -CH=), 7.52 (d, J= 6 Hz,3H, Ph-H),
7.67 (t, J = 7.6 Hz, 1H, Ph-H), 8.024 (t, 3H, Ph-H, -CH=), 8.6-9.2 (s, 1H, -OH) ppm; $^{13}$C NMR
(CDCl$_3$, 100 MHz): $\delta$ 128.951(2 C), 128.966 (2 C), 131.478 (2 C), 134.137 (1 C), 136.362 (1 C),
138.428 (1 C), 170.540 (-C=O), 189.341 (-C=O) ppm; IR (CDCl$_3$): 3812, 3599, 3183, 3118,
2966, 2932, 2647, 2550, 2379, 2298, 2172, 2125, 2027, 1981, 1929, 1851, 1771, 1760, 1732,
1716, 1669, 1634, 1596, 1450, 1403, 1329, 1285, 1267, 1240, 1182, 1105, 1059, 1033, 1012,
977, 892, 868, 841, 796, 767, 734, 696, 636, 618, 592, 485, 476 cm$^{-1}$. 

**Synthesis of (E)-methyl 4-oxo-4-phenylbut-2-enolate (1b)**

9.81 g (0.0557 mol) of (E)-4-oxo-4-phenylbut-2-enioic acid was dissolved in 30 mL of methanol. 
A spatula of (a catalytic amount of) para-Toluene sulfonic acid was added to the mixture. The 
reaction was allowed to stir for 20 hours while refluxing. An extraction was performed with
diethyl ether (50 mL) and H$_2$O (50 mL). Diethyl ether was separated and it was washed twice 
with H$_2$O and once with 100 mL of brine (saturated NaCl). The diethyl ether extract was dried 
using anhydrous MgSO$_4$. The diethyl ether was evaporated and yellow crude of (E)-methyl 4-
oxo-4-phenylbut-2-enolate (7.07g, 0.0372 mol) was obtained (% Isolated Yield = 67%). $^1$H 
NMR, $^{13}$C NMR and IR spectra were taken in CDCl$_3$. 

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Photolysis of 1a

Product Studies of 1a in Ar-saturated CDCl₃

A solution of 1a (~20 mg, 0.1 mmol) in CDCl₃ (2 mL) was purged with argon for 5 min and photolyzed via a Pyrex filter for 7 hours at 298 K. ¹H NMR analysis of the reaction mixture after 7 hours of photolysis shows 2a (100%). The products were characterized by GC-MS chromatography and ¹H-NMR spectroscopy of the reaction mixture.

2a: ¹H NMR (CDCl₃, 400 MHz): δ 3.615 (s, 3H, -OCH₃), 3.876 (s, 3H, -OCH₃), 6.260 (d, J = 12 Hz, 1H, -CH=), 6.934 – 6.963 (m, 3H, 1-CH=, 2-CH), 7.913 (d, J = 8.8 Hz, 2H, -CH) ppm.; ¹³C NMR (CDCl₃, 100 MHz): δ 192.58 (C=O), 165.40 (C=O), 164.03 (1 C), 141.48 (1 =CH), 131.08 (2 -CH), 128.94 (1 C), 125.26 (1 =CH), 114.01 (2 –CH), 55.53 (-OCH₃), 51.91 (-OCH₃) ppm.; IR (CDCl₃): 1664, 1650, 1598, 1576, 1511, 1458, 1437, 1420, 1387, 1306, 1254,
Product Studies of 1a in O₂-saturated CDCl₃

A solution of 1a (~ 20 mg, 0.1 mmol) in CDCl₃ (2 mL) was purged with argon for 5 min and photolyzed via a Pyrex filter for 8 hours at 298 K. ¹H NMR analysis of the reaction mixture after 7 hours of photolysis shows 2a (100%). The products were characterized by GC-MS chromatography and ¹H-NMR spectroscopy of the reaction mixture.

2a: ¹H NMR (CDCl₃, 400 MHz): δ 3.614 (s, 3H, -OCH₃), 3.875 (s, 3H, -OCH₃), 6.258 (d, J = 12 Hz, 1H, -CH=), 6.932 – 6.961 (m, 3H, 1-CH=, 2-CH), 7.911 (d, J = 8.8 Hz, 2H, -CH) ppm.; ¹³C NMR (CDCl₃, 100 MHz) : δ 192.58 (C=O), 165.40 (C=O), 164.03 (1 C), 141.48 (1 =CH), 131.08 (2 –CH), 128.94 (1 C), 125.26 (1 =CH), 114.01 (2 –CH), 55.53 (-(O)OCH₃), 51.91 (-(O)OCH₃) ppm.; IR (CDCl₃): 1664, 1650, 1598, 1576, 1511, 1458, 1437, 1420, 1387, 1306, 1254, 1220, 1163, 1113, 1021, 993, 913, 849, 822, 796, 743, 650, 602 cm⁻¹. GC/MS (EI): m/z 220 (M⁺), 189, 174, 161, 146, 135 (100%), 129, 120, 113, 107, 101, 92, 85, 77, 64, 54.

Product Studies of 1a in Ar-saturated CH₂Cl₂

A solution of 1a (~ 60 mg, 0.3 mmol) in CH₂Cl₂ (2 mL) was purged with argon for 15 min and photolyzed via a Pyrex filter for 16 hours at 298 K. GC-MS analysis of the reaction mixture showed the formation of 2a (100%). The products were characterized by GC-MS of the reaction mixture.
Product Studies of 1a in O₂-saturated CH₂Cl₂
A solution of 1a (~ 70 mg, 0.35 mmol) in CH₂Cl₂ (2 mL) was purged with oxygen for 15 min and photolyzed via a Pyrex filter for 16 hours at 298 K. GC-MS analysis of the reaction mixture showed 2a (22%) with 1a (78%). The products were characterized by GC-MS chromatography of the reaction mixture.

2a: GC/MS (EI): m/z 220 (M⁺), 189, 161, 135 (100%), 113, 107, 92, 85, 77, 64, 54.

Product Studies of 1b in Ar-saturated CDCl₃
A solution of 1b (~ 20 mg, 0.1 mmol) in CDCl₃ (2 mL) was purged with argon for 5 min and photolyzed via a Pyrex filter for 8 hours at 298 K. ¹H NMR analysis of the reaction mixture after 8 hours shows 2b (~100%). The products were characterized by ¹H-NMR spectroscopy of the reaction mixture.

2b: ¹H NMR (CDCl₃, 400 MHz): δ 3.604 (s, 3H, -OCH₃), 6.303 (d, J = 12 Hz, 1H, -CH=), 6.916 (d, J = 12 Hz, 1H, 1-CH=), 7.486 (t, J = 7.6 Hz, 2H, -CH), 7.598 (t, J = 7.6 Hz, 1H, -CH), 7.941 (d, J = 7.6 Hz, 2H, -CH) ppm.; ¹³C NMR (CDCl₃, 100 MHz) : δ 194.06 (C=O), 165.30 (C=O), 141.31 (1 =CH), 135.78 (1 C), 133.90 (1 =CH), 128.86 (3 -CH), 125.77 (2 -CH), 51.92 (-OCH₃) ppm.; GC/MS (EI): m/z 190 (M⁺), 159, 131, 113, 105 (100%), 85, 77, 71, 59, 51.
Product Studies of 1b in Oxygen-saturated CDCl₃

A solution of 1b (~ 20 mg, 0.1 mmol) in CDCl₃ (2 mL) was purged with oxygen for 15 min and photolyzed via a Pyrex filter for 8 hours at 298 K. ¹H NMR analysis of the reaction mixture after 8 hours shows 2b (~100%). The products were characterized by ¹H-NMR spectroscopy of the reaction mixture.

2b: ¹H NMR (CDCl₃, 400 MHz): δ 3.604 (s, 3H, -OCH₃), 6.303 (d, J = 12 Hz, 1H, -CH=), 6.916 (d, J = 12 Hz, 1H, 1-CH=), 7.486 (t, J = 7.6 Hz, 2H, -CH), 7.598 (t, J = 7.6 Hz, 1H, -CH), 7.941 (d, J = 7.6 Hz, 2H, -CH) ppm.; ¹³C NMR (CDCl₃, 100 MHz) : δ 194.06 (C=O), 165.30 (C=O), 141.31 (1 =CH), 135.78 (1 C), 133.90 (1 =CH), 128.86 (3 -CH), 125.77 (2 -CH), 51.92 (-OCH₃) ppm.; GC/MS (EI): m/z 190 (M⁺), 159, 131, 113, 105 (100%), 85, 77, 71, 59, 51.

Conclusions

We have demonstrated that 1a and 1b both undergo complete trans to cis isomerization upon irradiation. We did not observe a triplet 1,2 biradical for 1b but we observe a long lived intermediate with a lifetime ~70 μs from LFP for 1a. Further experiments are required to determine what this intermediate is.

Acknowledgment

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Chapter 10

Electron Withdrawing Substituent Effect on the Stability of C-based radical; Photochemistry of 2-azido-4-oxo-4-phenyl-butyric acid methyl ester
Electron Withdrawing Substituent Effect on the 
Stability of C-based radical; Photochemistry of 2- 
azido-4-oxo-4-phenyl-butyric acid methyl ester 

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ABSTRACT.

We investigated the photoreactivity of 1 to see the effect of an electron withdrawing group on the stability of the triplet nitrene upon irradiation. We used product studies, laser flash photolysis (LFP, \( \lambda=308 \) nm, 17 ns) and theoretical calculations in order to identify the intermediate formed by irradiating 1. Photolysis of 1 in argon-saturated CDCl\(_3\) yields 2 and 3, whereas photolysis in oxygen-saturated CDCl\(_3\) yields only 2. Further, photolysis of 1 in both argon- and oxygen-saturated methanol yielded only 2. We propose that upon excitation, 1 form the T\(_{1K}\) of 1 and then it mainly undergoes C-N bond cleavage in competition with energy transfer to the azido group.

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C-N bond cleavage results in 4 whereas energy transfer forms T_A of 1 which extrudes a N_2 molecule to form T_N of 1. T_N of 1 can intersystem cross to form 3 whereas 4 could abstract a H atom to form 2. Matrix isolation studies of 1 show the formation of T_N of 1 at 14 K.

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Nitrenes are intermediates which have a monovalent nitrogen atom.\(^1\) Non-bonded electrons on the nitrogen atom can be either paired, which gives a singlet nitrene, or unpaired, giving a triplet nitrene.\(^3\) Triplet nitrenes are known to be candidates for potential organic magnets. In this paper, we have designed 2-azido-4-oxo-4-phenyl-butyric acid methyl ester (1) and explored how a carbon based radical center (formed from azido cleavage) stabilized by an ester group behaves in comparison to a carbon based radical stabilized by a phenyl group (Scheme 1).

**Scheme 1**

Klima *et al.* have investigated the photo-induced C-N bond cleavage in 2-azido-1,3-diphenyl-propan-1-one and found that it is an excellent molecule to photorelease the hydrozoic acid (Scheme 2).\(^4\) Further, when Klima *et al.* studied 2-azido-2,2-dimethyl-1,3-diphenyl-propan-
According to Klima et al., both these molecules undergo C-N bond cleavage. Laser flash photolysis studies on 2-azido-1,3-diphenyl-propan-1-one shows that it exists for 14 μs in solution. We were curious to see whether 1 undergo C-N bond cleavage in the presence of an electron withdrawing group like a methyl ester chromophore.
Further, thermolysis studies carried on \( \alpha,\beta \)-unsaturated vinyl azides, such as the ones shown in Scheme 4 has shown to produce corresponding isoxazoles and oxazoles through a possible vinyl nitrene intermediate.\(^5\)\(^6\) This isoxazole formation is similar to the cyclization that we observed for 1.

**Results**

1. **Product Studies**

**Scheme 5**

\[
\begin{array}{c}
\text{Scheme 5} \\
\begin{array}{c}
\begin{array}{c}
\text{1} \\
\text{hv (> 300 nm)} \\
\text{CDCl}_3 \\
\text{20.5 hours} \\
\text{Ar}
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{2} \\
\text{74%}
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{3} \\
\text{15%}
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{2 + HN}_3 + N_2
\end{array}
\end{array}
\end{array}
\text{Note: Product studies have been carried out once, but in different solvents.}
\]
Photolysis of 1 in argon-saturated chloroform-d via a Pyrex filter at ambient temperature produced 2 and 3 (Scheme 5). GC-MS analysis of the reaction mixture shows 74% of 2, 15% of 3 and 11% of remaining starting material. As expected, we did not observe the formation of HN3 with GC-MS spectrometer. Irradiation of 1 in oxygen-saturated chloroform-d via a Pyrex filter at 298 K only yields 2. Irradiation via Pyrex filter ensures that only the ketone absorbs the light and forms the singlet excited state of the ketone (S1K) which then intersystem crosses to the triplet excited state of the ketone (T1K) of 1. The first and the second excited states of the ketone (T1K and T2K) of 1 are expected to be within a few kcal/mol of each other as observed for acetophenone.7 We propose that either the T1K or T2K of 1 can undergo energy transfer to its azide moiety from the triplet excited state of the azido chromophore, which results in extrusion of a N2 molecule and formation of triplet nitrene. Cyclization of the triplet nitrene, followed by intersystem crossing will yield 3. In addition, a triplet excited state of 1 can result in azido cleavage and formation of an azido radical and 4. We theorize that the azido radical can abstract a H atom from the α-carbon to give 2 and HN3.

2. Calculations

To better understand the reactivity of 1, we calculated stationary points on the triplet potential energy surface of 1 using the Gaussian098 at the B3LYP level of theory and with 6-31+G(d) basis set.9, 10 We used the calculations to identify the most favorable reaction on the triplet surface of 1 and to understand the factors that govern the reactivity of on the triplet surface of 1.
We optimized the ground-state ($S_0$) of 1 (Figure 1). TD-DFT calculations place the first excited state of the ketone ($S_{1K}$) of 1 at 88 kcal/mol above its ground state. Analysis of molecular orbitals shows that $S_{1K}$ of 1 has $(n, \pi^*)$ configuration where the major electronic excitation is from the non-bonding electrons of oxygen (Table 1, Figure 2) to $\pi^*$-orbital.

![Figure 1. Optimized $S_0$ Conformers of 1 (Energies are in kcal/mol).](image)

**Table 1.** Electronic transitions of 1 above 260 nm in gas phase

<table>
<thead>
<tr>
<th>Excited State</th>
<th>1: Singlet-A</th>
<th>3.8517 eV</th>
<th>321.89 nm</th>
<th>f=0.0001</th>
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</thead>
<tbody>
<tr>
<td>59 -&gt; 62</td>
<td>0.27175</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60 -&gt; 62</td>
<td>0.62168</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Excited State</td>
<td>2: Singlet-A</td>
<td>4.2776 eV</td>
<td>289.85 nm</td>
<td>f=0.0002</td>
</tr>
<tr>
<td>61 -&gt; 62</td>
<td>0.18717</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>61 -&gt; 63</td>
<td>0.64726</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Excited State</td>
<td>3: Singlet-A</td>
<td>4.4359 eV</td>
<td>279.50 nm</td>
<td>f=0.0059</td>
</tr>
<tr>
<td>61 -&gt; 62</td>
<td>0.67634</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Excited State 4: Singlet-A 4.6518 eV 266.53 nm f=0.0231

Figure 2. Molecular orbitals corresponds to electronic transitions of $S_1$ of 1 above 290 nm

TD-DFT calculations of 1 in gas phase show that the $T_{1K}$ of 1 is located 76 kcal/mol above the $S_0$ of 1 and has ($\pi,\pi^*$) configuration with the major electron transition being from the phenyl chromophore with minor contribution from the non-bonding electrons on oxygen. In comparison, the $T_{2K}$ of 1 is 77 kcal/mol above the $S_0$ of 1 and has (n,$\pi^*$) configuration with the major electron transition being from the non-bonding electrons on the oxygen with minor contribution from the phenyl chromophore.
We also optimized the T\(_{1K}\) of 1 and found that T\(_{1K}\) of 1 is located at 68 kcal/mol above S\(_0\) of 1, which is considerably lower than the energy obtained by TD-DFT calculations (Scheme 6). Analysis of bond lengths of the S\(_0\) of 1 shows C=O bond length of 1.22 Å. The optimized structure of T\(_1\) of 1 show that C=O bond length has been increased from 1.22 Å to 1.33 Å. Furthermore, the C-C bond between the carbonyl carbon atom and the quaternary phenyl carbon atom has been reduced from 1.50 Å to 1.42 Å, in T\(_{1K}\) of 1 in comparison to its ground state. In addition the dihedral angle of O-C\(_{\text{carbonyl}}\)-C\(_\alpha\)-H angle has increased from 12.4º in the ground state to 74.3º in the T\(_{1K}\) of 1. The analysis of bond lengths in the phenyl ring shows that only the C\(_{\text{carbonyl}}\)-C\(_{\text{ortho}}\) bond has increased from 1.40 Å in the ground state to 1.43 Å in the T\(_{1K}\) of 1. These analysis shows that optimized structure of the T\(_{1K}\) of 1 is delocalized mainly to the C=O chromophore, hence it has (n,\(\pi^*\)) configuration.

Energy transfer from the T\(_{1K}\) of 1 to azide moiety results the formation of T\(_A\) of 1. We also optimized the T\(_A\) of 1 and found that it is located at 42.6 kcal/mol above the S\(_0\) of 1 (Scheme 6). Analysis of bond lengths in the T\(_A\) of 1 shows the C=O bond being 1.22 Å, which is similar to the C=O bond in the S\(_0\) of 1. Further, it also shows that the bond between the carbonyl carbon atom and the quaternary phenyl carbon atom is the same for the S\(_0\) of 1 and the T\(_A\) of 1. More importantly, the angle between N-N-N atoms has been reduced from 172.8º in the S\(_0\) of 1 to
120.6° in the T_A of 1. In addition, the Nα-Nβ bond in T_A of 1 is 1.43 Å, which is somewhat longer than in the Nα-Nβ bond for the S0 of 1. Therefore the calculations show that in the optimized structure of the T_A of 1, triplet state is delocalized mainly on the N3 chromophore.

We calculated the transition state for the T_A of 1 to form the triplet nitrene (T_N) of 1 and found that it is located less than 1 kcal/mol (0.1 kcal/mol) above the T_A of 1 and 33.7 kcal/mol above T_N of 1. Intrinsic reaction coordinate (IRC) calculations confirm the transition state correlate to the T_A of 1 and the T_N of 1. Optimization of the T_N of 1 located it at 9 kcal/mol above the S0 of 1 (Scheme 6). The calculations show that the C-N bond length has been reduced from 1.45 Å in the T_A of 1 to 1.43 Å in the T_N of 1. Further, the C_carbonyl-Cα-Cβ-N dihedral angle has been increased from 77.9° in the T_A of 1 to 95.7° in the T_N of 1. This shows that the two unpaired electrons mainly localized on N atom which is somewhat orthogonal to the acetophenone and ester chromophores. Further, lesser C-N bond length change also indicates the lesser electron delocalization to ester chromophore from the N atom.

We calculated the transition state for the T1 of 1 to form 4 by azido cleavage and found that it is located 2 kcal/mol above the T1 of 1 and 12 kcal/mol above 4. IRC calculations show that the transition state does not correlate to the T1K of 1 and azido radical and 4. Instead, it shows that it correlates to a higher triplet state of 1 and to 4 and an azido radical. Optimization of 4 and azido radical located its energy at 58 kcal/mol above S0 of 1 (Scheme 6). The C=O bond in 4 is similar to the S0 of 1 or 1.22 Å. Further, the O-C_carbonyl-Cα-Cβ dihedral angle has been reduced from 12.3° in S0 of 1 to 0.0° in 4. Further, Cβ-Cγ bond distance has also been decreased from 1.54 Å in S0 of 1 to 1.45 Å in 4. C=O bond length of the ester moiety of 4 has been slightly increased from 1.21 Å in S0 of 1 to 1.23 Å in 4. C-O bond distance has also been increased from 1.34 Å in
$S_0$ of 1 to 1.36 Å in 4. This shows that ester chromophore has not been affected significantly upon the azido cleavage.

**Scheme 6**
Scheme 7. H abstraction by methanol radical from 4.

We calculated the transition state for the 4 to form T_{BR(1,2)} of 1 and found that it is located 11 kcal/mol above the 4 and methanol radical (Scheme 7). Intrinsic Reaction Coordinate (IRC) calculations confirm that this transition state correlates the 4 and T_{BR(1,2)} of 1. This transition state suggests that a methanol radical could easily abstract a H atom from 4 to form T_{BR(1,2)} of 1 followed by ISC to form 2.

Scheme 8. H abstraction of 4 from solvent to yield 9.

We calculated the enthalpy for formation of 9 from 4 by abstracting a H atom from solvent methanol (Scheme 8). Enthalpy of formation of 9 shows that it is an unfavorable process. This supports why we get 2 instead of 9 upon irradiation of 1.
Calculation of spin densities of $T_{1K}$ of 1 show that some of the spin density is delocalized on the C=O and the adjacent phenyl ring thus showing that $T_{1K}$ of 1 is mainly localized on the acetophenone chromophore (Figure 4). The general difference in spin density for a (n,\(\pi^*\)) and (\(\pi,\pi^*\)) chromophore is that for (n,\(\pi^*\)) ketone, the spin density is mainly localized on C=O chromophore whereas for (\(\pi,\pi^*\)) ketone, it is mainly localized on phenyl ring as suggested by alternating negative and positive spin density values. Analysis of $T_{1K}$ of 1 shows it has a mixed character but the major contribution is due to the (n,\(\pi^*\)) character of $T_{1K}$ of 1. Analysis of spin density on $T_N$ of 1 show that it is localized on N atom with a spin density of -1.88. In comparison, the spin density analysis of 4 shows that the major spin density is localized on C\(\beta\) atom (-0.82). However, some of the spin density is delocalized to the adjacent C=O chromophore, because the O-atom has a spin density of -0.15. This shows that the spin density on C\(\beta\) is stabilized by the adjacent C=O chromophore. Further, we also calculated the spin
density of peroxy radicals 6 and 7. Spin density calculations of 6 shows that spin density is mainly localized on two oxygen atoms with -0.71 spin density on radical oxygen atom. On the other hand, the spin density calculation of 7 shows that spin density is localized on two oxygen atoms and on nitrogen atom.

Scheme 9

The proposed mechanism for the intermediates and products are shown in Scheme 9.
3. Laser Flash Photolysis

(I). $\text{1 in CH}_3\text{CN}$

We performed laser flash photolysis to support the proposed reaction mechanism for $\text{1}$. Laser flash photolysis (Excimer laser, 308 nm, 17 ns) of $\text{1}$ in argon-saturated acetonitrile produced a transient absorption with $\lambda_{\text{max}}$ at $\sim$360 nm (Figure 5-6).

$1 \mu$s time window in Ar

![Absorption spectra](image)

**Figure 5.** Transient UV / Vis spectra obtained by laser flash photolysis of $\text{1}$ (a). 0.02 – 0.32 $\mu$s (red) (b).0.32 – 1.00 $\mu$s (blue) (c). 1.00 – 2.00 $\mu$s (black) (d). 2.00 – 7.01 $\mu$s (light green) over a time window of 1 $\mu$s in acetonitrile.
10 ms time window in Ar

**Figure 6.** Transient UV / Vis spectra obtained by laser flash photolysis of 1 (a) 0.16 – 2.08ms (red) (b) 2.08 – 5.56ms (blue) (c). 5.56 – 24.64ms (black) (d). 24.64 – 73.44ms (light green) in acetonitrile solvent.
We hypothesize the triplet ketone decays within the time resolution of the instrument (17ns). The calculated TD-DFT absorption spectrum of $T_{1K}$ of $\mathbf{1}$ in acetonitrile has the major electronic transfer at 427 ($f=0.0051$), 375 nm ($f=0.0288$), 309 nm ($f=0.0286$) and 303 nm ($f=0.0191$) (Figure 7). We assign the transient with $\lambda_{\text{max}} \sim 360$ nm to $\mathbf{4}$, based on the TD-DFT calculations, which show that the major electron transitions are located at 354 nm ($f=0.0252$), 324 nm ($f=0.0112$), 320 nm ($f=0.0231$) and 317 nm ($f=0.0145$) (Figure 7). Kinetic analysis of the
transient absorption further supports this assignment. The transient absorption at 340 nm decays with a rate constant of 54.3 s\(^{-1}\) (~\(\tau = 18.4\) ms) in argon saturated-solvent (Figure 8).

10 ms time window at 340 nm in Ar-saturated CH\(_3\)CN.

\[ k_1 = 54.302 \pm 0.751 \text{ s}^{-1}, \tau = 18.4 \pm 0.2 \text{ ms} \]

**Figure 8.** Kinetics obtained by laser flash photolysis of 1 in 10 ms time window at 420 nm in Ar-saturated CH\(_3\)CN.

**Quenching Studies of 1 in Air and Oxygen saturated CH\(_3\)CN**

In air-saturated acetonitrile solutions the intensity of the band around 360 nm is not quenched in a 1 \(\mu\)s time window (Figure 9). However, we observed that the absorbance slightly increases with the increase in time at 360 nm in air-saturated acetonitrile solutions. Transient UV/Vis absorption spectra at longer time scale shows that the absorption at 360 nm reduces with time (Figure 10). But, after ~73 ms, there is still significant absorbance (~0.01) remaining for the transient, unlike in argon-saturated acetonitrile (Figure 10). This suggests that in air saturated
acetonitrile solutions; the intermediate at 360 nm is somewhat longer lived. This was supported by the kinetic analysis of the transient at 360 nm in longer time window, which shows a mono-exponential decay with a rate constant of 41.2 s\(^{-1}\) \(\tau = 24.2\) ms\) (Figure 11). This indicates that the longer lived intermediate in air could be a different intermediate. This conclusion was further supported by the studies in oxygen-saturated solutions.

In air, 1 μs time window

**Figure 9.** Transient UV / Vis spectra of obtained from laser flash photolysis of 1 (a). 0.02 – 0.32 μs (red) (b).0.32 – 1.00 μs (blue) (c). 1.00 – 2.00 μs (green) (d). 2.00 – 7.01 μs (purple) in air-saturated acetonitrile.
In air, 10 ms time window

**Figure 10.** Transient UV / Vis spectra obtained by laser flash photolysis of 1 (a). 0.16 – 2.08 ms (red) (b). 2.08 – 5.56 ms (blue) (c). 5.56 – 24.64 ms (green) (d). 24.64 – 73.44 ms (purple) in air-saturated acetonitrile.

340 nm, 10 ms time window in air-saturated CH₃CN

k = 41.243 s⁻¹ ± 0.502 s⁻¹, τ = 24.2 ms ± 0.3 ms

**Figure 11.** Kinetics obtained by laser flash photolysis of 1 in 10 ms time window at 420 nm in Air-saturated CH₃CN.
In oxygen-saturated acetonitrile solutions the intensity of the band around 360 nm grew in at short time scale indicating that a new intermediate forms in oxygen-saturated acetonitrile unlike in argon saturated acetonitrile (Figure 12). This absorption grew in with a rate constant of $1.36 \times 10^6 \text{ s}^{-1} (\tau=738 \text{ ns})$ (Figure 13). We assign this growth to the formation of a peroxy radical by the reaction between 4 and O$_2$. Transient UV/Visible in longer time scale shows that the absorption at 360 nm decays with increase in time (Figure 14). But, after ~73 ms, there is some absorbance is remaining for the transient unlike in argon saturated acetonitrile. Kinetic analysis of the transient at 360 nm in longer time window shows a mono-exponential decay with a rate constant of $37.363 \pm 0.353 \text{ s}^{-1} (\tau = 26.8 \text{ ms} \pm 0.2 \text{ ms})$ (Figure 15). This indicates that the longer lived intermediate in oxygen is peroxy radical 6, rather than radical 4. This was further supported by TD-DFT calculations.

In oxygen, 1 μs time window
Figure 12. Transient UV / Vis spectra obtained by laser flash photolysis of 1 (a).0.02 – 0.32 μs (red) (b).0.32 – 1.00 μs (blue) (c). 1.00 – 2.00 μs (green) (d). 2.00 – 7.01 μs (purple) in acetonitrile

Figure 13. Kinetics obtained by laser flash photolysis of 1 in 1 μs time window at (a).320 nm in oxygen-saturated CH₃CN (b). 300 nm in oxygen-saturated CH₃CN
In oxygen, 10 ms time window

**Figure 14.** Transient UV / Visible spectra of obtained by laser flash photolysis of 1 (a).0.16 – 2.08 ms (red) (b). 2.08 – 5.52 ms (blue) (c). 5.52 – 24.64 ms (green) (d). 24.64 – 73.44 ms (purple) in acetonitrile

\[ k = 37.363 \text{ s}^{-1} \pm 0.353 \text{ s}^{-1}, \tau = 26.8 \text{ ms} \pm 0.2 \text{ ms} \]
**Figure 15.** Kinetics obtained by laser flash photolysis of 1 in 10 ms time window at 420 nm in oxygen-saturated CH$_3$CN

![Figure 15](image)

**Figure 16.** Calculated UV spectra for 7 (red) and 6 (blue) in acetonitrile using TD-DFT level of theory with UB3LYP/6-31+G(d) basis set.

![Figure 16](image)

We calculated the TD-DFT UV spectra for peroxy radical 6 and also for radical 7 that is formed from the reaction of T$_N$ of 1 with $^3$O$_2$ (Figure 16). TD-DFT calculations for 6 and 7 show major electronic transitions at 330 nm ($f$=0.0263) nm and 578 ($f$=0439) nm, respectively. The calculated electronic transition at 330 nm for 6 is in excellent agreement with the observed transient spectrum obtained in oxygen-saturated acetonitrile. Therefore, we assign the transient spectrum in oxygen-saturated acetonitrile to the peroxy radical 6. This was further supported by
the molecular orbital arrangement for the peak at 330 nm (Figure 17). The electron transition at 330 nm takes place from the phenyl chromophore to the half full oxygen orbital on the peroxy radical chromophore. Further, we also calculated the enthalpy for the formation of 6, 7 and 8; and the formation of 6 is favored over the formation of 7 and 8 (Scheme 10). The enthalpy for forming 6 is -21 kcal/mol and the transition state for forming peroxy radical 6 is 0.2 kcal/mol above the combined energy 4 and \(^{3}\text{O}_{2}\). In comparison, the enthalpy for forming 7 is +0.1 kcal/mol and the transition state for forming 7 is 12 kcal/mol above the combined energy of T\(_{N}\) of 1 and \(^{3}\text{O}_{2}\). Further, we also calculated the enthalpy for forming 8 on singlet surface and found that it is -16 kcal/mol. These calculations also support the assignment of transient peak at 340 nm to 6. Most aliphatic carbon radicals (sp\(^{3}\)) reacts exothermally (~ -35 kcal/mol) with molecular oxygen to form peroxy radicals.\(^{11}\) However, the formation of 6 is stabilized only by 21 kcal/mol indicating the precursor to 6, which is 4 is already a stable radical.

**Figure 17.** Molecular orbital involved in the electron transition at 330 nm for peroxy radical 6.
Scheme 10. Enthalpies for formation of 6, 7, 8 and transition state energy barrier for formation of 6 and 7 (TS = Transition State Energy barrier).

We also calculated the rate for formation of 6 in oxygen-saturated acetonitrile solutions by assuming the concentration of oxygen is 0.009 M.\textsuperscript{12} and by taking the rate constant for formation of 6 to be $9.46 \times 10^5$ s\textsuperscript{-1}, we found the rate for formation of 6 is $\sim 1.05 \times 10^8$ M\textsuperscript{-1} s\textsuperscript{-1} (Scheme 10). This rate of formation of 6 by reaction between molecular oxygen and 4 is in same order as what Rajam \textit{et al.} observed for his system in oxygen saturated solutions as shown in scheme 11.\textsuperscript{11}
Further, comparison of transient UV in shorter time scales for argon-, air- and oxygen-saturated acetonitrile solutions shows the formation of the peroxy radical 6 increase as the concentration of oxygen increases (Figure 18-19). As expected the rate of forming 6 increased with increased oxygen concentration. The decay of 6 shows more intense absorbance and somewhat longer lifetime than 4 (Figure 15). Calculations do not predict similar intensity for both 4 and 6. The calculations of 4 shows the major peaks has calculated oscillator strengths of $f=0.0252$ (at 354 nm) and $f=0.0231$ (at 320 nm) where as the calculations of 6 shows the major peak with an oscillator strength of $f=0.0263$ (at 330 nm) (Figure 7, Figure 16).

**Scheme 11.** Vinyl nitrene reactivity with oxygen
In argon, air and in oxygen, 1 μs time window

**Figure 18.** Transient UV / Vis spectra of 1 using laser flash photolysis (a). 2.00 – 7.01 μs in argon saturated acetonitrile (red) (b). 2.00 – 7.01 μs in air saturated acetonitrile (green) (c). 2.00 – 7.01 μs in oxygen saturated acetonitrile (blue)
(II). LFP of 1 in CH₃OH

We performed laser flash photolysis to support the proposed reaction mechanism for 1. Laser flash photolysis (Excimer laser, 308 nm, 17 ns) of 1 in argon-saturated methanol produced a transient absorption with $\lambda_{\text{max}}$ at $\sim$360 nm (Figure 20-21).
1 μs time window in Ar

**Figure 20.** Transient UV / Vis spectra obtained by laser flash photolysis of 1 (a). 0.02 – 0.30 μs (red) (b).0.32 – 1.01 μs (blue) (c). 1.01 – 2.01 μs (black) (d). 2.00 – 7.50 μs (light green) over a time window of 1 μs in methanol.

10 ms time window in Ar
Figure 21. Transient UV / Vis spectra obtained by laser flash photolysis of 1 (a) 0.16 – 4.00ms (red) (b). 4.00 – 10.00ms (blue) (c). 10.00 – 17.20ms (black) (d). 17.20 – 76.40ms (light green) in methanol solvent.
Figure 22. Calculated UV of T<sub>1K</sub> of 1 (red), T<sub>N</sub> of 1 (blue) and 4 (light green) in methanol using TD-DFT level of theory with UB3LYP/6-31+G(d) basis set.

We monitored the kinetics of 1 at 450 nm and we observed a kinetic trace which could fit into a bi-exponential decay. The rate constant for the shorter decay is 5.979 x 10<sup>5</sup> s<sup>-1</sup> ± 1.02 x 10<sup>5</sup> s<sup>-1</sup> (τ = 1.7 μs ± 0.3 μs) which we assign for the T<sub>1K</sub> of 1 in methanol. The calculated TD-DFT absorption spectrum of T<sub>1K</sub> of 1 in methanol has the major electronic transfer at 430 nm (f=0.0050), 375 nm (f=0.0291), 307 nm (f=0.0282) and 300 nm (f=0.0177) which fits well with the observed spectrum around 450 nm (Figure 22). The longer rate constant for the above mentioned decay is 7.459 x 10<sup>4</sup> s<sup>-1</sup> ± 1.53 x 10<sup>4</sup> s<sup>-1</sup> (τ = 13.4 μs ± 2.7 μs) which we do not assign to any intermediate since this time window is too short to estimate an accurate lifetime for this decay. We assign the transient with λ<sub>max</sub> ~360 nm to the 4, based on the TD-DFT calculations, which show that the major electron transitions are located at 349 nm (f=0.0260), 324.2 nm (f=0.0047), 323.7 nm (f=0.0358) and 316 nm (f=0.0058) (Figure 22). Kinetic analysis of the transient absorption further supports this assignment. The transient absorption at 360 nm decays with a rate constant of 50.621 s<sup>-1</sup> ± 0.379 s<sup>-1</sup> (τ = 19.8 ms ± 0.1 ms) in argon-saturated methanol (Figure 23).
10 ms time window at 360 nm in Ar-saturated CH₃OH.

\[ k_1 = 50.621 \text{s}^{-1} \pm 0.379 \text{s}^{-1}, \quad \tau = 19.8 \text{ms} \pm 0.1 \text{ms} \]

5 μs time window at 450 nm in Ar-saturated CH₃OH.

\[ k_1 = 5.979 \times 10^5 \text{s}^{-1} \pm 1.02 \times 10^5 \text{s}^{-1}, \quad \tau = 1.7 \text{μs} \pm 0.3 \text{μs} \]

\[ k_2 = 7.459 \times 10^4 \text{s}^{-1} \pm 1.53 \times 10^4 \text{s}^{-1}, \quad \tau = 13.4 \text{μs} \pm 2.7 \text{μs} \]

**Figure 23.** Kinetics obtained by laser flash photolysis of 1 in (a). 10 ms time window at 360 nm in Ar-saturated CH₃OH (b). 5 μs time window at 450 nm in Ar-saturated CH₃OH.
**Quenching Studies of 1 with Air and Oxygen saturated methanol**

In air-saturated methanol solutions the intensity of the band around 360 nm is reduced significantly in 1 μs time window (Figure 24, Figure 30-31). However, we observed that the absorbance at 300 nm is slightly increases with the increase in time in air-saturated methanol solutions. Transient UV/Vis absorption spectra at a longer time scale shows that the absorptions at 360 nm and 300 nm reduce with time (Figure 25). But, after ~76 ms, there is still significant absorbance (~0.012) is remaining for the transient at 360 nm unlike in argon-saturated methanol (Figure 21). This suggests that in air-saturated methanol solutions; the intermediate at 360 nm is somewhat longer lived. This was supported by the kinetic analysis of the transient at 360 nm in longer time window, which shows a mono-exponential decay with a rate constant of 27.461 s$^{-1}$ ± 0.737 s$^{-1}$ ($\tau = 36.4$ ms ± 0.9 ms) (Figure 26). We assign this decay to the decay of 4. The transient at 300 nm in longer time window, which shows a mono-exponential decay with a rate constant of 193.59 s$^{-1}$ ± 2.77 s$^{-1}$ ($\tau = 5.2$ ms ± 0.1 ms) (Figure 26). We assign this decay to the decay of 6. This indicates that the longer lived intermediate at ~300 nm in air could be a different intermediate. This conclusion was further supported by the studies in oxygen-saturated solutions.
In air, 1 μs time window

**Figure 24.** Transient UV / Vis spectra of obtained from laser flash photolysis of 1 (a). 0.02 – 0.30 μs (red) (b).0.32 – 1.01 μs (blue) (c). 1.01 – 2.01 μs (green) (d). 2.01 – 7.50 μs (purple) in air-saturated methanol.

In air, 10 ms time window
Figure 25. Transient UV / Vis spectra obtained by laser flash photolysis of 1 (a). 0.16 – 4.00 ms (red) (b). 4.00 – 10.00 ms (blue) (c). 10.00 – 17.20 ms (green) (d). 17.20 – 76.40 ms (purple) in air-saturated methanol.

300 nm, 10 ms time window in air-saturated CH₃OH

![Graph of absorbance vs time for 300 nm wavelength](image)

\[ k = 193.59 \text{ s}^{-1} \pm 2.77 \text{ s}^{-1}, \tau = 5.2 \text{ ms} \pm 0.1 \text{ ms} \]

360 nm, 10 ms time window in air-saturated CH₃OH

![Graph of absorbance vs time for 360 nm wavelength](image)

\[ k = 27.461 \text{ s}^{-1} \pm 0.737 \text{ s}^{-1}, \tau = 36.4 \text{ ms} \pm 0.9 \text{ ms} \]
340 nm, 2.5μs time window in air-saturated CH₃OH

\[ k = 1.921 \times 10^5 \text{ s}^{-1} \pm 8.29 \times 10^3 \text{ s}^{-1}, \tau = 5.2 \pm 0.2 \mu\text{s} \]

300 nm, 2.5 μs time window in air-saturated CH₃OH

\[ k = 2.685 \times 10^5 \text{ s}^{-1} \pm 6.59 \times 10^3 \text{ s}^{-1}, \tau = 3.7 \pm 0.1 \mu\text{s} \]

**Figure 26.** Kinetics obtained by laser flash photolysis of 1 in (a). 10 ms time window at 300 nm in Air-saturated CH₃OH. (b). 10 ms time window at 360 nm in Air-saturated CH₃OH. (c). 2.5μs
time window at 340 nm in Air-saturated CH\textsubscript{3}OH. (d) 2.5 \textmu s time window at 300 nm in Air-saturated CH\textsubscript{3}OH.

In oxygen-saturated methanol solutions the intensity of the band around 300 nm grew in at short time scale indicating that a new intermediate forms in oxygen-saturated methanol unlike in argon saturated acetonitrile (Figure 27). This absorption grew in with a rate constant of 1.365 x 10\textsuperscript{6} s\textsuperscript{-1} ± 3.22 x 10\textsuperscript{4} s\textsuperscript{-1} (\tau = 732 ns ± 17 ns) (Figure 29). We assign this growth to the formation of a peroxy radical 6 by the reaction between 4 and O\textsubscript{2}. Transient UV/Vis in longer time scale shows that the absorption at 300 nm decays with the increase in time (Figure 29). But, after ~76 ms, there is some absorbance at 340 nm (~0.01) is remaining for the transient like in argon saturated methanol. Kinetic analysis of the transient at 300 nm in longer time window shows a mono-exponential decay with a rate constant of 198.28 s\textsuperscript{-1} ± 1.96 s\textsuperscript{-1} (\tau = 5.0 ms ± 0.05 ms) (Figure 33). This indicates that the longer lived intermediate in oxygen peroxy radical 6, rather than radical 4. This was further supported by TD-DFT calculations. Further, we also hypothesize we may be observing little bit of triplet nitrene formation since we observe similar absorptions at 360 nm after 76 ms in methanol.
In oxygen, 1 μs time window

![Figure 27](image)

Figure 27. Transient UV / Vis spectra obtained by laser flash photolysis of 1 (a). 0.02 – 0.30 μs (red) (b). 0.30 – 1.01 μs (blue) (c). 1.01 – 2.01 μs (green) (d). 2.01 – 7.50 μs (purple) in oxygen-saturated methanol.

In oxygen, 10 ms time window

![Wavelength vs. Absorbance](image)
**Figure 28.** Transient UV / Vis spectra obtained by laser flash photolysis of 1 (a). 0.16 – 4.00 ms (red) (b). 4.00 – 10.00 ms (blue) (c). 10.00 – 17.20 ms (green) (d). 17.20 – 76.40 ms (purple) in oxygen-saturated methanol.

300 nm, 500 ns time window in oxygen-saturated CH$_3$OH

\[
k = 1.365 \times 10^6 \text{ s}^{-1} \pm 3.22 \times 10^4 \text{ s}^{-1}, \ \tau = 732 \text{ ns} \pm 17 \text{ ns}
\]

300 nm, 1 μs time window in oxygen-saturated CH$_3$OH

\[
k_1 = 2.079 \times 10^6 \text{ s}^{-1} \pm 2.57 \times 10^5 \text{ s}^{-1}, \ \tau = 481 \text{ ns} \pm 59 \text{ ns}
\]
\[
k_2 = 4.254 \times 10^5 \text{ s}^{-1} \pm 9.53 \times 10^4 \text{ s}^{-1}, \ \tau = 2.4 \mu\text{s} \pm 0.5 \mu\text{s}
\]
300 nm, 5 ms time window in oxygen-saturated CH$_3$OH

$$k = 198.28 \text{ s}^{-1} \pm 1.96 \text{ s}^{-1}, \tau = 5.0 \text{ ms} \pm 0.05 \text{ ms}$$

340 nm, 1μs time window in oxygen-saturated CH$_3$OH

$$k = 1.053 \times 10^6 \text{ s}^{-1} \pm 2.40 \times 10^3 \text{ s}^{-1}, \tau = 950 \text{ ns} \pm 22 \text{ ns}$$

**Figure 29.** Kinetics obtained by laser flash photolysis of 1 in (a). 500 ns time window at 300 nm in oxygen-saturated CH$_3$OH. (b). 1 μs time window at 300 nm in oxygen-saturated CH$_3$OH. (c).
5 ms time window at 300 nm in oxygen-saturated CH$_3$OH. (d). 1μs time window at 340 nm in oxygen-saturated CH$_3$OH.

In argon, air and in oxygen, 1 μs time window

**Figure 30.** Transient UV / Vis spectra of 1 using laser flash photolysis (a). 0.02 – 0.30 μs in argon saturated methanol (red) (b). 0.02 – 0.30 μs in air saturated methanol (green) (c). 0.02 – 0.30 μs in oxygen saturated methanol (blue)
In argon, air and in oxygen, 1 μs time window

**Figure 31.** Transient UV / Vis spectra of 1 using laser flash photolysis (a). 2.01 – 7.50 μs in argon saturated methanol (red) (b). 2.01 – 7.50 μs in air saturated methanol (green) (c). 2.01 – 7.50 μs in oxygen saturated methanol (blue)

In argon, air and in oxygen, 10 ms time window

---

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**Figure 32.** Transient UV / Vis spectra of 1 using laser flash photolysis (a). 0.16 ms – 4.00 ms in argon saturated methanol (red) (b). 17.20 ms – 76.40 ms in argon saturated methanol (red dotted) (c). 0.16 ms – 4.00 ms in air saturated methanol (green) (d). 17.20 ms – 76.40 ms in air saturated methanol (green dotted) (e). 0.16 ms – 4.00 ms in oxygen saturated methanol (blue) (b). 17.20 ms – 76.40 ms in oxygen saturated methanol (blue dotted).

**Figure 33.** Kinetic traces obtained from laser flash photolysis of 1 in Ar, Air and O₂ saturated acetonitrile (a) In 10 ms time scale (b) In 2.5 μs time scale.
Quenching with Isoprene

We investigated the quenching of the transient formed by laser flash photolysis of 1 with isoprene. We did laser flash photolysis of 1 in argon-saturated acetonitrile and measured the absorbance for 4 at ~420 nm (Figure 34-35).

Stern-Volmer equation is,

\[ \frac{I_0}{I} = 1 + k_q \tau_0 [Q] \]

where, \( I_0 \) = Intensity of 1 without the quencher, \( I \) = Intensity of 1 with q amount of quencher, \( k_q \) = Quencher rate co-efficient, \( \tau_0 \) = Lifetime of 1 without quencher, \( [Q] \) = Concentration of the quencher. By plotting \( A/A_0 \) versus the concentration of isoprene, we obtained the graph in Figure 34, which show that isoprene does not quench 4 because the lifetime of 4 is not affected by the isoprene concentration. Rather, isoprene reduces the yields of 4 and thus it must quench the precursor to 4. \( \tau_0 \) of \( T_{1K} \) of 1 is 0.24 – 2.44 ns if the \( k_q \) is \( 10^9 – 10^{10} \) by assuming the energy transfer is diffusion controlled. The \( A/A_0 \) vs. concentration trace becomes flat because there is no change in absorbance after 0.625 M isoprene. This could be due to complete quenching of \( T_{1K} \) of 1 by isoprene; hence there is no change in \( A/A_0 \) ratio. Figure 3535 was constructed by plotting \( A/A_0 \) data for isoprene concentrations less than or equal to 0.625 M. The lifetimes of the \( T_{1K} \) of 1 is comparable with Klima et al. since they have also not observed \( T_{1K} \) for their system since it is within the time resolution of the instrument they used.
<table>
<thead>
<tr>
<th>$Q_V$ (μL)</th>
<th>$Q_{\text{TOTAL}}$ (L)</th>
<th>Absorbance, $A$</th>
<th>$A_0/A$</th>
<th>[Q] (mol/L)</th>
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<tr>
<td>0</td>
<td>0.00150</td>
<td>0.0136 ± 0.0004</td>
<td>1.000 ± 0.029</td>
<td>0.000</td>
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<td>10</td>
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<td>0.00152</td>
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<td>30</td>
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<tr>
<td>40</td>
<td>0.00154</td>
<td>0.0079 ± 0.0006</td>
<td>1.722 ± 0.131</td>
<td>0.260</td>
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<td>50</td>
<td>0.00155</td>
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<td>0.625</td>
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<tr>
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<td>2.194 ± 0.035</td>
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<td>400</td>
<td>0.00190</td>
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<td>1.722 ± 0.654</td>
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</tr>
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<td>0.0059 ± 0.0006</td>
<td>2.305 ± 0.234</td>
<td>2.500</td>
</tr>
<tr>
<td>1000</td>
<td>0.00250</td>
<td>0.0061 ± 0000</td>
<td>2.230 ± 0.000</td>
<td>3.998</td>
</tr>
</tbody>
</table>

**Table 2.** Isoprene Quenching Data for 1
**Figure 34.** Stern-Volmer plot for quenching of 1 with isoprene at 420 nm in 500 μs time window for two trials

**Figure 35.** Stern-Volmer plot for quenching of 1 with isoprene at 420 nm in 500 μs time window, expansion of isoprene concentration below 0.40 M.

**Table 3.** Summary of lifetimes of intermediates formed upon irradiation of 1 in various solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( T_{1K} ) of 1 (from isoprene quenching studies)</th>
<th>( T_N ) of 1</th>
<th>4</th>
<th>6 (in O(_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>0.44-0.4 ns</td>
<td>Not observed</td>
<td>18.4 ms ± 0.2 ms</td>
<td>26.8 ms ± 0.2 ms</td>
</tr>
<tr>
<td>Methanol</td>
<td>1.7 μs ± 0.3 μs</td>
<td>~Similar lifetime to 4</td>
<td>19.8 ms ± 0.1 ms</td>
<td>5.0 ms ± 0.05 ms</td>
</tr>
</tbody>
</table>

Gradient (b) = 2.446 ± 0.463
Intercept (a) = 1 ± 0
4. Phosphorescence

We obtained the phosphorescence spectra of 0.1 M solution of 1 in ethanol at 77K. The spectra were not sufficiently resolved to obtain the (0,0) transition therefore, we used the onset of the emission at the shortest wavelength as an estimate for (0,0) transition. We located the onset at 380 nm (Figure 36). Therefore, the triplet energy of (0,0) transition is ~75 kcal/mol. This triplet energy obtained from phosphorescence is in very good agreement with the calculated triplet energy obtained from TD-DFT, which is 76 kcal/mol which also has (π,π*) configuration.
Figure 36. Phosphorescence spectrum of 0.1 M solution of 1 in ethanol at 77 K with (a). Excitation at 300 nm (b). Excitation at 280 nm (c). Excitation at 260 nm (d). Excitations at 300 nm, 280 nm and 260 nm.
5. Matrix Isolation

Figure 37. Matrix isolation IR spectra of 1 (a). Before irradiation (blue) (b). After 200 min of irradiation (red) (c). The difference spectrum (pink).

We investigated the photochemistry of 1 in argon matrices at 14 K to identify its reactivity in argon matrices. We deposited 1 into argon matrices in several different experiments, entraining the vapor pressure over a sample of pure 1 in flowing argon, and depositing the resulting sample on a 14 K cryogenic surface. Irradiation of 1 in argon matrices led to depletion of some bands and formation of new bands, mostly occurring very near those of the parent azide (Figure 37-39). This is expected since the acetophenone moiety is not significantly affected by irradiation and the majority of the observed vibrational bands belong to it. The infrared spectrum of 1 showed
intensive azido bands at 2142 cm\(^{-1}\), 2136 cm\(^{-1}\) and 2115 cm\(^{-1}\) (Figure 38), which are all depleted upon irradiation. The various azido bands are presumably either due to different conformers of 1, or entrapping in different matrix sites. After the irradiation, new bands were observed at 1245 cm\(^{-1}\), 1240 cm\(^{-1}\), 1221 cm\(^{-1}\) and 1217 cm\(^{-1}\) which we assign for T\(_N\) of 1 based on calculations (Figure 39). Calculations show that the calculated IR band at 1302 cm\(^{-1}\) for 1, which is due to coupled stretch or vibration of phenyl ring and aliphatic chain is expected shifts to lower wave numbers by about 28 cm\(^{-1}\) upon forming T\(_N\) of 1, which fits reasonably well with the experimental shift of 40 cm\(^{-1}\). The experimental peak at 1285 cm\(^{-1}\) of 1 disappeared upon irradiation and a new band grew in at 1245 cm\(^{-1}\) and 1240 cm\(^{-1}\) which we assign for T\(_N\) of 1. The calculated IR spectra of 4 does not show corresponding vibrational band to the calculated band at 1302 cm\(^{-1}\) of 1. Further, the calculated IR peak at 1222 cm\(^{-1}\) which is also due to a different coupled stretch or vibration of phenyl ring and aliphatic chain is calculated to shift to higher wave numbers (to 1247 cm\(^{-1}\)) by about 25 cm\(^{-1}\) upon forming T\(_N\) of 1, which is in good agreement with the experimental shift of 24-27 cm\(^{-1}\). The experimental IR peak at 1193 cm\(^{-1}\) of 1 disappeared upon irradiation while a new peak was observed at 1217 cm\(^{-1}\) and 1220 cm\(^{-1}\), which we assign for the formation of T\(_N\) of 1. These experimental shifts agree well with the calculated shift, hence we conclude that we observe the formation of T\(_N\) of 1 upon irradiation of 1 in argon matrices. Calculated IR peaks of 4 shows a very weak peak at 1242 cm\(^{-1}\), which shifts to higher wave numbers by 20 cm\(^{-1}\) from 1222 cm\(^{-1}\) band in 1. However, the comparison of the intensity of this band (Table 4) suggests that this band is not a significant band in 4. Further, we were able to identify a few other bands due to formation of T\(_N\) of 1 which are shown in Table 04. This shows that we have only T\(_N\) of 1 in argon matrices not 4. We hypothesize that azido radical and 4
formed after the C-N bond dissociation, recombines to form 1 again in argon matrices at 14 K, hence we only observe the formation of $T_N$ of 1.

**Figure 38.** Matrix isolation IR spectra of 1 show the depletion of azido bands (a). Before irradiation (blue) (b). After 200 min of irradiation (red) (c). The difference spectrum (pink).
Figure 39. Matrix isolation IR spectra of 1 show the depletion of azido bands. (a). Before irradiation (blue). (b). After 200 min of irradiation (red) (c). The difference spectrum (pink).

Table 4. Experimental and Calculated IR peaks for 1 and T_N of 1.

<table>
<thead>
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<th>Stretch</th>
<th>1</th>
<th>T_N of 1</th>
<th>4</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Observed</td>
<td>Calculated</td>
<td>Observed</td>
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<tr>
<td>N_3</td>
<td>2142, 2136,</td>
<td>2257 (608)</td>
<td>--</td>
</tr>
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<td>2115</td>
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<td>1766, 1755</td>
<td>1793 (228)</td>
<td>1765, 1752</td>
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<td>Ph-C=O</td>
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<td>1748 (183)</td>
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<td>1695</td>
<td>1696</td>
<td></td>
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<tr>
<td>Coupled</td>
<td>1285</td>
<td>1302 (410)</td>
<td>1245, 1240</td>
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<tr>
<td>Coupled</td>
<td>1193</td>
<td>1222 (136)</td>
<td>1220, 1217</td>
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</table>
6. **Steady-State EPR Spectroscopy**

Steady state EPR measurements of 1 were taken at 4 K (liquid He temperature) in ethanol glass in Brucker ESR E500 spectrometer with the laser source INDI-10 YAG laser with 355 nm irradiation. The center field is ~8400 Gauss which is consistent with what is reported in the literature for alkyl nitrenes. This has $D = 309$ Gauss. E value is not determined (Figure 40).

![Steady State EPR Spectrum of 1 in EtOH glass at 4 K.](image)

**Figure 40.** Steady State EPR Spectrum of 1 in EtOH glass at 4 K.
Discussion

Irradiation of 1 in argon saturated chloroform-d solutions yielded 2 and 3. In oxygen-saturated chloroform-d solutions, 1 yielded 2 as the major product. Therefore, 1 mainly undergoes C – N bond cleavage to give 2 in competition with triplet nitrene formation.

LFP studies showed that there is mainly one intermediate in acetonitrile with a rate constant of 54.302 s\(^{-1}\)± 0.751s\(^{-1}\) (\(\tau = 18.4\) ms ± 0.2 ms). We attribute this intermediate to 4. Quenching studies in air and oxygen saturated acetonitrile solutions shows the formation of 6 with a rate of 1.5 x 10\(^8\) M\(^{-1}\)s\(^{-1}\). Calculated enthalpy difference and TD-DFT spectra support the assignment of this transient to 6. Examination of the molecular orbitals supports this argument. We rule out the formation of another peroxy radical 7 based on calculated enthalpy difference and TD-DFT spectra. This new peroxy radical 6 has a lifetime of 26.8 ms ± 0.2 ms in oxygen saturated acetonitrile solutions.

\[
\begin{align*}
\text{CH}_3 + \text{CH}_3X & \rightarrow \text{CH}_2X + \text{CH}_4 \\
\text{RSE (CH}_2X) & = \Delta H (1) = \Sigma \Delta H_{\text{product}} - \Sigma \Delta H_{\text{reactant}}
\end{align*}
\]

Scheme 12. Definition of Radical Stabilization Energy (RSE)

The radical stabilization energy (RSE) of a substituent is defined as the enthalpy change of the isodesmic reaction (1) (Scheme 12).\textsuperscript{14} Enthalpy change can be obtained from the equation (2) using molecular modeling to calculate the heats of formation as shown in Scheme 12. We calculated the RSE for the reaction shown in Scheme 13 using DFT/B3LYP/6-31+G(d) and found that it has a RSE of -14 kcal/mol.
We have also calculated the ionization potential for 4 and methyl acetate radical using DFT/B3LYP/6-31+G(d) and results are shown in Table 5. The IP value for entry 1 is relatively higher so that we expected 4 to be inert towards oxygen; however, we observed the opposite of that. We compared IP value of entry 1 with entry 2, which shows that IP for forming carbocation for a system like 4 is unfavorable. Hence we hypothesize; the reactivity of 6 can only be explained from the transition state energy barrier to form 6 and enthalpy of formation of 6.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Radical</th>
<th>Cation</th>
<th>IP (eV)</th>
</tr>
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<td><img src="image" alt="Scheme 13" /></td>
<td>8.5</td>
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<tr>
<td>2</td>
<td><img src="image" alt="Scheme 13" /></td>
<td><img src="image" alt="Scheme 13" /></td>
<td>9.9</td>
</tr>
</tbody>
</table>

**Table 5.** Ionization potential for 4 and methyl acetate radical

Quenching studies in isoprene shows that the T₁ of 1 has a lifetime of 0.24 – 2.44 ns. Phosphorescence spectra give the energy of T₁K of 1 as 75 kcal/mol, which is in very good agreement with the calculated value of 76 kcal/mol using TD-DFT.
We also calculated the transition state energy barrier for 1A to undergo azido cleavage to yield 1B and found that it is located 7 kcal/mol above 1A. This indicates that azido cleavage for this molecule with an electron withdrawing CF$_3$ group is less likely than energy transfer to form 1C.

Spin density calculations of 4 shows that some of the spin density is delocalized to the ester chromophore. Therefore, 4 is highly stabilized from the electron withdrawing ester group. We also calculated the spin density of a similar molecule with electron withdrawing CF$_3$ group (Figure 41). The calculations show that the spin density on 1B is also more localized on C$_\beta$ indicating that 1B is less stable than 4. Therefore, we expect 1B to shorter lived than 4. Further, the spin density on 1C is more than T$_N$ of 1 indicating that the spin density is more localized on 1B. Therefore, I propose to study this system to see whether there is any effect on the stability of the triplet nitrene intermediate.
Matrix isolation studies of 1 show only the formation of T_N of 1. If the azido cleavage takes place in the matrices, they could recombine to give the starting material back since the two radical species could not diffuse apart.

**Conclusion**

Electron withdrawing substituent –C(O)-OCH$_3$ did not affect the stability of the triplet nitrene significantly based on the laser flash photolysis and DFT calculations. However, it certainly has an effect on the stability of 4 upon azido cleavage. This could be due to the radical stabilization by the electron withdrawing substituent –C(O)-OCH$_3$ by delocalizing radical on C to ester chromophore. This is supported by the spin density calculations. Hence, 4 is long lived based on laser flash photolysis studies compared to similar radicals formed from azido cleavage as shown Klima et al. In the presence of oxygen, 4 react to give 6 which also have similar or slightly higher lifetimes compared to 4. In argon matrices, we observe the formation of triplet nitrene since azido radical and 4 could recombine to give 1 back.

**Experimental**

**Calculations**

All geometries were optimized at B3LYP level of theory and with 6-31G+(d) basis set as implemented in the Gaussian03 and Gaussian09 programs.$^9$ $^{10}$ All transition states were confirmed to have one imaginary vibrational frequency by analytical determination of the second derivatives of the energy with respect to internal coordinates. Intrinsic reaction coordinates$^{15}$ calculations were used to verify that the located transition states corresponded to the attributed
reactant and product.\textsuperscript{16, 17} The absorption spectra were calculated using time-dependent density functional theory (TD-DFT).\textsuperscript{18-22} The effect of solvation was calculated using the self-consistent reaction field (SCRF) method with the integral equation formalism polarization continuum model (IEFPCM) with acetonitrile, methanol and dichloromethane as solvents.\textsuperscript{23-27}

**Laser Flash Photolysis.**

Laser flash photolysis was done with an Excimer laser (308 nm, 17 ns).\textsuperscript{28} The system has been described in detail elsewhere.\textsuperscript{28} A stock solution of 1 in CH$_3$CN was prepared with spectroscopic grade CH$_3$CN, such that the solutions had absorption between 0.3 and 0.6 at 308 nm. Typically, ~2 mL of the stock solution was placed in a 10 mm × 10 mm wide, 48 mm long quartz cuvette and was purged with argon for 5 min or oxygen for 15 min. The rates were obtained by fitting an average of three to five kinetic traces.

**Phosphorescence**

The solution of 1 (0.1M) were prepared in ethanol. The phosphorescence spectra were obtained on a phosphorimeter in ethanol glasses at 77K. The solutions were irradiated at 300 nm, 280 nm and 260 nm. The emission spectra were recorded between 280 and 800 nm.

**Matrix isolations**

Matrix isolation studies were performed using conventional equipment.\textsuperscript{29}
EPR Measurements

Steady state EPR measurements were taken at 4 K (liquid He temperature) in ethanol glass in Brucker ESR E500 spectrometer with the laser source INDI-10 YAG laser with 355 nm irradiation.

Synthesis of 1

Synthesis of (E)-4-oxo-4-phenylbut-2-enoic acid

7.80 g (0.099 mol) of benzene was dissolved in 30 mL of CH$_2$Cl$_2$. 15.00 g (0.153 mol, 1.5 eq) of maleic anhydride and 19.80 g (0.148 mol, 1.5 eq) of AlCl$_3$ was added to the mixture. The reaction was allowed to stir for 20 hours at room temperature. An extraction was performed with CH$_2$Cl$_2$ (50 mL) and H$_2$O (50 mL). CH$_2$Cl$_2$ was separated and it was washed twice with H$_2$O and once with 100 mL of brine (saturated NaCl). The CH$_2$Cl$_2$ extract was dried using anhydrous MgSO$_4$. The CH$_2$Cl$_2$ was evaporated and a yellow crude of (E)-4-oxo-4-phenylbut-2-enoic acid (9.81 g, 0.0557 mol) was obtained (%Yield = 56%). $^1$H NMR, $^{13}$C NMR and IR spectra were taken in CDCl$_3$.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 6.919 (d, J= 15.6 Hz, 1H, -CH=), 7.52 (d, J= 6 Hz, 3H, Ph-H), 7.67 (t, J = 7.6 Hz, 1H, Ph-H), 8.024 (t, 3H, Ph-H, -CH=), 8.6-9.2 (s, 1H, -OH) ppm; $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 128.951 (2 C), 128.966 (2 C), 131.478 (2 C), 134.137 (1 C), 136.362 (1 C), 138.428 (1 C), 170.582 (-C=O), 189.341 (-C=O) ppm; IR (CDCl$_3$): 3812, 3599, 3183, 3118, 2966, 2932, 2647, 2550, 2379, 2298, 2172, 2125, 2027, 1981, 1929, 1851, 1771, 1760, 1732, 1716, 1669, 1634, 1596, 1450, 1403, 1329, 1285, 1267, 1240, 1182, 1105, 1059, 1033, 1012, 977, 892, 868, 841, 796, 767, 734, 696, 636, 618, 592, 485, 476 cm$^{-1}$.
**Synthesis of (E)-methyl 4-oxo-4-phenylbut-2-enoate**

9.81 g (0.0557mol) of (E)-4-oxo-4-phenylbut-2-enoic acid was dissolved in 30 mL of methanol. A spatula of (a catalytic amount of) para-Toluene sulfonic acid was added to the mixture. The reaction was allowed to stir for 20 hours while refluxing. An extraction was performed with diethyl ether (50 mL) and H₂O (50 mL). Diethyl ether was separated and it was washed twice with H₂O and once with 100 mL of brine (saturated NaCl). The diethyl ether extract was dried using anhydrous MgSO₄. The diethyl ether was evaporated and yellow crude of (E)-methyl 4-oxo-4-phenylbut-2-enoate (7.07g, 0.0372 mol) was obtained. (% Isolated Yield = 67%) ¹H NMR, ¹³C NMR and IR spectra were taken in CDCl₃.

¹H NMR (CDCl₃, 400 MHz): δ 3.856 (s, 3H, -OCH₃), 6.902 (d, J = 15.6 Hz, 1H, -CH=), 7.522 (t, J = 7.6 Hz, 2H, Ph-H), 7.634 (t, J = 7.2 Hz, 1H, Ph-H), 7.933 (d, J = 15.6 Hz, 1H, =C-H), 8.004 (t, J= 7.2 Hz, 2H,Ph-H) ppm.; ¹³C NMR (CDCl₃, 100 MHz): δ 189.435 (C=O), 166.039 (C=O), 136.605 (CH), 136.579 (C), 133.897 (CH), 132.077 (CH), 128.907 (2 CH), 128.872 (2 CH), 52.373 (OCH₃) ppm.; IR (CDCl₃): 3631, 3554, 3443, 3287, 3060, 3029, 3002, 2954, 2846, 2595, 2344, 1983, 1910, 1730 (C(O)O), 1674 (C=O), 1633, 1597, 1580, 1449, 1437, 1390, 1367, 1307, 1272, 1220, 1194, 1169, 1130, 1067, 1002, 993, 976, 941, 887, 864, 824, 793, 757, 732, 690, 644, 631, 604, 529, 492, 456 cm⁻¹.
Synthesis of methyl 2-bromo-4-oxo-4-phenylbutanoate

(E)-methyl 4-oxo-4-phenylbut-2-enoate (7.07g, 0.0372 mol) was dissolved in 25 mL of CH₂Cl₂ and kept at -8 °C. SiO₂ (8.936g, 0.149 mol, 10eq) was added to (E)-methyl 4-oxo-4-phenylbut-2-enoate. PBr₃ (2.83g, 10.48mmol, 0.66 eq) in 10mL of CH₂Cl₂ was added dropwise to (E)-methyl 4-oxo-4-phenylbut-2-enoate using a dropping funnel for a period of 10 min. The mixture was allowed to stir overnight (20 hours). SiO₂ was filtered and CH₂Cl₂ was dried. CH₂Cl₂ was removed and the crude methyl 2-bromo-4-oxo-4-phenylbutanoate (4.14 g, 0.0153 mol) was obtained (% Isolated Yield = 41%).¹H NMR, ¹³C NMR and IR spectra were taken in CDCl₃.

¹H NMR (CDCl₃, 400 MHz): δ 3.667 (dd, J = 4.8 Hz, J = 4.8 Hz, 1H, -CH), 3.811 (s, 3H, -OCH₃), 3.968 (dd, J = 9.6 Hz, J = 9.6 Hz, 1H, -CH), 4.776 (dd, J = 4.8 Hz, J = 4.8 Hz, 1H, -CH), 7.476 (t, J = 7.2 Hz, 2H, Ph-H), 7.598 (t, J = 7.2 Hz, 1H, Ph-H), 7.948 (d, J = 7.2 Hz, 2H, Ph-H) ppm.; ¹³C NMR (CDCl₃, 100 MHz) : δ 38.25 (CH), 44.23 (CH₂), 53.26 (OCH₃), 128.14 (2 CH), 128.81 (2CH), 133.89 (CH), 135.58 (-C), 170.13 (C=O), 196.43 (C=O) ppm.; IR (CDCl₃): 3060, 2953, 1727, 1673, 1632, 1596, 1580, 1449, 1436, 1306, 1271, 1221, 1169, 1002, 974, 941, 824, 757, 731, 688 and 631 cm⁻¹. HRMS: m/z calculated for C₁₀H₁₀O₂Br₂Na⁺ [M+Na]⁺, 292.97838; found, 292.97834.
**Synthesis of methyl 2-azido-4-oxo-4-phenylbutanoate (1)**

Methyl 2-bromo-4-oxo-4-phenylbutanoate (4.14 g, 0.0153 mol) was dissolved in methanol at 0 °C. NaN₃ (4.89 g, 0.075 mol, 5eq) added to methyl 2-bromo-4-oxo-4-phenylbutanoate. The mixture was allowed to stir overnight (20 hours). Methanol was removed and an extraction was performed with diethyl ether (50 mL) and H₂O (50 mL). Ether layer was separated and it was washed twice with H₂O and once with 100 mL of brine (saturated NaCl). The ether extract was dried using anhydrous MgSO₄. The ether was evaporated and a viscous liquid of methyl 2-azido-4-oxo-4-phenylbutanoate (1) (1.88 g, 0.0081 mol) was obtained (Isolated Yield = 53%). ¹H NMR, ¹³C NMR and IR spectra were taken in CDCl₃.

¹H NMR (CDCl₃, 400 MHz) : δ 3.431 (dd, J = 6.8 Hz, J = 7.2, 1H, -CH), 3.561 (t, J = 5.2 Hz, 1H, -CH), 3.867 (s, 3H, -OCH₃), 4.664 (dd, J = 5.6 Hz, J = 5.2 Hz, 1H, -CH), 7.430 (t, J = 7.6 Hz, 2H, -Ph), 7.622 (d, J = 7.6 Hz, 2H, -Ph), 7.980 (t, J = 7.2 Hz, 1H, -Ph) ppm.; ¹³C NMR (CDCl₃, 100 MHz): δ 40.08, 52.97, 57.96, 128.16, 128.79, 133.80, 135.96, 170.31, 195.64 ppm.; IR (CDCl₃) : 2955, 2110 (-N₃), 1746 (C(=O)O), 1687 (C=O), 1597, 1581, 1449, 1437, 1403, 1367, 1269, 1213, 1021, 1002, 914, 756, 689, 571, 488, 470, 458 cm⁻¹. HRMS: m/z calculated for C₁₁H₁₁N₃O₃Na⁺ [M+Na]⁺, 256.06926; found, 256.06924. GC/MS (EI): m/z 204 (M⁺-N₂), 177, 146, 128, 120, 105 (100%), 100, 91, 77, 68, 59, 51.
Photolysis of 1

Product Studies of 1 in Ar-saturated CDCl₃

A solution of 1 (~28 mg, 0.5 mmol) in CDCl₃ (2 mL) was purged with argon for 5 min and photolyzed via a Pyrex filter for 20.5 hours at 298 K. GC analysis of the reaction mixture shows the formation of 2 (74%) with remaining 1 (11%) and 3 (15%). The products were characterized by GC-MS chromatography of the reaction mixture. The GC-MS values are consistent with what has been reported in literature.³⁰-³² Further, we separately injected an authentic sample of 2 to verify the formation of 2 in reaction mixture.

2: GC/MS (EI): m/z 190 (M⁺), 159, 131, 113, 105 (100%), 85, 77, 59, 51.

3: GC/MS (EI): m/z 204 (MH⁺, 100%), 172, 146, 128, 117, 105, 100, 77, 68, 59, 51.

Product Studies of 1 in O₂-saturated CDCl₃

A solution of 1 (~28 mg, 0.5 mmol) in CDCl₃ (2 mL) was purged with argon for 5 min and photolyzed via a Pyrex filter for 20.5 hours at 298 K. GC analysis of the reaction mixture shows the formation of 2 (100%). The products were characterized by GC-MS of the reaction mixture.

2: GC/MS (EI): m/z 190 (M⁺), 159, 131, 113, 105 (100%), 85, 77, 59, 51.

Product Studies of 1 in Ar-saturated CD₃OD

A solution of 1 (~2.3 mg, 0.01 mmol) in CD₃OD (2 mL) was purged with argon for 5 min and photolyzed via a Pyrex filter for 17.5 hours at 298 K. GC analysis of the reaction mixture shows
the formation of 2 (50%) with the remaining starting material. The products were characterized by GC-MS of the reaction mixture.

2: GC/MS (EI): m/z 190 (M⁺), 159, 131, 113, 105 (100%), 85, 77, 59, 51.

Product Studies of 1 in O₂-saturated CD₃OD

A solution of 1 (~2.8 mg, 0.05 mmol) in CD₃OD (2 mL) was purged with argon for 5 min and photolyzed via a Pyrex filter for 17.5 hours at 298 K. GC analysis of the reaction mixture shows the formation of 2 (75%) with the remaining starting material. The products were characterized by GC-MS of the reaction mixture.

2: GC/MS (EI): m/z 190 (M⁺), 159, 131, 113, 105 (100%), 85, 77, 59, 51.

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References


Chapter 11

Phenylethanol Derivatives as Triplet Sensitizers for 1-Azidoadamantane

Phenylethanol Derivatives as Triplet Sensitizers for 1-Azidoadamantane

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Abstract

Laser flash photolysis, phosphorescence and density functional calculations were used to characterize the triplet excited states of phenylethanol derivatives 1, 2, 3 and 4. In acetonitrile, the triplet excited states of these alcohols were formed at rate constants in the order of ~10^7 s^-1 and decayed at rate constants between 10^5 and 10^6 s^-1. The energies of these triplet excited states were between 80 and 83 kcal/mol. Furthermore, 3 can be used as a triplet sensitizer for alkyl azides to form triplet nitrene intermediates.

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Introduction

Triplet sensitization makes it possible to form various triplet excited states and reactive intermediates that cannot be formed by direct irradiation. For example, direct irradiation of alkyl azides does not lead to the formation of triplet alkyl nitrenes but rather to imine products either via a concerted reaction of the singlet excited state of the alkyl azide or by the formation of a singlet alkyl nitrene intermediate, which rearranges as shown in Scheme 1.\textsuperscript{[1-4]} Thus, intersystem crossing, either from the singlet excited state of the alkyl azide to its triplet excited state or from the singlet nitrene to its triplet configuration, must be slower than formation of the imine product. However, triplet alkyl nitrenes can be formed by inter- and intra molecular sensitization of alkyl azides with acetophenone derivatives.\textsuperscript{[5-10]} Acetophenone derivatives are excellent triplet sensitizers for alkyl azides because they absorb light at longer wavelengths than alkyl azides. In addition, acetophenone derivatives undergo intersystem crossing to their triplet states efficiently, with rate constants on the order of $10^{11}$ s\textsuperscript{-1} and with quantum yields approaching unity.\textsuperscript{[11-13]} In our continuing effort to study triplet intermediates using triplet sensitization, we characterized the triplet states of phenylethanol derivatives and showed that they can be used as triplet sensitizers for alkyl azides to form triplet nitrenes.
Here, we describe the characterization of the first excited triplet state (T$_1$) of phenylethanol derivatives 1, 2, 3 and 4 by product studies, phosphorescence, laser flash photolysis and density functional calculations (Scheme 2). The T$_1$s of 1, 2, 3 and 4 are located between 83 and 80 kcal/mol above their ground state (S$_0$). The T$_1$ of these phenylethanol derivatives have lifetimes of a few microseconds in acetonitrile, but the intersystem crossing rate constants to form the triplet excited states are only on the order of $\sim 10^7$ s$^{-1}$. However, alcohol 3 can be used to efficiently sensitize 1-azidoadamantane to form a triplet alkyl nitrene.
Experimental

Scheme 2.

Computational Details

The calculations were performed using density functional theory (DFT) with the B3LYP functional and with the 6-31+G(d) basis sets as implemented in Gaussian09. It has been shown that the B3LYP method can successfully predict energies for open-shell systems such as triplet nitrenes. All of the geometries were optimized at the B3LYP/6-31+G(d) level of theory, and for each stationary point, the second derivative of the energy was calculated to confirm that these structures represent local energy minimal. Solvation effects were evaluated for acetonitrile and methanol using the integral equation formalism polarizable continuum model with complete geometry optimizations and vibrational frequency analyses at the B3LYP/6-31+G(d) level of theory. The energies of the excited states and the absorption spectra were calculated using time-dependent density functional theory (TD-DFT). Spin contamination was negligible for all of these open-shell molecules. All of the calculations were performed at the Ohio Supercomputer Center.
Laser Flash Photolysis

Laser flash photolysis was performed with an Excimer laser (308 nm, 17 ns), using a previously described system. Stock solutions of alcohols 1, 2, 3 and 4 in methanol and acetonitrile were prepared with spectroscopic grade solvents such that the solutions had absorptions between 0.3 and 0.8 at 308 nm. Typically, ~2 mL of the stock solution was placed in a 48-mm-long quartz cuvette cell 10 mm × 10 mm in cross-section and was purged with argon for 5 min or oxygen for 15 min. The rates were obtained by fitting an average of three to eight kinetic traces.

Phosphorescence

The phosphorescence spectra were obtained on a phosphorimeter in ethanol glasses at 77K. The solutions were irradiated at 260 nm and the emission spectra recorded at between 300 and 600 nm.

Synthesis of starting materials

1-Azido adamantane and phenylethanol derivatives 1, 2 and 3 are commercially available. We prepared 4 as described below.

Synthesis of 1-(4-methoxy-2,5-dimethylphenyl)ethanone.

To a solution of 2-methoxy-1,4-dimethylbenzene (4.80 g, 0.035 mol) in dichloromethane (10 mL) at 0 °C was added CH₃COCl (2.75 g, 0.035 mol) in dichloromethane (10 mL). AlCl₃
(9.34 g, 0.070 mol) was added in small portions to the solution. The resulting mixture was stirred for 4 hours and poured into an ice bath. The mixture was acidified by adding a saturated solution of NH₄Cl. The reaction mixture was extracted with dichloromethane and washed with water. The organic layer was dried with anhydrous MgSO₄ and the solvent was removed under vacuum to yield 1-(4-methoxy-2,5-dimethylphenyl)ethanone (2.68 g, 0.015 mol, 43% yield).

**Synthesis of 1-(4-methoxy-2,5-dimethylphenyl)ethanol (4).**

CeCl₃·7H₂O (7.45 g, 0.02 mol) was added to a solution of 1-(4-methoxy-2,5-dimethylphenyl)ethanone (2.68 g, 0.015 mol) in methanol at ambient temperature while stirring.[28] The reaction mixture was cooled to 0 °C and NaBH₄ (0.76 g, 0.020 mol) was added in small portions. The resulting mixture was stirred for 25 minutes and saturated solution of NH₄Cl (15 mL) added. The reaction mixture was extracted with diethyl ether and washed with water. The organic layer was dried with anhydrous MgSO₄ and the solvent was removed under vacuum to 4 (2.079 g). The crude was purified on silica column eluted with ethyl acetate in hexane mixture (1:4) to yield 4 (0.74 g, 0.004 mol, 27% yield).

¹H NMR (CDCl₃, 400 MHz): δ 1.45 (d, J = 4.8 Hz, 3H), 1.62 (br s, 1H), 2.20 (s, 3H), 2.33 (s, 3H), 3.81 (s, 3H), 5.072 (q, J = 4.8 Hz, 1H), 6.59 (s, 1H), 7.26 (s, 1H) ppm. GC/MS (EI): m/z 180 (M⁺), 162 (100%), 147, 137, 131, 122, 115, 105, 91, 77, 65, 51.

**Triplet Sensitization.**

A mixture of 1, 2, 3 or 4 (0.2 mmol) and 1-adamantyl azide (35 mg, 0.2 mmol) was dissolved in CH₃CN (2 mL, 0.1 M solution), and the resulting solution was purged with argon for five
minutes. This solution was irradiated through a Pyrex® filter, and the reaction mixture was analyzed by gas chromatography-mass spectroscopy (GC-MS).

**Quenching Studies with 1-Adamantyl azide - Solution Preparation**

0.760 g (5 mmol) of 3 was dissolved in 200 mL of acetonitrile to make a stock solution of 25 mM. A series of solutions were made by dissolving 0.0046 g, 0.0089 g, 0.0240 g, 0.0316 g and 0.0438 g of 1-Adamantyl azide in 25 mL of stock solution to give concentrations of 1 mM, 2 mM, 5 mM, 7 mM and 10 mM of 1-Adamantyl azide respectively.

**Results and Discussion**

**Product Studies**

Prolonged irradiation of 1, 2, and 3 through a Pyrex® filter in both argon- and oxygen-saturated solution did not yield any photoproducts. Photolysis of 4 did result in formation of small amount of dimeric products which we did not characterize further. We photolyzed a 1:1 solution of 0.1 M 1, 2, 3 or 4 and 1-azidoadamantane through a Pyrex® filter. We followed the reaction with GC-MS and kept the conversion below 10%. p-Methoxyphenylethanol 3 yielded the azo-dimer 5 as its only product, whereas 1 and 4 resulted in the formation of 5 and 6 (Scheme 3). Dimer 5 has been shown to form by the dimerization of two triplet alkyl nitrene intermediates,[7] whereas 6 is formed via the singlet reactivity of 1-azidoadamantane to form 7,[29] which is trapped with an alcohol.[30, 31] Thus, 3 is an efficient triplet sensitizers for azidoadamantane, because it makes it possible to completely bypass the singlet reactivity of
azidoadamantane. In comparison, 1, 2 and 4 were not as efficient triplet sensitizer as 3.

Scheme 3.

Calculations

To better understand the ability of 1, 2, 3 and 4 to be used as sensitizers for azido compounds, we calculated their triplet excited states and compared it with Toluene. We optimized the $S_0$ of 1, 2, 3, 4 and Toluene and performed TD-DFT calculations to estimate the energies of their first excited singlet and triplet states ($S_1$ and $T_1$). We found that $S_1$ are located 120 kcal/mol above the $S_0$ for 1 and Toluene and at 116-114 kcal/mol for 2, 3 and 4 (Table 1). The $T_1$ of 1, 2, 3, 4 and Toluene were placed between 82 and 86 kcal/mol above their $S_0$ (Table 1). Inspection of the molecular orbital’s demonstrates that $S_1$ is due to a ($\pi,\pi^*$) electronic transition. In comparison, the $T_1$ in 1, 2 and 3 are due to a mixed electronic transition from a $\pi$-orbital and the lone pair on the alcohol moiety into a $\pi^*$-orbital (see Figure 1), whereas the $T_1$ of 4 is mainly due to a ($\pi,\pi^*$) electronic transition, like $T_1$ of Toluene. Solvation in ethanol or
acetonitrile did not change the calculated energies of $S_1$ and $T_1$ of 1, 2, 3, 4 and Toluene significantly.

Figure 1. The orbitals involved in the lowest energy electronic transitions for the $T_1$ of 3 (TD-DFT in CH$_3$CN).
In addition, we optimized the $T_1$ of 1, 2, 3 and 4. The most significant difference between the optimized $S_0$ and $T_1$ of 1, 2, 3 and 4 is that the carbon-carbon bonds in the aromatic chromophores (or moieties) are no longer equivalent; some of the bonds became longer and others shorter, as has been similarly observed for the $T_1$ of benzene and toluene.\textsuperscript{[32]} We found that the energies obtained from the optimized structures were 3-4 kcal/mol lower in energy than those obtained by TD-DFT calculations for 2, 3 and 4, whereas the energy calculated for the $T_1$ of 1 was the same by both methods. Thus, UB3LYP optimization of 1, 2, 3 and 4 yielded

**Figure 2.** Optimized Structure of the $T_1$ of 1, 2, 3 and 4 in gas phase.
energies that are in good agreement with those obtained from TD-DFT calculations. We have previously shown that UB3LYP significantly underestimates the adiabatic energy of triplet ketones with \((n,\pi^*)\) configuration, whereas UB3LYP assessment of the adiabatic energy of triplet ketones with \((\pi,\pi^*)\) configuration is excellent.\[^{33,34}\]

Table 1. Calculated energies in kcal/mol for \(S_1\) and \(T_1\) of 1, 2, 3, 4 and Toluene

<table>
<thead>
<tr>
<th></th>
<th>TD-DFT</th>
<th>Optimized (T_1)</th>
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<tbody>
<tr>
<td></td>
<td>(S_1) (T_1)</td>
<td>(T_2)</td>
</tr>
<tr>
<td></td>
<td>GP   EtOH MeCN</td>
<td>GP   EtOH MeCN</td>
</tr>
<tr>
<td>1</td>
<td>122  86 86 87</td>
<td>106  86 87 87</td>
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<tr>
<td>2</td>
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<td>94   80 80 80</td>
</tr>
<tr>
<td>4</td>
<td>114  82 82 82</td>
<td>96   78 78 78</td>
</tr>
<tr>
<td>Toluene</td>
<td>122  86 86 86</td>
<td>105  85</td>
</tr>
</tbody>
</table>

a) GP: Gas phase.

UV Absorption

We compared the absorption spectra of alcohols 1, 2, 3 and 4 with the absorption spectra of Toluene and acetophenone (see Table 2). Alcohols 3 and 4 have an absorption band at \(\sim 280\) nm that trails out to 300 nm (Figure 3), whereas 1 and 2 have weaker absorption bands at lower wavelength, similar to Toluene. The absorption of 1, 2, 3 and 4 above 300 nm is weaker than for the corresponding acetophenone derivatives, which have an \((n,\pi^*)\) absorption band around 320
nm ($\varepsilon = 50$, Table 2).\textsuperscript{[35]}

**Figure 3.** UV absorption spectra for 0.2 mM solutions of 1, 2, 3 and 4 in acetonitrile.

**Table 2.** The Ground State UV absorption $\lambda_{\text{max}}$ and $\varepsilon$ for 1, 2, 3 and 4.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{max}}$ ($\varepsilon$)</th>
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<td>nm (M$^{-1}$cm$^{-1}$)</td>
<td>nm (M$^{-1}$cm$^{-1}$)</td>
<td>nm (M$^{-1}$cm$^{-1}$)</td>
</tr>
<tr>
<td>Acetophenone</td>
<td>320 (50)</td>
<td>278 (1110)</td>
<td>240 (1.3 x 10$^4$)</td>
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<tr>
<td>Toluene</td>
<td>262 (174)</td>
<td>208 (2460)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>259 (300)</td>
<td>252 (300)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>277 (250)</td>
<td>268 (300)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>282 (2200)</td>
<td>276 (2400)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>284 (2600)</td>
<td>278 (2600)</td>
<td></td>
</tr>
<tr>
<td>1-Azido adamantane\textsuperscript{[36]}</td>
<td>286 (25)</td>
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Phosphorescence

**Figure 4.** Phosphorescence spectra for (a) 1, (b) 2, (c) 3 and (d) 4 obtained in ethanol at 77K with 260 nm irradiation.
Table 3. The (0, 0) bands obtained from phosphorescence spectra of 1, 2, 3 and 4 in ethanol at 77K.

<table>
<thead>
<tr>
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<th>(0,0) nm</th>
<th>kcal/mol</th>
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<tr>
<td>Acetophenone</td>
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<tr>
<td>Toluene</td>
<td></td>
<td></td>
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<tr>
<td>1</td>
<td>344</td>
<td>83</td>
</tr>
<tr>
<td>2</td>
<td>357</td>
<td>80</td>
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<tr>
<td>3</td>
<td>355</td>
<td>81</td>
</tr>
<tr>
<td>4</td>
<td>357</td>
<td>80</td>
</tr>
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</table>

We measured the phosphorescence of 1, 2, 3 and 4 in ethanol glasses at 77K. These spectra are shown in Figure 4, and the energies of the (0, 0) bands are listed in Table 3. The emission spectra for 1 and 2 have a resolved fine structure that makes it possible to locate their (0,0) transitions, whereas the emission for 3 and 4 are not sufficiently resolved to locate the (0,0) transitions. Therefore, we used the onset of the emissions at the shortest wavelength as an estimate for the (0, 0) transitions for 3 and 4. The intensity of the phosphorescence was somewhat lower for 4 than 1, 2 and 3.

The measured energies of the T1 in 1, 2, 3 and 4 in ethanol glasses and the calculated values are in good agreement. The calculated energies of the T1 for 1, 2, 3 and 4 are within ~3 kcal/mol of the measured energies. The energies of the T1 in 1, 2, 3 and 4 are similar to the reported energies of the T1 in toluene (82 kcal/mol) and benzene (81 kcal/mol). Furthermore, the calculated energy of T1 in Toluene fits well with the measured one.
**Laser Flash Photolysis**

Laser flash photolysis of 1 in acetonitrile resulted in a transient spectrum with \( \lambda_{\text{max}} \) at 320 and 350 nm. (Figure 5) The transient absorption was quenched in an oxygen-saturated solution. In addition, the rate constant of transient formation at 320 nm was \( 2 \times 10^7 \) s\(^{-1} \), whereas the transient decayed at a rate constant of \( 3 \times 10^5 \) s\(^{-1} \). Based on the TD-DFT calculations, we assigned this transient to the T\(_1\) of 1. Laser flash photolysis of 1 in methanol resulted in similar transient spectrum, whereas the decay rate constant for the T\(_1\) of 1 was somewhat slower at \( 4 \times 10^4 \) s\(^{-1} \).
Figure 5. Laser flash photolysis of 1. A) Kinetic trace obtained at 320 nm in argon-saturated methanol; B) Transient spectrum in argon-saturated acetonitrile immediately after the laser pulse; C) Calculated TD-DFT spectrum for the $T_1$ of 1 in acetonitrile.

Laser flash photolysis of 3 resulted in a broad transient spectrum with $\lambda_{\text{max}}$ at 410 nm.
(Figure 7) This transient was formed faster than the resolution of the laser flash apparatus (17 ns), but it was quenched in oxygen saturated-acetonitrile. The rate constant for the decay of this transient was measured at 410 nm and found to be $4.6 \times 10^5 \text{ s}^{-1}$.

Figure 7. Laser flash photolysis of 3 in argon-saturated acetonitrile. A) Kinetic trace obtained at 410 nm; B) Transient spectrum immediately after the laser pulse; C) Calculated TD-DFT spectrum for the T$_1$ of 3 in acetonitrile
Laser flash photolysis of 4 resulted in broad transient absorption as shown in Figure 8, and we assigned it to the T\textsubscript{1} of 4. This transient absorption was quenched efficiently in oxygen-saturated acetonitrile. The transient was formed at a rate constant of 7 \times 10^6 \text{ s}^{-1} and it decayed at a rate constant of 2 \times 10^5 \text{ s}^{-1}. 
**Figure 8.** Laser flash photolysis of 4 in argon-saturated acetonitrile. A) Kinetic trace obtained at 460 nm; B) Transient spectrum obtained immediately after the laser pulse; C) Calculated TD-DFT spectrum for the T1 of 4 in acetonitrile.

Thus, laser flash photolysis allowed for the direct detection of the T1 of 1, 2, 3 and 4 at ambient temperature. The T1 of 1, 3 and 4 have lifetimes of a several microseconds in acetonitrile, whereas the T1 of 2 is somewhat shorter lived. We were able to measure the formation rate constants for the T1 of 1, 2 and 4 directly, and they are on the order of $\sim 10^7$ s$^{-1}$. This is similar to the reported rate constants for the formation of the T1 of benzene and toluene. Furthermore, laser flash photolysis of p-methylphenylethanol has been reported to produce its T1, which has an absorption spectrum between 300 and 400 nm and a lifetime of 2 $\mu$s.$^{[38]}$

We measured the rate constant for quenching the T1 of 3 with azidoadamantane (see Figure 9). The decay rate constant of T1 of 3, increased with increasing concentration of azidoadamantane. A plot of the decay rate constant of T1 of 3 versus the azidoadamantane concentration can be fitted with a straight line, with a slope of $1.6 \times 10^8$ M$^{-1}$s$^{-1}$. The rate constant for azidoadamantane quenching the T1 of 3, is similar as to what is been reported as the rate constant of azidoadamantane quenching the T1 of acetophenone.
Figure 9. (A) Decay of triplet excited state of 3 with various concentrations of 1-Azidoadamantane (B). The rates of quenching the triplet excited state of 3 1-Azidoadamantane as a function of concentration of azidoadamantane

**Conclusion**

We used phosphorescence and laser flash photolysis to characterize the $T_1$ of 1, 2, 3 and 4. The $T_1$ are formed at rate constants of $\sim 10^7$ s$^{-1}$ and have lifetimes of several microseconds in
solution. The energies of the $T_1$ are between 80 and 83 kcal/mol, which make them valuable as high-energy triplet sensitizers. However, only, 3 is an efficient triplet sensitizer for 1-azidoadamantane, because it has the fastest intersystem crossing rate constants and thus singlet sensitization is not likely to compete with triplet sensitization. Presumably, due to the slow intersystem crossing in 4, it results in singlet and triplet sensitization of azidoadamantane. Alcohols 1 and 2 are not as good sensitizers, because their ground state absorptions do not differ sufficiently from 1-azidoadamantane in addition to slow intersystem crossing rate constants.

**Acknowledgements**

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We wish Professor Robert Moss happy 70th Birthday. At the same time we would like to congratulate him on his contribution to the field of reactive intermediates and thank him for many valuable advices on how to study reactive intermediates.

**References**


