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GENERATION AND STUDY OF BENZYLCHLOROCARBENE I.

REACTION OF NAPHTHYLCARBOMETHOXYCARBENE
WITH TETRAHYDROFURAN II.

Dissertation
Presented in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy in the Graduate School
of The Ohio State University

By
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*****
The Ohio State University 1999

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ABSTRACT

Plots of (carbene adduct)/(carbene-rearrangement product) versus carbene trapping agent, tetramethylene [TME] exhibit curvature when benzylchlorocarbene 2 is generated by photolysis of benzylchlorodiazirine 1. However, using a non-nitrogenous precursor, plots of this type are linear. Thus, any complex formed between benzylchlorocarbene and TME must collapse to form cyclopropane faster than it can fragment with rearrangement to β-chlorostyrene and TME. Diazirine 1 does photoisomerize to diazo compound 7 but this process is inefficient (\( \phi = 0.075 \)) and is not likely to be responsible for the curvature in plots of adduct/styrene versus [TME] observed with the diazirine precursor. Also, since β-chlorostyrene photoisomerizes and reacts with TME, the variation of the \( E/Z \) ratio of β-chlorostyrene produced on photolysis of 1 in the presence of TME is without mechanistic significance. Thus, the second, non-carbene, pathway to β-chlorostyrene is neither a carbene-olefin-complex nor a diazo intermediate. It is proposed that the second pathway involves a rearrangement in the excited state of the diazirine precursor.
DEDICATION

Dedicated to Sridhar
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SECTION I

CHAPTER 1

INTRODUCTION

1.1 General Review

Carbenes are very reactive intermediates that are divalent and possess two non-bonding electrons. The interest of organic chemists in carbenes dates back more than a century, when Dumas attempted the dehydration of methanol to generate a divalent carbon species.\(^1\) A few decades later, Geuther\(^2\) suggested that the basic hydrolysis of chloroform proceeds via dichlorocarbene as an intermediate. This was followed by Buchner's observation of carbene reactions in the pyrolysis of ethyl diazoacetate,\(^3\) and by Stuadinger in the photolysis of ketene.\(^4\) Modern carbene chemistry began in 1950 with the work of Hine.\(^5\) Hine carried out pioneering studies on the basic hydrolysis of chloroform and unequivocally demonstrated that dichlorocarbene was formed as an intermediate by \(\alpha\)-elimination of HCl from chloroform.

\[
\text{CHCl}_3 \rightleftharpoons \cdot\text{CCl}_3 \rightleftharpoons :\text{CCl}_2
\]

Scheme 1.1
Later, Doering and co-workers took one step further by trapping the dihalocarbenes with cyclohexene.\textsuperscript{6} Since then, both physical and synthetic organic chemists have performed extensive research on the synthetic and mechanistic aspects of this unique organic intermediate.\textsuperscript{7}

One of the most intriguing aspects of carbenes is their electronic configuration. Depending upon the method of generation and its structure, carbenes may be formed in either the singlet or triplet spin state. In a singlet state the two non-bonding electrons are of opposite spins and can either be paired in an in-plane, approximately \(\text{sp}^2\) orbital, leaving the \(\pi\) orbital empty (17) or can reside in two different non-bonding orbitals (18) (Scheme 1.2). Structure (18) normally is very high in energy and hence is not preferred. In the triplet state, the non-bonding electrons are unpaired, are of the same spin and occupy two different orbitals. The out of plane orbital is pure \(p\), the in plane orbital has substantial \(s\) character (19).

![Scheme 1.2](image)

Before the advent of modern spectroscopic techniques, chemists deduced the electronic states of carbenes based on the analysis of reaction mixtures. Skell and
Woodworth\textsuperscript{8} proposed that the reactivities of the two states are distinctly different in the reaction of carbene with alkenes to form cyclopropanes. Singlet state carbenes add to the alkenes in one concerted step, which retains the stereospecificity of the alkenes in the cyclopropanation products. On the other hand, triplet carbenes add to olefins by a stepwise mechanism, yielding a diradical intermediate with two unpaired electrons of the same spin. This eventually results in ring closure between two radical centers. However, since there is free rotation along the $\sigma$ bonds, there is a loss of stereospecificity of the cyclopropyl products. This is true only if bond rotation in the 1,3-diradical intermediate is much faster than the collapse of the diradical to give cyclopropyl product. If the rate of bond rotation is much slower than the rate of cyclopropanation, a diradical intermediate could still give stereoretention, and a stepwise process could “appear” to be concerted.

Herzberg has experimentally established that singlet carbenes are considerably bent.\textsuperscript{9} The bond angle H-C-H in singlet methylene has been found to be 102°. On the other hand, triplet carbenes in general have a larger R-C-R angle. The bond angle H-C-H in triplet methylene has been experimentally determined to be 136°.\textsuperscript{10} The triplet state of methylene (R=H) has been both experimentally and theoretically found to be the ground state. The triplet state is calculated to be about 8-9 kcal/mol lower in energy than the singlet state.\textsuperscript{11} Triplet methylene is the ground state of the carbene because when one electron is placed in the higher energy $\pi$ orbital, it gives a lower sum of orbital and electron-electron repulsion energies than when both electrons occupy the low lying $\sigma$ orbital.\textsuperscript{12}

Carbenes are very reactive intermediates with fleeting lifetimes in solution and in the gas phase. Many carbenes, as per methylene, have triplet ground states. Substituents
on the carbene center influence the relative energies of the singlet and triplet states. A general rule is that when hydrogen is replaced by an alkyl substituent, the electronic configuration of the carbene center is not significantly effected. Methyl carbene, for instance, is also calculated to have a triplet ground state, but the methyl substituent reduces the singlet-triplet energy difference to only 4.0 kcal/mol. Because of the low energy barrier to intramolecular rearrangements, alkyl carbenes are difficult to trap intermolecularly. Dialkylcarbenes are calculated to have singlet ground states and higher barriers to rearrangement than alkyl carbenes.

When a carbene center is adjacent to a heteroatom like a halogen or to substituents that possess electron pairs, it typically has a singlet ground state. This is due to the stabilization of the empty π orbital by delocalizing electrons from the substituent into the empty p orbital of the carbene (Scheme 1.3). This also makes the carbene more kinetically stable and as a result, diaryl, dihalo-, arylhalo-, and alkylhalo carbenes can be trapped intermolecularly in better yields than alkyl- or dialkyl carbenes.

\[ X = \text{F, Cl, OR, NR}_2 \]

Scheme 1.3
A variety of precursors have been reported in the literature which generate carbenes upon photochemical and thermal activation. Diaso compounds, diazirines, ketenes and tosyl hydrazone salts are commonly known carbene precursors. Thermal and direct photolysis of these precursors initially form singlet carbenes based on the spin conservation principle.

\[
\begin{align*}
\text{C} &= \text{C} = \text{O} \quad \rightarrow \quad \text{C} : + \text{CO} \\
\text{R} \quad \text{R} \\
\text{R} \quad \text{R} \\
\text{C} &= \text{N} = \text{N} \quad \rightarrow \quad \text{C} : + \text{N}_2 \\
\text{R} \quad \text{R} \\
\text{R} \quad \text{R} \\
\text{N} \quad \text{N} \\
\text{N} \quad \text{N} \\
\end{align*}
\]

Scheme 1.4

For those carbenes which possess a triplet ground state, the initially generated singlet carbene undergoes intersystem crossing to the triplet electronic configuration. Photosensitization is another process by which triplet carbenes can be obtained directly from the precursor by triplet energy transfer from a sensitizer. In this process, the sensitizer, such as a benzophenone derivative (which has rapid singlet to triplet intersystem crossing), and irradiating wavelength are chosen such that most of the light is absorbed by the sensitizer. The triplet excited state of the sensitizer (\(^{3}S^*\)) is then
quenched by the carbene precursor (P). This sequence generates the triplet excited state of the precursor, which undergoes decomposition to form the triplet carbene ($^3\text{CXY}$) (Equation 1.1a-d).

\[
\begin{align*}
\text{S} & \rightarrow ^1\text{S*} & \text{equation 1.1a} \\
^1\text{S*} & \rightarrow ^3\text{S*} & \text{equation 1.1b} \\
^3\text{S*} + \text{P} & \rightarrow \text{S} + ^3\text{P} & \text{equation 1.1c} \\
^3\text{P} & \rightarrow ^3\text{CXY} & \text{equation 1.1d}
\end{align*}
\]

Base induced $\alpha$-elimination of hydrogen halide is a common procedure used to prepare halocarbenes. In a typical case, under phase-transfer conditions, base-catalyzed decomposition of haloform generates both dichloro- and dibromocarbene, which can add to a variety of olefins.$^{14}$

\[
\begin{array}{c}
\text{CHCl}_3, \text{NaOH} \\
\text{PTC}
\end{array} \rightarrow
\begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array}
\]

PTC = Phase Transfer Catalyst

Scheme 1.5
1.2 Issues involved in the study of alkylcarbenes

Over the past few decades, alkyl carbenes have been studied in great detail. In 1964, Frey suggested three distinct stages that were involved in the study of the photochemistry of alkyl diazo compounds and diazirines. The first stage was to obtain the precursor in a pure state. The second stage involved an investigation of the photochemical decomposition, such as the nature and quantum yield of the products. Finally, the third stage attempts to elucidate the mechanism of the primary processes.

Before the development of simple and practical synthesis of diazirines by Paulson and by Schmitz and Ohme, the purification of alkyl diazirines often resulted in violent explosions. The new synthetic route enabled research on the mechanistic photochemistry of alkyl carbenes and many facets of the rearrangement of alkyl carbenes were discovered. In 1959, Friedman and Shechter reported that the photolysis and pyrolysis of diazirines and the salts of tosylhydrazones produce carbenic reaction products. In the following years, Mansoor and Stevens, and Frey and co-workers reported similar studies. They found that the pyrolysis of tosylhydrazone salt and pyrolysis and photolysis of diazirine produced the putative intermediate ethylmethylcarbene, which rearranges to a characteristic mixture of alkenes.
They found that although pyrolysis of 30 and 31 gave the same mixture of products, photolysis of 31 produced the products in different proportions (Table 1.1). This was an unexpected observation, leading to the conclusion that heat and light do not produce the same intermediate from the nitrogenous precursors. The authors proposed that due to the simple product mixtures, pyrolysis affords relaxed carbene. On the other hand, photolysis generated two intermediates that were responsible for the formation of products in different ratios. While the first intermediate was the relaxed carbene, the second intermediate was thought to involve a vibrationally or electronically excited state of the precursor or the carbene.
Table 1.1: Product distribution produced upon decomposition of various precursors of ethylmethylcarbene.\textsuperscript{21-23}

1.3 Benzylchlorocarbenes

The most common rearrangement reaction of alkyl substituted carbenes that have a hydrogen atom adjacent to the carbene center, is the migration of that hydrogen to the carbene center. This 1,2-H migration rearrangement can be in competition with intermolecular reactions such as addition to olefins to give cyclopropyl adducts. (Scheme 1.7).
1.3.1 A mechanistic aspect

In 1984 Tomioka, Liu and co-workers reported that photolysis of benzylchlorodiazirine 1 produced benzylchlorocarbene 2. The carbene generally undergoes a fast 1,2-H migration to give β-chlorostyrenes 3 as an E/Z mixture. Much knowledge has been acquired about the kinetics of this process in subsequent years. When olefins are added prior to the thermolysis or photolysis of the precursor, there is a competition between the intra- and intermolecular processes. Hence, when the photolysis was repeated in the presence of tetramethylethylene (TME), cycloaduct 4 was isolated. A simple mechanism as shown in Scheme 1.8 predicts a linear relationship between the ratio 4/3 as a function of TME concentration with a slope of $k_r/k_i$. 
Scheme 1.8

The expected linear dependence was not observed, however. The observed results, obtained under photolysis conditions, exhibited a curvature in plots of $4/3$ vs. [olefin] that could not be explained by the above mechanism. The curvature indicated that at higher olefin concentration, the yield of intramolecular product 3, was larger than expected. The data indicated that there must be two pathways which form $\beta$-chlorostyrene product. In the literature, there are quite a few explanations for this type of curvature; (i) formation of a carbene-olefin complex (COC), (ii) 1,2-H migration in the diazo intermediate, and (iii) rearrangement in the excited state (RIES) of the precursor.
Scheme 1.9

A mechanistic scheme, based on the Turro and Moss model\textsuperscript{18b} that involves a carbene-olefin complex (COC) has been proposed by Liu's group.\textsuperscript{18} They postulated that carbene-olefin complexes (COC) are formed prior to the formation of cyclopropane. It was proposed that carbene 2 reacts with TME to form a carbene-olefin π complex (COC) (5) which partitions between collapse to form cyclopropane 4 ($k^c_\text{a}$) and rearrangement ($k^c_\text{r}$) to β-chlorostyrene 3. Thus, not all of the carbene can be diverted to cyclopropane, even at infinite concentration of TME (Scheme 1.9). This mechanism could rationalize the variation of 4/3 as a function of [TME]. Calculations find that carbene-olefin complexes are not minima but collapse immediately to form cyclopropanes.\textsuperscript{5} However,
recent experimental and theoretical work indicates that carbenes do form bound complexes with benzene.\(^6\)

Furthermore, some dependence of the intercept of plots of \([3]/[4]\), versus \(1/[\text{alkene}]\) on the nature of the alkene was found, as predicted by the carbene-alkene complex mechanism\(^16\). Subsequently, it was found that the E/Z ratio of \(\beta\)-chlorostyrenes varies with [TME], which is also consistent with Scheme 1.9.

Other interpretations of the data are possible. Following Frey,\(^23\) the second pathway to beta chlorostyrene has been associated with an excited state of the carbene by Warner.\(^25\) This schemes also predict curvature of plots of \(4/3\) versus [TME] (Scheme 1.10).

\[
\frac{3}{4} = \frac{k_3}{k_1} + \frac{k_1 (k_1 + k_2)}{k_1 k_2 \text{[olefin]}} \quad \text{equation (1.2)}
\]

![Scheme 1.10](image-url)
Again, following Frey\textsuperscript{23} and early workers, Platz and co-workers have attributed the second $\beta$-chlorostyrene pathway to either a diazirine excited state\textsuperscript{24} (Scheme 1.11) and/or to the decomposition of an unstable diazo compound $7$ formed by photoisomerization of diazirine $1^{47}$ (Scheme 1.12). They also reported that 1,2-hydrogen migration in the excited state of benzylchlorodiazirine is a general phenomenon and that its importance is directly related to the bond dissociation energy of the migrating hydrogen. Accordingly, some $\beta$-chlorostyrene is formed directly from the excited state of the diazirine, by-passing the carbene intermediate. Hence, the $E/Z$ ratio of $3$ formed from the diazirine excited state will differ from the $E/Z$ ratio of $3$ formed from the free carbene.
The relative reactivity of benzylchlorocarbene with various alkenes has been reported and the relative amounts of intermolecular reaction (cyclopropane adduct) and intramolecular (β-chlorostyrenes) formed after complete photolysis of benzylchlorodiazirine 1 has been measured as a function of the concentration of several olefins.\textsuperscript{16b}

The change of the E/Z ratio of 3 with TME, and the dependence of 4/3 versus [alkene] type plots, on the nature of the alkene trap, is also consistent with the
intermediacy of a diazo compound (Scheme 1.12) which can react with alkenes.\textsuperscript{24} It has been suggested that all 3 pathways may be operating simultaneously in this system.\textsuperscript{2d,11,12}

\[ \text{PhCH}_2\text{N} \xrightarrow{hv} \text{PhCH}_2\text{N}^* \rightarrow \text{PhCH}_2\text{Cl} \]

Scheme 1.12

The stereochemical result of the E/Z ratio of chlorostyrenes formed during the photolysis of benzylchlorodiazirine 1 was found to be of utmost interest. In 1987, Tomioka\textsuperscript{16b} et al found that 3Z/3E ratio increases with increasing TME concentration. This group used the carbene-olefin complex (COC) mechanism (Scheme 1.8) to interpret the distribution of products formed. In this mechanism, the π complex has bonding
interactions between the empty orbital of the carbene and the filled olefinic $\pi$ orbital or between the filled orbital of the carbene and the empty olefinic $\pi^*$ orbital.

Liu, et al. suggested two limiting conformers, 21 and 22 were responsible for these results (Scheme 1.13). According to this theory, E-$\beta$-chlprostyrene arises from conformer 21, while the Z isomer is formed via conformer 22. It is clear from Scheme 1.13 that due to steric factors, conformer 23 is expected to be less stable than conformer 24. Hence with the increasing concentrations of TME, more Z isomer will be formed.

Scheme 1.13
If $k_{21}$ and $k_{22}$ are the rate constants for 1,2-H migration from 22 and 23 to give E and Z respectively, and $k_{23}$ and $k_{24}$ are a complex ratio of individual k’s involving the carbene-alkene complex, then, the kinetics will be as follows:

\[
\frac{Z}{E} = \frac{k_{22} + k_{24}[\text{TME}]}{k_{21} + k_{23}[\text{TME}]} \quad \text{equation (1.3)}
\]

During a study of the low temperature photolysis of diazirine 1 in a TME/benzene matrix at -196 °C and -121 °C, Liu, et al. found that the yield of cyclopropyl adduct 4 was only 3% of the total product formation and the $Z/E$ ratio of 3 was not dependent on the TME concentration. An explanation of this revealing information was once again provided with the help of Scheme 1.13.

At very low temperatures, as in the matrix studies, $k_{22} \gg k_{24}$ and $k_{22} \gg k_{23}$. Kinetic studies showed that the $Z/E$ ratio of 3 was invariant with TME concentration in the matrix. Also, at very high photolysis temperature (100 °C), intermolecular reaction to give cyclopropyl adduct 4 is much slower, $k_{22} \gg k_{24}$ and $k_{22} \gg k_{23}$. Hence, from equation (1.3), the $Z/E$ ratio of 3 was found to be independent of TME concentration. At intermediate temperatures, $k_{22}$ and $k_{24}$ are comparable and so are $k_{22}$ and $k_{23}$ and hence, $Z/E$ ratio becomes dependent on TME concentration.

1.3.2 Laser Flash Photolysis of Benzylchlorocarbenes

In the 1980’s, the Laser Flash Photolysis (LFP) technique emerged as a very important tool in the study of short-lived reactive intermediates. Prior to that, low
temperature rigid matrix, electron spin resonance spectroscopy\textsuperscript{39-31} and optical spectroscopy\textsuperscript{32,33} were the main experimental methods for studying carbenes. Due to the short lifetime of the carbenes, these standard kinetic methods could provide only a partial understanding of the structure and the chemical behavior of carbenes. Time resolved laser spectroscopy has allowed a new dimension in the study of carbenes.

Typically, a laser that can produce a high energy pulse at a certain selected wavelength is used as the photoexcitation source. This laser beam usually has a pulse width of several nanoseconds. Perpendicular to the incident laser beam, a xenon arc lamp serves as the probing light. The sample solution is placed in a quartz cuvette at the intersection of the probing light and the laser beam. The timing of the instrument and the recording of the data is controlled by a computer.

Since the LFP technique uses absorption spectroscopy as a tool for the detection of reactive species, the intermediate should have an appropriate chromophore in the UV-Vis region. For those intermediates, which lack a chromophore, a probe method is required. The probe method has gained much interest among carbene chemists. It uses a suitable substrate that forms UV-Vis active ylides with the "invisible" carbene. The kinetics of the "invisible" carbene can be deduced from the "visible" ylide. Even with carbenes that contain a chromophore, the LFP technique may suffer from overlap of absorption signals from the precursor, the resulting carbene and the carbene reaction product. Hence, the chemical probe method reduces complications from signal overlap and allows scientists to study carbenes with no suitable chromophores. In 1988, the Platz group introduced the carbene-pyridine ylide forming reactions to study the kinetics of carbenes in solutions.\textsuperscript{34}
In a typical experiment, a diazirine is photochemically decomposed in the presence of pyridine and the rate of formation of the ylide product is recorded. If $k_{\text{pyr}}$ is the absolute rate constant of reaction of carbene with pyridine, and $k_R$ is the rate constant of rearrangement of the carbene in the absence of pyridine, then according to Scheme 1.14,

$$k_{\text{obs}} = k_R + k_{\text{pyr}}[\text{Pyridine}]$$  \hspace{1cm} \text{equation (1.4)}

where, $k_{\text{obs}}$ is the observed rate constant of formation of the pyridine ylide.

The kinetics and spectroscopy of benzylchlorocarbene have been studied by laser flash photolysis techniques. Direct measurement of the rate constant of hydrogen
migration $k_R$ in the case of benzylchlorocarbene was rather difficult as this carbene does not absorb with a high extinction coefficient in the UV-Vis region of the spectrum. In 1990, Liu, et al. used, the "pyridine probe" strategy for the study of benzylchloro carbene.\textsuperscript{16a}

Liu and co-workers\textsuperscript{16a} found that Laser Flash Photolysis (LFP) of benzylchloro diazirine I in isooctane produces a transient absorption ($\lambda=310$ nm, and $\tau=16$ ns at $25^\circ$C) attributed to benzylchlorocarbene 2. Also, LFP of benzylchlorodiazirine I in the presence of pyridine in isooctane produces a transient species with an absorption maximum around 380 nm (Figure 1.1). This band is not observed in the absence of pyridine, hence it is associated with pyridine ylide 9 (Scheme 1.14).

![Figure 1.1: Transient spectra of pyridine-benzylchlorocarbene ylide 9 produced upon LFP of diazirine I in isooctane containing pyridine (0.6M) at 22 $^\circ$C.](image)
Plotting the observed rate constant of the formation of the pyridine ylide vs [pyridine] gives a straight line (Figure 1.2). The slope of this line is $k_{\text{pyr}}$, the absolute rate constant of reaction of the carbene with pyridine. The intercept of this plot is $k_R$, the absolute rate constant for the 1,2-hydrogen migration in benzylchlorocarbene 2.

Figure 1.2: Plot of the observed pseudo-first-order rate constants for the growth of the pyridine ylide 9 absorption at 380nm versus pyridine concentration at 22 $^\circ$C.$^{16a}$
Values of $k_R$ were measured at different temperatures. An Arrhenius plot of log $k_R$ vs $1/T$ obtained the kinetic parameters $E_i = 4.5 \text{ kcal/mol}$ and $A_R = 10^{11.1} \text{ s}^{-1}$ (Figure 1.3).

![Arrhenius plot](image)

**Figure 1.3:** Arrhenius plot of the rate constant for 1,2-H migration for benzylchlorocarbene $2$.\textsuperscript{16a}

Similar values were obtained upon LFP of I in the absence of pyridine. In this case, the carbene decay was monitored directly at 310 nm over the same temperature range. The authors also measured the rate constant of the addition of benzylchlorocarbene I to tetramethylethylene to be $(6.2 \pm 0.2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. In summary, the results were consistent with a mechanism involving formation of a complex between benzylchlorocarbene I and tetramethylethylene.
In 1992, White and Platz\textsuperscript{47} reported evidence of 1,2-H migration in the excited state of benzylchlorodiazirine and other alkyl diazirines. They found that this phenomenon was dependent upon the bond dissociation energy of the migrating hydrogen. The spectroscopic evidence of the formation of diazo compound 7 (Scheme 1.12), in combination with chemical trapping studies demonstrated that their results argued against the carbene-olefin complex (COC) theory in the reaction of benzylchlorodiazirine 1 with TME.
CHAPTER 2

PHOTOCHEMICAL STUDY OF
BENZYLCHLORODIAZIRINE

2.1 Previous investigation on benzylchlorocarbene

Apart from the 1,2-H migration reaction, benzylchlorocarbenes are known to undergo addition reactions with olefins. The relative reactivity of benzylchlorocarbene with various alkenes has been reported and the relative amounts of intermolecular reaction (cyclopropane adduct) and intramolecular (β-chlorostyrenes) formed after complete photolysis of benzylchlorodiazirine 1 has been measured as a function of the concentration of several olefins. In 1984, during studies on the competition between intramolecular 1,2-H shift and intermolecular addition of benzylchlorocarbenes to 2,3-dimethyl-2-butene, Tomioka, Liu and co-workers suggested a reversibly formed dissociable intermediate in the addition of carbene to alkene. They found that the intermolecular/intramolecular product ratio as a function of alkene concentration shows pronounced curvature.

Platz and co-workers have attributed the formation of β-chlorostyrene to other pathways. They have explained the curvature of the intermolecular/intramolecular product ratio as a function of alkene concentration to either a diazirine excited state or
to the decomposition of an unstable diazo compound 7 formed by photoisomerization of
diazirine 1.\textsuperscript{47}

To distinguish between these views, an independent precursor to
benzylchlorocarbene is needed. If a carbene-alkene complex 5 is the second route to
$\beta$-chlorostyrenes then the originally reported observations will be independent of
precursor, if not the anomalies should disappear. The first aim of this work was to
reproduce the original findings with benzylchlorodiazirine 1.

\subsection*{2.1.1 Synthesis of 3-Chloro-3-benzyldiazirine (1)}

3-Chloro-3-benzyldiazirine (1) was synthesized by Grahams method.\textsuperscript{55} Although
in the literature, benzyl imino ether, the product of the first step was not isolated, it was
done so in this procedure in order to get rid of excess ethanol and HCl.

![Scheme 2.1](image-url)
2.1.2 Photolysis of 3-chloro-3-benzyldiazirine (1)

Scheme 2.2

The photolysis (320-380nm, Rayonet reactor) of diazirine 1 in presence of TME, in isooctane produces both styrenes 3 and cyclopropane 4 (Table 2.1). The same experiment was repeated in dichloromethane (Table 2.2) to allow comparison with non-nitrogenous precursor 8, which was soluble in dichloromethane but not in isooctane. The plot of 4/3 as a function of TME, in both solvents shows curvature. The results are similar to that reported by Liu\textsuperscript{19} (Figure 2.3). The slight difference between our findings and those of the earlier workers is likely due to the small difference of temperature of the two studies or due to small difference in the Gas Chromatography response factors.
Figure 2.1: Total ion chromatogram obtained from the photolysis of diazirine 1 in isoctane with 0.1M TME at 15°C. This data is ± 4%.

The peak with the retention time of 11.89 minutes is that of 1-benzyl-1-chloro-2,2,3,3-tetramethyl cyclopropane 4. The peaks at 5.86 and 5.71 belong to E and Z β-chlorostyrene respectively.

<table>
<thead>
<tr>
<th>[TME] (M)</th>
<th>GC peak area for 4</th>
<th>GC peak area for 3E</th>
<th>GC peak area for 3Z</th>
<th>GC peak area ratio of 4/3</th>
<th>Ratio$^{(a)}$ of [4]/[3]</th>
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<td>0.11</td>
<td>0.23</td>
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<td>1</td>
<td>1.06</td>
<td>0.09</td>
<td>0.10</td>
<td>5.38</td>
<td>1.85</td>
</tr>
<tr>
<td>1.4</td>
<td>1.02</td>
<td>0.09</td>
<td>0.09</td>
<td>5.55</td>
<td>1.90</td>
</tr>
<tr>
<td>1.8</td>
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<td>0.09</td>
<td>0.10</td>
<td>5.65</td>
<td>1.94</td>
</tr>
<tr>
<td>2.2</td>
<td>1.04</td>
<td>0.08</td>
<td>0.10</td>
<td>5.80</td>
<td>1.99</td>
</tr>
</tbody>
</table>

(a) Peak area ratio of 3/4 was converted into mole ratio by multiplying by the response factor of 2.92.

Table 2.1: Product distribution after photolyzing diazirine 1 in isoctane containing TME at 350nm for 48 hours at 15°C.
Figure 2.2: Total ion chromatogram obtained from the photolysis of diazirine 1 in dichloromethane with 0.1M TME at 15°C. This data is ± 4%.

The peak with the retention time of 11.89 minutes is that of 1-benzyl-1-chloro-2,2,3,3-tetramethyl cyclopropane 4. The peaks at 5.86 and 5.71 belong to E and Z β-chlorostyrene respectively.

<table>
<thead>
<tr>
<th>[TME] (M)</th>
<th>GC peak area for 4</th>
<th>GC peak area for 3E</th>
<th>GC peak area for 3Z</th>
<th>GC peak area ratio of 4/3</th>
<th>Ratio$^a$ of [4]/[3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.21</td>
<td>0.14</td>
<td>0.35</td>
<td>0.43</td>
<td>0.15</td>
</tr>
<tr>
<td>0.2</td>
<td>0.31</td>
<td>0.17</td>
<td>0.22</td>
<td>0.80</td>
<td>0.27</td>
</tr>
<tr>
<td>0.4</td>
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<td>0.12</td>
<td>0.16</td>
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</tr>
<tr>
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<td>0.56</td>
<td>0.08</td>
<td>0.13</td>
<td>2.72</td>
<td>0.93</td>
</tr>
<tr>
<td>1</td>
<td>0.59</td>
<td>0.07</td>
<td>0.13</td>
<td>2.90</td>
<td>0.99</td>
</tr>
<tr>
<td>1.4</td>
<td>0.65</td>
<td>0.07</td>
<td>0.12</td>
<td>3.58</td>
<td>1.23</td>
</tr>
<tr>
<td>1.8</td>
<td>0.62</td>
<td>0.06</td>
<td>0.10</td>
<td>3.78</td>
<td>1.29</td>
</tr>
<tr>
<td>2.2</td>
<td>0.69</td>
<td>0.05</td>
<td>0.100</td>
<td>4.43</td>
<td>1.52</td>
</tr>
</tbody>
</table>

(a) Peak area ratio of 3/4 was converted into mole ratio by multiplying by the response factor of 2.92.

Table 2.2: Product distribution after photolyzing diazirine 1 in dichloromethane containing TME at 350nm for 48 hours at 15°C.
Figure 2.3: A plot of 4/3 vs [TME] obtained at 350nm from diazirine 1 (♦) at 15°C in CH₂Cl₂; (■) diazirine 1 at 15°C in isooctane, and (▲) data of Liu, et al. at 10°C in isooctane.

2.1.3 The study of E/Z ratio formed upon the photolysis of (1)

In the previous study, the ratio of E/Z of β-chlorostyrene 3 was found to be of particular interest. In general, it was found that the E/Z ratio decreases with an increase in the TME concentration. The results demonstrated the involvement of TME in the formation of chlorostyrene that linked the explanation to the carbene-olefin complex.

In our hands the E/Z ratio varies as shown in Table 2.3 and 2.4. The E/Z ratio was studied as a function of TME as shown in Figure 2.4.
(a) GC peak area ratios. Since 3E and 3Z are isomers, we assume that the response factors of the two compounds are the same. Hence, these values are taken as ratios of concentrations.

**Table 2.3:** Ratio of E/Z after photolyzing 1 in isooctane containing TME at 350nm for 48 hours at 15 °C. This data is ± 4%.

<table>
<thead>
<tr>
<th>[TME] (M)</th>
<th>GC peak area of 3E</th>
<th>GC peak area of 3Z</th>
<th>Ratio of [E]/[Z]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.11</td>
<td>0.23</td>
<td>0.50</td>
</tr>
<tr>
<td>0.2</td>
<td>0.12</td>
<td>0.15</td>
<td>0.78</td>
</tr>
<tr>
<td>0.4</td>
<td>0.11</td>
<td>0.12</td>
<td>0.92</td>
</tr>
<tr>
<td>0.8</td>
<td>0.10</td>
<td>0.11</td>
<td>0.93</td>
</tr>
<tr>
<td>1</td>
<td>0.09</td>
<td>0.10</td>
<td>0.90</td>
</tr>
<tr>
<td>1.4</td>
<td>0.09</td>
<td>0.09</td>
<td>0.95</td>
</tr>
<tr>
<td>1.8</td>
<td>0.09</td>
<td>0.10</td>
<td>0.89</td>
</tr>
<tr>
<td>2.2</td>
<td>0.08</td>
<td>0.01</td>
<td>0.84</td>
</tr>
</tbody>
</table>

(a) GC peak area ratios. Since 3E and 3Z are isomers, we assume the response factors of the two to be the same. Hence, these values are taken as ratios of concentrations.

**Table 2.4:** Ratio of E/Z observed after photolyzing 1 in dichloromethane containing TME at 350nm for 48 hours at 15 °C. This data is ± 4%.

<table>
<thead>
<tr>
<th>[TME] (M)</th>
<th>GC peak area of 3E</th>
<th>GC peak area of 3Z</th>
<th>Ratio of [E]/[Z]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.14</td>
<td>0.35</td>
<td>0.79</td>
</tr>
<tr>
<td>0.2</td>
<td>0.17</td>
<td>0.22</td>
<td>0.78</td>
</tr>
<tr>
<td>0.4</td>
<td>0.12</td>
<td>0.16</td>
<td>0.76</td>
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<tr>
<td>0.8</td>
<td>0.08</td>
<td>0.13</td>
<td>0.57</td>
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<td>0.13</td>
<td>0.56</td>
</tr>
<tr>
<td>1.4</td>
<td>0.07</td>
<td>0.12</td>
<td>0.58</td>
</tr>
<tr>
<td>1.8</td>
<td>0.06</td>
<td>0.10</td>
<td>0.59</td>
</tr>
<tr>
<td>2.2</td>
<td>0.06</td>
<td>0.11</td>
<td>0.52</td>
</tr>
</tbody>
</table>

31
Figure 2.4: The E/Z ratio of the β-chlorostyrenes formed at 15°C under various conditions; (♦) precursor 1, isooctane; (▲), precursor 1, dichloromethane; and (■), diazirine 1, data of Liu, et al. at 10°C in isooctane.

2.1.4 Time-Resolved Infrared Spectroscopy

Time-Resolved IR spectroscopy allows access to the entire mid-IR spectrum (4000-800 cm⁻¹) with high sensitivity and sufficient time (ca. 50ns) and frequency (4-16 cm⁻¹) resolution to probe a wide range of transient intermediates in solution. TRIR measurements are obtained from three different recordings of the emission spectrum of the IR light source. These include the spectrum of the IR source without the sample in the beam path (I₀), a spectrum of the IR source with the sample in the beam path (I), and
the IR intensity changes induced by photoexcitation ($\Delta I$). The absorption spectrum of the unexcited sample is derived from $I_0$ and $I$, $A = \log (I_0/I)$. The Time-resolved IR absorption spectrum is obtained in the form of a difference spectrum, $\Delta A = -\log (1 + \Delta I/I)$. Thus depletion of the reactant ground state gives rise to negative signals and the formation of transient intermediates or products leads to positive bands.

Laser flash photolysis of diazirine 1 produces a transient with a strong IR absorption at 2044 cm$^{-1}$. The transient is long lived ($\tau >> 200 \mu s$) and is associated with diazo compound 7 (Figure 2.5).

![Figure 2.5: TRIR spectra observed from 0.0-9.0 ps following 266 nm laser photolysis of diazirine 1 in argon saturated dichloromethane. The positive band at 2044 cm$^{-1}$ is due to the formation of diazo compound 7.](image-url)
Figure 2.6: TRIR spectra observed from 0.0-9.0 µs following 266 nm laser photolysis of diazirine 1 in argon saturated dichloromethane. The negative band at 1562 cm\(^{-1}\) is due to depletion of diazirine 1.

LFP of chloropropyldiazirine 12 and 13 produces diazo compounds 14 (2030 cm\(^{-1}\)) and 15 (2028 cm\(^{-1}\)), respectively.\(^{58}\)
Bonneau and co-workers have shown that the quantum yields of the formation of 14 from 12, and of 15 from 13 are approximately the same (0.10-0.13). Diazirines 1 and 13 were studied under identical conditions.

![TRIR spectra observed from 0.0-9.0 μs following 266 nm laser photolysis of diazirine 13 in argon saturated dichloromethane. The positive band at 2028 cm⁻¹ is due to the formation of diazo compound 15.](image)

**Figure 2.7:** TRIR spectra observed from 0.0-9.0 μs following 266 nm laser photolysis of diazirine 13 in argon saturated dichloromethane. The positive band at 2028 cm⁻¹ is due to the formation of diazo compound 15.
Figure 2.8: TRIR spectra observed from 0.0-9.0 μs following 266 nm laser photolysis of diazirine 13 in argon saturated dichloromethane. The negative band at 1555 cm\(^{-1}\) is due to depletion of diazirine 13.

Based on the analysis of the IR intensities of diazirine depletion bands and formation of diazo absorption bands, the quantum yield of diazo formation with benzylchlorodiazirine is about half of that of diazirines 12 and 13, or 0.075.
Although diazirine 1 does photoisomerize to compound 7, this process is inefficient ($\phi=0.075$) and is not likely to be responsible for the curvature in plots of $4/3$ versus [TME] observed with diazirine 1.

### 2.2 Study of mechanism using a non-nitrogenous precursor.

Phenanthridine 8 appeared to be a precursor, which would allow the differentiation of the various mechanistic proposals.

LFP of 8 produces carbene 2 which can be trapped with pyridine to form ylide 9 (Scheme 2.3). 

![Scheme 2.3](image_url)

Obviously 8 cannot form a diazo intermediate. Furthermore, if 8 opens to form biradical 10 upon photolysis, then this biradical (unlike 6, Scheme 1.11) will surely isomerize to 11 (Scheme 2.4) rather than somehow form β-chlorostyrene 3 as the thermal fragmentation of alkylcyclopropanes into a pair of alkenes (via cleavage with
rearrangement) is without precedent. Thus, there should not be a second pathway to form alkenes 3 when this precursor is employed.

\[
\begin{align*}
\text{10} & \quad \text{Cl} \quad \text{CH}_2\text{Ph} \\
\rightarrow & \\
\text{11} & \quad \text{Cl} \quad \text{CHCH}_2\text{Ph} \\
\rightarrow & \\
+ & \quad \text{PhCH} = \text{CHCl} \\
\text{3} & \quad \text{PhCH} = \text{CHCl}
\end{align*}
\]

Scheme 2.4

In the course of our investigation of the photochemistry of 8, in the presence and absence of TME, the results are consistent with Scheme 1.11 and rule out π complex 5, as a species capable of forming β-chlorostyrene at a rate comparable to its collapse to cyclopropane. The results do not exclude the possibility of the formation of π complex 5 but such a species, if formed, can only form cyclopropane 4 \((k_{fA} \gg k_{R}, \text{Scheme 1.9})\).
2.2.1 Synthesis of 8

Phenanthridine compounds are a useful source of alkylchlorocarbenes and have been successfully studied in the LFP studies. Their ability of this class of precursor to cleanly produce carbenes has been utilized in our chemical trapping studies of benzylchlorocarbenes.

![Scheme 2.5]

2.2.2 Photolysis of 8

![Scheme 2.6]
Photolysis of 8 in the presence of TME again produces β-chlorostyrenes 3 and cyclopropane 4 (Scheme 2.6). A plot of 4/3 versus [TME] in CH$_2$Cl$_2$ is linear over the range of [TME] (Figure 2.9) where such plots obtained with diazirine 1 are curved (Figure 2.3). Precursor 8 is insoluble in isooctane, hence the change of solvent. Photolysis of 8 was carried out both at 300nm and 350nm (Table 2.5 and Table 2.6).

Figure 2.9: A plot of 4/3 vs [TME] obtained from phenanthridine 8 (▲) at 15$^\circ$C in CH$_2$Cl$_2$ at 350nm; (◇) phenanthridine 8 at 15$^\circ$C in CH$_2$Cl$_2$ at 300nm, and (■) diazirine 1, data of Liu$^{19}$ et al at 10$^\circ$C in isooctane.
<table>
<thead>
<tr>
<th>[TME] (M)</th>
<th>GC peak area for 4</th>
<th>GC peak area for 3E</th>
<th>GC peak area for 3Z</th>
<th>GC peak area ratio of 4/3</th>
<th>Ratio$^a$ of [4]/[3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
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<td>0.2</td>
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<td>0.62</td>
<td>0.98</td>
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</tr>
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<td>0.4</td>
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<tr>
<td>0.8</td>
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<td>0.13</td>
<td>0.34</td>
<td>4.13</td>
<td>1.41</td>
</tr>
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<td>0.18</td>
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</tr>
<tr>
<td>1.8</td>
<td>2.24</td>
<td>0.08</td>
<td>0.18</td>
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<td>2.96</td>
</tr>
<tr>
<td>2.2</td>
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<td>0.06</td>
<td>0.13</td>
<td>9.57</td>
<td>3.28</td>
</tr>
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</table>

(a) Peak area ratio of 3/4 was converted into mole ratio by multiplying by the response factor of 2.92.

**Table 2.5**: Product distribution after photolyzing phenanthridine 8 in dichloromethane containing TME at 350nm for 48 hours at 15 °C. This data is ± 4%.

<table>
<thead>
<tr>
<th>[TME] (M)</th>
<th>GC peak area for 4</th>
<th>GC peak area for 3E</th>
<th>GC peak area for 3Z</th>
<th>GC peak area ratio of 4/3</th>
<th>Ratio$^a$ of [4]/[3]</th>
</tr>
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<td>0.2</td>
<td>1.12</td>
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<td>0.33</td>
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<td>0.41</td>
</tr>
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<td>0.8</td>
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<td>0.22</td>
<td>3.40</td>
<td>1.17</td>
</tr>
<tr>
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<td>1.52</td>
<td>0.23</td>
<td>0.18</td>
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</tr>
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<td>0.13</td>
<td>8.19</td>
<td>2.81</td>
</tr>
</tbody>
</table>

(a) Peak area ratio of 3/4 was converted into mole ratio by multiplying by the response factor of 2.92.

**Table 2.6**: Product distribution after photolyzing phenanthridine 8 in dichloromethane containing TME at 300nm for 2 hours at 15 °C. This data is ± 4%.
The curved plots of 4/3 first discovered by Tomioka, et al.\textsuperscript{15} are precursor dependent. Curvature is observed with diazirine 1 but not with phenanthridene 8. The curvature observed with precursor 1 cannot be due to a complex between carbene 2 and TME which was postulated to form styrene 3 in competition with collapse to cyclopropane 4.

Many scientists have speculated that carbenes form complexes with alkenes on the way to forming cyclopropanes.\textsuperscript{18} The putative complex is formed by the interaction of the empty p-orbital of the singlet carbene with the \( \pi \) electrons of the alkene (Scheme 1.9).

Theory predicts that these types of complexes are not minima on the potential surface in the gas phase.\textsuperscript{57} Our results do not rule out the possibility that a complex such as 5 is formed and has a finite lifetime in solution. However, the data requires that if 5 is indeed formed, it must form cyclopropane 3 much faster than it forms 2 plus TME (\( k_A \gg k_R \)).

Is this conclusion reasonable? Any complex of a carbene and an alkene must be enthalpically stable relative to its free components or it will not be formed. The rearrangement of an \( \alpha \)-hydrogen in a carbene is traditionally viewed as a hydride-like shift where the hydride moves to the empty p orbital of the carbene carbon (Scheme 2.7). The experimentally determined barrier to this rearrangement is 5.8 kcal/mol.\textsuperscript{16} Complexation must surely raise the barrier. In contrast, (according to theory)\textsuperscript{57} the barrier to collapse of the complex to form cyclopropane is close to zero, if it exists at all. Thus, complexation should make rearrangement even less competitive with cycloaddition as per the Reactivity Selectivity Principle.
2.2.3 The study of E/Z ratio formed upon the photolysis of (8)

Table 2.7: Ratio of E/Z after photolyzing 8 in dichloromethane containing TME at 350nm for 48 hours at 15 °C. This data is ± 4%.
(a) GC peak area ratios. Since 3E and 3Z are isomers, we are assuming the response factors of the two to be the same. Hence, these values are taken as ratios of concentrations.

**Table 2.8:** Ratio of E/Z after photolyzing 8 in dichloromethane containing TME at 300nm for 2 hours at 15 °C. This data is ± 4%.
Figure 2.10: The E/Z ratio of the β-chlorostyrenes formed at 15 °C under various conditions; (♦) precursor 8, 300nm, CH₂Cl₂; (▲), precursor 8, 350nm, CH₂Cl₂; and (■), diazirine 1, data of Liu,¹⁹ et al. at 10⁰ C in isooctane.
2.2.4 Study of 4/3 with varying concentration of TME as a function of temperature

<table>
<thead>
<tr>
<th>[TME] (M)</th>
<th>GC peak area for 4</th>
<th>GC peak area for 3E</th>
<th>GC peak area for 3Z</th>
<th>GC peak area ratio of 4/3</th>
<th>Ratio$^{(a)}$ of [4]/[3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
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<td>1.00</td>
<td>0.34</td>
</tr>
<tr>
<td>0.2</td>
<td>0.92</td>
<td>0.25</td>
<td>0.15</td>
<td>2.30</td>
<td>0.79</td>
</tr>
<tr>
<td>0.4</td>
<td>1.35</td>
<td>0.07</td>
<td>0.05</td>
<td>5.82</td>
<td>2.00</td>
</tr>
<tr>
<td>0.8</td>
<td>1.91</td>
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<td>0.13</td>
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<td>2.86</td>
</tr>
<tr>
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<td>0.06</td>
<td>10.51</td>
<td>3.60</td>
</tr>
<tr>
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<td>2.20</td>
<td>0.09</td>
<td>0.06</td>
<td>14.40</td>
<td>4.9</td>
</tr>
</tbody>
</table>

(a) Peak area ratio of 3/4 was converted into mole ratio by multiplying by the response factor of 2.92.

Table 2.9: Product distribution after photolyzing phenanthridine 8 in dichloromethane containing TME at 300nm for 48 hours at 9 °C. This data is ± 4%.

<table>
<thead>
<tr>
<th>[TME] (M)</th>
<th>GC peak area for 4</th>
<th>GC peak area for 3E</th>
<th>GC peak area for 3Z</th>
<th>GC peak area ratio of 4/3</th>
<th>Ratio$^{(a)}$ of [4]/[3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.25</td>
<td>0.21</td>
<td>0.09</td>
<td>0.82</td>
<td>0.28</td>
</tr>
<tr>
<td>0.2</td>
<td>0.49</td>
<td>0.26</td>
<td>0.11</td>
<td>1.31</td>
<td>0.45</td>
</tr>
<tr>
<td>0.4</td>
<td>0.76</td>
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<td>0.09</td>
<td>2.84</td>
<td>0.97</td>
</tr>
<tr>
<td>0.8</td>
<td>1.01</td>
<td>0.11</td>
<td>0.05</td>
<td>6.27</td>
<td>2.15</td>
</tr>
<tr>
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<td>0.08</td>
<td>0.05</td>
<td>9.48</td>
<td>3.25</td>
</tr>
<tr>
<td>1.4</td>
<td>1.28</td>
<td>0.07</td>
<td>0.03</td>
<td>12.20</td>
<td>4.18</td>
</tr>
</tbody>
</table>

(a) Peak area ratio of 3/4 was converted into mole ratio by multiplying by the response factor of 2.92.

Table 2.10: Product distribution after photolyzing phenanthridine 8 in dichloromethane containing TME at 300nm for 2 hours at 13 °C. This data is ± 4%.
<table>
<thead>
<tr>
<th>[TME] (M)</th>
<th>GC peak area for 4</th>
<th>GC peak area for 3E</th>
<th>GC peak area for 3Z</th>
<th>Ratio of 4/3</th>
<th>Ratio&lt;sup&gt;(a)&lt;/sup&gt; of [4]/[3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.27</td>
<td>0.17</td>
<td>0.19</td>
<td>0.72</td>
<td>0.25</td>
</tr>
<tr>
<td>0.2</td>
<td>0.45</td>
<td>0.14</td>
<td>0.18</td>
<td>1.37</td>
<td>0.47</td>
</tr>
<tr>
<td>0.4</td>
<td>0.84</td>
<td>0.17</td>
<td>0.20</td>
<td>2.31</td>
<td>0.79</td>
</tr>
<tr>
<td>0.8</td>
<td>0.87</td>
<td>0.12</td>
<td>0.06</td>
<td>4.83</td>
<td>1.66</td>
</tr>
<tr>
<td>1</td>
<td>1.95</td>
<td>0.23</td>
<td>0.11</td>
<td>5.77</td>
<td>1.98</td>
</tr>
<tr>
<td>1.4</td>
<td>1.14</td>
<td>0.10</td>
<td>0.03</td>
<td>8.58</td>
<td>2.94</td>
</tr>
</tbody>
</table>

(a) Peak area ratio of 3/4 was converted into mole ratio by multiplying by the response factor of 2.92.

Table 2.11: Product distribution after photolyzing phenanthridine 8 in dichloromethane containing TME at 300nm for 2 hours at 23 °C. This data is ± 4%.

<table>
<thead>
<tr>
<th>[TME] (M)</th>
<th>GC peak area for 4</th>
<th>GC peak area for 3E</th>
<th>GC peak area for 3Z</th>
<th>Ratio of 4/3</th>
<th>Ratio&lt;sup&gt;(a)&lt;/sup&gt; of [4]/[3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.29</td>
<td>0.30</td>
<td>0.36</td>
<td>0.45</td>
<td>0.15</td>
</tr>
<tr>
<td>0.2</td>
<td>0.50</td>
<td>0.36</td>
<td>0.30</td>
<td>0.76</td>
<td>0.26</td>
</tr>
<tr>
<td>0.4</td>
<td>0.90</td>
<td>0.34</td>
<td>0.15</td>
<td>1.82</td>
<td>0.62</td>
</tr>
<tr>
<td>0.8</td>
<td>1.29</td>
<td>0.28</td>
<td>0.14</td>
<td>3.04</td>
<td>1.04</td>
</tr>
<tr>
<td>1</td>
<td>1.54</td>
<td>0.21</td>
<td>0.12</td>
<td>4.71</td>
<td>1.62</td>
</tr>
<tr>
<td>1.4</td>
<td>1.83</td>
<td>0.22</td>
<td>0.18</td>
<td>5.47</td>
<td>1.87</td>
</tr>
</tbody>
</table>

(a) Peak area ratio of 3/4 was converted into mole ratio by multiplying by the response factor of 2.92.

Table 2.12: Product distribution after photolyzing phenanthridine 8 in dichloromethane containing TME at 300nm for 2 hours at 33 °C. This data is ± 4%.
<table>
<thead>
<tr>
<th>[TME] (M)</th>
<th>GC peak area for 4</th>
<th>GC peak area for 3E</th>
<th>GC peak area for 3Z</th>
<th>GC peak area ratio of 4/3</th>
<th>Ratio(^{(a)}) of [4]/[3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.17</td>
<td>0.58</td>
<td>0.30</td>
<td>0.19</td>
<td>0.07</td>
</tr>
<tr>
<td>0.2</td>
<td>0.33</td>
<td>0.39</td>
<td>0.20</td>
<td>0.56</td>
<td>0.19</td>
</tr>
<tr>
<td>0.4</td>
<td>0.56</td>
<td>0.36</td>
<td>0.19</td>
<td>1.01</td>
<td>0.35</td>
</tr>
<tr>
<td>0.8</td>
<td>0.98</td>
<td>0.27</td>
<td>0.16</td>
<td>2.27</td>
<td>0.78</td>
</tr>
<tr>
<td>1</td>
<td>1.39</td>
<td>0.29</td>
<td>0.20</td>
<td>2.81</td>
<td>0.96</td>
</tr>
<tr>
<td>1.4</td>
<td>1.42</td>
<td>0.19</td>
<td>0.13</td>
<td>4.51</td>
<td>1.54</td>
</tr>
</tbody>
</table>

(a) Peak area ratio of 3/4 was converted into mole ratio by multiplying by the response factor of 2.92.

Table 2.13: Product distribution after photolyzing phenanthridine 8 in dichloromethane containing TME at 300nm for 2 hours at 42 °C. This data is ± 4%.
Figure 2.11: A plot of [4]/[3] vs. [TME] obtained from phenanthridene 8 in CH$_2$Cl$_2$ at
(•) 9°C; (■) 13°C; (◆) 23°C; (▲) 33°C; and (○) 42°C at 300nm.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Temperature (K)</th>
<th>$1/T \times 10^{-3}$</th>
<th>Slope = $k_d / k_r$</th>
<th>$\ln (k_d / k_r)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>42</td>
<td>315</td>
<td>3.17</td>
<td>1.08</td>
<td>0.07</td>
</tr>
<tr>
<td>33</td>
<td>306</td>
<td>3.27</td>
<td>1.40</td>
<td>0.33</td>
</tr>
<tr>
<td>23</td>
<td>296</td>
<td>3.38</td>
<td>2.05</td>
<td>0.72</td>
</tr>
<tr>
<td>13</td>
<td>286</td>
<td>3.50</td>
<td>3.08</td>
<td>1.12</td>
</tr>
<tr>
<td>9</td>
<td>282</td>
<td>3.55</td>
<td>3.48</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Table 2.14: The data tabulated from Figure 2.5.
From Figure 2.12, values of $E_a^A - E_a^R = 1.6$ kcal/mol and $A^{A}/A^{R} = 10^{-4.3}$ M$^{-1}$ can be deduced. In literature, it has been reported that $E_a^R = 5.8$ kcal/mol and $A^{R} = 10^{11.9}$ s$^{-1}$. This indicates that $\Delta E_a^A = 4.2$ kcal/mol, which seems rather large, and $A^{A} = 10^{7.6}$ s$^{-1}$, which seems reasonable. Either our measured value of $\Delta \Delta E_a$ is too high (which seems unlikely given that it is only +1.6 kcal/mol) or the reported value of $\Delta E_a$ of the rearrangement is too large.
2.2.5 Photolysis of β-chlorostyrene 3 in presence of TME

The E/Z ratio of the β-chlorostyrenes produced on photolysis was studied as a function of precursor, photolysis wavelength, and solvent in the presence of TME. The results seem to be sensitive to each experimental parameter.

It was possible to synthesize a 90/10 mixture of 3 E/Z. The E/Z ratio varies upon photolysis (280-320 nm) in CH₂Cl₂ at 15°C (Table 2.15) and photolysis (320-380 nm) in CH₂Cl₂ at 15°C (Table 2.16) in the presence of TME (Figure 2.13).

<table>
<thead>
<tr>
<th>[TME] (M)</th>
<th>GC peak area of 3E</th>
<th>GC peak area of 3Z</th>
<th>Ratio² of [E]/[Z]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.21</td>
<td>0.13</td>
<td>1.6</td>
</tr>
<tr>
<td>0.2</td>
<td>0.27</td>
<td>0.14</td>
<td>1.87</td>
</tr>
<tr>
<td>0.4</td>
<td>0.21</td>
<td>0.13</td>
<td>1.55</td>
</tr>
<tr>
<td>0.8</td>
<td>0.20</td>
<td>0.10</td>
<td>2.00</td>
</tr>
<tr>
<td>1</td>
<td>0.19</td>
<td>0.09</td>
<td>2.21</td>
</tr>
<tr>
<td>1.4</td>
<td>0.20</td>
<td>0.08</td>
<td>2.52</td>
</tr>
<tr>
<td>1.8</td>
<td>0.26</td>
<td>0.07</td>
<td>3.45</td>
</tr>
<tr>
<td>2.2</td>
<td>0.29</td>
<td>0.07</td>
<td>4.25</td>
</tr>
</tbody>
</table>

(a) GC peak area ratios. Since 3E and 3Z are isomers, we are assuming the response factors of the two to be the same. Hence, these values are taken as ratios of concentrations.

Table 2.15: Product distribution after photolyzing 3 in dichloromethane containing TME at 300nm for 2 hours at 15°C. This data is ± 4%.
(a) GC peak area ratios. Since 3E and 3Z are isomers, we are assuming the response factors of the two to be the same. Hence, these values are taken as ratios of concentrations.

Table 2.16: Product distribution after photolyzing 3 in dichloromethane containing TME at 350nm for 48 hours at 15 °C. This data is ±4%.

<table>
<thead>
<tr>
<th>[TME] (M)</th>
<th>GC peak area of 3E</th>
<th>GC peak area of 3Z</th>
<th>Ratio$^3$ of [E]/[Z]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.10</td>
<td>0.47</td>
<td>0.22</td>
</tr>
<tr>
<td>0.2</td>
<td>0.09</td>
<td>0.46</td>
<td>0.20</td>
</tr>
<tr>
<td>0.4</td>
<td>0.08</td>
<td>0.46</td>
<td>0.17</td>
</tr>
<tr>
<td>0.8</td>
<td>0.06</td>
<td>0.42</td>
<td>0.14</td>
</tr>
<tr>
<td>1</td>
<td>0.13</td>
<td>0.40</td>
<td>0.34</td>
</tr>
<tr>
<td>1.4</td>
<td>0.28</td>
<td>0.20</td>
<td>1.37</td>
</tr>
<tr>
<td>1.8</td>
<td>0.30</td>
<td>0.17</td>
<td>1.81</td>
</tr>
<tr>
<td>2.2</td>
<td>0.32</td>
<td>0.16</td>
<td>2.04</td>
</tr>
</tbody>
</table>
Figure 2.13: A plot of 3E/3Z as a function of TME obtained by the photolysis of a 90% 3E in dichloromethane at (■) 300nm and (♦) 350nm.

Upon photolysis of 3 and TME, a photoproduct was formed in low percentage yield. The product was characterized by GC-MS and its fragmentation pattern (Figure 2.14) was consistent with that of [2+2] cycloadduct 17.
Figure 2.14: High resolution Mass Spectrum of [2+2] cycloadduct 17.

The E/Z ratio of 3 also changes from 90/10 E/Z to 50/50 in CH$_2$Cl$_2$ and to 33/66 in isooctane upon photolysis in the absence of TME. Considering that 3 both photoisomerizes and reacts with TME under our photolysis conditions, we feel it is unwise to attach much significance to the variation of the E/Z ratio in the presence of TME. 3Z and 3E may react with TME at different rates. Furthermore, 3Z and 3E may react with TME to form a biradical, which can fragment with net isomerization of the alkene (Scheme 2.8). Thus, we feel the variation of the 3 E/Z ratio with TME is of little mechanistic significance.
Previously, it has been postulated that the second pathway to β-chlorostyrene product is formed by a "Rearrangement in Diazirine Excited State" mechanism.\textsuperscript{34,47} Irradiation of the nπ* band of a diazirine leads to opening of the three membered ring to form a diradical\textsuperscript{27} which we postulate can migrate hydrogen in concert with nitrogen extrusion (Scheme 1.11). Of all the decay routes possible for diradical 6 this is surely the most exothermic route.\textsuperscript{33,34} In principal, biradical 6 can also be formed upon pyrolysis of diazirine 1.
It is also possible that hydrogen migrates in concert with ring opening of the
diazirine excited state to form biradical 16 (Scheme 2.9), although this process has not
been considered explicitly by theory.

\[
\begin{align*}
\text{PhCH}=\text{C} & \quad \text{PhCH}\
\text{Cl} & \quad \text{Cl} \\
\text{N} = \text{N} & \quad \text{N} = \text{N}
\end{align*}
\]

**Scheme 2.9**

Bonneau, *et al.* have made the reasonable suggestion that the importance of the
RIES mechanism varies with the structure of the diazirine.\(^{59}\) In fact, it is claimed that the
RIES mechanism accounts for only 6% of the disappearance of benzylchlorodiazirine.\(^{59}\)
It was further claimed in this study that the RIES mechanism cannot explain various
relative rate measurements.

Photolysis (320-380 nm) of diazirine 1 and phenanthridine 8 in a 1/1 (v/v)
mixture of TME and CH\(_2\)Cl\(_2\) at ambient temperature leads to ratios of [4]/[3] of 2/1 and
16/1, respectively. Under these conditions, nearly all photogenerated carbene should be
trapped with TME before it can rearrange\(^{16,58}\) but this is observed only with precursor 8.
As the quantum yield of diazo formation is 7.5% and the quantum yield of disappearance
of diazirines are typically unity,\(^{17}\) a 26% yield of β–chlorostyrene remains to be
explained with diazirine precursor 1. Although we cannot quantify the importance of
RIES to the 26% yield of the non-carbene pathway we posit that RIES makes a
substantial contribution to the second pathway to olefinic product with
benzylchlorodiazirine 1.
3.1 Review of Carboalkoxycarbenes

Carboalkoxycarbenes have been studied extensively since the early work by Doering and co-workers.\(^{35}\) They are an important class of synthetically useful intermediates as they can be generated from their readily available precursors such as \(\alpha\)-diazo esters. These precursors can undergo thermolysis or photolysis to produce carboalkoxycarbenes, which undergo typical carbene reactions and Wolff rearrangements.

3.1.1 Addition reactions

The addition of carboalkoxycarbenes to olefins has been a well-researched area for over a century. Buchner first reported the thermal decomposition of ethyl diazoacetate in presence of styrene to form two isomeric cyclopropyl adducts.\(^{3}\) It has been found that \(\alpha\)-diazo esters react with olefins via two major pathways. In the first
route, upon excitation, α-diazo esters decompose into carboalkoxy-carbenes followed by addition to the olefin. The second route involves a 1,3-dipolar addition of the diazo to the olefin to form a pyrazoline 43, which then decomposes into the cyclopropane adducts. Kirmse reported that the latter pathway is observed with electron deficient olefins.⁷

\[
\begin{align*}
\text{Scheme 3.1}
\end{align*}
\]

3.1.2 Insertions reactions

(a) C-H bond insertion. C-H insertion reactions were first examined systematically by Doering and Knox in 1961.⁷ They compared the selectivity of carboethoxy-carbene with methylene for various C-H insertion reactions. It was evident that carboethoxy-carbene was more selective in its C-H insertion reactions than methylene (Table 3.1). The Doering group attributed these results to the stabilization of carboethoxy-carbene by the ester group. This stabilization increases the lifetime of the
carbene, which gives it more time to differentiate between various types of C-H bonds, leading to better selectivity as per the reactivity-selectivity principle.

<table>
<thead>
<tr>
<th>Hydrocarbons</th>
<th>Ratio</th>
<th>:CH₂</th>
<th>:CHCO₂Et</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₃C=C–C–C–CH₃</td>
<td>3⁰/1⁰</td>
<td>1.2</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>CH₃CH₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₃C=C–C–CH₃</td>
<td>3⁰/1⁰</td>
<td>NA</td>
<td>3.1</td>
</tr>
<tr>
<td>H₃C=C–C–C–CH₃</td>
<td>2⁰/1⁰</td>
<td>1.0</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Table 3.1: Relative reactivities of methylene and carboethoxycarbene towards C-H insertion.

(b) O-H bond insertion. Apart from C-H bond insertion, carboalkoxycarbene also insert into O-H bonds to form ethers. Kirmse found that the insertion of carboalkoxycarbene into O-H bonds takes place first via an ylide formation. When dimethyl diazoglutaconate 44 was photolyzed in methanol, it gave products 46, 47 and 48 in a 1:1:1 ratio. While products 46 and 47 were formed by H-migration and ring closure respectively, product 48 was formed via ylide 45 which affords the more stable olefin by a proton transfer. The fact that product 49 was not observed, further confirmed that the O-H insertion takes place via an ylide mechanism.
3.1.3 Wolff rearrangement

Prior to 1965, carboalkoxycarbenes were thought to undergo only intermolecular reactions such as addition and insertion reactions (section 3.1.1 and 3.1.2). In 1965, Westheimer reported the first evidence of the Wolff Rearrangement (WR) of $\alpha$-diazo esters. Wolff rearrangement involves the decomposition of an $\alpha$-diazo carbonyl compound under photochemical or thermal conditions to generate a ketene. These ketenes could be trapped with a wide variety of nucleophiles to form carboxylic acids, esters or amides (Scheme 3.3). Due to these versatile reactions, organic chemists find the Wolff rearrangement to be a very important synthetic tool. It represents a key step in the Arndt-Eistert sequence for the one carbon homologation of carboxylic acids. Wolff
rearrangement also serves as an excellent tool for ring contraction and forming strained rings.\textsuperscript{38-41}

\begin{center}
\begin{align*}
&\begin{array}{c}
\text{hv} \\
\end{array} \\
&\begin{array}{c}
\text{WR} \\
\end{array} \\
&\begin{array}{c}
\text{ROH} \\
\end{array} \\
&\begin{array}{c}
\text{RNH}_2 \\
\end{array}
\end{align*}
\end{center}

\textbf{Scheme 3.3}

3.2 Mechanistic aspects of carbomethoxycarbene chemistry

Apart from their wide application in the field of synthetic organic chemistry, carboalkoxycarbenes have been of great interest to physical organic chemists. For the past three decades, there has been a considerable debate over the existence of diazo and diazirine excited states.\textsuperscript{21-23, 42} Some groups have provided considerable evidence for rearrangements in the excited state of diazocarbonyl compounds.\textsuperscript{43} Recently, quite a few groups have studied different mechanistic aspects of methyl 2-diazo-(2-naphthyl)acetate
50. The Platz group has performed Laser Flash Photolysis studies on 50, Bally and Zhu have examined this carbene by computational methods and studied the photochemical behavior of 50 in an Argon matrix at 10K. The McMahon group has used matrix EPR spectroscopy to study the triplet carbene, and Toscano and Yuzawa have performed time resolved IR studies to estimate the singlet-triplet energy gap of NAC (naphthylcarbomethoxycarbene).

\[
\begin{align*}
\text{50} & \quad \text{hv} \quad \text{NAC} \\
& \quad \text{hv} \quad \text{hv}
\end{align*}
\]

Scheme 3.4

3.2.1 Matrix studies

Bally and Zhu have reported that irradiation of 50 in an Argon matrix at 450 nm for 2 hours, results in an absorption spectrum that reveals the disappearance of the 320 nm band of the diazo precursor. This is followed by the rise of a new absorption band at around \(\lambda=360\) nm and \(\lambda>515\) nm. Upon subsequent irradiation of the sample with \(\lambda>515\) nm, the 360 nm band disappears and a new band is generated at 420 nm.

Upon the photolysis of diazo precursor 50, Bally and Zhu assigned the 360 nm band to the triplet state of naphthylcarbomethoxycarbene (\(^3\)NAC) and the 420 nm band to
the singlet naphthylcarboxethoxycarbene (\(^1\text{NAC}\)). They based their conclusions on the following observation:

(a) They found that photolysis of the sample containing \(^1\text{NAC}\) at 450 nm, or simply standing overnight at 12K in the dark, regenerates the 360 nm band (\(^3\text{NAC}\)) almost quantitatively. This evidence demonstrates photochemical and thermal interconversion from the singlet to the triplet species.

(b) \textit{Ab initio} calculations using the B3LYP/6-31G* level of theory shows a reasonable match with the experimental IR spectra for \(^3\text{NAC}\) and \(^1\text{NAC}\).

(c) IR spectroscopy showed that upon annealing the sample containing either \(^3\text{NAC}\) or \(^1\text{NAC}\) in the presence of CO and O\(_2\) gives keto ketene and carbonyl oxide respectively (Scheme 3.5). Also, photolysis of a sample that contains either species eventually gives IR spectra typical of a ketene with a strong absorption at 2100 cm\(^{-1}\). The ketene is formed as a result of Wolff rearrangement of either the singlet or triplet carbene.
Interconversion from the triplet to the singlet state of naphthylcarbomethoxy carbene (NAC) has also been demonstrated by low temperature EPR spectroscopy. McMahon and co-workers\(^{45}\) demonstrated that upon photoexcitation (\(\lambda > 515 \text{ nm}\)), the triplet state undergoes a reversible transformation to an EPR silent species (presumably, the singlet carbene). This "invisible" species can relax back to the triplet state either thermally or photochemically.
Bally and Zhu predict that diazo precursor 50 possesses a planar structure. The B3LYP/6-31G* optimized structures of the singlet and triplet carbenes are shown in Figure 3.1.

![Figure 3.1](image)

**Figure 3.1:** B3LYP/6-31G* optimized geometry of triplet (a) and singlet (b) naphthylcarbomethoxycarbene (NAC).

The figure illustrates that the COOMe moiety in the $^1$NAC is orthogonal to the plane of the naphthyl ring whereas $^3$NAC is planar. Photolysis of planar diazo compound 50 in a matrix gives a planar triplet carbene, which can be converted to its singlet state photochemically. The orthogonal structure allows the filled $\sigma^2$ orbital of the carbene to
conjugate with the \( \pi \) system of the carbonyl group. As the singlet state relaxes to the triplet ground state, it undergoes a drastic geometric change in the rigid matrix. It forces the ester group to be co-planar with the naphthyl ring. Based on the structural differences, slow intersystem crossing was explained. This effect is magnified in a rigid matrix at very low temperatures where \(^1\)NAC shows reasonable stability at 10K \((t_{1/2} = 2\) days). It was unusual for the higher lying singlet carbene to possess such a remarkable stability in the matrix. This was the first characterization of an excited state of a carbene by matrix spectroscopy.

3.2.2 Chemical Trapping and Laser Flash Photolysis

The Platz group\(^44\) has reported Laser Flash Photolysis (LFP) and solution-phase chemical analysis studies on methyl 2-diazo-(2-naphthyl)acetate (50). The results indicate that upon photolysis, diazo compound 50 releases singlet carbene \(^1\)NAC, which relaxes to the lower energy triplet state \(^3\)NAC within 350ps-1ns. They have addressed other issues related to naphthylcarbomethoxycarbene (NAC), including (a) evidence that Wolff rearrangement takes place via the carbene and not the diazo excited state, (b) the lifetime of triplet in different solvents and (c) the barrier to Wolff rearrangement.

LFP of 50 at low temperature and ambient temperature produced transient spectra, which could not be associated with the excited state of the diazo precursor. This led to the postulate that ketene 51, which is a product formed from the Wolff rearrangement (WR), is formed predominantly from the spin-equilibrated carbene rather than from a diazo excited state. This postulate was supported by chemical trapping experiments.
Platz's findings were consistent with Toscano's TRIR data, which will be discussed in the next section.

When diazo precursor 50 was photolyzed in Freon-113 with ethanol (0.04M-0.1M) as the trapping agent, Lithovorik determined that ethers 52 and 53 were formed. It was proposed that ether 52 was formed from trapping of $^1\text{NAC}$ while 53 was formed from ketene 51. The ratio of 52/53 as a function of ethanol concentration is shown in Table 3.2.

\[ \text{Scheme 3.6} \]
Table 3.2: Ratio of $52/53$ as a function of ethanol concentration.

The results demonstrate that ketene 51 is derived predominantly from the carbene (NAC) rather than the diazo excited state. From scheme 3.6, it is clear that the ether 53 is derived from a secondary reactive intermediate (ketene 51) which is produced from a primary intermediate (NAC) that reacts with ethanol. A plot of $52/53$ vs. [ethanol] was found to be linear clearly showing that formation of 53 is directly related to the ethanol concentration. In other words, ketene 51 arises from the carbene with very little, if any, contribution from the diazo excited state.

Laser Flash Photolysis (LFP) of 50 in Freon-113 produced a transient spectrum that had a lifetime of 2.2μs at ambient temperature. A similar transient was observed when the experiment was repeated in hexafluorobenzene and the lifetime of the transient was determined to be 2.5μs. The transient observed by LFP was attributed to the triplet ground state of naphthylcarbomethoxycarbene, $^3\text{NAC}$, based on the work of McMahon, Bally and Zhu. This group established that the triplet state is the ground state of the naphthylcarbomethoxycarbene (Section 3.2.1). Other evidence supported the assignment of the transient spectrum to $^3\text{NAC}$. The transient spectrum reported by Platz was very similar to the spectra obtained in an Argon matrix at 10K that was reported by Bally and Zhu. There was also the similarity of the transient spectrum to that of 2-naphthylcarbene ($\lambda_{\text{max}} = 362, 380\text{nm}$) reported by Horn et al. Even the lifetime
measurement of $^3$NAC was similar to the lifetime of triplet phenylcarbomethoxycarbene as reported by Tomioka, et al. According to Tomioka's work, triplet phenylcarbomethoxycarbene has a lifetime of 461ns in Freon-113 and 433ns in hexafluorobenzene.

Yet another experiment supported the spectroscopic assignment of Platz and co-workers. The lifetime of the transient was found to be shorter in the presence of oxygen. LFP of 50 in aerated Freon-113 produces a transient spectrum of carbonyl oxide 58. This was consistent with the findings of Bally and Zhu who observed 58 in an Argon Matrix at 10K.

Platz and co-workers found that the lifetime of this transient was dependent on the nature of the solvent in which it was studied. In reactive solvents such as CCl$_4$ the lifetime is short (150ns). A steady-state photolysis of 50 (rayonet, 350nm) in CCl$_4$ produced a complex mixture of products. The carbene formed a spectrum of stable products by abstracting a chlorine atom from CCl$_4$, which is a rich chlorine atom donor. This is not observed when photolysis is performed in Freon-113, which is a poor chlorine atom donor. Thus, it was concluded that the lifetime of $^3$NAC in Freon-113 is controlled by a unimolecular process, specifically, the Wolff Rearrangement.
The lifetime of triplet carbene $^{3}\text{NAC}$ was measured as a function of temperature, between of 249 K (3.6$\mu$s) and 313 K (1.5$\mu$s). An Arrhenius treatment of the data could not be fit to a straight line. This type of non-linear behavior of an Arrhenius plot in carbene reactions have been observed previously and explanations have been advanced.\textsuperscript{50} It has been proposed that for long-lived carbenes, decay at high temperatures is classical and an Arrhenius treatment will be linear. But at lower temperatures, either quantum mechanical tunneling occurs or the data are associated with reactions of carbene with oxygen, adventitious water or even the diazo precursor. Since all of these processes have little temperature dependence, at lower temperatures, there is not much change in the lifetime of carbene. When the same experiment was repeated in hexafluorobenzene, the Arrhenius plot of $(1/\tau)$ vs. $1/T$ could be fitted to a straight line to give $E_a=3.4$ kcal/mol.

Platz and co-workers determined that $^{3}\text{NAC}$ was formed within 1 ns of the laser pulse and is long lived with a lifetime of several microseconds in Freon-113 and hexafluorobenzene. Since singlet to triplet intersystem crossing (ISC) usually proceeds on the timescale of hundreds of picoseconds, it was clear that spin equilibration of NAC was complete in Freon-113 and hexafluorobenzene and was faster than Wolff rearrangement to form ketene 51 (Scheme 3.7). From Toscano's determination of the singlet-triplet gap ($\Delta G = 0.2$ kcal/mol) in solution \textit{vide infra},\textsuperscript{46} Platz and co-workers have determined the activation energy to Wolff rearrangement.

If $k_{WR}$ is the rate of formation of ketene 51 and $K$ is the equilibrium constant for the singlet to triplet interconversion, then the rate constant of the Wolff Rearrangement is $k_{WR}K$ and the observed barrier will be $\Delta E_a^{WR} + \Delta H_{ST}$, where $\Delta E_a^{WR}$ is the barrier to Wolff Rearrangement and $\Delta H_{ST}$ is the enthalpy difference between $^{1}\text{NAC}$ and $^{3}\text{NAC}$.\textsuperscript{70}
From this equation, Platz and co-workers calculated the activation energy to WR of \(^1\)NAC to be close to 3.4 kcal/mol. This was consistent with results reported by Bally and Zhu\(^45\) in an Argon Matrix at low temperature, where they found that \(^1\)NAC does not rearrange to ketene 51 at low temperature. This demonstrates that at low temperatures, there is a barrier to Wolf Rearrangement of the carbene.

3.2.3 Time Resolved Infrared Spectroscopy

Toscano and co-workers have studied the photochemistry of diazo compound 50 by time resolved infrared (TRIR) spectroscopy.\(^46\) The detection of IR bands from both singlet and triplet states of carbene NAC, following laser excitation of diazo 50 allowed
the first direct measurement of the singlet-triplet gap in solution at ambient temperatures. Furthermore, they directly monitored the rate of growth of ketene which revealed that the ketene arises almost exclusively from a carbene intermediate and not from the excited state of diazo. The lifetime of NAC by TRIR spectroscopy were found to be significantly shorter than that reported by Platz and co-workers from their LFP studies of NAC. This discrepancy will be explained later.

Laser excitation of in argon-saturated Freon-113 resulted in a spectrum in the region 1870-1550 cm\(^{-1}\). The band at 1650 cm\(^{-1}\) was attributed to triplet carbene (NAC) while those at 1620 and 1584 cm\(^{-1}\) were attributed to the singlet carbene (NAC). The negative band at 1715 cm\(^{-1}\) represented the depletion of diazo compound. This assignment was in agreement with results of Bally and Zhu obtained by a low temperature matrix IR experiment. Toscano, et al. further confirmed the identities of these positive bands by kinetic studies. Platz and co-workers already established that the singlet-triplet spin equilibration of carbene (NAC) is much faster than reaction from either spin state. Toscano's observation was consistent with those results. All three positive bands decayed at equal rates. The kinetic data at 1650 cm\(^{-1}\) indicated that the lifetime of NAC was 830ns.

The lifetime of NAC determined by TRIR analysis was much shorter than the lifetime reported by Platz and co-workers (2.2 \(\mu\)s) in the LFP studies discussed in the previous section. This observation was explained as follows. TRIR studies require a high concentration of diazo compound in order to achieve comparable optical densities at the photolysis wavelength (266nm). It was found that the lifetime of carbene depended upon the initial concentration of diazo compound. When the rate constant
of carbene decay at 1650 cm$^{-1}$ was measured in Freon-113 as a function of the concentration of diazo compound 50, the kinetics could be explained by the following pseudo first-order equation:

$$k_{\text{obsd}} = k_0 + k_{\text{diazo}}[1]$$  \hspace{1cm} \text{equation (3.1)}

where $k_{\text{diazo}}$ is the second-order rate constant for reaction of diazo compound 50 with carbene (NAC) to form azine 55 (Scheme 3.8) and $k_0$ is the rate of carbene decay at infinitely dilute concentrations of diazo 50.

\[ \begin{align*}
\text{2-Np} \quad \text{OMe} \quad \text{2-Np} \\
\text{N} \quad \text{2-Np} \quad \text{OMe} \quad \text{O} \\
\text{50} \\
\text{hv} \\
\text{2-Np} \quad \text{OMe} \quad \text{2-Np} \\
\text{55} \\
\end{align*} \]

\[ \begin{align*}
\text{2-Np} \quad \text{OMe} \quad \text{2-Np} \\
\text{3NAC} \\
\text{hv} \\
\text{2-Np} \quad \text{OMe} \quad \text{2-Np} \\
\text{1NAC} \\
\text{hv} \\
\text{OMe} \quad 2-\text{Np} \\
\text{51} \\
\end{align*} \]

\[ \begin{align*}
\text{2-Np} \quad \text{OMe} \quad \text{2-Np} \\
\text{55} \\
\end{align*} \]  

\text{Scheme 3.8}
At low concentrations, the second term in equation 3.1 disappears. At higher concentrations of 50 (5mM), a new long lived IR band appears at 1746 cm\(^{-1}\) which is formed at the same rate as the IR bands of the carbene decay. On the basis of the kinetics and the previously reported IR spectrum of the phenyl analogue,\(^{51}\) this band was assigned to azine 55. Thus, from equation 3.1, at higher concentration of diazo 50, \(k_{\text{obs}}\) will be higher and hence, the lifetime would appear to be shorter.

Toscano et al also examined the reaction of NAC in reactive solvents such as hexane and acetonitrile. The lifetime of \(^3\)NAC in hexane decreased to 130ns, and to 420ns in acetonitrile. The quenching of \(^3\)NAC by oxygen reduced the lifetime to 100ns. These results were in agreement with the results reported by Platz and co-workers.\(^{44}\)

The observation of IR signals for both singlet and triplet NAC allowed Toscano and co-workers to experimentally estimate the singlet/triplet energy gap in solution. This was the first time a carbene singlet /triplet gap was directly measured in solution. Previously, product studies and kinetic measurements had been employed for the estimate of these splittings which usually relied on many assumptions concerning the spin selectivity of carbene trapping agents.\(^{51}\) Toscano and co-workers found that the relative intensities of the IR signals of the singlet and the triplet NAC were directly related to the extinction coefficient of the singlet and the triplet IR bands. Bally and Zhu observed that at 12K, \(^1\)NAC thermally relaxes to \(^3\)NAC and calculated the ratio of \(^3\)NAC/\(^1\)NAC to be 1.5.\(^{44}\) From this data and the TRIR-determined ratio of \(^3\)NAC/\(^1\)NAC being 2.1 at 21 °C in Freon-113 solution, Toscano and co-workers found the equilibrium constant to be 1.4. This value eventually lead to the standard free energy difference of 0.2 kcal/mol, with the triplet carbene being lower in energy.
Similar to the finding of Platz and co-workers\textsuperscript{44} and Bally and Zhu,\textsuperscript{45} Toscano, \textit{et al.} found that ketene 51 arises entirely from the carbene and not the excited state of the diazo precursor. TRIR experiments elucidated that the rate of the ketene growth equaled the rate of carbene decay in both Freon-113 and acetonitrile, leading to the conclusion that ketene 51 arises entirely from the carbene. It has been shown previously that concerted rearrangement to ketene from an excited state is facile from the \textit{syn} configuration, whereas carbene is produced from the \textit{anti} form of the precursor.\textsuperscript{52-54} Thus, the preferred conformation of 50 (\textit{anti}), upon photolysis leads to efficient production of carbene NAC which eventually rearranges to ketene 51.

Toscano, \textit{et al.} also observed a relatively weak band at 1840 cm\textsuperscript{-1} several microseconds after laser photolysis of diazo compound 50. They assigned this band to $\beta$-lactone 56. This observation was in agreement with the 1846 cm\textsuperscript{-1} band detected by low-temperature matrix IR experiments of Bally and Zhu\textsuperscript{45} and steady state photolysis of diazo compound 50 by Platz and co-workers.\textsuperscript{44} Bally and Zhu observed that in an Argon matrix, $\beta$-lactone 56 is converted to 2-vinylnaphthalene 57 and carbon dioxide (Scheme 3.8). It was not possible to detect 2-vinylnaphthalene 57 in Argon by IR spectroscopy, but the formation of carbon dioxide in the matrix was clear. Consequently, after steady state photolysis of diazo compound 50, Platz and co-workers reported formation of 2-vinylnaphthalene 57 rather than $\beta$-lactone 56.\textsuperscript{44} To determine if the formation of $\beta$-lactone 56 was mediated by a carbene intermediate or from the excited state of diazo compound 50, Toscano and co-workers monitored the growth of $\beta$-lactone 56 by TRIR spectroscopy. It was understood that formation of $\beta$-lactone 56 via an excited state of diazo compound 50 would be associated with a fast, unresolvable growth, whereas
formation via a carbene intermediate would be revealed by rate of growth of β-lactone 56
equal to rate of decay of carbene. Toscano and co-workers reported kinetic traces that
indicated that the rate of growth of β-lactone 56 was equal to rate of decay of carbene
demonstrating that β-lactone 56, like ketene 51, arises predominantly from carbene rather
than the excited state of diazo compound 50.

\[
\text{Scheme 3.9}
\]
CHAPTER 4

REACTION OF
2-NAPHTHYLCARBOMETHOXYCARBENE
WITH TETRAHYDROFURAN

4.1 Review

The reactions of carbenes with ether to form ylides has been long considered in the literature. However, until recently, there was no direct spectroscopic evidence that was reported. In 1996, Wang reported the first direct observation of a carbene-THF ylide during the Laser Flash Photolysis of 2-diazo-2- (2-naphthyl) acetate 50. The transient absorption signals obtained by Wang demonstrated two absorption signals, one at 330 nm and other at 380 nm. He assigned the first band to the carbene-THF ylide 59.

![Scheme 4.1](image)

Scheme 4.1
Wang assigned the band at 380 nm to 2-naphthyl carbomethoxymethyl radical 60. This assignment was based on the studies on 2-naphthyl diazomethane, reported by Horn and Chateauneuf who found that Laser Flash Photolysis of 2-naphthyl diazomethane in pentane generated 2-naphthyl methyl radical.48a

\[
\begin{array}{c}
\text{H} \\
\text{CO}_2\text{CH}_3 \\
\end{array}
\]

The absorption maxima at 330 nm exhibited biphasic growth kinetics containing both a fast and a slow process (Figure 4.1). The rate of growth of the fast process was beyond the time resolution of LFP system in use at that time, but the rate of growth of the slow process was dependent on the concentration of THF. Wang assigned the fast component to the growth of the ylide from the initially formed singlet carbene and assigned the slow growth to the formation of the carbene-THF ylide from the triplet carbene.

![Figure 4.1](image)

**Figure 4.1:** Rate of growth of 330 nm band in Freon-113 in presence of THF (0.05M).
4.2 Laser Flash Photolysis of 2-diazo-2-(2-naphthyl) acetate 50

LFP of diazo compound 50 in neat tetrahydrofuran (THF) produces the transient spectrum shown in Figure 4.2. The spectrum exhibits a sharp band at 330nm, which is assigned to the carbene-THF ylide on the basis of Wang's assignment.\textsuperscript{70}

![Transient absorption spectrum](image)

**Figure 4.2:** The transient absorption spectrum obtained upon LFP (308nm) of diazo compound 50 in de-aerated, neat THF at ambient temperature. The spectrum was recorded 200ns after the laser excitation, over a window of 200ns.

LFP of diazo compound 50 in Freon-113 in 5.0M tetrahydrofuran (THF) produces the same transient spectrum when the spectrum is recorded 0ns after the laser excitation (Figure 4.3) or 3\(\mu\)s after laser excitation (Figure 4.4).
Figure 4.3: The transient absorption spectrum obtained upon LFP (308nm) of diazo compound 50 in de-aerated Freon-113 containing 5.0M THF at ambient temperature. The spectrum was recorded 0 ns after the laser excitation, over a window of 200ns.

Figure 4.4: The transient absorption spectrum obtained upon LFP (308nm) of diazo compound 50 in de-aerated Freon-113 containing 5.0M THF at ambient temperature. The spectrum was recorded 3μs after the laser excitation, over a window of 200ns.
4.3 Ylides formed with other ethers:

Since it has been recognized that carbenes react with tetrahydrofuran to form an ylide, other ethers were studied to determine the generality of this observation. The following five ethers were chosen for the study:

1. 1,4-Dioxane
2. 1,2-Dimethoxyethane
3. 15-Crown-5
4. Trimethylene oxide
5. Diethyl ether

Figure 4.5: The transient absorption spectrum obtained upon LFP (308nm) of diazo compound 50 in de-aerated neat 1,4-dioxane at 308nm at ambient temperature. The spectrum was recorded 400ns after the laser excitation, over a window of 200ns.
Figure 4.6: The transient absorption spectrum obtained upon LFP (308nm) of diazo compound 50 in de-aerated neat 1,2-dimethoxyethane at ambient temperature. The spectrum is recorded 400ns after the laser excitation, over a window of 200ns.

Figure 4.7: The transient absorption spectrum obtained upon LFP (308nm) of diazo compound 50 in de-aerated neat 15-crown-5 at ambient temperature. The spectrum is recorded 400ns after the laser excitation, over a window of 200ns.
Transient absorption at 330nm was not observed upon LFP of diazo compound 50 in the presence of trimethylene oxide and diethylether.

Figure 4.8: The transient absorption spectrum obtained upon LFP (308nm) of diazo compound 50 in de-aerated neat trimethylene oxide at ambient temperature. The spectrum was recorded 400ns after the laser excitation, over a window of 200ns.

Figure 4.9: The transient absorption spectrum obtained upon LFP (308nm) of diazo compound 50 in de-aerated neat diethyl ether at ambient temperature. The spectrum was recorded 400ns after the laser excitation, over a window of 200ns.
4.4 Study of the rate of formation of carbene-THF ylide 59 as a function of temperature

It was observed that the rate of formation of carbene-THF ylide 59 does not depend upon temperature over the investigated range.

![Graph](image)

**Figure 4.10**: Rate of growth of transient absorption at 330nm observed in neat THF at 23.2 °C.

![Graph](image)

**Figure 4.11**: Rate of growth of transient absorption at 330nm observed in neat THF at 7.9 °C.
Figure 4.12: Rate of growth of transient absorption at 330nm observed in neat THF at -3.0 °C.

Figure 4.13: Rate of growth of transient absorption at 330nm observed in neat THF at -33.0 °C.
Figure 4.14: Rate of growth of transient absorption at 330nm observed in neat THF at -47.0 °C.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Temperature (K)</th>
<th>(k_{\text{growth}} \times 10^{-9})</th>
<th>(1/k_{\text{growth}} = \tau \text{ (ns)}^{(a)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.2</td>
<td>296.2</td>
<td>0.10</td>
<td>10</td>
</tr>
<tr>
<td>7.9</td>
<td>288.8</td>
<td>0.25</td>
<td>4.0</td>
</tr>
<tr>
<td>-3.0</td>
<td>270</td>
<td>0.18</td>
<td>5.6</td>
</tr>
<tr>
<td>-33</td>
<td>240</td>
<td>0.25</td>
<td>4.0</td>
</tr>
<tr>
<td>-47</td>
<td>226</td>
<td>0.19</td>
<td>5.3</td>
</tr>
</tbody>
</table>

(a) The data has error bar of ± 2ns.

Table 4.1: The lifetime of NAC at various temperatures.

As is evident from Table 4.1, there is not much change in the lifetime (\(\tau\)) of the carbene with the change in temperature. This is discussed in section 3.2.2.
4.5 Study of the rate of decay of carbene-THF ylide 59 at different THF concentrations

The rate of growth of carbene-THF ylide 59 was studied to determine if the rate of decay was dependent on the concentration of the trapping agent, THF. The carbene-THF ylide 59 was found to be long-lived and exhibited minimal decay at both 0.05M THF and 5.0M THF. A small decay was observed at low THF concentrations. The rate of decay did not depend on [THF] but the amplitude of this decay was [THF] dependent. We can not explain this observation at this time.

![Figure 4.15: Rate of decay of transient absorption at 330nm observed in 0.05M THF at 23 °C.](image-url)
Figure 4.16: Rate of decay of transient absorption at 330nm observed in 5.0M THF at 23 °C.

4.6 Photochemistry of 2-diazo-2(2-naphthyl) acetate

Photolysis of the 2-diazo-2(2-naphthyl) acetate (50) in neat tetrahydrofuran produces four carbene-derived products 21, 22, 23, and 24. These products were analyzed by GC-MS spectrometry (Figure 4.17) and were isolated and characterized by $^1$H NMR, $^{13}$C NMR and high resolution mass spectrometry.
Figure 4.17: Total ion chromatogram obtained after photolysis of diazo compound 50 in tetrahydrofuran.
Scheme 4.2

Table 4.2: Relative yields of products from decomposition of 2-diazo-2- (2-naphthyl) acetate (50) in tetrahydrofuran.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>21</th>
<th>22</th>
<th>23</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>6.7</td>
<td>14.6</td>
<td>2.2</td>
<td>1</td>
</tr>
</tbody>
</table>
Based on the spectral characterization of the photo-products, further evidence of the formation of carbene-THF ylide 59 was provided (Appendix C). While product 21, 22 and 24 were formed via a carbene-THF ylide, only a small percentage of product 23 was formed via C-H insertion of NAC to THF.

Product 21 and 22 demonstrate the existence of a THF ylide. They are formed via 1,4 proton transfer and 1,5-carbon migration in the carbene-THF ylide, respectively (Scheme 4.3 and 4.4).
Product 24 is formed in a stepwise process involving 1,6-carbon migration and 1,3-hydrogen transfer to give product 24 (Scheme 4.5). Product 23 is formed from the insertion reaction of the carbene into the C-H bond of THF (Scheme 4.6).
The above results indicate that the Carbene-THF ylide is a long-lived species (τ >> 20μs). The formation of the ylide can be observed, but the ylide is so long-lived that its decay cannot be observed by laser flash photolysis. The rate of formation of the carbene-THF ylide as a function of temperature was studied. There was no change in the rate of formation with temperature, indicating that the activation energy of formation of the ylide is close to zero. This is consistent with a very small singlet-triplet energy gap.

The formation of an ylide 15-crown-5, 1,4-dioxane and 1,2-dimethoxyethane was observed. However, laser flash photolysis of diazo precursor 50 in diethyl ether and trimethylenedioxi failed to produce a transient spectrum typical of an ylide formation.
CHAPTER 5

EXPERIMENTAL

5.1 General methods

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AC 200 200MHz NMR spectrometer. Dr. Karl Vermillion obtained the DEPT and proton spin decoupled spectra on a Bruker AC 500 MHz NMR spectrometer. Chemical shifts are reported in $\delta$ ppm with tetramethylsilane as internal standard. Infrared spectra were recorded using a Perkin Elmer 1700 Series FTIR interfaced with a Perkin Elmer 3700 data station. UV/Vis spectra were recorded on a Milton Roy Spectronic 3000 Diode Array Spectrophotometer. Gas Chromatographic analysis were obtained with a Perkin Elmer 8500 Gas Chromatograph equipped with a flame ionization detector, using a Supleco fused silica capillary column cross-linked with methyl silicone (column i.d. 0.32mm, column length 30m, phase film thickness 3 µm). GC/MS mass spectral analysis were performed on a Hewlett Packard 6889 GC using a 30m x 0.25mm x 0.25µm column packed with 5% PH ME Siloxane and HP 5973 MS detector. Samples for laser flash photolysis studies were contained in quartz cells for excitation at 308nm. The sample cells were fabricated from square tubing purchased from Vitro Dynamics. Excitation
with the Nd/YAG picosecond laser required Suprasil® Quartz Fluorescence-free static cells purchased from Scientific Products. Low temperature LFP experiments were performed using a Fluorescence-free cell in a variable-temperature sample holder and a NESLAB RTE-110 Proportional Temperature Controller to regulate temperature.

All reagents were purchased from commercial sources and used without purification, unless noted otherwise. 2,3-Dimethyl-2-butene and Freon-113 were purified by passage through a neutral alumina column, just prior to use. Diethyl ether and tetrahydrofuran were distilled over sodium and benzophenone. The distillations were performed under an inert atmosphere.

5.2 Time Resolved Infrared Protocols

TRIR experiments were performed at Johns Hopkins University following the method of Hamaguchi and co-workers. This method allows access to the entire mid-IR spectrum (4000 - 800 cm⁻¹) with high sensitivity and sufficient time (ca. 50 ns) and frequency (4 - 16 cm⁻¹) resolution to probe a wide range of transient intermediates in solution. The broadband output of a newly developed MoSi₂ infrared source (JASCO) is crossed with excitation pulses (266 nm, 10 ns, 0.4 mJ) from a Continuum HPO-300 diode-pumped Nd:YAG laser. Changes in infrared intensity are monitored by an MCT photovoltaic IR detector (Kolmar Technologies, KMPV11-1-J1), amplified by an NF Electronic Instruments 5305 low noise amplifier, and digitized with a Tektronix TDS520A oscilloscope. Data are collected at a repetition rate of 200 Hz, the maximum data handling speed of the digitizing oscilloscope, and acquisition is synchronized with
the stepwise scan of a JASCO TRIR-1000 dispersive spectrometer. In order to obtain spectra with sufficient sensitivity, several thousand laser shots are typically signal averaged at each IR frequency of interest. Since data are collected at relatively high repetition rates, a flow cell is necessary to prevent excessive sample decomposition. A reservoir of ca. 15-mL of solution is continually circulated between two calcium fluoride salt plates.

5.3 Laser Flash Photolysis

Two kinds of laser sources were used for the LFP studies. A Lambda Physik LPX-100 excimer laser (308nm, 120mJ, 17ns) and Continuum PY62C-10 Nd:YAG laser (266nm, 12mJ, 0.15ns) were used to obtain kinetics and transient spectra. The intensities of these lasers remained stable for a period of several hours to meet the experimental requirement of constant laser output. For experiments involving the Lambda Physik excimer laser, the cells were made from square quartz tubing and were approximately 1 cm in length. Excitation with the Nd/YAG picosecond laser required Suprasil® Quartz Fluorescence-free static cells purchased from Scientific Products. An almost perfectly flat surface of this type of quartz cell results in the minimum scattering of laser light.

The stock solutions of the 2-diazo-2-(2-naphthyl)acetate were prepared just prior to the LFP experiments. For experiments with the Lambda Physik excimer laser, the absorbance of the diazo samples used in the kinetic studies was close to 0.5 at 308nm, which was the wavelength of laser emission. The LFP studies were carried out in Freon-113 as the solvent. A constant volume (1 mL) of stock solution were added to the
cuvette. To each cuvette, varying amounts of trapping agent (THF) were added and Freon-113 was added to each cuvette to maintain a total volume of 2 mL. In the LFP experiments that required the use of the Nd/YAG laser, the diazo solution was made in neat trapping agent, THF. For all LFP experiments, the appropriate sample cells were fitted with a rubber septum and the solutions were de-aerated by passing a stream of argon through the samples for 2 minutes.

**Experimental Setup**

![Schematic diagram of Laser Flash Photolysis apparatus.]

*Figure 5.1: Schematic diagram of Laser Flash Photolysis apparatus.*

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The sample cells were then irradiated with the laser pulse. The shutter was open for a few milliseconds before the laser pulse to allow the monitoring light to pass the sample at a right angle to the laser beam. The monitoring beam was generated by a 150W Xe arc lamp that was fitted with an aspherab beam columnator that could be pulsed to temporarily increase its brightness. After passing the sample, the monitoring beam was focussed on the slit of an Oriel 77200 monochromator. The monochromator was used to select the wavelength of interest, and both the front and rear slits were set to a width between 0.2 to 0.3 mm. The signal was obtained with an IP 28 photomultiplier tube detector and was digitized with a Tektronix 7912 A/D transient digitizer. The data collection and storage was performed by a Macintosh IX computer, which controlled the entire apparatus. The data analysis was performed by a program written by Shamim Ahemad, which is based on Marquad Algorithm and the program Igor®, designed by Wavemetrics.

Transient absorption spectra were obtained with an EG&G Princeton Allied Research model 1460 Optical Multichannel Analyzer that was connected to an EG&G PARC 1304 Pulse amplifier, an EG&G PARC 1024 UV detector and a Jarrel-Ash 1234 Grating. The excitation source was the excimer laser operating at 308nm (Lambda Physik LPX-100). The diazo solution was made in a variety of trapping agents and the absorbance of the diazo samples used in kinetic studies was close to 0.8 at 308nm, which was the wavelength of laser emission. For all transient absorbance experiments, the appropriate sample cells were fitted with a rubber septum and the solutions were deaerated by passing streams of argon through the samples for 2 minutes.
5.4 Product Analysis

5.4.1 Photolysis of 3-chloro-3-benzyldiazirine (1)

In a typical photolysis experiment, 20mM solutions of 3-chloro-3-benzyldiazirine (1) in isooctane or dichloromethane were placed in a pyrex cuvette and the solutions were degassed for two minutes with an argon flow. The solutions were photolyzed at 320-380 nm using a rayonet reactor equipped with RPR-3500 bulbs for 48 hours, at 15 °C in the presence of varying amounts of teramethylethylene (TME) ranging from 0.1M-2.2M. The photolytic reaction gave the carbene trapped product 1-benzyl-1-chloro-2,2,3,3-tetramethylcyclopropane (4) and the 1,2 H-migration produce (E)-and (Z)-chlorostyrenes (3).

5.4.2 Photolysis of 1-benzyl-1-chloro-1a,9b-dihydrocyclopropa[1]phenanthridene (8)

In a typical photolysis experiment, 20mM solutions of 1-benzyl-1-chloro-1a,9b-dihydrocyclopropa[1]phenanthridene (8) in dichloromethane were photolyzed at 320-380 nm or at 280-320 nm using a rayonet reactor equipped with RPR-3500 and RPR-3000 bulbs respectively for 48 hours, at various temperatures and in the presence of varying amounts of tetramethylethylene (TME) ranging from 0.1M-2.2M. The solutions were degassed with a strong Argon flow for 2 minutes before the photolysis. The photolytic reaction gave the carbene trapped product 1-benzyl-1-chloro-2,2,3,3-tetramethylcyclopropane (4) and the 1,2 H-migration products (E)-and (Z)-chlorostyrenes (3). Products 3 and 4 were identified by NMR and GC-MS analysis. The relative yields of
products were analyzed on a HP 6890 GC using a 30m x 0.25mm x 0.25μm column packed with 5% PH ME Siloxane and HP 5973 MS detector. The peak area ratio 3/4 was multiplied by a response factor of 2.92 to convert into a molar ratio. This was calculated using the following equations:

\[
\frac{\text{Area}_3}{\text{Area}_{\text{STD}}} = \frac{R_3}{R_{\text{STD}}} x \frac{[3]}{[\text{STD}]} \quad \text{Equation 5.1a}
\]

\[
\frac{\text{Area}_4}{\text{Area}_{\text{STD}}} = \frac{R_4}{R_{\text{STD}}} x \frac{[4]}{[\text{STD}]} \quad \text{Equation 5.1b}
\]

where \(\text{Area}_3\), \(\text{Area}_4\) and \(\text{Area}_{\text{STD}}\) are area of 3, 4 and a standard (dimethylterphthalate) respectively; \(R_3\), \(R_4\) and \(R_{\text{STD}}\) are the response factor of 3, 4 and dimethylterphthalate respectively and \([3]\), \([4]\) and \([\text{STD}]\) are the concentration of 3, 4 and dimethylterphthalate respectively.

\(\frac{R_3}{R_{\text{STD}}}\) was calculated from Equation 5.1a when a known concentration of β-chlorostyrene 3 and the standard (dimethylterphthalate) were injected in the GC together. Similarly, \(\frac{R_4}{R_{\text{STD}}}\) was calculated from Equation 5.1b when a known concentration of 1,benzyl-1,chloro-2,2,3,3,tetramethyl cyclopropane 4 and the standard (dimethylterphthalate) were injected in the GC together.

Dividing Equation 5.1a by Equation 5.1b \(\frac{R_3}{R_4}\) was calculated to be 2.92.
5.5 Synthesis

5.5.1 Preparation of 7,7-dichlorodibenzobicyclo [4.1.0] heptane

To a solution of phenanthrene (17.8g, 0.1mol) and cetyltrimethylammonium bromide (0.8g, 0.54mmol) in chloroform (200ml), was added sodium hydroxide (80% aqueous w/w) and the reaction mixture was stirred for 3 days at room temperature. The resulting emulsion was poured into water (1L), diluted with chloroform (250ml) and the separated organic phase carefully washed with water (4 x 1L) to avoid reformation of the emulsion. The organic phase was filtered through basic alumina (300g) and the alumina washed with chloroform (200mL). The combined organic extracts were concentrated in vacuum and the resulting yellow solid was recrystallized with ethanol (300mL) to give the desired product (12.0g, 46%) m.p. 140-141.5 °C (lit.144 °C).

$^1$H NMR (CDCl$_3$, TMS) δ ppm 3.41, (s, 2H), 7.35 (m, 6H), 8.03 (d, 2H).

$^{13}$C NMR (CDCl$_3$, TMS) δ ppm 36.50, 122.98, 127.92, 128.02, 128.15, 130.91, 131.25.
5.5.2 Preparation of 7-benzyl, 7-chloro dibenzo[a,c] bicyclo[4.1.0] heptane

7, 7- dichlorodibenzobicyclo [4.1.0] heptane 7 (3.06g, 11.4mmol) and 90mL of freshly distilled THF were combined in a 250mL, three-necked round bottomed flask, equipped with magnetic stir bar and argon inlet and outlet. The flask was cooled to -78°C in a dry ice/acetone bath and 6.0mL (1.1equivalent) of 2.0M (12.4mmol) n-BuLi was added dropwise via syringe. The solution turned dark green and was stirred at -78°C for 40 minutes. The temperature was raised to -50°C and was held at that temperature for 10 minutes. The temperature was lowered again to -78°C and to this reaction mixture, benzyl bromide (18ml, 0.15mol) was added to the flask via syringe and the resulting yellow solution was held at -78°C for 2 hours. The reaction mixture was then allowed to come to room temperature with continued stirring overnight. The reaction mixture was washed twice with brine (25mL), dried over sodium sulfate, filtered and concentrated on a rotary evaporator. The crude solution was distilled over high vacuum to get rid of liquid impurities and the crude was recrystallized with ethanol to yield 7-benzyl, 7-chloro dibenzo[a,c] bicyclo[4.1.0] heptane (1.18g, 33%) m.p. 122-123 °C (lit. 123.5-125.5 °C).

$^1$H NMR (CDCl$_3$, TMS) δ ppm 2.94, (s, 2H), 3.40 (s, 2H), 7.38 (m, 6H), 8.05 (d, 2H).
$^{13}$C NMR (CDCl$_3$, TMS) $\delta$ ppm 31.21, 42.71, 46.62, 122.74, 126.87, 127.24, 127.68, 128.42, 129.34, 130.26, 130.34, 131.82, 137.52.

5.5.3 Preparation of benzyl imino ether$^{55}$

\[
\begin{align*}
\text{OC}_2\text{H}_5 \\
\text{NH} \cdot \text{HCl}
\end{align*}
\]

A solution of freshly distilled benzyl cyanide (22.0ml, 0.2mol) was prepared in absolute ethanol (13.0ml, 0.22mol) contained in a three-necked round bottomed flask and cooled in an ice-bath. The flask was tared and HCl gas (that was dried by passing through concentrated sulfuric acid) was bubbled through the solution with vigorous stirring. Upon addition of 1.1 molar equivalents of HCl (7.3g, 0.2mol), the flask was capped with a rubber septum and stored in the freezer for 3 days. Crystals appeared, which were isolated by suction filtration and dried under high vacuum over a sheet of sodium hydroxide to get rid of excess acid. When the pH paper showed no excess acid, the crystals were removed from the vacuum chamber and stored under argon (26.39g, 66%) m.p. 276 °C (decomposition). $^1$H NMR (DMSO, TMS) $\delta$ ppm 1.14, (t, 3H), 3.62 (s, 2H), 4.05, (q, 4H), 7.26 (m, 5H), 7.5 (b, 2H). $^{13}$C NMR (DMSO, TMS) $\delta$ ppm 13.99, 42.12, 60.15, 126.14, 126.70, 128.02, 128.25, 128.97, 129.17, 171.05.
5.5.4 Preparation of benzyl amidine hydrochloride

\[
\begin{align*}
\text{NH}_2 \\
\text{NH} \cdot \text{HCl}
\end{align*}
\]

To a three-necked flask, one neck fitted with an ammonia inlet and another neck fitted with a 4Å molecular sieves outlet, absolute ethanol (11.0mL, 0.19mol) was introduced. The flask was immersed in an ice-water-salt bath and ammonia (1.0g, 0.06mol) was added to the flask. Meanwhile, in another three neck flask, benzyl imino ether (12.0g, 0.06mol) in ethanol (2.5mL) was added. Using a syringe, the ammonia solution was introduced into the second flask, cooled in an ice-water bath. The reaction mixture was allowed to stir for 3 hours. At the end of the reaction, ethanol was evaporated and white crystals of the desired benzyl amidine hydrochloride appeared (7.9g, 77%) m.p. 148-151.5 °C (lit. 151-153 °C). \[^{1}H\ NMR\ (DMSO,\ TMS)\ δ\ ppm\ 3.73 \ (s,\ 2H),\ 7.38\ (m,\ 5H),\ 9.05\ (b,\ 2H).\ \[^{13}C\ NMR\ (DMSO,\ TMS)\ δ\ ppm\ 37.41,\ 127.46,\ 128.61,\ 128.88,\ 134.22,\ 169.20.\]

5.5.5 Preparation of benzyl chloro diazirine

\[
\begin{align*}
\text{Cl} \\
\text{N} = \text{N}
\end{align*}
\]
A 500mL three neck round bottomed flask, fitted with a magnetic stirrer was charged with 75mL of DMSO and 150mL of hexanes. To this mixture of solvents, was added benzyl amidine hydrochloride (3.5g, 20.5mmol) that had been ground in a mortar and pestle with 10g of lithium chloride. The flask was fitted with an addition funnel that had been charged with a solution of sodium chloride (10.0g) in 5% NaOCl (Clorox) (150ml). The reaction flask was cooled to about 0°C. The bleach solution was added dropwise over a period of 2.5 hours of stirring, so that the temperature was maintained below 15°C. After an additional 2 hours of stirring, 100mL of distilled water was added to dissolve the precipitated salts. The organic layer was separated from the aqueous layer and was set aside. The aqueous layer was washed with 3x100mL of hexanes. The combined organic layer was dried with MgSO₄ and the solvent removed by evaporation. The crude diazirine was purified by column chromatography using pentane as the eluent. The solvent was evaporated to yield the desired benzylchlorodiazirine (1.0g, 30%). ¹H NMR (CDCl₃, TMS) δ ppm 3.34 (s, 2H), 7.37 (m, 5H). ¹³C NMR (CDCl₃, TMS) δ ppm 43.62, 127.76, 128.89, 129.62, 132.84.

5.5.6 Preparation of chloromethyl triphenyl phosphonium iodide⁶²

\[
\text{(PH}_3\text{P─CH}_2\text{Cl)}^+I^-
\]

Triphenylphosphine (5.9g, 22.64mmol) was dissolved in 28.3mL THF in a 100mL three necked round bottomed flask, equipped with a magnetic stirrer, a pressure
equilibrating dropping funnel, a thermometer and a Widmer reflux condenser topped with argon inlet-outlet tube. The mixture was stirred rapidly while chloroiodomethane (5.0g, 28.3mmol, 2.06mL) was added dropwise. The flask was then immersed in an oil-bath and the mixture was heated at reflux for 20 hours. The resulting white precipitate was washed with 5x10mL of THF in a nitrogen atmosphere. The phosphonium salt was then dried in vacuum at 50°C for several hours (5.0g, 51%) m.p. 94-97 °C (lit. 95-98 °C). \(^{1}H\) NMR (CDCl\(_3\), TMS) δ ppm 3.36 (s, 2H), 7.85 (m, 5H).

5.5.7 Preparation of E-chlorostyrene\(^{63}\)

\[
\text{Ph} \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \text{Cl}
\]

Under a nitrogen atmosphere, ethanol (10mL) was placed in a 100mL three neck round bottom flask, equipped with a magnetic stirrer, thermometer and a condenser topped with a nitrogen inlet and outlet tube. Potassium (0.64g, 16mmol) was added and the reaction mixture was refluxed for one hour to afford a potassium ethoxide solution. The reaction flask was then immersed in a water bath. A powder dropping funnel, which contained chloromethyl triphenyl phosphonium iodide (4.4g, 10.0mmol) was attached to the flask and the phosphonium salt was added to the potassium ethoxide solution over a period of five minutes. The funnel was washed with another 3.0mL of ethanol. The reaction mixture was stirred for 1.5 hours at ambient temperature after which, the powder dropping funnel was replaced with a pressure equilibrating addition funnel which
contained benzaldehyde (0.85g, 8.1mmol) in 4.0mL ethanol. The benzaldehyde solution was added over a 20-minute period. The reaction mixture was stirred at ambient temperature for four hours and then refluxed for three hours. At the end of the reaction, the mixture was shaken with 20mL of pentane and 20mL of saturated sodium bisulfate and the layers were separated. The aqueous layer was extracted with 3x20mL of pentane. The combined organic phase was washed with 3x10mL of water and dried over magnesium sulfate. The solvent was evaporated to yield purified 9/1 E/Z-chlorostyrene (0.18g, 17%). $^1$H NMR (CDCl$_3$, TMS) $\delta$ ppm 6.5-6.9 (dd, 2H), 7.45 (m, 5H).

5.5.8 Preparation of propyl imino ether$^{64}$

A solution of freshly distilled propyl cyanide (25.0g, 0.36mol) was prepared in absolute ethanol (25.0mL, 0.40mol) contained in a three-necked round bottomed flask and cooled in an ice-bath. The flask was tared and HCl gas (that was dried by passing through concentrated sulfuric acid) was bubbled through the solution with vigorous stirring. Upon addition of 1.1 molar equivalents of HCl (14.6g, 0.4mol), the flask was capped with a rubber septum and stored in the freezer for 7 days. The solution turned viscous and after the removal of ethanol, crystals appeared, which were isolated by suction filtration and dried under high vacuum over a sheet of sodium hydroxide to remove excess acid. When the pH paper showed no excess acid, the crystals were
removed from the vacuum chamber and stored under argon (33.5g, 61%) m.p. 74-76.5 °C (lit. 75.77 °C). ¹H NMR (DMSO, TMS) δ ppm 0.80, (t, 3H), 0.86 (t, 3H), 1.46 (m, 2H), 2.59 (t, 2H), 4.5 (q, 2H). ¹³C NMR (DMSO, TMS) δ ppm 13.28, 18.40, 33.82, 36.93, 68.97, 178.80.

5.5.9 Preparation of isopropyl imino ether⁶⁵

\[ \text{NH}^{-} \text{HCl} \]
\[ \text{OC}_2 \text{H}_5 \]

A solution of freshly distilled isopropyl cyanide (25.0g, 0.36mol) was prepared in absolute ethanol (25.0mL, 0.40mol) contained in a three-necked round bottomed flask and cooled in an ice-bath. The flask was tared and HCl gas (that was dried by passing through concentrated sulfuric acid) was bubbled through the solution with vigorous stirring. Upon addition of 1.1 molar equivalents of HCl (14.6g, 0.4mol), the flask was capped with a rubber septum and stored in the freezer for 7 days. The solution turned viscous and after the removal of ethanol, crystals appeared, which were isolated by suction filtration and dried under high vacuum over a sheet of sodium hydroxide to remove excess acid. When the pH paper showed no excess acid, the crystals were removed from the vacuum chamber and stored under argon (33.5g, 61%) m.p. 87 °C.
89 °C). $^1$H NMR (DMSO, TMS) $\delta$ ppm 1.15 (d, 6H), 1.33 (t, 3H), 2.96 (m, 1H), 4.43 (q, 2H). $^{13}$C NMR (DMSO, TMS) $\delta$ ppm 13.17, 18.45, 19.41, 32.35, 69.10, 182.10.

5.5.10 Preparation of propyl amidine hydrochloride

\[
\begin{align*}
\text{NH} & \cdot \text{HCl} \\
\text{NH}_2 & \quad \text{C} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

To a three-necked flask, one neck fitted with an ammonia inlet and another neck fitted with a 4Å molecular sieves outlet, absolute ethanol (18.0mL, 0.3mol) was introduced. The flask was immersed in an ice-water-salt bath and ammonia (2.0g, 0.12mol) was added to the flask. Meanwhile, in another three necked flask, propyl imino ether (15.0g, 0.1mol) in ethanol (2.5mL) was added. Using a syringe, the ammonia solution was introduced in the second flask cooled with an ice-water bath. The reaction mixture was allowed to stir for 3 hours. At the end of the reaction, ethanol was evaporated and white crystals of the desired propyl amidine hydrochloride appeared (10.75g, 89%) m.p. 107-109 °C (lit.109 °C). $^1$H NMR (DMSO, TMS) $\delta$ ppm 0.87 (t, 3H), 1.60 (m, 2H), 2.33 (t, 2H), 8.80 (b, 2H). $^{13}$C NMR (DMSO, TMS) $\delta$ ppm 12.85, 19.80, 33.09, 170.95.
5.5.11 Preparation of isopropyl amidine hydrochloride

\[
\begin{align*}
\text{NH}_3 & \rightarrow \text{H} \quad \text{Cl} \\
& \quad \text{NH}_2 \\
& \quad \text{CH}_3
\end{align*}
\]

To a three-necked flask, one neck fitted with an ammonia inlet and another neck fitted with a 4Å molecular sieves outlet, absolute ethanol (18.0mL, 0.3mol) was introduced. The flask was immersed in an ice-water-salt bath and ammonia (2.0g, 0.12mol) was added to the flask. Meanwhile, in another three necked flask, isopropyl imino ether (15.0g, 0.1mol) in ethanol (2.5mL) was added. Using a syringe, the ammonia solution was introduced in the second flask cooled in an ice-water bath. The reaction mixture was allowed to stir for 3 hours. At the end of the reaction, ethanol was evaporated and white crystals of the desired isopropyl amidine hydrochloride appeared (11.6g, 95%) m.p. 162-164 °C (lit. 167 °C). \(^1H\) NMR (DMSO, TMS) \(\delta\) ppm 1.14 (d, 6H), 2.74 (m, 1H), 8.91 (b, 2H). \(^13C\) NMR (DMSO, TMS) \(\delta\) ppm 19.00, 31.71, 175.53.

5.5.12 Preparation of propyl chloro diazirine

\[
\begin{align*}
\text{N} & \equiv \text{N} \\
& \quad \text{Cl}
\end{align*}
\]

Propyl chloro amidine hydrochloride (3.1g, 0.25mol) and lithium chloride (10.0g, 0.24mol) were ground in a mortar with a pestle and introduced into a modified
500mL round bottom flask equipped with magnetic stirrer and DMSO (75mL). The suspension was cooled with an ice-water bath to 0°C. One neck of the flask was connected to a pasteur pipette fitted to an argon line which was extended below the level of solvent. The flask was also fitted with a 250mL addition funnel to which a solution of NaOCl (150mL, 5% Clorox) with sodium chloride (30.0g, 0.51mol) was introduced. The third neck of the flask extended horizontally and was attached to a tube filled with potassium pellets as drying agent, which was held in place at each end by glass wool. The other end of the drying tube was fitted with a cold finger condensing trap with a small joint for venting argon. The cold finger trap was charged with 25mL of dichloromethane and it was cooled to -78°C with a dry ice-acetone bath. Argon flow was established for 15 minutes to purge the oxygen and the apparatus was covered with aluminum foil. NaOCl solution was added drop-wise to the flask over a period of an hour maintaining the temperature to 0°C. After the addition of NaOCl solution, the reaction flask was stirred for 2 hours. The solution from the cold finger condenser was then transferred to a dry round bottom flask and propyl chloro diazirine was stored in the freezer in solution (UV λmax = 336nm).
Isopropyl chloro amidine hydrochloride (3.1g, 0.25mol) and lithium chloride (10.0g, 0.24mol) were ground in a mortar with a pestle and introduced into a modified 500mL round bottom flask equipped with magnetic stirrer and DMSO (75mL). The suspension was cooled with an ice-water bath to 0°C. One neck of the flask was connected to a pasteur pipette fitted to an argon line which was extended below the level of solvent. The flask was also fitted with a 250mL addition funnel to which a solution of NaOCl (150mL, 5% Clorox) with sodium chloride (30.0g, 0.51mol) was introduced. The third neck of the flask extended horizontally and was attached to a tube filled with potassium pellets as drying agent, which was held in place at each end by glass wool. The other end of the drying tube was fitted with a cold finger condensing trap with a small joint for venting argon. The cold finger trap was charged with 25mL of dichloromethane and it was cooled to -78°C with a dry ice-acetone bath. Argon flow was established for 15 minutes to purge the oxygen and the apparatus was covered with aluminum foil. NaOCl solution was added drop-wise to the flask over a period of an hour maintaining the temperature to 0°C. After the addition of NaOCl solution, the reaction flask was stirred for 2 hours. The solution from the cold finger condenser was
then transferred to a dry round bottom flask and isopropyl chloro diazirine was stored in the freezer in solution (UV $\lambda_{\max} = 352\text{nm}$).

5.5.13 Preparation of methyl-2-naphthylacetate$^{68}$

\[
\text{To 2-naphthyl acetic acid (5.0g, 27mmol) in a round bottom flask, methanol (8.5mL) was added along with concentrated sulfuric acid (0.85mL). The reaction mixture was refluxed for 3 hours, after which it was cooled and poured into water (40mL). It was extracted with 3x20mL dichloromethane. The total organic layer was dried over sodium sulfate and concentrated. The ester appeared as a pale yellow liquid (5.2g, 97%).}^{1}\text{H NMR (CDCl$_3$, TMS) $\delta$ ppm 3.76 (s, 3H), 3.85 (s, 2H), 7.52 (m, 3H), 7.84 (m, 4H).}^{13}\text{C NMR (CDCl$_3$, TMS) $\delta$ ppm 41.35, 52.05, 125.88, 126.22, 127.42, 127.74, 127.75, 128.03, 128.29, 131.59, 132.58, 133.55, 172.00.}
5.5.14 Preparation of 2-diazo-2-(2-naphthyl) acetate

In a 50mL round bottomed flask, methyl 2-naphthylacetate (1.6g, 8.0mmol) was placed with 4-acetamidobenzenesulfonyl azide (3.27g, 13.6mmol) in dichloromethane. To this solution was added 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) (1.5mL, 10.0mmol). The flask was wrapped in aluminum foil and was stirred for 16 hours at room temperature. The solution was concentrated to give a red oil that was chromatographed on silica gel using 2:1 petroleum ether and dichloromethane as the eluant. The compound appeared as an orange colored solid. The diazo was then recrystallized with methanol to give flaky orange crystals (1.0g, 56%) m.p. 79-80 °C (lit. 79 °C). IR (CHCl₃, cm⁻¹) 3058.8, 2980.7, 2079.7, 1706. ¹H NMR (CDCl₃, TMS) δ ppm 3.91 (s, 3H), 7.46 (m, 3H), 7.82 (m, 3H), 8.02 (d, 1H). ¹³C NMR (CDCl₃, TMS) δ ppm 51.99, 121.85, 122.54, 122.62, 125.74, 126.57, 127.58, 127.60, 128.64, 131.47, 133.60, 165.67.
5.5.15 Characterization of products derived from decomposition of benzyl chloro carbene precursors in the presence of 2,3-dimethyl-2-butene

When benzyl chloro carbene precursors were photolyzed in the presence of neat carbene-trapping agent, TME, two major products were formed. The addition product with TME, 1,benzyl-1,chloro-2,2,3,3,tetramethyl cyclopropane 4, and the rearrangement products, E-and Z-chloro styrene 3.

[Diagram of compounds 4 and 3]

Compound 4 was isolated from the reaction mixture by column chromatography using pentane as the eluent and characterized. $^1$H NMR (CDCl$_3$, TMS) $\delta$ ppm 1.18 (s, 6H), 1.29 (s, 6H), 3.24 (s, 2H), 7.28 (m, 5H). $^{13}$C NMR (CDCl$_3$, TMS) $\delta$ ppm 18.68, 20.08, 39.48, 59.95, 125.99, 128.09, 128.79, 138.84. MS m/e (relative intensity) M$^+$ 222 (2.0), 187 (42), 171 (42), 156 (20), 145 (51), 143 (18), 131 (32), 91 (79). Alkene 3 was identified by comparison with an authentic sample synthesized independently.

5.5.16 Characterization of products derived from photolysis of 2-diazo-2- (2-naphthyl) acetate in the presence of tetrahydrofuran

In the photolysis experiment, 300mg of 2-diazo-2- (2-naphthyl) acetate (50) in 25mL tetrahydrofuran was placed in a pyrex tube and the solution was degassed for five
minutes with an argon flow. The solutions was photolyzed at 320-380 nm using a rayonet reactor equipped with RPR-3500 bulbs for 20 hours, at 15 °C. The photolytic reaction gave the following four carbene-trapped products 21, 22, 23, and 24 in the ratio 7:15:2:1 respectively, which were isolated by column chromatography using 2:1 petroleum ether and dichloromethane.

![Chemical Structure](image)

**Compound 21:** Compound 21 was isolated in a pure state as an oil (50mg). $^1$H nmr (δ ppm) 2.45 (q, 2H), 3.55 (dd, 2H), 3.70 (s, 3H), 5.1 (m, 3H), 5.8 (m, 4H), 7.5 (m, 3H), 7.8 (m, 4H). $^{13}$C nmr (δ ppm) 34.25, 52.50, 69.49, 81.44, 116.90, 124.77, 126.52, 126.60, 126.90, 127.93, 128.35, 128.70, 133.36, 133.67, 134.16, 134.89, 171.50. DEPT spectra revealed that δ 34.25, 69.49, 116.90 are secondary carbon centers. MS m/e (relative intensity) M⁺ exact mass 270 (3), 211 (61), 181 (17), 171 (21), 157 (32), 155 (25), 129 (35), 127 (33), 55 (100).
Compound 22: Compound 22 was isolated in a pure state as a yellow solid (90mg), m. p. 62 °C. $^1$H nmr ($\delta$ ppm) 1.7 (m, 4H), 1.8 (m, 1H), 2.6 (m, 1H), 3.72 (s, 3H), 3.85-4.0 (mdd, 2H), 7.4 (m, 2H), 7.65 (dd, 1H), 7.8 (m, 3H), 8.0 (d, 1H). $^{13}C$ nmr ($\delta$ ppm) 20.80, 25.13, 33.68, 52.59, 65.18, 80.94, 123.13, 124.44, 126.17, 126.21, 127.54, 128.21, 128.40, 132.84, 133.21, 138.41, 173.14. DEPT spectra revealed that $\delta$ 20.8, 25.13, 33.68 and 65.18 are the secondary carbon centers. MS m/e (relative intensity) $M^+$ exact mass 270 (0.65), 211 (100), 155 (73), 127 (54).

Compound 23: Compound 23 was isolated in a pure state as a colorless oil (12mg). $^1$H nmr ($\delta$ ppm) 1.55 (m,3H), 2.15 (m, 1H), 3.66 (s, 3H), 3.80 (m, 3H), 4.6 (dd,
1H), 7.50 (m, 3H), 7.80 (m, 4H). $^{13}$C nmr (δ ppm) 25.86, 30.42, 52.27, 57.15, 68.57, 80.18, 126.06, 126.24, 126.71, 127.82, 127.96, 128.15, 128.41, 133.10, 133.61, 134.30, 172.76. DEPT spectra revealed that δ 25.86, 30.42, and 68.57 are the secondary carbon centers. MS m/e (relative intensity) M$^+$ exact mass 270 (3), 200 (58), 141 (24), 71 (100), 43 (43).

[Chemical structure image]

**Compound 24:** Compound 24 was isolated in a pure state as a colorless oil (10mg). $^1$H nmr (δ ppm) 1.65 (m, 2H), 1.85 (m, 2H), 3.30 (m, 1H), 3.70 (s, 3H), 3.75 (m, 3H), 5.49 (s, 1H), 7.32 (d, 1H), 7.56 (m, 2H), 7.75 (d, 1H), 7.80 (m, 1H), 8.15 (m, 1H). $^{13}$C nmr (δ ppm) 35.36, 36.85, 37.47, 62.20, 78.71, 89.69, 133.67, 135.52, 135.82, 136.21, 138.54, 141.43, 141.70, 143.75, 147.36, 181.30. DEPT spectra revealed that δ 35.36, 36.85, 37.47 and 78.71 are the secondary carbon centers. MS m/e (relative intensity) M$^+$ exact mass 270 (40), 211 (84), 193 (20), 169 (57), 152 (25), 141 (100), 115 (39).

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SYNTHESIS OF POLYSUBSTITUTED PHENYL AZIDES

Organic azides are compounds containing the RN₃ unit. Upon photolysis or thermolysis, they eliminate nitrogen and form nitrenes. Physical organic chemists have a longstanding interest in the photochemical reactions of organic azides. The reactivity of the azides and the intermediates they form have been studied extensively, but there are still many questions that remain unanswered. Azides have applications in polymer chemistry, as light-sensitive agents in biochemistry, in photographic processes and in the field of lithography.¹ Because of these practical applications and their fundamental interest, physical organic chemists continue to focus their attention in the studies of these compounds.

In order to investigate some of the issues concerning the reactivity of nitrenes, this study focuses on the synthesis of the substituted phenyl azides. It is hoped that once the basic understanding of phenyl nitrene has been achieved, the effect on the nature of substituents with electron-withdrawing or electron-donating groups on the nitrenes can be studied.
A.1 Synthesis of 2-azido-benzoic acid methyl ester

\[
\begin{align*}
\text{COOCH}_3 & \quad \text{(a) NaNO}_2, \text{HCl, } 0 \, ^\circ\text{C} \quad \text{(b) NaN}_3, \text{H}_2\text{O, } 0 \, ^\circ\text{C.}
\end{align*}
\]

A solution of 2-amino-benzoic acid methyl ester (3.77g, 25mmol) in HCl (5M, 120mL, 1:1 HCl and H\text{\textsubscript{2}}O) was cooled to 0 °C and diazotized by the slow addition of a solution of sodium nitrite (1.93g, 28mmol) in water (15mL). The resulting diazonium chloride was stirred for 10 minutes at 0 °C. A solution of sodium azide (1.63g, 25mmol) and sodium acetate (20.5g, 250mmol) in water (50mL) was slowly added to the diazonium chloride. The reaction mixture was stirred for 2 hours at 0 °C and then it was extracted with ether. The product was purified by column chromatography using dichloromethane as the eluent. The first few fractions contained the azide, which was stored under nitrogen in a freezer at -20 °C (2.5g, 71%). \( ^1\text{H} \text{NMR} (\text{CDCl}_3, \text{TMS}) (\delta \text{ ppm}) \), 3.87 (s, 3H), 7.1-7.8 (m, 4H). \( ^{13}\text{C} \text{NMR} (\text{CDCl}_3, \text{TMS}) (\delta \text{ ppm}) \), 52.19, 119.81, 122.50, 124.38, 131.71, 133.11, 139.92, 165.67. IR (CCl\text{\textsubscript{4}}, cm \text{\textsuperscript{-1}}) 2113.8, 1727, 1435.4, 1337.9, 1250.5.

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A.2 Synthesis of 1-azido-2-methoxy benzene

\[
\begin{align*}
\text{OMe} & \quad \text{NH}_2 & \quad \text{OMe} & \quad \text{N}_3 \\
\text{(a)} & \quad \text{(b)} & \quad \text{(a)} & \quad \text{(b)}
\end{align*}
\]

(a): NaNO\textsubscript{2}, HCl, 0 °C (b): NaN\textsubscript{3}, H\textsubscript{2}O, 0 °C.

A solution of 2-methoxy aniline (1.0g, 8.1mmol) in HCl (5M, 40mL, 1:1 HCl and H\textsubscript{2}O) was cooled to 0 °C and diazotized by the slow addition of a solution of sodium nitrite (0.62g, 9.0mmol) in water (5mL). The resulting diazonium chloride was stirred for 10 minutes at 0 °C. A solution of sodium azide (0.6g, 8.1mmol) and sodium acetate (6.7g, 81mmol) in water (17mL) was slowly added to the diazonium chloride. The reaction mixture was stirred for 2 hours at 0 °C and then it was extracted with ether. The product was purified by column chromatography using dichloromethane as the eluent. The first few fractions contained the azide, which was stored under nitrogen in a freezer at -20 °C (0.53g, 50%). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, TMS) (δ ppm), 3.87 (s, 3H), 6.8-7.1 (m, 4H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, TMS) (δ ppm), 55.19, 110.64, 111.24, 119.46, 129.95, 140.27, 160.87. IR (CCl\textsubscript{4}, cm\textsuperscript{-1}) 2115.3, 1592.7, 1500, 1298.3, 1247.9.
A.3 Synthesis of 1-azido-3-methoxybenzene²

\[
\begin{align*}
\text{NH}_2 \\
\text{OMe} \\
\text{N}_3 \\
\text{OMe}
\end{align*}
\]

(a): NaNO₂, HCl, 0 °C (b): NaN₃, H₂O, 0 °C.

A solution of 3-methoxy aniline (1.0g, 8.1mmol) in HCl (5M, 40mL, 1:1 HCl and H₂O) was cooled to 0 °C and diazotized by the slow addition of a solution of sodium nitrite (0.62g, 9.0mmol) in water (5mL). The resulting diazonium chloride was stirred for 10 minutes at 0 °C. A solution of sodium azide (0.6g, 8.1mmol) and sodium acetate (6.7g, 81mmol) in water (17mL) was slowly added to the diazonium chloride. The reaction mixture was stirred for 2 hours at 0 °C and then it was extracted with ether. The product was purified by column chromatography using dichloromethane as the eluent. The first few fractions contained the azide, which was stored under nitrogen in a freezer at -20 °C (0.96g, 88%).¹ H NMR (CDCl₃, TMS) (δ ppm), 3.78 (s, 3H), 6.5-7.3 (m, 4H).¹³C NMR (CDCl₃, TMS) (δ ppm), 55.21, 104.97, 110.64, 111.24, 130.38, 141.27, 160.85. IR (CCl₄, cm⁻¹) 2109.5, 1602.4, 1489.3, 1297.4, 1229.1.
A.4  Synthesis of 5-azido-isophthaiic acid

\[
\begin{align*}
\text{HOOC-} & \text{NH}_2 \quad \rightarrow \quad \text{HOOC-} \quad N_3 \\
\text{COOH} & \quad \text{(a)} \quad \text{COOH} \\
\end{align*}
\]

(a): NaNO₂, HCl, 0 °C  (b): NaN₃, H₂O, 0 °C.

A solution of 5-amino-isophthalic acid (1.0g, 5.5 mmol) in HCl (5M, 30mL, 1:1 HCl and H₂O) was cooled to 0 °C and diazotized by the slow addition of a solution of sodium nitrite (0.48g, 7.0 mmol) in water (4.2mL). The resulting diazonium chloride was stirred for 10 minutes at 0 °C. A solution of sodium azide (0.41g, 6.4 mmol) and sodium acetate (5.0g, 61 mmol) in water (14mL) was slowly added to the diazonium chloride. The reaction mixture was stirred for 2 hours at 0 °C and then it was extracted with ethyl acetate. After the removal of the solvent, the product appeared as a white solid (0.96g, 88%). \(^1\)H NMR (DMSO, TMS) (δ ppm), 7.67 (s, 2H), 8.17 (s, 1H). \(^{13}\)C NMR (DMSO, TMS) (δ ppm), 123.26, 126.09, 132.88, 140.46, 165.66. IR (CCl₄, cm \(^{-1}\)) 3439, 2119.7, 1734.5, 1243.8.
A.5 Schematic synthesis of 1-azido-2,5-dimethoxy-3,6-dicarboxylic acid dimethyl ester

\[ \text{(a): Br}_2, \text{CHCl}_3, 40^\circ\text{C} \text{ (b): CH}_3\text{l, K}_2\text{CO}_3, \text{acetone, reflux 8hrs (c): HNO}_3 \text{ (concentrated), CH}_3\text{COOH (glacial) r.t. (d): SnCl}_2, \text{HCl, r.t. (e): NaNO}_2, \text{HCl, 0}^\circ\text{C (f): NaN}_3, \text{H}_2\text{O, 0}^\circ\text{C.}} \]

A.5.1 Synthesis of 2,5-dihydroxy-terphthalic acid dimethyl ester

\[ \text{OH} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{OH} \]

\[ \text{COOCH}_3 \]

\[ \text{OH} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]

\[ \text{OMe} \]

\[ \text{H}_3\text{COOC} \]

\[ \text{COOCH}_3 \]
A cold solution of bromine (4.26mL) in chloroform (100mL, at 0 °C) was added to a cold solution of 2,5-dioxo-1,4-cyclohexane dicarboxylate (9.4g, 41.2 mmol) in chloroform (100mL). The solution was stirred at room temperature for 2 hours and then at 40 °C for 2 hours. The reaction mixture was washed with 10% sodium thiosulfate solution, then with water and finally dried with potassium carbonate. Upon the evaporation of the solvent, a yellow solid was obtained (9.2g, 99%) m.p. 177-178 °C (lit. m.p. 177-179 °C). \(^1\text{H NMR} \ (\delta \text{ ppm}) \ 3.85 \ (s, \ 6\text{H}), \ 7.25 \ (s, \ 2\text{H}), \ 9.8 \ (s, \ 2\text{H}). \ ^1\text{H NMR} \ (\text{DMSO, TMS}) \ (\delta \text{ ppm}), \ 7.67 \ (s, \ 2\text{H}), \ 8.17 \ (s, \ 1\text{H}). \ ^{13}\text{C NMR} \ (\text{DMSO, TMS}) \ (\delta \text{ ppm}), \ 52.53, \ 117.55, \ 119.90, \ 150.50, \ 167.27.
A.5.2 Synthesis of 2,5-dimethoxy-terphthalic acid dimethyl ester

Anhydrous potassium carbonate (13.66g, 97.7mmol) and 2,5-dihydroxy-terphthalic acid dimethyl ester (4.87g, 21.5mmol) were stirred for 8 hours in refluxing acetone (150mL) containing iodomethane (24.46g, 0.17mol). The reaction mixture was then cooled and washed with water to dissolve excess potassium carbonate and extracted with dichloromethane. The organic layer was dried and solvent was removed to yield the desired product (5.22g, 96%) m.p. 139 °C (lit.4 m.p. 141-142 °C). ¹H NMR (DMSO, TMS) (δ ppm), 3.80 (d, 12H), 7.33 (s, 2H). ¹³C NMR (DMSO, TMS) (δ ppm), 52.20, 56.42, 114.42, 123.99, 151.01, 165.50.

A.5.3 Synthesis of 2,5-dimethoxy-3-nitro-terphthalic acid dimethyl ester

To a cooled mixture of 1:1 concentrated nitric acid and glacial acetic acid (192mL), 2,5-dimethoxy-terphthalic acid dimethyl ester (24g, 95mmole) was added slowly such that the temperature did not rise above 0 °C. The reaction mixture was allowed to stir overnight. The solution was then poured into an ice-water mixture and stirred for 1 hour. A yellow solid was obtained which was filtered and dried (8.7g, 31%) m.p. 90 °C (lit.° m.p. 91-92 °C). \(^1\)H NMR (DMSO, TMS) (δ ppm) 3.80 (d, 6H), 3.90 (d, 6H), 7.71 (s, 1H). \(^1^3\)C NMR (DMSO, TMS) (δ ppm), 61.29, 61.61, 65.39, 72.64, 125.63, 127.37, 137.11, 152.07, 152.28, 160.11, 170.37, 171.86.

A.5.4 Synthesis of 3-amino-2,5-dimethoxy-terphthalic acid dimethyl ester

To a stirred mixture of stannous chloride dihydrate (10.0g, 44mmol) and concentrated hydrochloric acid (65mL) was added 2,5-dimethoxy-3-nitro-terphthalic acid dimethyl ester (1.5g, 5mmol) in small quantities over 30 minutes. The reaction mixture was stirred for 3 hours and then diluted with water and extracted with ethyl acetate. The organic layer was dried over sodium sulfate and the solvent removed. The product crystallized as a brown solid containing a slight impurity of starting material (1.2g, 89%) m.p. 276-278 °C. \(^1\)H NMR (DMSO, TMS) (δ ppm), 3.64 (s, 3H), 3.69 (s, 3H), 3.77 (s, 3H), 3.81 (s, 3H) 6.39 (s, 1H). \(^1^3\)C NMR (DMSO, TMS) (δ ppm), 29.16, 47.12, 59.28, 72.64, 106.02, 134.15, 148.29, 150.46, 161.70, 174.06, 174.76, 180.15. MS m/e (relative
A.5.5 Synthesis of 3-azido-2,5-dimethoxy-terphthalic acid dimethyl ester

A solution of 3-amino-2,5-dimethoxy-terphthalic acid dimethyl ester (2g, 7.4mmol) in HCl (5M, 35mL, 1:1 HCl and H₂O) was cooled to 0 °C and diazotized by the slow addition of a solution of sodium nitrite (0.6g, 8.3mmol) water (4.5mL). The resulting diazonium chloride was stirred for 10 minutes at 0 °C. A solution of sodium azide (0.5g, 7.5mmol) and sodium acetate (6g, 74mmol) in water (15mL) was slowly added to the diazonium chloride. The reaction mixture was stirred for 2 hours at 0 °C and then it was extracted with dichloromethane. The azide was purified by column chromatography using dichloromethane as eluent. The first few fractions contained the azide (0.4g, 20%) m.p. 64-67 °C. ¹H NMR (CDCl₃, TMS) (δ ppm), 3.80 (s, 3H), 3.86 (s, 3H), 3.92 (s, 3H), 3.93 (s, 3H) 7.10 (s, 1H). ¹³C NMR (CDCl₃, TMS) (δ ppm), 52.60, 52.74, 63.39, 109.35, 126.12, 132.57, 147.92, 152.08, 165.07. MS m/e (relative intensity) M⁺ 295(8.24), 267 (17.01), 264 (17.65), 234 (55.90), 220 (100), 207 (52.84), 175 (43.50), 162 (48.15), 59 (81.06). IR (CCl₄, cm⁻¹) 2115, 1733.5, 1601.1, 1411.7, 1224.5, 1038.1.
A.6 Schematic synthesis of 2-azido-3,4,5-trimethoxy-benzoic acid methyl ester

(a) \text{HCl (gas), CH}_3\text{OH, reflux.} \hspace{1cm} (b): \text{HNO}_3 \text{ (concentrated), CH}_3\text{COOH (glacial) 0 °C (c): SnCl}_2, \text{HCl, r.t.} \hspace{1cm} (d): \text{NaNO}_2, \text{HCl, 0 °C (e): NaN}_3, \text{H}_2\text{O, 0 °C.}

A.6.1 Synthesis of 3,4,5-trimethoxy-benzoic acid methyl ester

To absolute methanol (50mL) saturated with hydrogen chloride gas at 0 °C, 3,4,5-trimethoxy benzoic acid was added (20g, 94.2 mmol). The reaction mixture was heated at reflux for 4.5 hours in oil-bath. A white solid appeared at the end of reaction, which
was extracted with ethyl acetate and water to give the desired ester (20.5g, 96%) m.p. 82-
84 °C (lit. m.p. 84°C). \(^1\)H NMR (DMSO, TMS) (δ ppm), 3.72 (s, 3H), 3.82 (s, 9H), 7.22
(s, 2H). \(^1\)C NMR (DMSO, TMS) (δ ppm), 52.10, 55.93, 60.06, 106.40, 124.62, 152.67,
184.24.

A.6.2 Synthesis of 3,4,5-trimethoxy-2-nitro-benzoic acid methyl ester

\[
\begin{align*}
\text{COOCH}_3 \\
\text{NO}_2 \\
\text{MeO} \quad \text{OMe} \\
\text{MeO} \\
\end{align*}
\]

To a cooled mixture of 1:1 concentrated nitric acid and glacial acetic acid (300mL), 3,4,5-trimethoxybenzoic acid methyl ester (0.16 mole) was added slowly such that the temperature did not rise above 0 °C. The reaction mixture was allowed to stand for 1 hour at the same temperature. The solution was then poured into an ice-water mixture and stirred overnight. The product crystallized as a yellow solid and was filtered and dried (6.35g, 14%) m.p. 67 °C (lit. m.p. 68 °C). \(^1\)H NMR (DMSO, TMS) (δ ppm),
3.81 (s, 3H), 3.88, (s, 3H), 3.90 (s, 3H), 3.92 (s, 3H), 7.32 (s, 1H). \(^1\)C NMR (DMSO,
TMS) (δ ppm), 53.00, 56.57, 60.98, 62.48, 108.67, 117.18, 144.94, 145.59, 154.10,
162.73.

NOTE Distillation was attempted in order to retrieve the product from the mother liquor. A massive explosion occurred probably due to the formation of nitroacetate.
A.6.3 Synthesis of 2-amino-3,4,5-trimethoxy-benzoic acid methyl ester

To a stirred mixture of stannous chloride dihydrate (50.0 g, 0.22 mol) and concentrated hydrochloric acid (300 mL) was added 3,4,5-trimethoxy-2-nitro-benzoic acid methyl ester (7.5 g, 27 mmol) in small quantities over 30 minutes. The reaction mixture was stirred for 2.5 hours then diluted with water and extracted with ethyl acetate. The organic layer was dried over sodium sulfate and the solvent removed. The product crystallized as a brown solid (4.19 g, 63%) m.p. 40 °C (lit. 7 m.p. 41 °C). $^1$H NMR (DMSO, TMS) (δ ppm), 3.69 (s, 3H), 3.72 (s, 3H), 3.77 (s, 3H), 3.82 (s, 3H), 7.05 (s, 1H). $^{13}$C NMR (DMSO, TMS) (δ ppm), 51.33, 56.07, 60.01, 60.35, 103.26, 108.06, 139.89, 141.03, 142.58, 147.25, 167.28.

A.6.4 Synthesis of 2-azido-3,4,5-trimethoxy-benzoic acid methyl ester
A solution of 2-amino-3,4,5-trimethoxybenzoic acid methyl ester (1g, 4.1mmol) in HCl (5M, 20mL, 1:1 HCl and H₂O) was cooled to 0 °C and diazotized by the slow addition of a solution of sodium nitrite (0.33g, 4.6mmol) in water (2.5mL). The resulting diazonium chloride was stirred for 10 minutes at 0 °C. A solution of sodium azide (0.3g, 4.1 mmol) and sodium acetate (3.36g, 40mmol) in water (9mL) was slowly added to the diazonium chloride. The reaction mixture was stirred for 2 hours at 0 °C and then it was extracted with dichloromethane. The azide was purified by column chromatography using dichloromethane as eluent. The first few fractions contained the azide (0.3g, 29%) m.p. 36-37 °C. \[^1\text{H} \text{NMR (CDCl}_3, \text{TMS}) (\delta \text{ ppm}), 3.82 (\text{s, 3H}), 3.85 (\text{s, 3H}), 3.89 (\text{s, 6H}), 7.09 (\text{s, 1H}).\] \[^{13}\text{C} \text{NMR (CDCl}_3, \text{TMS}) (\delta \text{ ppm}), 52.25, 56.11, 60.93, 61.71, 109.31, 118.15, 127.31, 146.14, 148.22, 149.98, 165.52.\] MS m/e (relative intensity) M⁺ 267 (6.61), 244 (2.28), 227 (25.56), 225 (39.40), 182 (9.16), 162 (17.42), 133 (8.83), 113 (19.2), 95 (10.38), 84 (74.72), 66 (100), 46 (26.57). IR (CCl₄, cm⁻¹) 2118.6, 1724.1, 1594.2, 1498, 1217.8, 1116.5.
A.7  Schematic synthesis of 2-azido-terphthalic acid dimethyl ester

(a): \( \text{HNO}_3 \) (concentrated), \( \text{H}_2\text{SO}_4 \) (concentrated) r.t. (b): \( \text{SnCl}_2, \text{HCl} \), r.t. (c): \( \text{NaNO}_2, \text{HCl} \), 0 °C (d): \( \text{NaN}_3, \text{H}_2\text{O} \), 0 °C.

A.7.1  Synthesis of 2-nitro-terphthalic acid dimethyl ester

To a cooled mixture of 1:1 fuming nitric acid and concentrated sulfuric acid (200mL), terphthalic acid dimethyl ester (15g, 25.7 mmole) was added slowly such that the temperature does not rise above 0 °C. The reaction mixture was allowed to stir for 2 hours at room temperature. The product crystallized as a yellow solid and was filtered and isolated (18.35g, 99%) m.p. 73-74 °C (lit. m.p. 75-76 °C). \( ^1\text{H} \) NMR (DMSO, TMS)
(δ ppm), 3.87 (s, 3H), 3.91 (s, 3H), 7.97 (d, 1H), 8.32 (d, 1H), 8.46 (s, 1H). $^{13}$C NMR (DMSO, TMS) (δ ppm), 52.97, 53.42, 124.50, 130.50, 133.89.

A.7.2 Synthesis of 2-amino-terphthalic acid dimethyl ester

\[
\begin{align*}
&\text{COOCH}_3 \\
&\text{NH}_2 \\
&\text{COOCH}_3
\end{align*}
\]

To a stirred mixture of stannous chloride dihydrate (50.0g, 0.22 mol) and concentrated hydrochloric acid (300mL) was added 2-nitro-terphthalic acid dimethyl ester (7g, 29.4 mmol) in small quantities over 30 minutes. The reaction mixture was stirred for 30 minutes and then the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layer was dried over sodium sulfate and the solvent removed. The product crystallized as a yellow solid (2.5g, 41%) m.p. 133-134 °C (lit. m.p. 134 °C). $^1$H NMR (DMSO, TMS) (δ ppm), 3.82 (d, 6H), 6.85 (s, 2H), 7.01 (d, 1H), 7.43 (s, 1H), 7.76 (d, 1H). $^{13}$C NMR (DMSO, TMS) (δ ppm), 51.63, 52.17, 111.81, 114.34, 117.56, 131.07, 134.08, 150.93, 165.82, 167.17.
A solution of 2-amino-terphthalic acid dimethyl ester (1g, 4.7mmol) in HCl (5M, 23mL, 1:1 HCl and H2O) was cooled to 0 °C and diazotized by the slow addition of a solution of sodium nitrite (0.36g, 5.2mmol) in water (2.8mL). The resulting diazonium chloride was stirred for 10 minutes at 0 °C. A solution of sodium azide (0.31g, 4.7 mmol) and sodium acetate (3.85g, 47mmol) in water (9.4mL) was slowly added to the diazonium chloride. The reaction mixture was stirred for 2 hours at 0 °C and then it was extracted with dichloromethane. The azide was purified by column chromatography using dichloromethane as eluent. The first few fractions contained the azide (0.31g, 29%) m.p. 76 °C (lit. m.p. 76 °C). 1H NMR (CDCl3, TMS) (δ ppm), 3.91 (s, 3H), 3.94 (s, 3H), 7.85 (m, 3H). 13C NMR (CDCl3, TMS) (δ ppm), 52.54, 52.63, 120.76, 125.18, 126.22, 131.70, 134.31, 140.26, 165.28. IR (CCl4, cm⁻¹) 2116, 1724, 1401, 1298.3, 1250.
A.8 Schematic synthesis of 2-azido-isophthalic acid dimethyl ester

(a): KMnO₄, H₂O, reflux (b): HCl (gas), CH₃OH, reflux. (c): SnCl₂, HCl, r.t. (d): NaNO₂, HCl, 0 °C (e): NaN₃, H₂O, 0 °C.

A.8.1 Synthesis of 2-nitro-isophthalic acid

In a 1-L flask, fitted with stirrer and reflux condenser, were added 2-nitro m-xylene (13.3g, 87 mmoles), potassium permanganate (54.53g, 0.34 moles) and water (665mL). This mixture is slowly heated and refluxed for 5 hours until the purple color of KMnO₄ disappeared. The reaction mixture was then distilled (to remove unreacted starting material that distilled off with water). The hot mixture is then filtered under suction to remove MnO₂. The combined filtrate was distilled again to concentrate the
reaction mixture and the solution was acidified with concentrated HCl (46mL) with continual agitation. When the mixture was cooled, a white precipitate of the desired product was isolated (12.5g, 68%) m.p. 315 °C (lit.11 m.p. 314-315). \(^1\)H NMR (DMSO, TMS) (\(\delta\) ppm), 7.78 (3, 1H), 8.15 (t, 2H). \(^1\)C NMR (DMSO, TMS) (\(\delta\) ppm), 124.74, 131.09, 134.45, 164.02.

A.8.2 Synthesis of 2-nitro-isophthalic acid dimethyl ester\(^{12}\)

\[
\begin{align*}
\text{H}_3\text{C} \text{O}_2\text{C} & \quad \text{NO}_2 \\
\text{C}_2\text{H}_5 \text{CO}_2\text{C} \quad \text{C}_2\text{H}_5
\end{align*}
\]

To absolute methanol (112mL) saturated with hydrogen chloride gas at 0 °C, 2-nitro isophthalic acid was added (12g, 56 mmol). The reaction mixture was heated at reflux for 5 hours in oil-bath. A white solid appeared at the end of reaction, which was extracted with ethyl acetate and water to give the desired ester (13.44g, 99%) m.p. 129-130 °C (lit.\(^{12}\) m.p. 133-134 °C). \(^1\)H NMR (DMSO, TMS) (\(\delta\) ppm), 3.85 (s, 6H), 7.87 (t, 1H), 8.22 (d, 2H). \(^1\)C NMR (DMSO, TMS) (\(\delta\) ppm), 52.32, 123.47, 131.66, 134.95, 162.80.
A.8.3 Synthesis of 2-amino-isophthalic acid dimethyl ester\textsuperscript{12}

\[
\begin{align*}
\text{H}_3\text{CO}_2\text{C} & \quad \text{NH}_2 \\
\text{CO}_2\text{CH}_3 & \quad \text{C} \quad \text{C}
\end{align*}
\]

To a stirred mixture of stannous chloride dihydrate (50.0g, 0.22 mol) and concentrated hydrochloric acid (300mL) was added 2-nitro-isophthalic acid dimethyl ester (7g, 29.4 mmol) in small quantities over 30 minutes. The reaction mixture was stirred for 30 minutes and then the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layer was dried over sodium sulfate and the solvent removed. The product crystallized as a yellow solid (4.4g, 72\%) m.p. 101-103 °C (lit.\textsuperscript{12} m.p. 103-104 °C). \textsuperscript{1}H NMR (DMSO, TMS) (δ ppm), 3.80 (s, 6H), 6.61 (t, 1H), 8.01 (d, 2H). \textsuperscript{13}C NMR (DMSO, TMS) (δ ppm), 51.76, 111.14, 113.50, 113.73, 137.09, 152.01, 167.27.

A.8.4 Synthesis of 2-azido-isophthalic acid dimethyl ester\textsuperscript{12}

\[
\begin{align*}
\text{H}_3\text{CO}_2\text{C} & \quad \text{N}_3 \\
\text{CO}_2\text{CH}_3 & \quad \text{C} \quad \text{C}
\end{align*}
\]

A solution of 2-amino-isophthalic acid dimethyl ester (1g, 4.7mmol) in HCl (5M, 23mL, 1:1 HCl and H\textsubscript{2}O) was cooled to 0 °C and diazotized by the slow addition of a
solution of sodium nitrite (0.36g, 5.2mmol) in water (2.8mL). The resulting diazonium chloride was stirred for 10 minutes at 0 °C. A solution of sodium azide (0.31g, 4.7 mmol) and sodium acetate (3.85g, 47mmol) in water (9.4mL) was slowly added to the diazonium chloride. The reaction mixture was stirred for 2 hours at 0 °C and then it was extracted with chloroform. The azide was purified by column chromatography using chloroform as eluent. The first few fractions contained the azide (0.51g, 48%) m.p. 48 °C (lit.12 m.p. 67 °C). 1H NMR (CDCl3, TMS) (δ ppm), 3.93 (s, 6H), 7.27 (t, 1H), 7.90 (d, 2H). 13C NMR (CDCl3, TMS) (δ ppm), 52.64, 125.14, 126.85, 134.33, 139.09, 165.69. IR (CCl4, cm⁻¹) 2134.3, 1728.4, 1590.1, 1435.5, 1216.8, 1113.6.

A.9 Schematic synthesis of 5-azido-isophthalic acid dimethyl ester

(a): SnCl2, HCl, r.t. (b): NaNO2, HCl, 0 °C (c): NaN3, H2O, 0 °C.
A.9.1 Synthesis of 5-amino-isophthalic acid dimethyl ester

\[
\text{H}_3\text{COOC}\begin{array}{c}
\text{NH}_2 \\
\text{COOCH}_3
\end{array}
\]

To a stirred mixture of stannous chloride dihydrate (26.0g, 0.12 mol) and concentrated hydrochloric acid (200mL) was added 5-nitro-isophthalic acid dimethyl ester (3.5g, 15 mmol) in small quantities over 30 minutes. The reaction mixture was stirred for 1.5 hour and then the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layer was dried over sodium sulfate and the solvent removed. The product appeared as a white solid (0.7g, 26%) m.p. 176-178 °C (lit.\textsuperscript{13} m.p. 178-180 °C). \textsuperscript{1}H NMR (DMSO, TMS) (δ ppm), 3.82 (s, 6H), 7.39 (s, 2H), 7.64 (s, 1H). \textsuperscript{13}C NMR (DMSO, TMS) (δ ppm), 52.07, 116.57, 118.02, 130.59, 149.49, 165.93.

A.9.2 Synthesis of 5-azido-isophthalic acid dimethyl ester

\[
\text{H}_3\text{COOC}\begin{array}{c}
\text{N}_3 \\
\text{COOCH}_3
\end{array}
\]

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A solution of 2,5-amino-isophthalic acid dimethyl ester (0.68g, 3.2 mmol) in HCl (5M, 15.3mL, 1:1 HCl and H₂O) was cooled to 0 °C and diazotized by the slow addition of a solution of sodium nitrite (0.25g, 3.5 mmol) in water (2mL). The resulting diazonium chloride was stirred for 10 minutes at 0 °C. A solution of sodium azide (0.21g, 3.2 mmol) and sodium acetate (2.6g, 32 mmol) in water (6.5mL) was slowly added to the diazonium chloride. The reaction mixture was stirred for 2 hours at 0 °C and then it was extracted with chloroform. The azide isolated was pure (0.67, 93%) m.p. 103-106 °C. ¹H NMR (CDCl₃, TMS) (δ ppm), 3.94 (s, 6H), 7.82 (s, 2H), 8.39 (s, 1H). ¹³C NMR (CDCl₃, TMS) (δ ppm), 52.53, 123.94, 126.81, 132.24, 141.20, 165.29. MS m/e (relative intensity) M⁺ 235 (4.72), 207 (84.26), 192 (44.19), 164 (62.34), 59 (100). IR (CCl₄, cm⁻¹) 2113.6, 1728.4, 1435.5, 1338.2, 1217.4, 1152.4.
REFERENCES FOR APPENDIX A


APPENDIX B

GC-MS TRACES OF THE PRODUCT STUDIES

Gas Chromatograph/ Mass spectral analysis were performed on a Hewlett Packard 6890 GC using a 30m x 0.25mm x 0.25μm column packed with 5% PH ME Siloxane and HP 5973 MS detector. The carrier gas was helium and the runs utilized the following method:

- Injector temp. 250 °C
- Detector temp. 250 °C
- Oven temp. 1 80 °C
- Iso time 1 3 min
- Ramp rate 1 10 °/min
- Oven temp. 2 250 °C
GC/MS traces of the product mixture formed upon photolysis of benzylchlorodiazirine 1 in isooctane (15°C) containing TME.

1-benzyl-1-chloro-2,2,3,3-tetramethylcyclopropane (4) (r.t.=11.89);
(E) beta-chlorostyrene (3E) (r.t.=5.71); (Z) beta-chlorostyrene (3Z) (r.t.=5.86).

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(h) $[\text{TME}] = 2.2\text{M}$

Retention Time | Area | Area % | Ratio %
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5.842 | 5307988 | 6.082 | 7.748
11.614 | 3215138 | 3.684 | 4.693
11.895 | 68505426 | 78.500 | 100.000

153
GC/MS traces of the product mixture formed upon photolysis of benzylchlorodiazirine 1 in dichloromethane (15 °C) containing TME.

1-benzyl-1-chloro-2,2,3,3-tetramethylcyclopropane (4) (r.t.=11.89);
(E) beta-chlorostyrene (3E) (r.t.=5.71); (Z) beta-chlorostyrene (3Z) (r.t.=5.86).

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(b) [TME] = 0.2 M
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GC/MS traces of the product mixture formed upon photolysis of 1-benzyl-1-chloro-1a,9b-dihydrocyclopropa[1]phenanthridene (8) in dichloromethane (15 °C) containing TME.

1-benzyl-1-chloro-2,2,3,3-tetramethylcyclopropane (4) (r.t.=10.83);
phenanthrene (r.t.=13.29);
(E) beta-chlorostyrene (3E) (r.t.=5.10); (Z) beta-chlorostyrene (3Z) (r.t.=4.87).
1-benzyl-1-chloro-1a,9b-dihydrocyclopropa[1]phenanthridene (8) (r.t.=20.15)

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APPENDIX C

MISCELLANEOUS SPECTRA
Figure C.1: UV-vis spectrum of propylchlorodiazirine 12 in dichloromethane.
Figure C.2: UV-vis spectrum of isopropylchlorodiazirine 13 in dichloromethane.
Figure C.3: $^1$H NMR spectrum of benzyl imino ether in DMSO.
Figure C.4: $^1$C NMR spectrum of benzyl imino ether in DMSO.

$\text{Benzyl imino ether}$

$\text{FW} = 18400$
$\text{D2} = 4450.000$
$\text{DP} = 20\text{H CPD}$

$\text{LB} = 200$
$\text{SB} = 0.0$
$\text{CX} = 24.00$
$\text{CY} = 0.0$
$\text{F1} = 220.000\text{DP}$
$\text{F2} = -4.992\text{P}$
$\text{H2/CM} = 589.633$
$\text{PPM/CM} = 9.375$
$\text{SR} = -3711.90$

PPM 0 20 40 60 80 100 120 140 160 180 200

-4.992P 0.0 24.00 0.0 220.000 DP 4450.000 D2 18400 FW 3711.90 SR -3.992 P F2 -4.992P H2/CM 589.633 PPM/CM 9.375 F1 220.000 DP CX 24.00 SB 0.0 LB 200 DP 20H CPD F2 -4.992P H2/CM 589.633 PPM/CM 9.375 SR -3711.90 FW 18400 D2 4450.000 D2 20H CPD LB 200 SB 0.0 CX 24.00 CY 0.0
Figure C.5: $^1$H NMR spectrum of benzyl amidine hydrochloride in DMSO.
Figure C.6: $^{13}$C NMR spectrum of benzyl amidine hydrochloride in DMSO.
Figure C.7: $^1$H NMR spectrum of benzylchlorodiazirine in CDCl$_3$. 

169
Figure C.8: $^{13}$C NMR spectrum of benzylchlorodiazirine in CDCl$_3$. 
Figure C.9: $^1$H NMR spectrum of 1-benzyl-1-chloro-2,2,3,3-tetramethyl cyclopropane in CDCl$_3$. 
Figure C.10: $^{13}$C NMR spectrum of 1-benzyl-1-chloro-2,2,3,3-tetramethyl cyclopropane in CDCl$_3$. 
Figure C.11: $^1$H NMR spectrum of chloromethyl triphenyl phosphonium iodide in DMSO.
Figure C.12: $^{13}$C NMR spectrum of chloromethyl triphenyl phosphonium iodide in DMSO.
Figure C.13: $^1$H NMR spectrum of 90:10 E/Z-betachlorostyrene in CDCl$_3$. 

175
Figure C.14: $^1$H NMR spectrum of propyl imino ether in DMSO.
Figure C.15: $^{13}$C NMR spectrum of propyl imino ether in DMSO.
Figure C.16: $^1$H NMR spectrum of isopropyl imino ether in DMSO.
Figure C.17: $^{13}$C NMR spectrum of isopropyl imino ether in DMSO.
Figure C.18: $^1$H NMR spectrum of propyl amidine hydrochloride in DMSO.
Figure C.19: $^{13}\text{C}$ NMR spectrum of propyl amidine hydrochloride in DMSO.
Figure C.20: $^1$H NMR spectrum of isopropyl amidine hydrochloride in DMSO.
Figure C.21: $^{13}$C NMR spectrum of isopropyl amidine hydrochloride in DMSO.
Figure C.22: $^1$H NMR spectrum of 7, 7- dichlorodibenzobicyclo [4.1.0] heptane in CDCl$_3$. 
Figure C 23: $^{13}$C NMR spectrum of 7, 7'-dichlorodibenzobicyclo [4.1.0] heptane in CDCl$_3$. 
Figure C.24: $^1$H NMR spectrum of 7-benzyl, 7-chloro dibenzo[a,c] bicyclo[4.1.0] heptane in CDCl$_3$. 
Figure C.25: $^{13}$C NMR spectrum of 7-benzyl, 7-chloro dibenzo[a,c] bicyclo[4.1.0] heptane in CDCl$_3$. 
Figure C.26: $^1$H NMR spectrum of methyl-2-naphthylacetate in CDCl$_3$. 
Figure C.27: $^{13}$C NMR spectrum of methyl-2-naphthylacetate in CDCl$_3$. 
Figure C.28: $^1$H NMR spectrum of 2-diazo-2-(2-naphthyl) acetate in CDCl$_3$. 
Figure C.29: $^{13}$C NMR spectrum of 2-diazo-2- (2-naphthyl) acetate in CDCl$_3$. 
Figure C.30: $^1$H NMR spectrum of compound 21 in CDCl$_3$. 
**Figure C.31:** $^{13}$C NMR spectrum of compound 21 in CDCl$_3$. 

193
Figure C.32: DEPT spectrum of compound 21 in CDCl$_3$. 

194
Figure C.33: Mass spectrum of compound 21.
Figure C.34: $^1$H NMR spectrum of compound 22 in CDCl$_3$. 
Figure C.35: $^{13}$C NMR spectrum of compound 22 in CDCl$_3$. 
Figure C.36: DEPT spectrum of compound 22 in CDCl₃.
Figure C.37: Mass spectrum of compound 22.
Figure C.38: $^1$H NMR spectrum of compound 23 in CDCl$_3$. 
Figure C.39: $^{13}$C NMR spectrum of compound 23 in CDCl$_3$. 
Figure C.40: DEPT spectrum of compound 23 in CDCl₃.
Figure C.41: Mass spectrum of compound 23.
Figure C.42: $^1$H NMR spectrum of compound 24 in CDCl$_3$. 
Note: All the peaks in the spectrum are shifted by 9.6ppm due to incorrect SR values.

**Figure C.43:** $^{13}$C NMR spectrum of compound 24 in CDCl$_3$. 

205
Note: All the peaks in the spectrum are shifted by 9.6 ppm due to incorrect SR values.

Figure C.44: DEPT spectrum of compound 24 in CDCl₃.
Figure C.45: Mass spectrum of compound 24.
Figure C.46: $^1$H NMR spectrum of 2-azido-benzoic acid methyl ester in CDCl$_3$. 

208
Figure C.47: $^{13}$C NMR spectrum of 2-azido-benzoic acid methyl ester in CDCl$_3$. 

209
Figure C.48: IR spectrum of 2-azido-benzoic acid methyl ester in CHCl₃.
Figure C.49: $^1$H NMR spectrum of 1-azido-2-methoxy benzene in CDCl$_3$. 

211
Figure C.50: IR spectrum of 1-azido-2-methoxy benzene in CCl₄.
Figure C.51: $^1$H NMR spectrum of 1-azido-3-methoxy benzene in CDCl$_3$. 

213
Figure C.52: $^{13}$C NMR spectrum of 1-azido-3-methoxy benzene in CDCl$_3$. 
Figure C.53: IR spectrum of 1-azido-3-methoxy benzene in CCl₄.
Figure C.54: $^1$H NMR spectrum of 5-azido-isophthalic acid in DMSO.
Figure C.55: $^{13}$C NMR spectrum of 5-azido-isophthalic acid in DMSO.
Figure C.56: IR spectrum of 5-azido-isophthalic acid in CHCl₃.
Figure C.57: $^1$H NMR spectrum of 2,5-dihydroxy-terphthalic acid dimethyl ester in DMSO.
Figure C.58: $^{13}$C NMR spectrum of 2,5-dihydroxy-terphthalic acid dimethyl ester in DMSO.
Figure C.59: $^1$H NMR spectrum of 2,5-dimethoxy-terphthalic acid dimethyl ester in DMSO.
Figure C.60: $^{13}$C NMR spectrum of 2,5-dimethoxy-terphthalic acid dimethyl ester in DMSO.
Figure C.61: $^1$H NMR spectrum of 2,5-dimethoxy-3-nitro-terphthalic acid dimethyl ester in DMSO.
Figure C.62: $^{13}$C NMR spectrum of 2,5-dimethoxy-3-nitro-terphthalic acid dimethyl ester in DMSO.
Figure C.63: $^1\text{H}$ NMR spectrum of 3-amino-2,5-dimethoxy-terphthalic acid dimethyl ester in DMSO.
Figure C.64: $^{13}$C NMR spectrum of 3-amino-2,5-dimethoxy-terphthallic acid dimethyl ester in DMSO.
Figure C.65: Mass spectrum of 3-amino-2,5-dimethoxy-terphthalic acid dimethyl ester.
Figure C.66: $^1$H NMR spectrum of 3-azido-2,5-dimethoxy-terphthalic acid dimethyl ester in CDCl$_3$. 
Figure C.67: $^{13}$C NMR spectrum of 3-azido-2,5-dimethoxy-terphthalic acid dimethyl ester in CDCl$_3$. 
Figure C.68: IR spectrum of 3-azido-2,5-dimethoxy-terphthalic acid dimethyl ester in CHCl₃.
Figure C.69: Mass spectrum of 3-azido-2,5-dimethoxy-terphthalic acid dimethyl ester.
Figure C.70: $^1$H NMR spectrum of 3,4,5-trimethoxy-benzoic acid methyl ester in DMSO.
**Figure C.71:** $^{13}$C NMR spectrum of 3,4,5-trimethoxy-benzoic acid methyl ester in DMSO.
Figure C.72: $^1$H NMR spectrum 3,4,5-trimethoxy-2-nitro-benzoic acid methyl ester in DMSO.
Figure C.73: $^{13}$C NMR spectrum of 3,4,5-trimethoxy-2-nitro-benzoic acid methyl ester in DMSO.
Figure C.74: $^1$H NMR spectrum 2-amino-3,4,5-trimethoxy-benzoic acid methyl ester in DMSO.
Figure C.75: $^{13}$C NMR spectrum of 2-amino-3,4,5-trimethoxy-benzoic acid methyl ester in DMSO.
Figure C.76: $^1$H NMR spectrum 2-azido-3,4,5-trimethoxy-benzoic acid methyl ester in DMSO.
Figure C.77: $^{13}$C NMR spectrum of 2-azido-3,4,5-trimethoxy-benzoic acid methyl ester in DMSO.
Figure C.78: IR spectrum 2-azido-3,4,5-trimethoxy-benzoic acid methyl ester in CHCl₃.
Figure C.79: Mass spectrum of 2-azido-3,4,5-trimethoxy-benzoic acid methyl ester.
Figure C.80: $^1$H NMR spectrum 2-nitro-terphthalic acid dimethyl ester in DMSO.
Figure C.81: $^{13}$C NMR spectrum of 2-nitro-terphthalic acid dimethyl ester in DMSO.
Figure C.82: $^1$H NMR spectrum 2-amino-terphthalic acid dimethyl ester in DMSO.
Figure C.83: $^{13}$C NMR spectrum of 2-amino-terphthalic acid dimethyl ester in DMSO.
Figure C.84: $^1$H NMR spectrum 2-azido-terphthalic acid dimethyl ester in CDCl$_3$. 

246
Figure C.85: $^{13}$C NMR spectrum of 2-azido-terphthalic acid dimethyl ester in CDCl$_3$. 
Figure C.86: IR spectrum of 2-azido-terphthalic acid dimethyl ester in CHCl$_3$.  

248
Figure C.87: $^1$H NMR spectrum 2-nitro-isophthalic acid in DMSO.
Figure C.88: $^{13}$C NMR spectrum of 2-nitro-isophthalic acid in DMSO.
Figure C.89: $^1$H NMR spectrum 2-nitro-isophthalic acid dimethyl ester in DMSO.
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Figure C.92: $^{13}$C NMR spectrum of 2-amino-isophthalic acid dimethyl ester in DMSO.
Figure C.93: $^1$H NMR spectrum 2-azido-isophthalic acid dimethyl ester in CDCl$_3$.  

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Figure C.94: $^{13}$C NMR spectrum of 2-azido-isophthalic acid dimethyl ester in CDCl$_3$. 

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Figure C.95: IR spectrum 2-azido-isophthalic acid dimethyl ester in CHCl$_3$.  

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Figure C.96: $^1$H NMR spectrum 5-amino-isophthalic acid dimethyl ester in DMSO.
Figure C.97: $^{13}$C NMR spectrum of 5-amino-isophthalic acid dimethyl ester in DMSO.
Figure C.98: $^1$H NMR spectrum 5-azido-isophthalic acid dimethyl ester in CDCl$_3$. 

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Figure C.99: $^{13}$C NMR spectrum of 5-azido-isophthalic acid dimethyl ester in CDCl$_3$. 
Figure C.100: IR spectrum 5-azido-isophthalic acid dimethyl ester in CHCl₃.
Figure C.101: Mass spectrum of 5-azido-isophthalic acid dimethyl ester.