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CHEMISTRY AND KINETICS OF DIMETHYLCARBENE AND THE FLUORESCENCE SPECTRA, LIFETIMES AND THE REARRANGEMENT OF THE EXCITED STATES OF DIALKYLDIAZIRINES

DISSERTATION

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

by

Francis C. Ford

*****

The Ohio State University

1998

Dissertation Committee:
Professor Matthew S. Platz, Adviser
Professor Gideon A. Fraenkel
Professor Christopher M. Hadad

Approved by

Adviser
Department of Chemistry
ABSTRACT

Product studies, laser flash photolysis, and fluorescence spectroscopy were used to study the chemistry and kinetics of dimethylcarbene. The absence of reports of bimolecular chemistry of dimethylcarbene has been attributed either to the absence of a barrier to 1,2-hydrogen migration or to rearrangement in the excited state the precursor. Product studies were performed by photochemical decomposition of two dimethylcarbene precursors: 3,3-dimethyl-3H-diazirine and 2-methoxy-2-methyl-5,5-trideuteromethyl-Δ1-1,3,4-oxadiazoline. Dimethylcarbene was trapped in various solvents and Stern-Volmer quenching methods were used to confirm the reactivity of the carbene with the particular solvent. Significant bimolecular chemistry was observed.

The barrier to 1,2-hydrogen migration was experimentally determined by laser flash photolysis of 3,3-dimethyl-3H-diazirine and 3,3-dimethyl-3H-diazirine-δ6. In Freon-113 and α,α,α-trifluoromethylbenzene the carbenes decayed by rearrangement and by reaction with solvent. This observation was supported by results from product analysis in these solvents. In perfluorohexane the carbene decay appears to be predominantly unimolecular. The Arrhenius parameters indicate that the rearrangement of dimethylcarbene in perfluorohexane has a large component of quantum mechanical tunneling (QMT) while
QMT makes only a minor contribution to the deuterated system under the conditions of this study. The barrier to rearrangement of 5.6 kcal/mole of dimethylcarbene-$d_1$ in prefluorohexane is consistent with \textit{ab initio} molecular orbital calculations.

Rearrangement in the excited state of the diazirine precursor was studied by fluorescence spectroscopy. The fluorescence lifetimes, fluorescence quantum yields, and quantum yields of carbene formation of several diazirines with structural features allowing the blocking of 1,2-hydrogen migrations were determined. Activation energies for excited state disappearance were not affected by deuteration at the $\alpha$-carbon while a small isotope effect was observed for quantum yields of fluorescence ($\Phi_F$) and carbene formation ($\Phi_C$). It was postulated that various competing processes involving ring opening to a diradical from the ($n \rightarrow \pi^*$) excited state to a diradicaloid ($n \rightarrow \sigma^*$) state followed by fragmentation to propene accounts for isotope effects observed. The involvement of reactions other than carbene formation from the excited state of diazirines is responsible for the inability to trap dimethylcarbene in significant yields.
ACKNOWLEDGMENTS

I would like to express my sincerest appreciation to my adviser, Professor Matthew Platz for his intellectual guidance and inspiration during the course of this research. I also would like to thank him for his patience encouragement and understanding.

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VITA

September 16, 1967 Born-Manila, Philippines

1988......................................................... B. S. Chemistry
University of the Philippines
Diliman, Quezon City

1991-1997.............................................. GAANN Fellow
Department of Chemistry
The Ohio State University
Columbus, Ohio

FIELD OF STUDY

Major Field: Chemistry
Division: Organic Chemistry
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CHAPTER 1

INTRODUCTION

Carbenes are neutral, bivalent carbon species wherein the carbon atom has two covalent bonds to two other groups and two nonbonding orbitals containing two electrons between them. The distribution of nonbonding electrons determines the electronic state of a carbene and ultimately the type of reactions it undergoes. If the energy separation between the nonbonding orbitals is greater than the pairing energy for the two electrons, then both electrons will occupy the lower-energy orbital. A reasonable approximation of a carbene in this state is a bent sp² hybrid 1. Structure 1 represents the lowest singlet state and the reactivity of a carbene in this state is thought to resemble that of the carbonium ion 2.

If, on the other hand, the difference in molecular orbital energies is less than the pairing energy, then the two nonbonding electrons will occupy different orbitals. Structure 3 shows the carbene in a low energy triplet state configuration. A carbene in the triplet state exhibits reactivity similar to that of a free radical 4.
The excited state configuration of carbenes may also be achieved especially when generated from the direct photolysis of carbene precursors. Structures 5 and 6 represent excited states of carbenes with 6 being the more energetic of the two structures.

### 1.1 Reactivity of Carbenes

Alkyl and dialkyl carbenes generally undergo two types of reactions: (1) intermolecular insertion/addition (σ-bond insertion and π-bond cycloaddition) and (2) intramolecular isomerization (hydrogen and carbon migrations). Intermolecular processes include concerted three-center insertions (Scheme 1.1)
Scheme 1.1: Concerted three-centered insertion mechanism.

Particularly common examples are the C-H insertion reactions of singlet carbenes.\(^1\) Stepwise reaction mechanisms are possible and are exhibited by triplet carbenes.

Since the triplet carbene is thought of as a free radical\(^1,2\), a two step abstraction-recombination mechanism is thought to occur (Scheme 1.2).

Scheme 1.2: Abstraction-recombination mechanism.
Doering\textsuperscript{3} has shown that methylene inserts into C-H bonds of (-)-S-2-methoxypropionate with retention of configuration. Had an abstraction-recombination mechanism occurred, racemization would have been expected. This provides chemical evidence of the electronic state of a carbene.

Ylide formation is another type intermolecular reaction which carbenes undergo (Scheme 1.3). This usually involves nucleophilic attack of donor lone pairs on an electrophilic carbene.

\[ \begin{array}{c}
\text{R} \\
\text{R}
\end{array} + \text{X—Y} \rightarrow \text{R—X—Y} \rightarrow \text{R—X—Y} \rightarrow \text{R—X—Y} \]

Scheme 1.3: Ylide formation mechanism.

The ring expansion of cyclic ethers resulting from the attack of methylene in the gas phase illustrates the ylide forming mechanism followed by hydrogen or carbon migration.\textsuperscript{4} With alcohols, the product is usually insertion into O-H bonds\textsuperscript{5-8}. Reactions with nitrogen\textsuperscript{9}, sulfur\textsuperscript{10,11} and phosphorous nucleophiles occur in an analogous manner. With thiols and amines, the products are those of insertion into S-H or N-H bonds.

Laser Flash Photolysis (LFP) of alkyl and dialkylidazirines produces alkyl and dialkylcarbenes (Scheme 1.4). The carbenes formed react with pyridine to form ylides\textsuperscript{7} which are intensely absorbent and relatively long-lived.\textsuperscript{12,13}
Scheme 1.4: Carbene-pyridine ylide formation.

Cycloadditions to multiple bonds resulting in cyclopropanation are possibly the most well known reactions of carbene intermediates (Scheme 1.5). Following Hine’s initial work with dichlorocarbene\(^1\), Doering and Hoffmann showed that CCl\(_2\) or CBr\(_2\) could be intercepted by olefins to form cyclopropanes\(^1\)\(^5\).

Scheme 1.5: Cycloaddition of dihalocarbenes CCl\(_2\) and CBr\(_2\).
The stereospecificity of addition is thought to reflect the electronic state of the carbene.\textsuperscript{16} For example, most addition reactions of methylene are stereospecific \textit{cis}-additions; thus, the carbene is thought to be in the singlet state (Scheme 1.6). The transition state for the reaction involves a three-centered (yet not necessarily symmetrical) transition state with the carbene adding to one face of the alkene thus resulting in a stereospecific addition.

\begin{center}
\begin{tikzpicture}
  \node (a) at (0,0) {H};
  \node (b) at (1,0) {R_1};
  \node (c) at (2,0) {R_2};
  \node (d) at (3,0) {H};
  \node (e) at (4,0) {R_1};
  \node (f) at (5,0) {R_2};
  \node (g) at (6,0) {H};
  \draw (a) -- (b) -- (c) -- (d) -- (e) -- (f) -- (g);
  \draw (a) -- (g);
\end{tikzpicture}
\end{center}

\textbf{Scheme 1.6:} Stereospecific addition of singlet methylene.

In a triplet carbene, addition occurs through a stepwise mechanism resulting in the formation of a 1,3-diradical (Scheme 1.7). If bond rotation in the diradical is faster than intersystem crossing, then loss of stereospecificity is observed; otherwise, an apparently stereospecific adduct is formed.
Scheme 1.7: Non-stereospecific addition of triplet methylene.

Besides the question of stereospecificity as related to carbene multiplicity, addition of a carbene to certain olefins may occur from only one direction and afford only one product. For example, bicyclic olefins in Scheme 1.8 will react with carbenes only from the exo direction affording only exo cyclopropanes. The effect may originate from steric hindrance to endo attack.17
Intramolecular reactions occur with great rapidity and are often used to explain the paucity of intermolecular reactions. Hydrogen migration may be regarded as a hydride shift in a singlet carbene analogous to carbonium 1,2-hydrogen shifts (Scheme 1.9). It is widely believed that the alignment of the migrating C-H bond with the empty $p$-orbital of the carbene controls the rate of 1,2-migration.\textsuperscript{18-24}

\begin{center}
\textbf{Scheme 1.8}: Exo-addition of carbenes to bicyclic olefins.
\end{center}

\begin{center}
\textbf{Scheme 1.9}: 1,2-Hydrogen migration mechanism for dimethylcarbene.
\end{center}
When α-hydrogens are absent, 1,2-carbon migration and β-hydrogen migration may occur. β-hydrogen migration results in cyclopropane formation (Scheme 1.10) while 1,2-carbon migrations, which are relatively uncommon, results in alkene formation similar to 1,2-hydrogen shifts.

Scheme 1.10: 1,3-Hydrogen migration and cyclopropane formation.

1.2 Carbene Precursors

The intermediacy of a carbene is often deduced from results of product analysis of reaction mixtures. However free carbenes may not necessarily be involved in product formation. The intermediacy of a free carbene usually depends on the type of precursor and the generative method. Using a variety of precursors, one can demonstrate whether a free carbene is involved in a given reaction. If the same products are formed with a multitude of precursors, this is often taken as evidence of a free carbene intermediate.

The most common method of generating carbenes is by heat or light-induced decomposition of diazirines, diazo compounds, and ketenes. Due to the instabilities of
alkyl diazo compounds, modifications in generating the diazo precursors are desirable. Tosylhydrazone salts and N-nitroso derivatives of sulfonamides can be used to generate diazo compounds in situ thus circumventing the difficulty of handling the sensitive precursor.

Base-induced α-elimination methods have been used to generate alkyl and dialkyl carbenes. In some cases, the products obtained are characteristic of free carbene intermediates but more often, of carbenoid species. Carbenoids undergo reactions which are characteristic of free divalent carbon species but exhibit reactivities and selectivities different from carbenes generated from other precursors. A single intermediate is thus difficult to pinpoint with this technique and is thus satisfactory only for qualitative studies. Cycloelimination reactions can provide reasonable non-nitrogenous precursors for alkyl and dialkyl carbenes if they are readily available and if cycloreversion and rearrangement does not compete with carbene formation.

1.2.1 Diazirines

Diazirines are useful as photochemical sources of highly reactive carbene intermediates. As such they are valuable compounds for mechanistic and synthetic organic chemistry. In addition, they are widely employed as reagents in photoaffinity labeling (PAL) experiments with biological macromolecules. Diazirines are cyclic isomers of diazo compounds with the N-N double bond in a three-membered ring. The first diazirines were prepared by Schmitz in 1960 and, unlike their acyclic isomers, are surprisingly stable compounds that are easy to handle.
Several routes toward the synthesis of diazirines are available in the literature.\textsuperscript{25,40} The method of choice usually depends on whether the diazirine derives from a ketone or an aldehyde. Ketones are converted to the corresponding diaziridines by amination with chloramine or hydroxylamine-\textit{O}-sulfonic acid (Scheme 1.11).\textsuperscript{41,42}

\begin{equation}
\begin{align*}
\text{R} \quad \text{N} \quad \text{R} \\
\text{R} \quad \text{N} \quad \text{R}
\end{align*}
\end{equation}

\begin{equation}
\begin{align*}
\text{R} \quad \text{N} \quad \text{R} \\
\text{R} \quad \text{N} \quad \text{R}
\end{align*}
\end{equation}

\begin{equation}
\begin{align*}
\text{R} \quad \text{N} \quad \text{R} \\
\text{R} \quad \text{N} \quad \text{R}
\end{align*}
\end{equation}

\begin{equation}
\begin{align*}
\text{R} \quad \text{N} \quad \text{R} \\
\text{R} \quad \text{N} \quad \text{R}
\end{align*}
\end{equation}

X = -Cl, -\text{OSO}_3\text{H}

[O] = \text{CrO}_3/\text{H}_2\text{SO}_4; \text{KMnO}_4/\text{OH}^-; \text{Ag}_2\text{O}

\textbf{Scheme 1.11:} Diazirine preparation by amination-oxidation.

The diaziridines synthesized to date are isolated in 3-35\% yield and can be then converted to the diazirine using chromium trioxide in dilute sulfuric acid\textsuperscript{43}, aqueous basic potassium permanganate or silver oxide.\textsuperscript{39,44}
Aldehydes can be converted to the diazirine by first converting the aldehyde to the cyclic triazolidine 10. The cyclic trimer is then converted to the diazirine using the previous oxidants. The trimers of acetaldehyde and trimethyl acetaldehyde have been synthesized in 40-50% yield using this method.

Diazirines may also be produced by exposure of aldehydes and ketones to chlorine and ammonia and in situ oxidation leading to diazirines. The parent diazirine is prepared by the oxidation of methylene diammonium sulfate with sodium hypochlorite or by the reaction of the t-octylazomethine in dichloramine in buffered aqueous solution (Scheme 1.12).

\[ R = -\text{C(CH}_3\text{)}_2\text{CH}_2\text{C(CH}_3\text{)}_3; -\text{C(CH}_3\text{)}_3 \]

**Scheme 1.12:** Diazirine preparation by amination-oxidation of N-alkylimines.
Modifications of Graham's procedure usually involves initial preparation of a tertiary imine (tert-butyl or cyclohexylimine) followed by cyclization with hydroxylamine sulfonic acid. Oxidation with tert-butylhypochlorite yields the diazirine. Related methods employing this strategy involve the use of O-tosyl ketoximes followed by cyclization/elimination with attack of alkoxyamines.

In this work, several diazirines have been synthesized using the aforementioned modifications to literature preparations, including: dimethyl diazirine, cyclohexyldiazirine, adamantyldiazirine and 1-adamantyldiazirine. A major problem in diazirine preparation is that most simple alkyl, dialkyl and some spirocyclic diazirines are generally low boiling liquids (Table 1.1). Thus, the diazirine is collected at -70°C in the solvent used for laser flash photolysis, after first passing through a column of potassium hydroxide and Drierite.

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Boiling Point</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C (760 torr)</td>
<td></td>
</tr>
<tr>
<td>Diazirine</td>
<td>-14 °C</td>
<td>46</td>
</tr>
<tr>
<td>3,3-Dimethyldiazirine</td>
<td>21 °C</td>
<td>39</td>
</tr>
<tr>
<td>3-Ethyl-3-methyldiazirine</td>
<td>41 °C</td>
<td>44</td>
</tr>
<tr>
<td>3,3-Tetramethylenediazirine</td>
<td>23 °C</td>
<td>51</td>
</tr>
<tr>
<td>3,3-Pentamethylenediazirine</td>
<td>33 °C</td>
<td>39</td>
</tr>
</tbody>
</table>

**Table 1.1:** Boiling points of alkyl-, dialkyl-, and spirocyclic diazirines.
1.2.2 Oxadiazolines

Warkentin has extensively investigated the synthesis and chemistry of oxadiazolines over the past 20 years. Oxadiazolines are readily prepared from aldehydes or ketones via an N-acetylhydrazone. Oxidation of an aldehyde or ketone N-acetylhydrazone in methanol with lead tetraacetate furnishes the oxadiazoline in quantitative yields (Scheme 1.13).

![Scheme 1.13: Preparation of oxadiazolines.]

It has been demonstrated that oxadiazolines decompose by two possible paths when subjected to heat or light (Scheme 1.14): (1) Fragmentation into diazoalkanes and carbonyl derivatives; (2) cycloreversion to nitrogen gas and carbonyl diradical or ylide, which can further dissociate to a carbonyl compound and a carbene.
Scheme 1.14: Thermal and photochemical decomposition pathways of oxadiazolines.

Dialkyldiazo compounds may be generated by direct or sensitized photolysis of oxadiazolines. Pyridine-trappable products such as carbenes may be obtained by subsequent photolysis of the diazoalkane.

The volatility of simple alkyl and dialkyl diazirines introduces problems in quantitation and ease of handling. The oxadiazoline precursor seems to be a reasonable alternative to diazirines due to ease in preparation, handling and quantitation. Oxadiazolines also allow us an alternative precursor to a carbene if the diazirine is not available. If we can provide evidence of similar chemical reactivity between diazirines and oxadiazolines, then we can conclude that the two precursors are equivalent.
1.3 Alkyl and Dialkyl Carbenes

The parent carbene, methylene 11a, has been the object of much research and is by now a rather well-understood compound. Singlet and triplet geometries have been determined for this species and the energy gap between these states calculated to be about 9 kcal/mol in favor of the triplet state.\textsuperscript{61-63} Substitution of alkyl groups for hydrogens in methylene gives the corresponding alkyl and dialkyl carbenes. Calculations indicate that alkyl substitution decreases the singlet-triplet gap.\textsuperscript{64}

\textbf{Scheme 1.15:} Structures of simple alkyl and dialkyl carbenes (methylene-$h_1$ and $d_1$ 11a and 11b; ethylidene-$h_1$ and $d_1$ 12a and 12b; dimethylcarbene-$d_4$ and $h_3$ 13a and 13b).

Methylcarbene 12a also has a triplet ground state with a 5 kcal/mol separation between the two states.\textsuperscript{65} Dimethylcarbene 13a, the parent dialkyl carbene, is calculated to have a singlet ground state with a singlet-triplet split of 1.64 kcal/mole.\textsuperscript{66}
1.3.1 Chemical Trapping Studies

Few alkyl and dialkyl carbenes have been successfully studied by chemical trapping and spectroscopic studies. These species are thought to be so evasive as to preclude trapping by virtue of their very rapid intramolecular reactions, particularly 1,2-hydrogen migration. However, several studies have shown that for simple alkyl and dialkyl carbenes, intermolecular trapping is possible.

Methylcarbene 12a or ethylidene is the simplest alkyl substituted carbene which can undergo 1,2-hydrogen migration to form ethylene. Attempts by Kramer and Wright\textsuperscript{67} to intercept 12a have resulted in low yields (5\%) of ethylphenylsilane (Scheme 1.16).

\[
\begin{array}{c}
\text{Si} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\quad + \quad \begin{array}{c}
\text{PhSiH}_3
\end{array}
\quad \rightarrow \quad \begin{array}{c}
\text{Ph} \\
\text{H} \\
\text{H} \\
\text{CH}_2\text{CH}_3
\end{array}
\]

**Scheme 1.16:** Interception of methylcarbene 12a with phenylsilane.

Using diazoethane 14 as the carbene precursor, Frey\textsuperscript{68} showed that gas phase photolysis of 14 with propylene (Scheme 1.17) produces small amounts of cis- and trans-1,2-dimethylcyclopropanes which he attributed to the trapping of 12. Extension of these experiments to the photolysis of 14 in 2-butene resulted in only trace formation of
cyclopropane while photolysis of 14 in propane and butane provided no C-H insertion products.

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{hv} \quad \text{H}_2\text{C} \quad \text{H} \quad \text{H}_2\text{C} \quad \text{CH}_3 \\
\text{14} & \quad \text{propylene} \\
& \quad \text{H}_2\text{C} = \text{CH}_2
\end{align*}
\]

**Scheme 1.17:** Interception of methylcarbene 12a with propylene.

In a cryogenic matrix, the low temperatures and rigid conditions should effectively slow down intramolecular processes thereby allowing the observation of the carbene. McMahon and Seeburg\(^\text{69}\) demonstrated that the photolysis of 3-methylidiazirine 15a and its trideuterio isotopomer 15b in an argon matrix at 8 K results in the formation of singlet carbenes 12a and 12b. Upon photolysis of 15a and 15b in a CO doped argon matrix, the formation of triplet state of 12a and 12b is not observed but ethylene and small amounts of ketenes are produced. The ketenes are thought to be derived from small amounts of singlet ethylidenes (12a and 12b) that have been trapped by CO. The authors\(^\text{69}\) concluded that even at low temperatures (8 K), 1,2-hydrogen migration is so fast that it effectively competes with bimolecular trapping of 12a and 12b thus resulting in a
failure to observe an isotope effect in the product ratios and in the production of trace yields of ketene (Scheme 1.18).

Scheme 1.18: Interception of methylcarbene-$h$ $12a$ and methylcarbene-$d$ $12b$ with carbon monoxide.

Recent studies by Modarelli and Platz$^{70}$ with ethylidene-$d$ $12b$ demonstrated that the carbene may be trapped with pyridine (Scheme 1.4) and methanol (Scheme 1.19). They observed that upon photolysis of 3-methylidiazirine-$h$ $15a$ and 3-methylidiazirine-$d$ $15b$ in methanol and methanol-$d$, the ethers (16 and 17) from O-H or O-D insertion are formed. Deuteration of the $\alpha$-hydrogens was found to increase the carbene yield by 36%. The authors attributed this increase to the influence of several kinetic isotope effects on the
migration of H or D in the carbene and in the diazirine excited state and in the insertion into the O-H(D) bond of the alcohol.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{N} \quad \text{N} \quad \text{H} \\
\text{N} & \quad \text{N} \quad \text{H} \\
& \text{CD}_3\text{OD} \quad \text{hv} \quad \rightarrow \\
& \text{H}_3\text{C} \quad \text{N} \\
\text{OCD}_3 & \quad \text{D} \quad \text{H} \\
& \text{H}_2\text{C} \equiv \text{CH}_2 \\
\text{16} & \quad (22\%) \\
\text{D}_3\text{C} & \quad \text{N} \quad \text{N} \quad \text{D} \\
\text{D} & \quad \text{N} \quad \text{D} \\
& \text{CH}_3\text{OH} \quad \text{hv} \quad \rightarrow \\
& \text{D}_3\text{C} \quad \text{N} \\
\text{OCH}_3 & \quad \text{D} \quad \text{H} \\
& \text{D}_2\text{C} \equiv \text{CD}_2 \\
\text{17} & \quad (30\%)
\end{align*}
\]

**Scheme 1.19:** Product studies of methylidiazirine (15a and 15b) photolysis in methanol.

In contrast to the bimolecular chemistry found in methylcarbene, very little was known about dimethylcarbene 13a, the parent dialkyl carbene at the outset of this work. Attempts to trap the carbene by photolysis of the 3,3-dimethylidiazirine 18a in cyclohexene in solution have been unsuccessful. Matrix isolation studies have failed to generate dimethylcarbene as a persistent species that may be characterized by spectroscopy. In 1991, Modarelli et al. were able to trap dimethylcarbene (13a and 13b) as a pyridine ylide (Scheme 1.4) by laser flash photolysis of a solution of 3,3-dimethylidiazirine 18a in pyridine. Chemical trapping of the carbene 13a and its perdeuterated analog 13b was also
accomplished with methanol and methanol-d₄ (Scheme 1.20). Ethers 19 and 20 were formed in 40% and 52% yield. Deuteration was found to increase the carbene yield by 30%. As with ethylidene-d₄, the yield increased due to several isotope effects operating on hydrogen migration and on solvent capture. The remaining 48% of untrapped product was attributed to propylene formation from an excited state of the diazirine.⁶⁴,⁷⁰

Scheme 1.20: Product studies of dimethyl diazirine (18a and 18b) photolysis in methanol.
1.3.2 Theoretical Studies

Due to the low yields obtained for intermolecular trapping reaction of methylcarbene and the apparent lack of data for dimethylcarbene, the lifetimes of alkyl and dialkylcarbenes were thought to be exceedingly short. Early semi-empirical MINDO calculations corroborated this view by placing the barrier to rearrangement from within 0 to 20 kcal/mol. The MINDO method was considered unreliable because it tended to favor cyclic structures. With the development of *ab initio* methods, the calculated values decreased dramatically to 3 kcal/mol or less. A summary of the various theoretical treatments for the 1,2-hydrogen migration barrier for methylcarbene is shown in Table 1.2. Depending on the level of theory, the values for $\Delta E'$ tended to disagree on the actual height of the barrier. Introduction of polarized functions and correlation effects reduced the barrier to 2.1 kcal/mol.\textsuperscript{73} The highest level of calculation to date (MP4SDTQ/6-311G\textsuperscript{*}/MP2/6-31G\textsuperscript{*}+ZPE) yields a 0.6 kcal/mol barrier for 1,2-hydrogen migration in singlet methylcarbene.\textsuperscript{74}

In the case of dimethylcarbene, early theoretical estimates by Evanseck and Houk\textsuperscript{24} placed the barrier to 1,2-hydrogen migration at 4.7 kcal/mol. More recent predictions by Matzinger and Fülscher placed the barrier to rearrangement at 7.4 kcal/mol.\textsuperscript{78} The discrepancy of 2.4 kcal/mol between the two values is attributed to: (1) a 0.98 kcal/mol difference between the lowest energy structure favored by Evanseck and Houk over that of Matzinger and Fülscher and (2) the fact that MP2 methods tend to underestimate barrier heights by 2 kcal/mol.\textsuperscript{78}
Table 1.2: Calculated activation barriers for 1,2-hydrogen shift in methylcarbene.

For ethylidene, the results of theoretical calculations raise the question of whether the carbene is an intermediate or a transition structure on the reaction surface from the diazirine to ethylene. Dimethylcarbene, on the other hand, appears to be an intermediate in a potential energy minimum from the calculated barrier and hence should be relatively long-lived and have appreciable bimolecular chemistry.

1.3.3 Carbene Formation and Excited States

Observations from the preceding product studies do not agree with the implications of the theoretical studies on dimethylcarbene. A plausible explanation could be the possible involvement of chemical reactions in the excited state of the diazirine upon photochemical
Accordingly, many results obtained from studies of diazirines are suspected to have been derived partly from excited electronic states of diazirines and/or carbenes. It has been postulated that the participation of excited states in 1,2- and 1,3-hydrogen migration accounts for short lifetimes and the apparent inability to trap some alkyl and dialkyl carbenes.64

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reference</th>
</tr>
</thead>
</table>
| \[
\begin{align*}
\text{NNHT}_x \\
\text{NaOCH}_3, \Delta
\end{align*}
\] | 3.5 66.5 29.5 0.5 81 |
| \[
\begin{align*}
\text{NNH}_x \\
\Delta
\end{align*}
\] | 23 38 35 4 81 |

Table 1.3: Intramolecular product distribution from the decomposition of ethylmethylcarbene precursors in solution.
The products derived from photolysis and thermolysis of ethylmethylidiazirine and its corresponding tosyldrazide salts were found to be very different (Table 1.3). This was surprising considering that the same carbene should be formed from each precursor. In all cases, photolyses of the diazirine led to much more indiscriminate intramolecular reactions than did thermolysis of the diazirine and salt of the analogous tosylhydrazide. The difference in results have been rationalized on the basis that one intermediate cannot be common to both photolytic and thermally initiated decomposition of the precursors. A more reactive and less selective intermediate is generated with light than with thermal decomposition of diazirines.

The direct photochemical formation of an alkene from a diazirine excited state was first proposed by Frey in 1965. In the photolysis of methyldiazirine, Frey proposed the mechanism in Scheme 1.21 to account for the relative yields of the volatile products obtained. Step k₁ corresponds to carbene formation and extrusion of nitrogen upon absorption of radiation. The resulting carbene formed in this step then decomposes (Step k₂) into vibrationally excited or "hot" ethylene. "Hot" ethylene may then decompose by two pathways: (1) through loss of hydrogen resulting in acetylene or (2) by collisional deactivation to ethylene. What was novel in the mechanism was Frey’s proposal of a pathway yielding unexcited ethylene from an excited state of the diazirine (Steps k₁ and k₂). This conclusion was arrived at based on the following observation: at sufficiently low pressures, collisional deactivation (k₄) becomes unimportant and thus all excited ethylene molecules should produce acetylene. A plot of the yield of ethylene against pressure should extrapolate to zero. Experimentally, the yield of ethylene extrapolates to 60% at zero pressure (Figure 1.1). To account for the missing yield of acetylene, a pathway was proposed wherein ethylene molecules are produced but with insufficient energy to decompose to acetylene.
Scheme 1.21: Mechanism of acetylene and ethylene formation from methylidiazirine 15a.
Figure 1.1: Percentage yield of acetylene in the photolysis of 3-methyl diazirine; y-axis. percentage yield; x-axis, pressure (mm).\textsuperscript{84}

Excited state reactions have also been observed on comparing photolysis and thermolysis results of dimethyl diazirine. Photolysis of dimethyl diazirine has been investigated in the gas phase at various pressures. The primary photolytic step is believed to be the production of energy-excessive dimethyl carbene which decomposes into vibrationally excited propylene.\textsuperscript{85} At high pressures, most of the excited propylene is collisionally deactivated; hence, a product distribution of 99% propylene was observed. At lower pressures, increasing amounts of other hydrocarbons were observed (particularly 2-butenes) and the propylene to nitrogen ratio decreased to less than unity. With decreased collisional deactivation at lower pressures, the possibility of excited state decomposition to other radical fragments results in the formation of hydrocarbon products other than propylene. Thermolytic decomposition of dimethyl diazirine gave only propylene and
nitrogen by a unimolecular process. The possibility of a diazo intermediate could not be ruled out in the photochemical and thermal study of dimethyldiazirine decomposition but the authors clearly demonstrated that different intermediates are involved in the two processes.

The inefficiency of diazirine precursors and the participation of diazirine excited states in photolysis can also explain the product distribution obtained by Modarelli et al.\textsuperscript{64,70} in the photolysis of 3-methyldiazirine-$d_3$ and dimethyldiazirine-$d_5$ in methanol (Schemes 1.19 and 1.20). If methanol effectively captures all carbene produced from the diazirines 15b and 18b, then propylene (48\%) and ethylene (70\%) must be rearrangement products from an intermediate other than the carbene, presumably the excited state of the diazirine.

In more recent theoretical treatments of diazirine excited states, Yamamoto et al.\textsuperscript{87} proposed that in the photolysis of diazirines, an electronically excited $n \rightarrow \pi^*$ 21 state is initially formed (Scheme 1.22).\textsuperscript{88} From this $n \rightarrow \pi^*$ state, the diazirines may undergo decay to the diazo compound or may undergo carbene formation by passing through diradicaloid structures 22 and 23. Excitation or conversion of the $n \rightarrow \pi^*$ state into an $n \rightarrow \sigma^*$ state followed by decay into a bent diradicaloid 22 was the most efficient route (path a) to carbene and nitrogen. From the $n \rightarrow \pi^*$ minimum, decay may occur via a bent-in-plane linear diradicaloid structure 23 to ground state diazomethane (path b). Carbene formation from the bent-in-plane linear diradicaloid 23 was found to be the least efficient in generating carbene and nitrogen (path c).\textsuperscript{87}
Scheme 1.22: Proposed mechanism of diazo isomerization and carbene formation in diazirines.

For dimethyldiazirine, Mueller-Remmers and Jug$^{89}$ calculated that a radiationless transition from the n$\rightarrow$$\sigma^*$ state could result in the formation of rearrangement products such as propylene.

Theoretical and chemical evidence indicate that diazirines may not be efficient precursors for carbenes due to the involvement of diazirine excited states.

1.3.4 Laser Flash Photolysis Studies

Methylcarbene and dimethylcarbene are species which lack chromophores that would render them visible in the UV-Vis region. Since laser flash photolysis (LFP)
methods use absorption spectroscopy for detection, a method is required to enable these species to be monitored in an LFP experiment.

Scaiano\textsuperscript{90-92} developed the use of kinetic probes in rendering "invisible" species observable by UV-Vis detection. Several conditions must be satisfied in order to find a suitable trap: (1) the trap must not react with the precursor, (2) it should not absorb pulsed laser radiation, (3) it must react rapidly with the photogenerated reactant, and (4) the product of the trap and the reactant must provide a species with a chromophore that is sufficiently long-lived.\textsuperscript{93} Based on Scaiano's use of kinetic probes, Jackson and Platz\textsuperscript{12,94,95} introduced pyridine ylide probes in the study of solution kinetics of carbenes.
The interception of a carbene with pyridine in a laser flash photolysis study is shown in Scheme 1.23. The carbene is formed upon absorption of pulsed laser radiation and reacts rapidly with pyridine $k_{\text{PYR}}[\text{pyridine}]$. The ylide concentration at any time $[Y]_t$ is represented as an exponential growth function (equation 1.1) where $[Y]_\infty$ is the ylide concentration after its formation is complete but the decay is still insignificant.

$$[Y]_t = [Y]_\infty \left(1 - e^{-kt}\right) \quad \text{(eq. 1.1)}$$
The time constant $k_{\text{obs}}$ for the exponential growth of the ylide can be broken down into the sum of all the first-order and pseudo first-order rate constants that account for the decay of the carbene (equation 1.2).

$$k_{\text{obs}} = k_{\text{pyr}}[\text{PYR}] + k_{\text{sx}}[\text{SX}] + k_{\text{R}} = k_{\text{pyr}}[\text{PYR}] + k_{\text{R}} \quad \text{(eq. 1.2)}$$

By varying the concentration of pyridine, a set of $k_{\text{obs}}$ are obtained and extrapolation to zero pyridine concentration yields $k_{\text{R}}$. The rate constant $k_{\text{R}}$ represents the decay processes of the carbene in the absence of pyridine and the reciprocal of $k_{\text{R}}$ is the lifetime ($\tau$) of the carbene. The above method constitutes a direct method for measuring the absolute rate constant of carbene decay. The quantity $k_{\text{R}}$ can be dissected into its components $k_{\text{R}}$ and $k_{\text{sx}}[\text{SX}]$ using product analysis, isotope effects, and intuition.

Due to limitations of laser spectrometers, indirect methods relying on double reciprocal plots of carbene yield and pyridine concentration are employed to determine carbene lifetimes. The theory behind this process relies on relating the carbene quantum yield with the optical yield of the pyridine ylide produced. The quantum yield of ylide formation ($\phi_y$) in a laser pulse is given in equation 1.3, where $\phi_c$ is the quantum yield of carbene formation.

$$\phi_y = \frac{\phi_c k_{\text{pyr}}}{k_{\text{pyr}}[\text{PYR}] + k_{\text{R}}} \quad \text{(eq. 1.3)}$$

The optical yield of ylide ($A_y$) is related to $\phi_y$ by equation 1.4 where $A_y^{\text{max}}$ is the maximum yield of ylide that can be obtained when [pyridine] is sufficiently large to capture every carbene produced in the laser pulse.

$$A_y = A_y^{\text{max}} \phi_y \quad \text{(eq. 1.4)}$$

Combining and rearranging equations 1.3 and 1.4 leads to equation 1.5

$$\frac{1}{A_y} = \frac{1}{\phi_c A_y^{\text{max}} k_{\text{pyr}}} \left[ \frac{k_{\text{R}}}{k_{\text{pyr}}[\text{PYR}]} \right] + \frac{1}{\phi_c A_y^{\text{max}}} \quad \text{(eq. 1.5)}$$
A plot of $1/A_v$ versus $1/[\text{PYR}]$ is predicted to be linear. Division of the intercept by the slope of this plot gives the ratio $\frac{k_{\text{PYR}}}{k_r}$ or $k_{\text{PYR}} \tau$.

The double reciprocal method of analysis is based on several assumptions: (1) the rate reaction of singlet carbene with pyridine ($k_{\text{PYR}}$) is $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (2) $k_{\text{PYR}}$ does not vary significantly with solvent, and (3) all the decay processes of the carbene proceed through the singlet state. Since the double reciprocal method depends on the optical yield of ylide, processes which affect the absolute yield of ylide will be reflected in the lifetime of the carbene.

Methylcarbene and dimethylcarbene were previously studied by LFP methods and their lifetimes estimated using double reciprocal plots. Ethylidene-$d_2$ was found to have a lifetime of 0.5 ns, i.e., 42 times as short as that of dimethylcarbene. The lifetime agrees with Frey's estimate of 700 ps for the lifetime of methylcarbene. Deuteration of the $\alpha$-hydrogens was found to increase the lifetime of dimethylcarbene which resulted in an isotope effect ($\tau_{d}/\tau_{u}$) of 3.2 in pentane at ambient temperature. A polar solvent was found to shorten the carbene lifetime for both dimethylcarbene and methylcarbene. Stabilization of the polar transition state (Scheme 1.9) by increasing solvent polarity results in a lowering of the barrier to 1,2-hydrogen migration, hence, a shorter lifetime is observed.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Lifetime (ns)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimethylcarbene</td>
<td>pentane</td>
<td>21</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>(\alpha,\alpha,\alpha)-Trifluoromethylbenzene</td>
<td>27</td>
<td>64</td>
</tr>
<tr>
<td>acetonitrile</td>
<td></td>
<td>8.0</td>
<td>64</td>
</tr>
<tr>
<td>acetonitrile-(d_1)</td>
<td></td>
<td>9.0</td>
<td>64</td>
</tr>
<tr>
<td>chloroform</td>
<td></td>
<td>6.8</td>
<td>64</td>
</tr>
<tr>
<td>chloroform-(d)</td>
<td></td>
<td>7.3</td>
<td>64</td>
</tr>
<tr>
<td>dimethylcarbene-(d_6)</td>
<td>pentane</td>
<td>67</td>
<td>64</td>
</tr>
<tr>
<td>methylcarbene-(d_4)</td>
<td>pentane</td>
<td>0.5</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>acetonitrile</td>
<td>0.3</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>acetonitrile-(d_1)</td>
<td>0.4</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>chloroform</td>
<td>0.1</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>chloroform-(d)</td>
<td>0.1</td>
<td>70</td>
</tr>
</tbody>
</table>

'Assuming \(k_{PV} = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}\)

Table 1.4: Deduced lifetimes of methylcarbene\(^70\) \((12b)\) dimethylcarbene\(^64\) \((13a\) and \(13b\))

1.4 Statement of the Problem

In the preceding sections, we have reviewed the chemistry of methyl and dimethylcarbene. There is very little data in the literature describing the bimolecular chemistry of dimethylcarbene and this has always been attributed to (1) the very facile 1,2-hydrogen rearrangement that precludes capture of the carbene and (2) rearrangements in the
excited state of the diazirine precursor. Modarelli’s work on the lifetime of
dimethylcarbene and theoretical calculations on the height of the barrier to rearrangement
indicate that dimethylcarbene should be sufficiently long-lived for bountiful bimolecular
chemistry. For dimethylcarbene, there are no experimental values available for the height
of the rearrangement barrier. The pyridine ylide method using double reciprocal plots is an
indirect method of measuring the lifetime of the carbene. This method is limited by its
dependence on the assumed value of $k_{pyr}$ and on the absolute yield of the ylide. In
determining the activation barriers, a more direct method is required. With improvements
in our LFP equipment, we are now in the position to determine the absolute kinetics for
1,2-hydrogen migration in dimethylcarbene and determine the activation parameters for this
rearrangement.

Precursor inefficiency may account for the apparent inability to trap the carbene by
traditional methods. Diazirines may undergo 1,2-hydrogen rearrangements upon
photochemical activation to excited states. Carbene formation may thus account for a
fraction of the quantum yield. Theory predicts that a fluorescent excited state is formed
upon photochemical activation of a diazirine. It is unclear whether 1,2-hydrogen migration
occurs from this state or from a non-fluorescent excited state. Intramolecular
rearrangements in the excited state may be studied by controlling the structural features of
the diazirine. The effect of isotopic substitution on the fluorescence lifetime ($\tau_f$),
fluorescence quantum yield ($\Phi_f$) and carbene quantum yield ($\Phi_c$) will enable us to determine
(1) if 1,2-hydrogen migration competes with fluorescence and (2) the barrier for this
rearrangement in the fluorescent excited state.

To complement our work on the kinetics of 1,2-hydrogen rearrangement in
dimethylcarbene, we will conduct product and Stern-Volmer quenching studies to survey
its bimolecular chemistry. Due to diazirine volatility, a quantitative treatment of the
resulting photoproducts may not be possible. To solve this problem, we will use oxadiazolines (2-methoxy-2,5,5-trimethyl-\(\Delta^1\)-1,3,4-oxadiazoline and 2-methoxy-2-methyl-5,5-trideuteromethyl-\(\Delta^1\)-1,3,4-oxadiazoline) as alternative precursors to diazirines. Product studies and Stern-Volmer quenching studies will allow us to relate the observed absolute kinetics with the reactivity of dimethylcarbene. These studies will also allow us to determine if oxadiazolines are equivalent precursors to diazirines.

It is our hope that the succeeding chapters answer the basic questions we have raised concerning the ease of hydrogen migration and precursor efficiency in relation to the bimolecular chemistry of dimethylcarbene.
CHAPTER 2

PRODUCT STUDIES ON DIMETHYLCARBENE

In this chapter we present product studies on dimethylcarbene. The present study involves the investigation of the bimolecular chemistry of dimethylcarbene derived from diazirine and oxadiazoline precursors. To develop the reactivity profile for dimethylcarbene, dimethyldiazirine 18a and dimethyloxadiazoline 24a were photolyzed in various solvents to illustrate: (1) cycloaddition reactions (alkenes and aromatics) and (2) insertion reactions (C-H, Si-H, N-H, C-O and C-Cl).

Dimethyldiazirine 18a and dimethyloxadiazoline 24a were condensed into the desired solvent (Table 2.1) and photolyzed for 24 hours at 5 °C with the appropriate wavelength of 350 nm for the diazirine and 300 nm for the oxadiazoline. The products resulting from the photolysis were analyzed by gas chromatography-mass spectrometry (GC-MS).
### Table 2.1: Product studies of dimethylcarbene reaction in various solvents.

<table>
<thead>
<tr>
<th>Carbene Precursor</th>
<th>Cycloaddition Reactions</th>
<th>Insertion Reactions</th>
<th>Ylide Forming Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,3-Dimethylidiazirine and</td>
<td>Tetramethylethylene</td>
<td>Cyclohexane</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>Dimethyloxadiazoline</td>
<td>Cyclopentene</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Norbornene</td>
<td>Triethylsilane</td>
<td>Isopropylamine</td>
</tr>
<tr>
<td></td>
<td>Benzene</td>
<td></td>
<td>Freon-113</td>
</tr>
<tr>
<td></td>
<td>N,N-Dimethylaniline</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Trifluoromethylbenzene</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**2.1 Cycloaddition Reactions**

The reaction of tetramethylethylene with dimethylcarbene derived from either diazirine 18a or oxadiazoline 24a is shown in Scheme 2.1. Continuous photolysis of either precursor in neat tetramethylethylene fails to produce hexamethycyclopropane (Scheme 2.1).
Scheme 2.1: Reaction of dimethylcarbene 13a with tetramethylethylene.

We can rationalize this result for dimethylcarbene based on Hoffmann's theory of the cycloaddition of methylene to ethylene. In this reaction, the bent singlet methylene approaches the alkene through an unsymmetrical transition state (Scheme 2.2). In the transition state, the carbene lies over the olefin parallel to the plane defined by the olefin and the α substituents. There is overlap between the carbene's vacant \( p \) orbital and the filled olefinic \( \pi \) orbital (electrophilic attack of the carbene on the olefin).
Scheme 2.2: Transition state for the cycloaddition of carbenes to alkenes.

Ethylene and methylene can then correlate with the ground state cyclopropane and result in a symmetry-allowed cycloaddition process. It is possible that for larger sized substituents on the alkene and carbene, this situation may significantly raise the barrier to cycloaddition; hence, the carbene undergoes reactions with more favorable pathways.

The results for the photolysis of diazirine 18a and oxadiazoline 24a in cyclopentene and norbornene are summarized in Table 2.2. With both precursors, the formation of cyclopropanes 25 and 26 were observed (Schemes 2.3 and 2.4).
Scheme 2.3: Reaction of dimethylcarbene 13a with cyclopentene.

Cyclopropane 25 was identified based on the observed parent ion mass (m/e = 110) and the fragmentation pattern obtained. Upon the loss of a methyl group, a stable ion fragment C₅H₁₂⁺ with mass (m/e = 95) was observed. This ion is believed to have the bicyclo[3.1.0] ring, which would imply cycloaddition of dimethylcarbene. Extrusion of propylene gave the base peak for ion C₅H₁₊ (m/e = 67) which is believed to have a cyclopentyl ring in the structure.
**Scheme 2.4:** Reaction of dimethylcarbene 13a with norbornene.

Dimethylcarbene addition to norbornene gave cyclopropane 26 (Scheme 2.4). The parent ion which has an \( m/e = 136 \) was found for the peak eluting at 4.52 minutes. Analysis of the fragmentation pattern shows that the loss of an ethylene molecule yields an ion \( C_3H_6^+ \) with \( m/e = 108 \) while extrusion of propylene results in an ion \( C_5H_9^+ \) with \( m/e = 93 \). The overall fragmentation pattern indicates that cyclopropane 26 was formed.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>25</th>
<th>26</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time (min.)</td>
<td>Parent (m/e)</td>
</tr>
<tr>
<td>18a</td>
<td>4.21</td>
<td>110</td>
</tr>
<tr>
<td>24a</td>
<td>4.52</td>
<td>110</td>
</tr>
</tbody>
</table>

**Table 2.2:** Products of dimethylcarbene addition to cyclopentene and norbornene.
Singlet carbenes are electrophilic species and hence may also add to aromatic hydrocarbons. We photolyzed dimethyldiazirine 18a in benzene and an addition product 27 was observed from GC-MS analysis of the photolysis products. The results are listed in Table 2.3. The parent ion with m/e = 120 was observed along with a fragment resulting from the loss of a methyl group (m/e = 105). Comparison with an authentic sample of isopropyl benzene results in a complete match in fragmentation patterns of the authentic sample and photoproduct 27.

![Scheme 2.5: Reaction of dimethylcarbene 13a with benzene.](image)

<table>
<thead>
<tr>
<th>Precursor</th>
<th>27</th>
</tr>
</thead>
<tbody>
<tr>
<td>18a</td>
<td></td>
</tr>
<tr>
<td>Time (min.)</td>
<td>Parent (m/e)</td>
</tr>
<tr>
<td>3.45</td>
<td>120</td>
</tr>
</tbody>
</table>

**Table 2.3: Product of dimethylcarbene addition to benzene.**

The photolysis of dimethyldiazirine and dimethyloxadiazoline in N,N-dimethylaniline (Scheme 2.6) resulted in a complex mixture of products (28, 29, and 30).

43
Dimethylcarbene may attack N,N-dimethylaniline by ylide formation followed by rearrangement on the nitrogen (28), by C-H insertion with either of the two methyl groups (29) and by cycloaddition to the ring (30). The results (Table 2.4) showed that electrophilic attack on the ring occurs with both the oxadiazoline and the diazirine precursor. The ion fragment with $m/e = 120$ was observed indicating addition of an isopropyl group to the aromatic ring. The parent ion which has an $m/e = 161$ was found for the peak eluting at 6.0 minutes. The fragmentation pattern furnishes ions $C_{10}H_{12}N^+$ with $m/e = 146$ resulting from the loss of a methyl group while extrusion of a second methyl group results in an ion $C_{9}H_{10}N^+$ with $m/e = 132$. From this analysis of the fragmentation pattern, it is believed that photoproduct 28 was formed. Ylide formation followed by rearrangement was observed in the diazirine while insertion into the methyl groups was not observed. The precursor dependence may be indicative of inefficient photolysis of the oxadiazoline. Since initial formation of a diazomethane is theorized$^{56,58,59}$, a second wavelength of radiation may required to efficiently form the carbene.$^{60}$
Scheme 2.6: Reaction of dimethylcarbene 13a with N,N-dimethylaniline.
<table>
<thead>
<tr>
<th>Precursor</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>Time (min.)</td>
</tr>
<tr>
<td>18a</td>
<td>6.0</td>
</tr>
<tr>
<td>24a</td>
<td>_</td>
</tr>
</tbody>
</table>

Table 2.4: Products of dimethylcarbene addition to N,N-dimethylaniline.

Initially, we thought that α,α,α-trifluoromethylbenzene would be unreactive towards attack of dimethylcarbene due to the deactivation of the ring by the trifluoromethyl group. However, the photolysis of dimethyldiaziprine in this solvent produced a complex mixture of products that were difficult to identify. The addition of dimethylcarbene to the ring should result in the compound 31 with a mass m/e = 188. We were unable to find a parent ion with the mass of 188. However, we did find fragments that would indicate addition of dimethylcarbene. A fragment with mass m/e = 156 was found which we assume to be the result of the loss of a methyl group and a fluorine atom from 31. Although the results are not overwhelming, it is reasonable to surmise that there is some reaction of dimethylcarbene with trifluoromethylbenzene.
Scheme 2.7: Reaction of dimethylcarbene 13a with α,α,α-trifluoromethylbenzene.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>31</th>
</tr>
</thead>
<tbody>
<tr>
<td>18a</td>
<td></td>
</tr>
<tr>
<td>Time (min.)</td>
<td>Parent (m/e)</td>
</tr>
<tr>
<td>15.10</td>
<td>156</td>
</tr>
</tbody>
</table>

Table 2.5: Product of dimethylcarbene addition to α,α,α-trifluoromethylbenzene.
2.2 Insertion Reactions

2.2.1 Reaction with C-H Bonds

Insertion reactions are among the most common reactions of carbenes. A singlet carbene insertion occurs through a concerted three-centered transition state mechanism.

Scheme 2.8: Reaction of dimethylcarbene 13a with cyclohexane.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>32</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (min.)</td>
<td>Parent (m/e)</td>
</tr>
<tr>
<td>18a</td>
<td>3.49</td>
</tr>
<tr>
<td>24a</td>
<td>3.48</td>
</tr>
</tbody>
</table>

Table 2.6: Product of dimethylcarbene reaction with cyclohexane.
(Scheme 1.2). The photolysis of dimethyldiazirine and oxadiazoline with cyclohexane resulted in the formation of isopropylcyclohexane (Scheme 2.8). This was verified by comparison with an authentic sample of the compound. Table 2.6 gives a summary of the chromatographic data for the diazirine and oxadiazoline. Quantification of the extent of C-H insertion was possible since the oxadiazoline was easily handled and a fixed quantity could be weighed out. Using isopropylcyclohexane as an external standard, a standard curve for the response of the instrument is obtained (Figure 2.1). The yield of isopropylcyclohexane formed from photolysis of a known quantity of oxadiazoline is determined. Insertion into C-H bonds occurs to an extent of approximately 13% while C-D insertion at 9%. The C-H/C-D insertion ratio is 1.5 which is slightly smaller than that determined by laser flash photolysis of the diazirine.
Figure 2.1: Standard curve for the calculated GC peak area of isopropylcyclohexane versus concentration.
2.2.2 Reaction With Si-H Bonds

Photochemical decomposition of dimethylidiazirine or oxadiazoline in triethylsilane resulted in the formation of isopropyltriethylsilane (Scheme 2.9). The formation of 33 is deduced from the observed m/e = 158 of the peak eluting at 3.37 minutes. The fragmentation pattern of 33 gives rise to fragment peaks at m/e = 130, 115 and 87 resulting from the loss of ethylene, propylene or both. The presence of these peaks (Table 2.7) indicate that a propyl group had inserted into the Si-H bond. Standard 33 was not available for comparative study.

Scheme 2.9: Reaction of dimethylcarbene 13a with triethylsilane.
**Table 2.7:** Product of dimethylcarbene reaction with triethylsilane.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>33</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Time (min.)</td>
<td>m/e</td>
</tr>
<tr>
<td>18a</td>
<td>3.34</td>
</tr>
<tr>
<td>24a</td>
<td>3.42</td>
</tr>
</tbody>
</table>

### 2.2.3 Reaction With N-H Bonds

The reaction of dimethylcarbene with amines should be analogous to the reactivity with pyridine and oxygen nucleophiles. With a primary amine, the expected product should be insertion into the N-H bond (Scheme 2.10). The amine adds to the electrophilic carbene to form an ylide which can then migrate a hydrogen resulting in the formation of diisopropylamine 34. Gas chromatographic analysis of the products from photolysis of dimethyldiazirine with isopropylamine shows the formation of diisopropylamine \( m/e = 101 \) at 5.0 minutes (Table 2.8). The molecular ion peak \( m/e = 101 \) was quite weak. A base peak corresponding to the fragment \( C_5H_{10}N^+ \) has an \( m/e = 84 \) and was found in the mass spectrum of the peak believed to be 34. The structure of this ion can arise from diisopropylamine. Comparison with an authentic sample of diisopropylamine results in a 100% peak to peak match of the mass spectrum. A series of diisopropylamine standards were prepared and the areas for each concentration determined giving the standard curve for the instrument response (Figure 2.2). The carbene yield was taken to be proportional to the amount of insertion product and this was determined to be approximately 60 ± 7%.
Scheme 2.10: Reaction of dimethylcarbene 13a with isopropylamine.

Table 2.8: Product of dimethylcarbene reaction with isopropylamine.
Figure 2.2: Standard curve for the calculated GC peak area of diisopropylamine versus concentration.
2.2.4 Reaction With C-O Bonds

Carbenes may react with ethers by: (1) electrophilic attack on the oxygen lone pairs forming an ylide followed by rearrangement to 35 and (2) insertion into C-H bonds (Scheme 2.11) adjacent to oxygen resulting in 36. Photolysis of dimethyldiazirine and oxadiazoline in tetrahydrofuran resulted in the formation of the C-H insertion product. We did not observe any products resulting from initial ylide formation followed by rearrangement.

Identification of the insertion product was based on the fragmentation pattern observed. The peak of interest elutes at 4.6 minutes and, from its mass spectrum, has a parent ion with mass of 114 (Table 2.9). Analysis of the fragmentation pattern for 36 shows that loss of a propylene molecule leads to the formation of a cation C₄H₄O⁺ with an m/e = 71. If a tetrahydropyran ring was formed (implying an ylide mechanism) then a
cation \( \text{C}_4\text{H}_7\text{O}^+ \) with an \( m/e = 99 \) would be expected to appear in the fragmentation pattern. The fragment peaks (\( \text{C}_4\text{H}_7\text{O}^+, m/e = 99 \) and \( \text{C}_4\text{H}_7\text{O}^+, m/e = 71 \)) were very indicative of an isopropyl branch at the \( \alpha \)-carbon rather than a tetrahydropyran ring. This observation is not surprising considering that, in ethers, C-H bonds adjacent to oxygen are relatively weak.

\[ \text{Scheme 2.11: Reaction of dimethylcarbene 13a with tetrahydrofuran.} \]
2.2.5 Reaction With C-Cl Bonds

Carbenes show a strong preference for insertion into carbon-chlorine (C-Cl) bonds but are unreactive towards carbon-fluorine (C-F) bonds. In our present work, some mechanistic studies have been performed in chlorinated solvents. We were thus interested in determining if chlorine abstraction was a possibility in the solvents used. We photolyzed dimethyldiazirine in carbon tetrachloride (CCl₄), Freon-113 and perfluorohexane (C₆F₁₄) and analyzed the photolysis products for evidence of halogen abstraction. Table 2.10 summarizes our results.
Scheme 2.12: Reaction of dimethylcarbene 13a with carbon tetrachloride.

Insertion of dimethylcarbene into a C-Cl bond probably occurs through an initial electrophilic attack of the carbene followed by rearrangement (Scheme 2.12). The product resulting from the insertion of dimethylcarbene in CCl₄, 37 was observed and identified based on the parent mass m/e = 195.

Diazirine photolysis in Freon-113 (Scheme 2.13) followed by GC-MS analysis gave an ion C₅H₄Cl,F⁺ with m/e = 194.5 which we believe to be derived from the insertion product 38. This ion may fragment by loss of either a Cl or a CClF₂ radical resulting in ions with C₅H₃ClF⁺ (m/e = 157.6) and C₅H₃ClF₂⁺ (m/e = 107.5). The ion C₅H₃ClF⁺ may lose a fluorine radical to give C₅H₄ClF⁺ (m/e = 137.0). All ions observed had masses indicating the inclusion of a three carbon fragment (from dimethylcarbene) into the structure of Freon-113. Thus, halogenated solvents particularly Freon-113 cannot be considered inert towards dimethylcarbene.
Scheme 2.13: Reaction of dimethylcarbene 13a with Freon-113.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>37</th>
<th>38</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time (min.)</td>
<td>(m/e)</td>
</tr>
<tr>
<td>18a</td>
<td>13.5</td>
<td>120</td>
</tr>
</tbody>
</table>

Table 2.10: Products of dimethylcarbene addition to CCl₄ and Freon-113.

Photolysis of dimethyl diazirine in prefluoroexane followed by GC-MS analysis did not reveal the formation of any carbon fluorine insertion products (39). The only identifiable product was azine presumably derived from reaction of carbene with diazopropane formed in the photolysis.
CHAPTER 3

INDIRECT KINETICS AND STERN-VOLMER QUENCHING STUDIES OF DIMETHYLCARBENE

The product studies gave us a general idea of carbene reactivity. In this chapter, we will reinvestigate the kinetics of dimethylcarbene using the pyridine ylide method. The pyridine ylide method used in this chapter will rely on the ylide yield to determine carbene lifetimes. Factors affecting this yield such as bimolecular reactivity of the carbene need to be investigated. Stern-Volmer quenching experiments allow us to determine the absolute reactivity of several carbene quenchers relative to pyridine. Using the pyridine ylide technique, the kinetics of dimethylcarbene reactivity with other compounds may be evaluated and related to the previous product studies.

3.1 Pyridine Ylide Formation

In order to apply LFP techniques to the study of dimethylcarbene, a UV-Vis active transient must be obtained to allow the reactive species to be monitored. The transient spectrum of the dimethylcarbene-pyridine ylide has been reported previously. Excimer laser photolysis (351 nm) of a solution of dimethyl Diazirine and pyridine in Freon-113 was monitored using an optical multichannel analyzer (OMA). The spectra obtained from the OMA experiment is shown in Figure 3.1. The wavelength of maximum optical density
for ylide 40 obtained in this work was recorded at 363 nm which agrees with the previously obtained value of 364 nm. 

Scheme 3.1: Mechanism for carbene formation, pyridine ylide formation and 1,2-hydrogen migration in the photolysis of dimethyldiazirine 18a.
In Chapter 1 we used oxadiazolines as an alternative source for dimethylcarbene. If oxadiazolines and diazirines are equivalent precursors to dimethylcarbene, pyridine ylide formation is expected and we should be able to monitor the ylide at the region where the diazirine derived ylide absorbs.

LFP at 308 nm of dimethyloxadiazoline with pyridine in Freon-113 yields the OMA spectrum shown in Figure 3.2. The maximum optical density for this ylide falls within the 363-365 nm range. On comparison with the reported value of 364 nm\(^6\) and our result from dimethyldiazirine of 363 nm, we believe that dimethylcarbene is produced upon photolysis of dimethyloxadiazoline and that the pyridine ylide obtained from the oxadiazoline is equivalent to that obtained from the diazirine.

![Figure 3.1](image.png)

**Figure 3.1:** Transient spectrum of the ylide 40 produced by LFP of dimethyldiazirine 18a in Freon-113 containing 2.00 M pyridine at ambient temperature. The spectrum was recorded over a window of 175 ns, 50 ns after the laser pulse.
3.2 Lifetime of Dimethylcarbene

The mechanism of carbene formation from dimethyldiazirine is shown in Scheme 3.1. The rate constant $k_{\text{PR}}$ represents the bimolecular rate constant for the reaction of dimethylcarbene with pyridine while $k_r$ represents the sum of all the first-order and pseudo first-order processes which consume dimethylcarbene in the absence of pyridine. We

Figure 3.2: Transient spectrum of the ylide 40 produced by LFP of 2-methoxy-2,5,5-trimethyl-$\Delta^1$-1,3,4-oxadiazoline 24a in Freon-113 containing 2.00 M pyridine at ambient temperature.
know from Chapter 1 that the optical yield of ylide ($A_y$) may be represented as a function of the pyridine concentration (equation 1.5).

The optical yield ($A_y$) is measured by determining the change in absorbance as a function of time at the wavelength of maximum ylide absorption (Figure 3.3). The difference of the maximum height of the signal from the base of the signal is taken as the optical yield ($A_y$).

A plot of the inverse of the optical yield ($A_y$) against the reciprocal of the pyridine concentration yields a straight line. Division of the intercept by the slope yields the value $k_c/k_{PyR}$. To determine $k_T$, we assume the value of $k_{PyR}$ to be $1 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ (as determined for other carbenes). We can calculate $k_T$ and the inverse ($1/k_T$) which is the lifetime ($\tau$) of the carbene.
Figure 3.3: The formation of transient 40 following LFP (351 nm) of \textbf{18a} monitored at 364 nm in Freon-113 at ambient temperature.
The lifetime of dimethylcarbene was deduced in pentane, cyclohexane, Freon-113, acetonitrile, and chloroform. The effect of deuterium substitution on the carbene lifetime was investigated with diazirine (18a and 18b) and oxadiazoline (24a and 24b) precursors. Solvent isotope effects on the lifetime were also determined in the deuterated modifications of cyclohexane (d_{12}), chloroform (d_{13}) and acetonitrile (d_{14}).

The plots of optical yield (A_{obs}) versus pyridine are shown in Figures 3.4 to 3.15. The yield of ylide reaches saturation at concentrations of pyridine above 1M pyridine in pentane, Freon-113 and cyclohexane (d_{12} and h_{12}). In more polar solvents (acetonitrile and chloroform), we were unable to saturate the carbene with pyridine, indicating a very short-lived carbene. The double reciprocal plots are shown in Figures 3.16 to 3.27 and the lifetime data summarized in Table 3.1.

On comparison of the lifetime data, it is apparent that the oxadiazoline duplicates the results obtained for the diazirine precursor of dimethylcarbene both in the protiated and in the deuterated case. Deuterium substitution of the carbene α-hydrogens increases the lifetime in pentane and Freon-113 which is consistent with Modarelli's observation.
The magnitude of the isotope effects are much smaller than that previously mentioned\(^{64}\) (Chapter I, Table 1.3). This could be due to variations in \(k_{pyr}\), or in inaccuracies introduced by points at very low pyridine concentrations. Since dimethylcarbene-\(d_n\) is longer lived, the saturation point is reached at a lower pyridine concentration (0.08 M) thus narrowing the range over which we may accurately measure small quantities of pyridine. Errors in the region of the double reciprocal plot could effectively skew results by as much as 20 ns.

The lifetimes of dimethylcarbene 13a in cyclohexane and in cyclohexane-\(d_{12}\) were estimated by double reciprocal analysis of the data and a solvent isotope effect of \(\tau C_nH_{1,2}/\tau C_nD_{1,2} = 2.3\) was observed. This is close to the kinetic isotope effect observed for intermolecular C—H insertion reactions of other singlet carbenes and indicates that intermolecular processes significantly contribute to the disappearance of this carbene in a hydrocarbon solvent.\(^{99,100}\) This result also agrees with the solvent isotope effect \((C_nH_{1,2}/C_nD_{1,2} = 1.5)\) we have determined from product analysis in Chapter 2 (Section 2.2.1).

Our lifetime measurements in acetonitrile and chloroform are consistently smaller than those observed by Modarelli. The variation of about 2-5 ns in the measurements is within the range of \(k_{pyr}\) of \(1-5 \times 10^9 \text{ M}^{-1} \text{s}^{-1}\).

The lifetime of dimethylcarbene in chloroform and acetonitrile could be shortened two factors: (1) reaction of dimethylcarbene with the solvent and (2) the effect of solvent polarity. The reaction of dimethylcarbene with solvent may effectively decrease carbene yield hence the pyridine saturation level is not reached. Solvent polarity stabilizes the transition state in hydrogen migration which should decrease the lifetime.

From our product studies in Chapter 1, we have clearly demonstrated that dimethylcarbene inserts into C-Cl bonds. The combined effect of polar solvent stabilization
of the transition state and chemical reaction with the solvent should account for the short lifetime of dimethylcarbene in chloroform. In acetonitrile, ylide formation was not observed in OMA experiments and C-H insertion may be a minor process in this solvent. Thus, the decrease in lifetime relative to pentane may be due to solvent polarity effects.
**Figure 3.4**: A plot of the optical yield of ylide 40 as a function of pyridine concentration produced by LFP (351 nm) of dimethyldiazirine-$h_6$ 18a in pentane at ambient temperature.
Figure 3.5: A plot of the optical yield of ylide 40 as a function of pyridine concentration produced by LFP (351 nm) of dimethyl diazirine-$d_5$ 18b in pentane at ambient temperature.
Figure 3.6: A plot of the optical yield of ylide 40 as a function of pyridine concentration produced by LFP (351 nm) of dimethylazirine-\( \text{H}_8 \) 18a in Freon-113 at ambient temperature.
Figure 3.7: A plot of the optical yield of ylide 40 as a function of pyridine concentration produced by LFP (351 nm) of dimethyldiazirine-$d_3$, 18b in Freon-113 at ambient temperature.
Figure 3.8: A plot of the optical yield of ylide 40 as a function of pyridine concentration produced by LFP (351 nm) of dimethylazirine-$h_8$ 18a (351 nm) in acetonitrile at ambient temperature.
Figure 3.9: A plot of the optical yield of ylide 40 as a function of pyridine concentration produced by LFP (351 nm) of dimethyldiazirine-\( h_s \), 18a in acetonitrile-\( d_3 \) at ambient temperature.
Figure 3.10: A plot of the optical yield of ylide 40 as a function of pyridine concentration produced by LFP (351 nm) of dimethyldiazirine-$\overset{18}{\text{a}}$ in chloroform at ambient temperature.
Figure 3.11: A plot of the optical yield of ylide 40 as a function of pyridine concentration produced by LFP (351 nm) of dimethyldiazirine-\textit{h}_n 18a in chloroform-\textit{d} at ambient temperature.
Figure 3.12: A plot of the optical yield of ylide 40 as a function of pyridine concentration produced by LFP (351 nm) of dimethyldiazirine-\textsubscript{a} 18\textsubscript{a} in cyclohexane at ambient temperature.
Figure 3.13: A plot of the optical yield of ylide 40 as a function of pyridine concentration produced by LFP (351 nm) of dimethylidazirine-\(h_8\) 18a in cyclohexane-\(d_12\) at ambient temperature.
Figure 3.14: A plot of the optical yield of ylide 40 as a function of pyridine concentration produced by LFP (308 nm) of 2-methoxy-2,5,5-trimethyl-$\Delta^1$-1,3,4-oxadiazoline 24a in Freon-113 at ambient temperature.
Figure 3.15: A plot of the optical yield of ylide 40 as a function of pyridine concentration produced by LFP (308 nm) of 2-methoxy-2-methyl-5,5-trideuteromethyl-$\Delta^1$-1,3,4-oxadiazoline 24b in Freon-113 at ambient temperature.
Figure 3.16: A plot of $1/A_{364}$ for ylide 40 as a function of $1/[\text{pyridine}]$ resulting from LFP (351nm) of dimethylidiazirine-$h_6$ 18a in pentane at ambient temperature.
Figure 3.17: A plot of $1/A_{364}$ for ylide 40 as a function of $1/[\text{pyridine}]$ resulting from LFP (351 nm) of dimethyldiazirine-$d_9$ 18b in pentane at ambient temperature.
Figure 3.18: A plot of $1/A_{364}$ for ylide 40 as a function of $1/[\text{pyridine}]$ resulting from LFP (351 nm) of dimethyldiazirine-$h_8$ 18a in Freon-113 at ambient temperature.
Figure 3.19: A plot of $\frac{1}{A_{364}}$ for ylide 40 as a function of $\frac{1}{[\text{pyridine}]}$ resulting from LFP (351 nm) of dimethyldiazirine-$d_5$ 18b in Freon-113 at ambient temperature.
Figure 3.20: A plot of $1/A_{364}$ for ylide 40 as a function of $1/\text{[pyridine]}$ resulting from LFP (351nm) of dimethylaziridine-$h_6$ 18a in acetonitrile at ambient temperature.
Figure 3.21: A plot of $1/A_{364}$ for ylide 40 as a function of $1/[\text{pyridine}]$ resulting from LFP (351 nm) of dimethyldiazirine-$h_8$ 18a in acetonitrile-$d_3$ at ambient temperature.
Figure 3.22: A plot of $1/A_{364}$ for ylide 40 as a function of $1/[\text{pyridine}]$ resulting from LFP (351nm) of dimethyldiazirine-$h_9$ 18a in chloroform at ambient temperature.
Figure 3.23: A plot of $1/A_{364}$ for ylide 40 as a function of $1/[^{[\text{pyridine}]}]$ resulting from LFP (351nm) of dimethyldiazirine-$h_8$ 18a in chloroform-$d$ at ambient temperature.
Figure 3.24: A plot of $1/A_{364}$ for ylide 40 as a function of $1/[\text{pyridine}]$ resulting from LFP (351nm) of dimethyldiazirine-$h_9$ 18a in cyclohexane at ambient temperature.
Figure 3.25: A plot of $1/A_{364}$ for ylide 40 as a function of $1/[[\text{pyridine}]]$ resulting from LFP (351 nm) of dimethyl diazirine-$H_8$ 18a in cyclohexane-$d_{12}$, at ambient temperature.
Figure 3.26: A plot of $1/A_{364}$ for ylide 40 as a function of $1/[\text{pyridine}]$ resulting from LFP (308nm) of 2-methoxy-2,5,5-trimethyl-$\Delta^1$-1,3,4-oxadiazoline 24a in Freon-113 at ambient temperature.
Figure 3.27: A plot of $1/A_{364}$ for ylide 40 as a function of $1/[\text{pyridine}]$ resulting from LFP (308nm) of 2-methoxy-2-methyl-5,5-trideuteromethyl-$\Delta^1$.1.3.4-oxadiazoline 24b in Freon-113.
<table>
<thead>
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<th>Precursor</th>
<th>Solvent</th>
<th>Lifetime (ns)</th>
<th>$\tau_1/\tau_0$</th>
</tr>
</thead>
<tbody>
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<td>dimethyldiazirine-$h_\alpha$ (18a)</td>
<td>pentane</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Freon-113</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>acetonitrile</td>
<td>6.0 (8.0)$^a$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>acetonitrile-$d_1$</td>
<td>7.0 (9.0)$^a$</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>chloroform</td>
<td>4.4 (6.8)$^a$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>chloroform-$d_1$</td>
<td>5.0 (7.3)$^a$</td>
<td>1.14</td>
</tr>
<tr>
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<td>cyclohexane</td>
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</tr>
<tr>
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<td>2.3</td>
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</tr>
<tr>
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<td>1.43</td>
</tr>
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<td>Freon-113</td>
<td>35</td>
<td>1.94</td>
</tr>
</tbody>
</table>

Assuming $k_{pyr} = 1 \times 10^7$ M$^{-1}$ s$^{-1}$

$^a$Data of Modarelli et. al.$^{64}$. see also Table 1.4

**Table 3.1:** Lifetimes of carbenes deduced using the pyridine ylide technique from diazirine and oxadiazoline precursors in this work and in a previous study$^{64}$.

### 3.3 Stern-Volmer Quenching

The Stern-Volmer method allows us to interpret the lifetime of a reactive intermediate in the presence of a known quencher in solution. This provides an estimate of the amount of intermolecular insertion expected for dimethylcarbene in solution. The possible decay pathways for singlet carbene is shown in Scheme 3.1. The optical yield
(Φₙ) of the singlet carbene can be represented in eq. 3.1 where kᵣ is the sum of all the pseudo first-order rate constants (kᵣ + kₓ[SX]) for the singlet state in the absence of the quencher.

\[
Φ₀ = \frac{k_{PYR}[PYR]}{kᵣ + k_{PYR}[PYR]} \quad \text{(eq. 3.1)}
\]

In the presence of a singlet carbene quencher, the optical yield of the pyridine ylide (Φ) is shown in eq. 3.2.

\[
Φ = \frac{k_{PYR}[PYR]}{kᵣ + k_{PYR}[PYR] + k_Q[Q]} \quad \text{(eq. 3.2)}
\]

Thus, division of eq. 3.1 by eq. 3.2 affords eq. 3.3, where

\[
\tau' = \frac{1}{kᵣ + k_{PYR}[PYR]}
\]

(\(\tau'\)) is the lifetime of the singlet carbene in the presence of a specific constant concentration of pyridine. A plot of Φ₀/Φ against the quencher concentrations is predicted to be linear with a slope equals to \(k_Q\tau\). Assuming the singlet carbene reacts with the quencher in a diffusion controlled rate (\(k_Q = 10^{9-10} \text{ M}^{-1}\text{s}^{-1}\)), then the lifetime of the singlet state can be estimated by the use of a Stern-Volmer plot.

\[
\frac{Φ₀}{Φ} = \frac{kᵣ + k_{PYR}[PYR] + k_Q[Q]}{kᵣ + k_{PYR}[PYR]} = 1 + \frac{k_Q}{kᵣ + k_{PYR}[PYR]}[Q] = 1 + k_Q\tau'[Q] \quad \text{(eq. 3.3)}
\]

At higher pyridine concentration, where \(k_{PYR}[PYR] \gg kᵣ\), the above equation 3.3 can be simplified as

\[
\frac{Φ₀}{Φ} = 1 + \frac{k_Q}{k_{PYR}[PYR]}[Q] \quad \text{(eq. 3.4)}
\]

The rate constant for the reaction of dimethylcarbene with the quencher can be determined from equation 3.4, where Φ₀ represents the yield of pyridine ylide in the absence of quencher, Φ is the yield of pyridine ylide at various concentration of quencher. The optical
yield of pyridine ylide \((A^)\) is proportional to its yield \((\Phi)\), so the relationship in equation 3.3 may be expressed in equation 3.5 if the concentration of pyridine is held constant.

\[
\frac{A^0}{A^} = 1 + \frac{k_Q}{k_{PYR}[PYR]}[Q] \quad \text{(eq. 3.5)}
\]

Plotting \(A^0/A^\) versus \([Q]\) at a constant pyridine concentration results in a straight line with the slope equal to \(\frac{k_Q}{k_{PYR}[PYR]}\). This treatment of the data is valid only when \(k_{PYR}[PYR] \gg k_c\). This corresponds to the saturation region of plots of \(A^\) versus pyridine where every carbene produced in a laser pulse is captured by pyridine.

### 3.3.1 Reactivity With Alkenes

Dimethylcarbene was found to be surprisingly unreactive toward olefins. The resulting Stern-Volmer plot for the diazirine and oxadiazoline precursors are shown in Figures 3.28 to 3.33. Inspection of these plots gives us a slope \(k_Q/k_{PYR} = 0\) indicating that the pyridine ylide is not quenched by tetramethylethylene (TME). This is not surprising considering our previous discussion on the steric constraints on the transition state of cycloaddition (Chapter 2). Pyridine trapping and 1,2-hydrogen migration may consume the carbene before cycloaddition to TME occurs.

\[\text{Scheme 3.2: Steric effects on carbene cycloaddition to alkenes.}\]
Cyclopentene and norbornene were both found to quench pyridine ylide formation. Cyclopentene was found to be the most reactive of all the alkenes toward dimethylcarbene. The $k_{ij}$ values for cyclopentene and norbornene are shown in Table 3.2. Values of $k_{ij}$ are obtained by assuming $k_{pr} = 3 \times 10^9$ M$^{-1}$s$^{-1}$ obtained from the results in Chapter 4 of this work. Cyclopentene was found to be 60-70% more reactive while norbornene was found to be 15-20% more reactive than pyridine. We may again rationalize these results based on steric effects in the cycloaddition of the carbene to an alkene. For norbornene, the exo-adduct is favored over the endo-adduct due to decreased axial hydrogen interactions. Since reaction with norbornene will entail more motion on the part of the carbene and alkene, other processes can occur before cycloaddition and thus, minimal product formation and a lower value of $k_{ij}$ was observed. The less hindered cyclopentene ring may favor cycloaddition and hence bimolecular chemistry becomes competitive with hydrogen migration (Scheme 3.2). We are thus able to trap the carbene with cyclopentene and consequently measure a larger value of $k_{ij}$. 

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Figure 3.28: Stern-Volmer treatment of the quenching of 40 by tetramethylethylene in Freon-113 at ambient temperature. Ylide 40 was obtained by LFP (351nm) of dimethylidiazirine-\(h_\alpha\) 18a with [pyridine] = 1.37M.
Figure 3.29: Stern-Volmer treatment of the quenching of 40 by tetramethylethylene in Freon-113 at ambient temperature. Ylide 40 was obtained by LFP (308nm) of 2-methoxy-2,5,5-trimethyl-\(\Delta^3\)-1,3,4-oxadiazoline 24a with [pyridine] = 1.37M.
Figure 3.30: Stern-Volmer treatment of the quenching of 40 by cyclopentene in Freon-113 at ambient temperature. Ylide 40 was obtained by LFP (351 nm) of dimethyl(diazirine-h_ex 18a with [pyridine] = 1.37 M.
Figure 3.31: Stern-Volmer treatment of the quenching of 40 by cyclopentene in Freon-113 at ambient temperature. Ylide 40 was obtained by LFP (308nm) of 2-methoxy-2,5,5-trimethyl-Δ1-1,3,4-oxadiazoline 24a with [pyridine] = 1.37M.
Figure 3.32: Stern-Volmer treatment of the quenching of 40 by norbornene in Freon-113 at ambient temperature. Ylide 40 was obtained by LFP (351nm) of dimethyldiazirine-$h_v$ 18a with [pyridine] = 1.37M.
Figure 3.33: Stern-Volmer treatment of the quenching of 40 by norbornene in Freon-113 at ambient temperature. Ylide 40 was obtained by LFP (308nm) of 2-methoxy-2,5,5-trimethyl-Δ1-1,3,4-oxadiazoline 24a with [pyridine] = 1.37M.
3.3.2 Reactivity With Alcohols and Ethers

Stern-Volmer plots for the reaction of 13a with methanol, tert-butanol and tetrahydrofuran (THF) are shown in Figures (3.34 to 3.39) while the $k_d/k_{pyr}$ values are shown in Table 3.2. The values of $k_d/k_{pyr}$ are deduced from Stern-Volmer plots with $[ROH] < 4.0$M. At larger $[ROH]$, plots of $A^0/A$ exhibit curvature due to oligomerization of the alcohol. Values of $k_o$ are obtained by assuming $k_{pyr} = 3 \times 10^3$M$^{-1}$s$^{-1}$ obtained from the results in Chapter 4 of this work.

We observed alcohols to be more reactive toward dimethylcarbene than THF. This could be due to a steric effect on dimethylcarbene addition to THF. Carbenes can "add" to lone electron pairs, forming ylides. Laser flash optical multichannel analyzer experiments failed to produce ylides for dimethylcarbene reaction with alcohols and ethers. Although no ylides have been observed this does not preclude their formation since ylides may be consumed by subsequent reactions thus rendering them invisible. Tetrahydrofuran was found to be 80% less reactive than pyridine in trapping dimethylcarbene. Since the carbene is electrophilic in character, we expected it to react readily with lone pairs on oxygen. From our product analysis results, dimethylcarbene reacts with THF by inserting into the $\alpha$-C-H bonds. We have not observed dimethylcarbene ylide formation with THF through OMA and product studies.

Increased reactivity of methanol may be due to its higher acidity compared to tert-butanol. A proton transfer mechanism may be operating in the reactivity of alcohols with dimethylcarbene as opposed to other possible mechanisms such as ylide formation and concerted O-H insertion. Stern-Volmer kinetics reveal that C-H insertion may not be as competitive with O-H insertion reactions in trapping dimethylcarbene.
Figure 3.34: Stern-Volmer treatment of the quenching of 40 by methanol in Freon-113 at ambient temperature. Ylide 40 was obtained by LFP (351 nm) of dimethylidiazirine-\(h_s\), 18a with [pyridine] = 1.37 M.
Figure 3.35: Stern-Volmer treatment of the quenching of 40 by methanol in Freon-113 at ambient temperature. Ylide 40 was obtained by LFP (308nm) of 2-methoxy-2,5,5-trimethyl-Δ1,1,3,4-oxadiazoline 24a with [pyridine] = 1.37M.
Figure 3.36: Stern-Volmer treatment of the quenching of 40 by tert-butanol in Freon-113 at ambient temperature. Ylide 40 was obtained by LFP (351 nm) of dimethyldiazirine-$h_x$ 18a with [pyridine] = 1.37M.
Figure 3.37: Stern-Volmer treatment of the quenching of 40 by tert-butanol in Freon-113 at ambient temperature. Ylide 40 was obtained by LFP (308nm) of 2-methoxy-2,5,5-trimethyl-Δ^1-1,3,4-oxadiazoline 24a with [pyridine] = 1.37M.
Figure 3.38: Stern-Volmer treatment of the quenching of 40 by tetrahydrofuran in Freon-113 at ambient temperature. Ylide 40 was obtained by LFP (351nm) of dimethyldiazirine-\(h_a\) 18a with [pyridine] = 1.37M.
Figure 3.39: Stern-Volmer treatment of the quenching of 40 by tetrahydrofuran in Freon-113 at ambient temperature. Ylide 40 was obtained by LFP (308nm) of 2-methoxy-2,5,5-trimethyl-Δ1,3,4-oxadiazoline 24a with [pyridine] = 1.37M.
3.3.3 Reactivity With Silanes

Stern-Volmer analysis of the reaction of dimethylcarbene 13a with triethylsilane results in $k_d/k_{pyr} = 0$ (Figures 3.40-3.41). This implies that the reaction between dimethylcarbene and triethylsilane is not competitive with pyridine capture of the carbene. Diazirine and oxadiazoline derived dimethylcarbene do not react rapidly with triethylsilane. Our results from the product studies indicate formation of isopropyltriethylsilane however products are formed only upon photolysis of both diazirine 18a or oxadiazoline 24a in neat triethylsilane. A previous study of the reaction of dimethylcarbene with phenylsilane reported a yield of 5%. Thus, it is reasonable to conclude that trapping dimethylcarbene through Si-H insertion reactions will be low yielding and inefficient.
Figure 3.40: Stern-Volmer treatment of the quenching of 40 by triethylsilane in Freon-113 at ambient temperature. Ylide 40 was obtained by LFP (351 nm) of dimethylidiazirine-$h_2$, 18a with [pyridine] = 1.37M.
**Figure 3.41:** Stern-Volmer treatment of the quenching of 40 by triethylsilane in Freon-113 at ambient temperature. Ylide 40 was obtained by LFP (308nm) of 2-methoxy-2.5.5-trimethyl-Δ1-1.3.4-oxadiazoline 24a with \([\text{pyridine}] = 1.37\text{M}\).
3.3.4 Reactivity With Amines

The Stern-Volmer plots for the reaction of dimethylcarbene with isopropylamine are shown in Figures 3.42 to 3.43. The values of $k_q/k_{pyr}$ are deduced from Stern-Volmer plots with $[RNH_2] < 0.4M$. At larger $[RNH_2]$, plots of $A_n/A_0$ exhibit curvature due to oligomerization of the amine. Values of $k_q$ are obtained by assuming $k_{pyr} = 3 \times 10^7 M^{-1}s^{-1}$ obtained from the results in Chapter 4 of this work.

Isopropylamine was found to be more reactive than pyridine in trapping dimethylcarbene 13 (Table 3.2). A precursor effect on $k_q/k_{pyr}$ was observed. This could be due to the two photon process in the formation of carbene 13a from the oxadiazoline. Since the Stern-Volmer method depends on the optical yield of ylide, factors affecting formation of 40 such as inefficient carbene formation may result in lower values measured for $k_q/k_{pyr}$.

Isopropylamine is a very efficient trap of dimethylcarbene. From the studies described earlier (Chapter 2), the absolute yield of amine was 60% upon photolysis of the oxadiazoline in neat isopropylamine. The carbene yield of 60% is close to Modarelli's yield using the diazirine precursor and methanol as the trap. If we assume that all the carbene formed is trapped by isopropylamine (being more reactive than pyridine) then the 40% yield of propene may be due to reactions in the excited state of the oxadiazoline. We may conclude from this result that although oxadiazolines duplicate results obtained from diazirines, they may be used as alternative precursors to the diazirines but are not much better in terms of the efficiency of carbene formation.
Figure 3.42: Stern-Volmer treatment of the quenching of 40 by isopropylamine in Freon-113 at ambient temperature. Ylide 40 was obtained by LFP (351nm) of dimethylidiazirine-κ8 18a with [pyridine] = 1.37M.
Figure 3.43: Stern-Volmer treatment of the quenching of 40 by isopropylamine in Freon-113 at ambient temperature. Ylide 40 was obtained by LFP (308nm) of 2-methoxy-2,5,5-trimethyl-Δ1,1,3,4-oxadiazoline 24a with [pyridine] = 1.37M.
### Table 3.2: Reactivities of carbene quenchers relative to pyridine from Stern-Volmer analysis in Freon-113 at ambient temperature.

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<th>Quencher</th>
<th>Precursor</th>
<th>24a</th>
<th>18a</th>
</tr>
</thead>
<tbody>
<tr>
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<td>$k_Q / k_{PYR}$</td>
<td>$k_Q$</td>
<td>$k_Q / k_{PYR}$</td>
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<td>cyclopetene</td>
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<td>norbornene</td>
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<td>$3.45 \times 10^7$</td>
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<tr>
<td>triethysilane</td>
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<td>N/A</td>
<td>0</td>
</tr>
<tr>
<td>methanol</td>
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<td>$1.23 \times 10^9$</td>
<td>0.564</td>
</tr>
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<td>tert-butanol</td>
<td>0.417</td>
<td>$1.25 \times 10^9$</td>
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<td>tetrahydrofuran</td>
<td>0.177</td>
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<tr>
<td>isopropylamine</td>
<td>1.65</td>
<td>$4.95 \times 10^7$</td>
<td>4.27</td>
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</table>

$^a[PYR] = 1.37 \text{ M}$  
$^b$Assuming $k_{PYR} = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
CHAPTER 4

ABSOLUTE KINETICS OF DIMETHYLCARBENE

Dimethylcarbene (DMC) 13a is the prototypical dialkyl carbene. Despite its fundamental place in dissecting the nature of carbene reactivity, there is a dearth of knowledge about this species. The lack of data concerning dimethylcarbene has generally been attributed to a facile rearrangement to propene precluding chemical trapping and analysis by conventional photochemical techniques. Presumably the hydrogen shift is faster than the bimolecular trapping rate. On the basis of bond additivity arguments, the rearrangement to propene is calculated to be more than 60 kcal/mole.106,107 A similar system that decomposes in a highly exothermic manner (>30-50 kcal/mole), tetramethylethylene, has a lifetime in the femtosecond region.108,109 It is thus reasonable to deduce that the lifetime of dimethylcarbene should lie within a similar range and thus render it untrappable. Modarelli, et. al.13,64,70,93 were able to trap dimethylcarbene with pyridine in solution at ambient temperature. Thus for a seemingly untrappable carbene, bimolecular chemistry is observed. Furthermore, modern theory predicts a barrier of 7.4 kcal/mole for the rearrangement of dimethylcarbene to propene.78 It is thus reasonable to infer a lifetime quite longer than that of tetramethylethylene. Herein we present our efforts to dissect the absolute kinetics of dimethylcarbene.
4.1 Direct Measurement of the Absolute Rate Constants for Dimethylcarbene Decay

Photolysis of 3,3-dimethylazonine 18a in the presence of pyridine produces the ylide 40 whose growth may be fitted satisfactorily to an exponential. Excimer laser flash photolysis yields a carbene lifetime of 20-30 ns in Freon-113 (Table 3.1). This value is limited by the time resolution of the excimer laser flash photolysis system, which is estimated to be about 20 ns thus rendering direct measurement of the ylide growth impossible. Recent upgrading of the laser flash photolysis equipment was done by introduction of a 150 picosecond Nd-YAG laser (Figure 7.1) and a new photomultiplier tube (PMT) with a faster time response. The time resolution of current system was then determined to be 1-2 ns and thus with the new system, it is possible to resolve the growth of the pyridine ylide.

Upon LFP of dimethylazonine in solution with added pyridine, the absorption of pyridine ylide 40 can be resolved as an exponential growth curve described by equation 4.1.

\[ [Y]_t = [Y]_0 \left(1 - e^{-kt} \right) \]  \hspace{1cm} (eq. 4.1)

Fitting the curve to the described exponential function furnishes the observed rate constant for the growth of the pyridine ylide \( k_{obs} \). The observed growth rate \( k_{obs} \) is a linear function of the pyridine concentration (equation 4.2). A plot of the observed growth rate against pyridine concentration results in a straight line. The plots of the observed growth rate versus pyridine concentration are shown in Figures 4.1 to 4.30.

\[ k_{obs} = k_{PYR}[PYR] + k_T \]  \hspace{1cm} (eq. 4.2)
From equation 4.2, the slope and the intercept of the plot represent $k_{pr}$ and $k_r$, respectively where $k_{pr}$ describes the absolute rate constant from the reaction of dimethylcarbene with pyridine and $k_r$ is the absolute rate constant for 1,2-hydrogen migration in dimethylcarbene. The lifetime of the carbene ($\tau$) at a particular temperature is then determined as the inverse of $k_r$. The absolute rate constants $k_{pr}$ and $k_r$ of dimethylcarbene in Freon-113, $\alpha,\alpha,\alpha$-trifluoromethylbenzene and perfluorohexane at different temperatures by direct measurement are presented in Tables 4.1 to 4.3.

On comparison of the $\tau$ values from the direct time resolved method with the pyridine ylide method (Chapter 3), we find that the lifetime is consistently smaller at ambient temperature in Freon-113 and $\alpha,\alpha,\alpha$-trifluoromethylbenzene. Factors which affect the ylide yield will be reflected in the pyridine ylide method much more than in the direct time resolved method. Variations in diazirine concentration due to volatility and through degassing may lead to a larger intercept to slope ratio thereby resulting in an apparently longer lived intermediate. In the double reciprocal plot method, points at very low pyridine concentrations may be poorly defined as a result of errors introduced in measuring small volumes of pyridine and the added complication of laser noise which may contribute to the absorption signal ($A_y$) at low pyridine concentration. Uncertainties introduced at this region of the double reciprocal plot can significantly skew intercept/slope ratios.

The direct method of measurement does not rely on ylide intensities and double reciprocal plots but on the growth of the ylide. Fluctuations in diazirine/pyridine concentrations, laser intensity and noise do not affect the results in determining the value of $k_{obs}$. We are convinced that the values obtained for the lifetime of dimethylcarbene by time resolved methods are more accurate.

Another assumption we have made in the indirect pyridine ylide method was on the value of $k_{pyr}$. From the direct method, the measurements of the $k_{pyr}$ resulted in values.
ranging from $1-5 \times 10^9 \text{M}^{-1} \text{s}^{-1}$ and shows little variation with temperature. Our original assumption for the value of $k_{pyr}$ of $1-5 \times 10^9 \text{M}^{-1} \text{s}^{-1}$ is valid. Thus in comparing the lifetimes obtained by the direct and indirect methods: (1) the direct method is more accurate and predicts a smaller lifetime for dimethylcarbene at ambient temperature and (2) the indirect method provides a good estimate of the lifetime in solution and in different solvents. The main source of inconsistency between the two methods lies in the double reciprocal analysis and not in the assumed value of $k_{pyr}$.

<table>
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<th>Carbene</th>
<th>Solvent</th>
<th>T (K)</th>
<th>$\tau$ (ns)</th>
<th>$k_T$ $(\text{x} \ 10^7 \text{s}^{-1})$</th>
<th>$k_{pyr}$ $(\text{x} \ 10^9 \text{M}^{-1} \text{s}^{-1})$</th>
<th>$\tau_D/\tau_H$</th>
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<td>CF$_2$CICFCI$_2$</td>
<td>298</td>
<td>5.7 ± 0.3</td>
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<tr>
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Table 4.1: Values of $k_T$ and $k_{pyr}$ for DMC-$h_a$ 13a and DMC-$d_a$ 13b in Freon-113 as a function of temperature.
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Table 4.2: Values of $k_\tau$ and $k_{\text{pyr}}$ for DMC-d$_4$ 13b and DMC-d$_4$ 13b in α,α,α-trifluoromethylbenzene as a function of temperature.
<table>
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<th>Carbene</th>
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<th>T (K)</th>
<th>$\tau$ (ns)</th>
<th>$k_r$ ($x 10^7 \text{s}^{-1}$)</th>
<th>$k_{pyr}$ ($x 10^7 \text{M}^{-1}\text{s}^{-1}$)</th>
<th>$\tau_r/\tau_{ll}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>13a</td>
<td>C$<em>n$F$</em>{14}$</td>
<td>298</td>
<td>7.0 ± 1.2 ± 2.8 ± —</td>
<td>0.1</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>13b</td>
<td>C$<em>n$F$</em>{14}$</td>
<td>298</td>
<td>8.3 ± 1.0 ± 1.3 ± 1.18 ±</td>
<td>0.2</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>13a</td>
<td>C$<em>n$F$</em>{14}$</td>
<td>291</td>
<td>8.4 ± 1.9 ± 4.1 ± —</td>
<td>0.6</td>
<td>0.9</td>
<td>0.7</td>
</tr>
<tr>
<td>13b</td>
<td>C$<em>n$F$</em>{14}$</td>
<td>291</td>
<td>10.4 ± 1.6 ± 3.9 ± 1.24 ±</td>
<td>0.4</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>13a</td>
<td>C$<em>n$F$</em>{14}$</td>
<td>286</td>
<td>9.1 ± 1.0 ± 3.0 ± —</td>
<td>0.3</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>13b</td>
<td>C$<em>n$F$</em>{14}$</td>
<td>286</td>
<td>12.3 ± 8.1 ± 5.5 ± 1.35 ±</td>
<td>0.8</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>13b</td>
<td>C$<em>n$F$</em>{14}$</td>
<td>279</td>
<td>12.6 ± 7.9 ± 1.98 ± —</td>
<td>0.6</td>
<td>0.4</td>
<td>—</td>
</tr>
<tr>
<td>13a</td>
<td>C$<em>n$F$</em>{14}$</td>
<td>275</td>
<td>9.8 ± 10.2 ± 3.4 ± —</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>13b</td>
<td>C$<em>n$F$</em>{14}$</td>
<td>275</td>
<td>21.3 ± 4.7 ± 5.0 ± 2.05 ±</td>
<td>0.9</td>
<td>0.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 4.3: Values of $k_r$ and $k_{pyr}$ for DMC-$d_8$ 13b and DMC-$d_8$ 13b in perfluorohexane as a function of temperature.
Figure 4.1: A plot of $k_{\text{obs}}$ as a function of pyridine concentration for DMC-$d_3$ 13b in Freon-113 at 243K.
Figure 4.2: A plot of $k_{obs}$ as a function of pyridine concentration for DMC-$d_6$ 13b in Freon-113 at 253K.
Figure 4.3: A plot of $k_{obs}$ as a function of pyridine concentration for DMC-$d_6$ 13b in Freon-113 at 273K.
Figure 4.4: A plot of $k_{obs}$ as a function of pyridine concentration for DMC-$d_6$ 13b in Freon-113 at 288K.
Figure 4.5: A plot of $k_{\text{obs}}$ as a function of pyridine concentration for DMC-$d_3$ 13b in Freon-113 at 298K.
Figure 4.6: A plot of $k_{\text{obs}}$ as a function of pyridine concentration for DMC-$h_s$ 13a in Freon-113 at 243K.
Figure 4.7: A plot of $k_{obs}$ as a function of pyridine concentration for DMC-$h_a$ 13a in Freon-113 at 253K.
Figure 4.8: A plot of $k_{obs}$ as a function of pyridine concentration for DMC-$h_6$ 13a in Freon-113 at 263K.
Figure 4.9: A plot of $k_{obs}$ as a function of pyridine concentration for DMC-$h_e$ 13a in Freon-113 at 273K.
Figure 4.10: A plot of $k_{\text{obs}}$ as a function of pyridine concentration for DMC-$d_\text{13b}$ in $\alpha\alpha\alpha$-trifluoromethylbenzene at 245K.
Figure 4.11: A plot of $k_{obs}$ as a function of pyridine concentration for DMC-$d_3$ 13b in $\alpha.\alpha.\alpha$-trifluoromethylbenzene at 253K.
Figure 4.12: A plot of $k_{\text{obs}}$ as a function of pyridine concentration for DMC-$d_1$, 13b in $\alpha,\alpha,\alpha$-trifluoromethylbenzene at 259K.
Figure 4.13: A plot of $k_{\text{obs}}$ as a function of pyridine concentration for DMC-$d_6$ 13b in $\alpha,\alpha,\alpha$-trifluoromethylbenzene at 266K.
Figure 4.14: A plot of $k_{\text{obs}}$ as a function of pyridine concentration for DMC-$d_6$ 13b in $\alpha.\alpha.\alpha$-trifluoromethylbenzene at 271K.
Figure 4.15: A plot of $k_{obs}$ as a function of pyridine concentration for DMC-$d_6$ 13b in $\alpha.\alpha.\alpha$-trifluoromethylbenzene at 278K.
Figure 4.16: A plot of $k_{obs}$ as a function of pyridine concentration for DMC-$d_4$, 13b in $\alpha,\alpha,\alpha$-trifluoromethylbenzene at 288K.
Figure 4.17: A plot of $k_{\text{obs}}$ as a function of pyridine concentration for DMC-$d_6$ 13b in $\alpha\alpha\alpha$-trifluoromethylbenzene at 298K.
Figure 4.18: A plot of $k_{obs}$ as a function of pyridine concentration for DMC-$h_6$ 13a in $\alpha,\alpha,\alpha$-trifluoromethylbenzene at 245K.
Figure 4.19: A plot of $k_{\text{obs}}$ as a function of pyridine concentration for DMC-$h_6 13a$ in $\alpha.\alpha.\alpha$-trifluoromethylbenzene at 253K.
Figure 4.20: A plot of $k_{\text{obs}}$ as a function of pyridine concentration for DMC-$h_{13a}$ in $\alpha,\alpha,\alpha$-trifluoromethylbenzene at 278K.
Figure 4.21: A plot of $k_{obs}$ as a function of pyridine concentration for DMC-$h$, 13a in $\alpha,\alpha,\alpha$-trifluoromethylbenzene at 288K.
Figure 4.22: A plot of $k_{\text{obs}}$ as a function of pyridine concentration for DMC-$d_6$ 13b in perfluoroheptane at 275K.
Figure 4.23: A plot of $k_{obs}$ as a function of pyridine concentration for DMC-$d_6$ 13b in perfluorohexane at 279K.
Figure 4.24: A plot of $k_{\text{obs}}$ as a function of pyridine concentration for DMC-$d_6$ 13b in perfluorohexane at 286K.
Figure 4.25: A plot of $k_{obs}$ as a function of pyridine concentration for DMC-$d_6$, 13b in perfluorohexane at 291K.
Figure 4.26: A plot of $k_{\text{obs}}$ as a function of pyridine concentration for DMC-$d_6$ 13b in perfluorohexane at 298K.
Figure 4.27: A plot of $k_{obs}$ as a function of pyridine concentration for DMC-$h_8$ 13a in perfluorohexane at 275K.
Figure 4.28: A plot of $k_{obs}$ as a function of pyridine concentration for DMC-$h_8$ 13a in perfluorohexane at 286K.
Figure 4.29: A plot of $k_{obs}$ as a function of pyridine concentration for DMC-$h$, 13a in perfluorohexane at 291K.
Figure 4.30: A plot of \( k_{\text{obs}} \) as a function of pyridine concentration for DMC-\( h_6 \) 13a in perfluorohexane at 298K.
4.2 Activation Parameters for the Disappearance of Dimethylcarbene

Since it has been established that dimethylcarbene has a finite lifetime, it remains for us to determine the barriers to the various pathways which consume the carbene. Barring reaction with the solvent, 1,2-hydrogen migration should be the primary decay path of dimethylcarbene. Early theoretical estimates of this barrier (Evanseck and Houk) have placed it at 4.7 kcal/mole. More recent predictions by Matzinger and Fülscher have placed the barrier to rearrangement at 7.4 kcal/mole.

\[ \log k = \frac{-E_a}{2.303R} \left( \frac{1}{T} \right) + \log A \]  

(eq. 4.3)

The Arrhenius equation (eq. 4.3) illustrates the relationship between reaction rates and reaction temperature, and allows the evaluation of the activation parameters (enthalpy and entropy) of a chemical reaction. If the lifetime of dimethylcarbene in solution is controlled by 1,2-hydrogen migration, variation in the temperature and isotopic substitution should manifest itself as an isotope effect on the activation parameters. From the values of the absolute rate constant for 1,2 hydrogen migration obtained in the previous section, a plot of the logarithm of \( k_r \) against the reciprocal of the temperature should yield a straight line. The slope of the line (-\( E_a/2.303R \)) gives the energy of activation (\( E_a \)) for the 1,2-hydrogen migration process and the intercept, the preexponential factor (A) related to the entropy of activation (\( \Delta S^* \)). Arrhenius treatment of the \( 1/r \) data in Freon-113, \( \alpha,\alpha,\alpha \)-trifluoromethylbenzene and perfluorohexane are shown in Figures 4.31 to 4.33. The activation parameters (\( E_a \) and \( \log A \)) are summarized in Tables 4.4 and 4.5. Entropies of activation were calculated at 298 K using equation 4.4 with the factor \( kT/h \) equal to \( 10^{12.8} \) s\(^{-1}\).

\[ A = \frac{kT}{h} \exp \left( \frac{\Delta S^*}{R} \right) \]  

(eq 4.4)
<table>
<thead>
<tr>
<th>Solvent</th>
<th>$E_a$ (kcal/mole)</th>
<th>$\Delta S^\ddagger$ (298 K) (cal-mole$^{-1}$ K$^{-1}$)</th>
<th>log $A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$\textsubscript{2}$CFCClF$\textsubscript{2}$</td>
<td>3.11 ± 0.05</td>
<td>-9.6 ± 0.7</td>
<td>10.7 ± 0.3</td>
</tr>
<tr>
<td>C$\textsubscript{n}$H$\textsubscript{5}$CF$\textsubscript{1}$</td>
<td>2.90 ± 0.05</td>
<td>-11.0 ± 0.7</td>
<td>10.4 ± 0.3</td>
</tr>
<tr>
<td>C$\textsubscript{n}$F$\textsubscript{14}$</td>
<td>2.56 ± 0.05</td>
<td>-12.8 ± 0.7</td>
<td>10.0 ± 0.3</td>
</tr>
</tbody>
</table>

**Table 4.4**: Activation parameters of the reaction of DMC-$h_\textsubscript{a}$ 13a determined from the intercept ($k_r$) in plots of $k_{\text{obs}}$ versus [pyridine].

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$E_a$ (kcal/mole)</th>
<th>$\Delta S^\ddagger$ (298 K) (cal-mole$^{-1}$ K$^{-1}$)</th>
<th>log $A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$\textsubscript{2}$CFCClF$\textsubscript{2}$</td>
<td>3.36 ± 0.05</td>
<td>-9.6 ± 0.7</td>
<td>10.7 ± 0.3</td>
</tr>
<tr>
<td>C$\textsubscript{n}$H$\textsubscript{5}$CF$\textsubscript{1}$</td>
<td>3.85 ± 0.05</td>
<td>-8.2 ± 0.7</td>
<td>11.0 ± 0.3</td>
</tr>
<tr>
<td>C$\textsubscript{n}$F$\textsubscript{14}$</td>
<td>5.63 ± 0.03</td>
<td>-2.7 ± 0.7</td>
<td>12.2 ± 0.3</td>
</tr>
</tbody>
</table>

**Table 4.5**: Activation parameters of the reaction of DMC-$d_\textsubscript{a}$ 13b determined from the intercept ($k_r$) in plots of $k_{\text{obs}}$ versus [pyridine].

The observed activation barrier to the disappearance of DMC varies with the solvent and the isotopic composition of the carbene and is significantly smaller than the value (7.4 kcal/mol) of the 1,2-hydrogen migration predicted by Matzinger and Fülscher's$^{78}$ calculations. In Freon-113 the activation energy observed for the disappearance of DMC-
\( h_{13a} \) and DMC-\( d_{13b} \) are the same within experimental error (3.1-3.3 kcal/mol, see Table 1). There are many possible reasons for this discrepancy. In determining the Arrhenius parameters for the disappearance of \( 13a \) and \( 13b \), the carbene can be consumed by both intra- and intermolecular reactions and the measured \( E_a \) reflects all of the decay routes followed.

Carbenes may be consumed by reaction with excess precursor in solution. This possibility was ruled out because the carbenes are short-lived and the concentration of diazirine precursor is low (millimolar). Thus, it is unlikely that reaction of carbene with diazirine consumes \( 13a \) or \( 13b \). Indeed doubling the diazirine concentration in \( \alpha,\alpha,\alpha \)-trifluoromethylbenzene has no effect on \( \tau \), outside of experimental error.

Consumption of \( 13a \) by reaction with solvent is a likely possibility for the more rapid than predicted disappearance of \( 13a \). This is not a surprising deduction considering our results concerning the significant bimolecular chemistry exhibited by dimethylcarbene. Our ylide quenching studies coupled with GC-MS analysis illustrate this point.

Photolysis of a cyclohexane solution of dimethyldiazirine led to the formation of isopropylcyclohexane \( 32 \) which was confirmed by comparison with an authentic sample. The lifetimes of DMC in cyclohexane and in cyclohexane-\( d_{12} \) were estimated by excimer laser flash photolysis methods and double reciprocal analysis of the data yields \( \tau \) \( C_{4}H_{12} / \tau \) \( C_{4}D_{12} = 2.3 \). Intermolecular processes thus contribute to the disappearance of dimethylcarbene in hydrocarbon solvents.

As mentioned earlier, carbenes have a greater affinity for C-Cl bonds than C-H bonds possibly due to electrophilic attack of the carbene on the halogen. In Freon-113 the most likely bimolecular reaction of \( 13a \) is abstraction of chlorine atoms from the solvent.54,99,100,111,112 This was investigated by GC-MS. Prolonged, continuous, irradiation (350 nm) of \( 18a \) in Freon-113 was followed by GC-MS analysis. A complex
mixture of volatile products were formed including several which contain the fragment 
(CH₄).CCl, apparently derived from products formed by the reaction of 13a.
Identification of a fragment 37 which corresponds to a C-Cl insertion product in Freon-113
strengthens our case for solvent reactivity with the carbene.

The lack of any isotope effect on the carbene lifetime in Freon-113 is consistent
with the GC-MS study which demonstrated that 13a reacts with Freon-113. There is no
conflict with theory in Freon-113 as 13a does not disappear in this solvent by a clean
unimolecular reaction.

In α, α, α-trifluoromethylbenzene, an isotope effect of 0.95 kcal/mol on the
disappearance of dimethylcarbene is observed. This demonstrates that the lifetime of
dimethylcarbene is controlled, in part, by rearrangement to propylene but the isotope effects
on the Arrhenius parameters are too small, however, to indicate that quantum mechanical
tunneling (QMT) is influencing the reaction dynamics. One can argue that as in Freon-113
part of the decay of dimethylcarbene must be bimolecular, hence the low activation
parameters.

The most likely mode of reaction of dimethylcarbene with α,α,α-
trifluoromethylbenzene is addition to the aromatic ring.¹ ² Photolysis of a benzene
solution of 18a led to the formation of cycloadduct 27. The possibility of electrophilic
addition of 13a to a benzene ring was thus confirmed. Repeating the photolysis in α,α,α-
trifluoromethylbenzene results in a complex mixture of products with a fragment 31
indicating addition of an isopropyl group to the ring. Due to the deactivated benzene ring in
α,α,α-trifluoromethylbenzene, electrophilic addition may not be as facile a process as in
benzene allowing us to partially observe the isotope effect of 1,2-hydrogen migration in
dimethylcarbene.
There is a possibility of complexation between DMC with the \( \pi \) electrons of the aromatic ring or with the non-bonding electrons on the halogen with these solvents.\(^{113-122} \) However, calculations of Sulzbach and Hadad\(^{123} \) indicate that complexation should raise the barrier to hydrogen migration. Thus complexation does not explain the low \( E_1 \) values measured in Freon-113.

The results in Freon-113 and \( \alpha,\alpha,\alpha \)-trifluoromethylbenzene led us to search for a solvent that might be unreactive to DMC such as perfluorohexane. The isotope effects observed in perfluorohexane were large and dramatic (\( \Delta E^D_1 - \Delta E^H_1 = 3.18 \text{ kcal/mol}, \frac{A_D}{A_H} = 158 \)) and the enthalpic barrier to disappearance of DMC in perfluorohexane was actually smaller than in the presumably more reactive solvents and was very much smaller than predicted by calculations. The observed results cannot be explained by transition structure theory.

The effect of tunneling on the reaction rate would be to make the reaction faster than expected from the transition state picture. Since hydrogen is about half the mass of deuterium, the effects will be greater for hydrogen. As a result, the isotope effects and preexponential factor \( (A) \) ratios would be anomalously large. This was clearly observed in the isotope effects for \( 13a \) and \( 13b \) in perfluorohexane. Thus we conclude that the decay of \( 13a \) and \( 13b \) in perfluorohexane is intramolecular and that of \( 13a \) proceeds by a QMT mechanism in perfluorohexane. Since the barrier to disappearance of \( 13b \) in perfluorohexane is close to that predicted by theory, the decay of DMC under these conditions may not have a component of QMT.
Figure 4.31: Arrhenius plot of $k_r$ data obtained in Freon-113.
Figure 4.32: Arrhenius plot of $k_T$ data obtained in $\alpha,\alpha,\alpha$-trifluoromethylbenzene.
Figure 4.33: Arrhenius plot of $k_T$ data obtained in perfluorohexane.
CHAPTER 5

FLUORESCENCE SPECTRA AND LIFETIMES OF ALKYL AND DIALKYLDIAZIRINES

The photochemistry of diazirines is complex. Upon photoexcitation, several processes may occur that introduce difficulties in distinguishing carbene chemistry from the excited state chemistry of diazirines. In diazirine photolysis, it is theorized that an excited n→π* state is produced. This excited n→π* state may decay by several pathways which include: fluorescence (k_F), internal conversion (k_{IC}), intersystem crossing (k_{ISC}), carbene formation (k_C), diazo formation (k_A) and 1,2-hydrogen migration (k_R). The total rate for the disappearance of the n→π* state k_d is the sum of all the photophysical processes which consume the excited state and is represented in equation 5.1.

\[ k_d = k_F + k_{IC} + k_{ISC} + k_C + k_R + k_A + ... \]  

(eq 5.1)

The photolysis is further complicated by the interrelationships between the products formed in excited state processes with those products derived from carbene chemistry (Scheme 5.1). Since 1,2-hydrogen migration can occur from the diazirine excited state and from the carbene, it will be difficult to distinguish carbene rearrangement products from diazirine excited state derived products.
Scheme 5.1: Excited state participation in the photolysis of diazirines.

The involvement of diazirine excited states in 1,2-hydrogen migration may be probed by fluorescence spectroscopy. The measurement of the fluorescence lifetime ($\tau_f$) and the fluorescence quantum yield ($\Phi_f$) will allow us to measure the effect of processes which consume the excited $n\rightarrow\pi^*$ state. The kinetic equations for the quantum yields, lifetimes, and first order rate constants for any of the events that take place in the
photochemistry of diazirines may be derived and are shown in Table 5.1. Any enhancement of a competing process (such as 1,2-hydrogen migration) will be reflected as a decrease in the lifetime and quantum yield measurements. In order to study diazirine excited states, several diazirines were synthesized (Scheme 5.2) and the effect of structure on the quantum yields and lifetimes were determined.

Deuteration of the carbene carbon should have no effect on the measured quantum yields ($\Phi_f$ and $\Phi_C$) and lifetimes ($\tau_f$) provided that vibrational relaxation (internal conversion) is a minor process in diazirines. On the other hand, deuteration of the $\alpha$-carbons of diazirines should decrease $k_R$ from the excited state of the diazirine. If rearrangement is a major process in diazirine photochemistry, deuteration should increase the quantum yields ($\Phi_f$ and $\Phi_C$) and lifetime ($\tau_f$).

<table>
<thead>
<tr>
<th>Photophysical Quantity</th>
<th>Symbol</th>
<th>Relation to Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorescence</td>
<td>$\Phi_f$</td>
<td>$\frac{k_F}{k_f + k_{IC} + k_C + k_R + ...}$</td>
</tr>
<tr>
<td>Quantum Yield</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbene</td>
<td>$\Phi_C$</td>
<td>$\frac{k_C}{k_f + k_{IC} + k_C + k_R + ...}$</td>
</tr>
<tr>
<td>Quantum Yield</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorescence</td>
<td>$\tau_f$</td>
<td>$\frac{1}{k_f + k_{IC} + k_C + k_R + ...}$</td>
</tr>
<tr>
<td>Lifetime</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 5.1:** Kinetic equations for the quantum yields and lifetimes for the photophysical processes studied.
5.1 Determination of Relative Fluorescence Quantum Yields

The determination of the relative fluorescence quantum yields of two substances, both in solution at room temperature, is a relatively simple matter. The total rate of emission fluorescence is proportional to $I_0e^{c_l0}$, which is proportional to the integrated area under the curve. The ratio of the two observed fluorescence intensities is given by:

$$\frac{Q_{\text{std}}}{Q_{\text{sol}}} = A_{\text{std}} \frac{A_{\text{sol}}}{\Phi_{\text{std}}} = \frac{I_0 \varepsilon_{\text{std}} c_{\text{std}}}{I_0 \varepsilon_{\text{sol}} c_{\text{sol}}} \frac{\Phi_{\text{std}}}{\Phi_{\text{sol}}} = \left( \frac{\Phi_{\text{std}}}{\Phi_{\text{sol}}} \right) \left( \frac{OD_{\text{std}}}{OD_{\text{sol}}} \right) \tag{eq. 5.2}$$

If the absolute fluorescence efficiency ($\phi$) of one of the substances is known, that of the other is then simply calculated. The ratio of fluorescence intensities measured ($Q_{\text{std}}/Q_{\text{sol}}$) is equal to the ratio of the absolute rates of fluorescence by the two solutions only.
if the geometrical arrangement of the specimen and optics is identical for the two measurements. A change in the refractive index (n) of the solution results in a variation in the angles of the rays emerging from the plane of the cuvette-air interface. Thus if the two substances to be compared are dissolved in different solvents the observed intensities must be corrected by multiplying by n^2 (equation 5.3).

\[ \frac{\Phi_{\text{std}}}{\Phi_{\text{sol}}} = \left( \frac{A_{\text{std}}}{A_{\text{sol}}} \right) \left( \frac{\text{OD}_{\text{std}}}{\text{OD}_{\text{sol}}} \right) \left( \frac{n_{\text{std}}^2}{n_{\text{sol}}^2} \right) \]  

(eq 5.3)

The designators "std" and "sol" indicate the standard reference and sample solution respectively and Φ is the fluorescence quantum yield. The term \( \left( n_{\text{std}}^2/n_{\text{sol}}^2 \right) \) is a correction factor for the refractive index and \( \left( A_{\text{std}}/A_{\text{sol}} \right) \) the ratio of integrated intensities under the emission spectra. The ratio of the absorbance of solution and standard \( \left( \text{OD}_{\text{std}}/\text{OD}_{\text{sol}} \right) \) is factored in to correct for concentration variations within samples.

Diazirine solutions were prepared with matched absorbances for comparison of isotope effects. The fluorescence quantum yields of the diazirine solutions were measured by comparing the integrated fluorescence intensities with that of the standard 9,10-diphenylanthracene (Φ_{std} = 1.00). Applying equation 5.3, the quantum yields Φ_{f} were calculated and shown in Table 5.2. The fluorescence spectra of diazirines (Scheme 5.2) are shown in Figures 5.1-5.5.
<table>
<thead>
<tr>
<th>Diazirine</th>
<th>( \Phi_e )</th>
<th>( \Phi_I^{\text{rel}} )</th>
<th>( \Phi_I^{11}/\Phi_I^{11} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>18a</td>
<td>0.00272 ± 0.00004</td>
<td>0.15 ± 0.02</td>
<td>1.26 ± 0.02</td>
</tr>
<tr>
<td>18b</td>
<td>0.00345 ± 0.00006</td>
<td>0.19 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>41a</td>
<td>0.00016 ± 0.00002</td>
<td>0.0090 ± 0.0001</td>
<td>1.1 ± 0.2</td>
</tr>
<tr>
<td>41b</td>
<td>0.00017 ± 0.00003</td>
<td>0.009 ± 0.0001</td>
<td></td>
</tr>
<tr>
<td>42a</td>
<td>0.00315 ± 0.00005</td>
<td>0.174 ± 0.003</td>
<td>1.18 ± 0.02</td>
</tr>
<tr>
<td>42b</td>
<td>0.0037 ± 0.0002</td>
<td>0.21 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>43a</td>
<td>0.00113 ± 0.00007</td>
<td>0.062 ± 0.005</td>
<td>1.18 ± 0.08</td>
</tr>
<tr>
<td>43b</td>
<td>0.00133 ± 0.00003</td>
<td>0.073 ± 0.005</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>0.0181 ± 0.0002</td>
<td>1.0000 ± 0.0002</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2: Absolute and relative quantum yields of fluorescence for diazirines (Scheme 5.2) measured at ambient temperature in Freon-113.

Spirocyclic diazirines have greater values of \( \Phi_e \) than the simpler dialkyldiazirines (compare 44 and 42a versus 18a, Scheme 5.3). Since spirocyclodiazirines are relatively stiff molecules, coupling of C—C vibrational modes to the diazirine moiety will be relatively inefficient. Thus, internal conversion in spirocyclidiazirines will be slower (lower \( k_{1c} \)) resulting in an increase in \( \Phi_e \).
Deuteration at the diazirine carbon will have little effect on $\Phi_F$ if internal conversion is a minor process in diazirines. This is observed in 41a and 41b but a larger isotope effect is observed for 43a and 43b. Diazirines 43a and 43b were prepared to be used as alternative models for diazirine 41a and 41b which are gases at room temperature. Internal conversion may be a major process in diazirines 43a resulting in a 20% increase in $\Phi_F$. Another possible reason for the isotope effect may be that a very facile carbon migration to 3-homoadamantene has been observed for the N-tosylhydrazone derivative.\textsuperscript{127-129} We may be observing a secondary kinetic isotope effect of this carbon migration to a relatively stable 3-homoadamantene\textsuperscript{130} from the excited state of the diazirine. This explanation may be highly unlikely and a simpler reason may be due to internal conversion in the excited state of 43a.
Deuteration alpha to the diazirine carbon increases $\Phi_F$ and dialkyldiazirines are observed to be more fluorescent than monoalkyldiazirines which are more fluorescent than parent diazirine (44, 42a, and 18a versus 43a and 41a). This suggests that the fluorescent excited state is not ring opening. In addition to this, the isotope effects observed for 43a and 43b indicate that internal conversion is important. Thus, based on measurements of $\Phi_F$, we cannot conclude that the concerted hydrogen migration and ring opening (Scheme 5.4) in the fluorescent $n\rightarrow\pi^*$ state of the diazirine is occurring.

The observed isotope effects could be due to enhanced vibrational coupling and internal conversion in the protio relative to the deuterio forms. However, it seems unlikely that remote deuteration should influence internal conversion to the same extent as isotopic substitution on the diazirine carbon. Rather, the isotope effect observed upon deuteration of the $\alpha$-carbon of the diazirine could be due to hydrogen migration taking place further on in the reaction path of the $n\rightarrow\pi^*$ state of the diazirine.
Figure 5.1: Fluorescence spectrum of 44 ($\lambda_x = 350$ nm; slit widths: 3.5 mm, 1.5 mm, 5.5 mm, and 3.5 mm) in Freon-113 at ambient temperature.
Figure 5.2: Fluorescence spectrum of 43a and 43b ($\lambda_{ex} = 350$ nm; slit widths: 3.5 mm, 1.5 mm, 5.5 mm, and 3.5 mm) in Freon-113 at ambient temperature.
Figure 5.3: Fluorescence spectrum of 41a and 41b ($\lambda_{ex} = 320$ nm; slit widths: 3.5 mm, 1.5 mm, 5.5 mm, and 3.5 mm) in Freon-113 at ambient temperature.
Figure 5.4: Fluorescence spectrum of 18a and 18b (λc = 350 nm; slit widths: 3.5 mm, 1.5 mm, 5.5 mm, and 3.5 mm) in Freon-113 at ambient temperature.
Figure 5.5: Fluorescence spectrum of 42a and 42b ($\lambda_{ex} = 350$ nm; slit widths: 3.5 mm, 1.5 mm, 5.5 mm, and 3.5 mm) in Freon-113 at ambient temperature.
5.2 The Single-Photon Technique

The time-correlated single photon counting (TCSPC) method is capable of measuring fluorescence lifetimes in the picosecond regime and its excellent signal to noise ratio makes it useful for weak fluorophores. Figure 7.2 shows the layout of a typical time-correlated single photon counting fluorimeter. A pulsed light source, usually a flashlamp or mode locked laser, generates multiphoton excitation pulses which stimulate absorption in an assembly of sample molecules. At low levels of excitation power, each sample molecule absorbs one photon at most, on a timescale which is effectively instantaneous. The subsequent de-excitation of these molecules via the emission of fluorescence photons occurs with a distribution of time delays normally described by equation 5.4 that is, exponential. The single photon timing technique records this distribution by measuring the time delays of individual fluorescence photons with respect to the excitation pulse.

\[ t_p(t) = \frac{1}{\tau} e^{-\frac{t}{\tau}} \]  

(eq. 5.4)

The heart of the technique lies in what is known as the time-to-amplitude converter (TAC). When the excitation pulse occurs, a synchronization pulse or "start" timing pulse triggers the charging of a capacitor in the TAC. The voltage on the capacitor increases linearly until either a pre-selected time range is reached or a "stop" timing pulse is detected. The latter is initiated by the detection of a fluorescence photon, and the "start"-"stop" time interval generates a proportional voltage across the capacitor. This voltage pulse is stored according to amplitude using an analog-to-digital converter within a multichannel analyzer (MCA) and thereby allocated a proportional channel number. On repeating the "start"-"stop" cycle many times, a histogram representative of the fluorescence decay is acquired in
the MCA memory. The decay parameters can then be extracted using on-line data analysis of the histogram using numerical and statistical procedures.

The fluorescence decays are adequately described by a single exponential function for more than 6 percent of the decay. The fluorescence lifetimes are listed in Table 5.3 and an Arrhenius treatment of the data is presented in Figures 5.7 to 5.9.

The lifetime of spirocyclohexyldiazirine 42a is only 98 ps at 283 K in pentane and that of dimethyl diazirine 18a is 40 ps at 283 K in CF₂ClCFCl₂. The rigidity of spirocycldiazirines reduces coupling of C—C vibrational modes in the diazirine. As reasoned earlier, internal conversion in spirocyclic diazirines will be less efficient than a simple diazirine (lower k_{ic}) resulting in an increase in \( \tau_p \). It appears that the influence of internal conversion is on the A factor rather than on the activation energy. This is demonstrated in the larger A factor for diazirine 18a (7.66 x 10^{-12} \text{ s}^{-1}) compared to diazirine 42a (1.31 x 10^{-12} \text{ s}^{-1}).

The increase in fluorescence intensity and fluorescence decay time observed at low temperatures confirms that fluorescence competes with several activated processes in the excited states of 42a and 18a. Arrhenius treatment of the fluorescence lifetime data yielded activation energies of 2.80 kcal/mole for spirocyclohexyldiazirine 42a and 3.20 kcal/mole for dimethyl diazirine 18a. The barrier to ring opening of diazirines is lower than that of monocyclic diazirines due to greater strain release.

Calculations indicate that the \( n\rightarrow\pi^* \) state (\( S_1 \)) requires \( = 3 \text{ kcal/mol} \) to reach the \( n\rightarrow\pi^*/n\rightarrow\sigma^* (S_1/S_2) \) surface crossing. At this point the \( S_1 \) excited state becomes \( n\rightarrow\sigma^* (S_2) \) in nature and the C—N bond cleaves to form a biradical. Spiro cyclic diazirines 44 and 42a have greater strain energy than acyclic dimethyl diazirine 18a. Strain is
released in 44 and 42a when the C—N bond cleaves hence destabilization of the S₁ state in
44 and 42a lowers the activation barrier to cleavage.

There were no discernible isotope effects observed on the fluorescence lifetimes of
diazirines 42a and 18a. However, our studies on the fluorescence quantum yields Φ,
indicate that there is a finite isotope effect on Φ₁ which appears to contradict our
observations on τₚ. From Table 5.3 and equation 5.1, the fluorescence lifetime τₚ should
be equal to the reciprocal of kₚ. In determining τₚ, we are thus measuring the sum of all the
decay processes that consume the S₁ state which is equal to (kₚ + k_isc + k_Ic + k_r)^⁻¹ = k_d⁻¹
where the rate constants correspond to fluorescence, intersystem crossing, internal
conversion, and cleavage to form a diradical. If kₚ makes only a minuscule contribution to
k_d the small isotope effect cannot be seen upon measurement of τₚ. In measuring Φₚ, from
Table 5.2, the quantum yield should be equal to the ratio of kₚ and k_d. The absolute values
of Φₚ that we have determined for diazirines 42a and 18a are very small relative to
adamantyldiazirine. For adamantyldiazirine, the value of the quantum yield Φₚ was
estimated to be 0.0012. Thus, upon taking a ratio of small numbers
the isotope effect is discernible.

From τₚ measurements, we surmise that the S₁ state traverses a small barrier of
~3.2 kcal/mole to an S₂ diradical 45 (Figure 5.10). The diradical 45 may decay by
several pathways such as diazo formation, hydrogen migration and carbene formation.
Migration of an α-hydrogen after ring opening may explain the small isotope effect
observed on Φₚ.
<table>
<thead>
<tr>
<th>Diazirine (Solvent)</th>
<th>Temp (K)</th>
<th>$\tau$(ns)</th>
<th>A(s$^{-1}$)</th>
<th>$E_r$(kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>44 (methylcyclohexane)</td>
<td>230</td>
<td>2.120</td>
<td>7.99 x 10$^{11}$</td>
<td>3.40</td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>0.930</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>291</td>
<td>0.444</td>
<td></td>
<td></td>
</tr>
<tr>
<td>42a (pentane)</td>
<td>213</td>
<td>0.528</td>
<td>1.56 x 10$^{12}$</td>
<td>2.86</td>
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<tr>
<td></td>
<td>221</td>
<td>0.375</td>
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<td>233</td>
<td>0.340</td>
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<tr>
<td></td>
<td>243</td>
<td>0.259</td>
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<tr>
<td></td>
<td>253</td>
<td>0.198</td>
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<td></td>
<td>263</td>
<td>0.375</td>
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<tr>
<td></td>
<td>273</td>
<td>0.123</td>
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<td></td>
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<tr>
<td></td>
<td>283</td>
<td>0.098</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>293</td>
<td>0.080</td>
<td></td>
<td></td>
</tr>
<tr>
<td>42b (pentane)</td>
<td>213</td>
<td>0.514</td>
<td>1.31 x 10$^{12}$</td>
<td>2.81</td>
</tr>
<tr>
<td></td>
<td>223</td>
<td>0.438</td>
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<td></td>
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<tr>
<td></td>
<td>233</td>
<td>0.353</td>
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<td></td>
</tr>
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<td></td>
<td>243</td>
<td>0.262</td>
<td></td>
<td></td>
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<td></td>
<td>253</td>
<td>0.215</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>263</td>
<td>0.172</td>
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<td>273</td>
<td>0.132</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>283</td>
<td>0.110</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>0.088</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18a (CF$_2$ClCFCl$_2$)</td>
<td>238</td>
<td>0.115</td>
<td>8.39 x 10$^{12}$</td>
<td>3.261</td>
</tr>
<tr>
<td></td>
<td>248</td>
<td>0.087</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>257</td>
<td>0.076</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>268</td>
<td>0.049</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>283</td>
<td>0.040</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18b (CF$_2$ClCFCl$_2$)</td>
<td>238</td>
<td>0.118</td>
<td>7.66 x 10$^{12}$</td>
<td>3.19</td>
</tr>
<tr>
<td></td>
<td>248</td>
<td>0.084</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>257</td>
<td>0.060</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>268</td>
<td>0.052</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>283</td>
<td>0.040</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.3: Temperature dependence of the fluorescence lifetime for diazinnes (18a, 18b, 42a, 42b and 44).
Figure 5.6: Arrhenius treatment of the fluorescence lifetime of 44.
Figure 5.7: Arrhenius treatment of the fluorescence lifetime of 42a and 42b.
Figure 5.8: Arrhenius treatment of the fluorescence lifetime of 18a and 18b.
5.3 Quantum Yield of Dimethylcarbene

Carbene formation and 1,2-hydrogen migration are other processes which contribute to the consumption of diazirine excited states. If 1,2-hydrogen migration occurs in an excited state, the quantum yield of carbene formation ($\Phi_c^r$) may be used as a probe for this process. From Table 5.2, we can see how the value of $k_R$ will affect $\Phi_c$. Upon deuterium substitution of the $\alpha$-hydrogens in a carbene, $k_R$ is decreased and $\Phi_c$ should increase resulting in an isotope effect $\Phi_c^H/\Phi_c^D$. Since we do not observe hydrogen migration process in the parent diazirine, deuteration of the carbene center should have no effect on the ratio $\Phi_c^H/\Phi_c^D$.

The quantum yield of carbene formation ($\Phi_c$) is measured by determining the optical density ($A_{\nu}^{\text{SAT}}$) of the carbene-pyridine ylide at the saturating concentration of pyridine. At a concentration of 1M pyridine, essentially all carbene formed from the diazirine will be trapped (for all carbenes studied). Photolysis of a diazirine solution in 1M pyridine with 351 nm laser pulse produces the signal shown in Figure 5.10. The height of the signal represents the optical yield of the carbene-pyridine ylide at the saturating pyridine concentration ($A_{\nu}^{\text{SAT}}$). Since the transient absorption of the ylide is proportional to the quantum yield of carbene formation, $A_{\nu}^{\text{SAT}}$ is taken to represent $\Phi_c$. Diazirines 18a, 41a, 42a and their deuterated isotopomers (18b, 41b, and 42b) were prepared and photolyzed at 351 nm. The quantum yields of carbene formation obtained are shown in Table 5.4.
Figure 5.9: The growth curve for pyridine ylide 40 produced upon LFP with an XeF excimer laser (351 nm) and monitored at 364 nm in Freon-113 at ambient temperature.
<table>
<thead>
<tr>
<th>Carbene</th>
<th>Transient Absorption</th>
<th>$A_{y}^{SAT}$</th>
<th>$\frac{A_{y}^{SAT-H}}{A_{y}^{SAT-D}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure 41a" /></td>
<td>0.22 ± 0.04</td>
<td>1.0 ± 0.2</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Structure 41b" /></td>
<td>0.23 ± 0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Structure 43a" /></td>
<td>0.24 ± 0.03</td>
<td>1.0 ± 0.1</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Structure 43b" /></td>
<td>0.24 ± 0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Structure 18a" /></td>
<td>0.072 ± 0.004</td>
<td>1.22 ± 0.08</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Structure 18b" /></td>
<td>0.088 ± 0.004</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 5.4:** Optical yields of ylide formation for diazirines photolyzed in 2.0 M pyridine in Freon-113 at ambient temperature.
The results listed in Table 5.4 reveal that deuteration of the diazirine carbon has no effect on the quantum yield of carbene formation. By this measure, it seems clear that coupling of the diazirine C—H (D) vibration to the excited state does not play a major role in the deactivation of $S_1$ by internal conversion (IC). This is not completely consistent with relative quantum yield measurements (Table 5.2) where small isotope effect were realized.

Deuteration on the carbon alpha to the diazirine moiety does have a significant effect on carbene yield. Twenty percent more dimethylcarbene-$d_6$ 13b is produced than dimethylcarbene-$h_6$ 13a, per laser pulse. It is unlikely that this is an effect of internal conversion because IC effects are not pronounced when deuterium is exchanged for hydrogen on the diazirine carbon. We believe that carbene formation from an excited state must compete with hydrogen/deuterium migration from α carbon perhaps from a state other than the $S_1$.

Calculations indicate that carbene formation does not proceed from $S_1$, an $n\rightarrow\pi^*$ excited state. The $S_1$ state crosses the $S_2$ state ($n\rightarrow\sigma^*$) at a point a few kcal/mol above $S_1$, hence the apparent activation barrier to the fluorescence lifetime ($\tau_f$). The $S_2$ is biradical in nature (e.g. 45, Figure 5.10). We speculate that 45 migrates hydrogen to form propene in concert with nitrogen extrusion (Figure 5.11, path a) at a rate comparable to carbene formation (Figure 5.11, path b) or isomerization to diazo compound (Figure 5.11, path c). This explains the isotope effects on transient absorption yields ($\Delta A_{\nu}^{\text{SAT}}$) with dimethyldiazirine and its isotopomer.
Figure 5.10: Proposed mechanism for the photochemistry of dimethyldiazirine.
CHAPTER 6

CONCLUSION

The product studies and Stern-Volmer quenching experiments indicate that dimethylcarbene can exhibit significant bimolecular chemistry. The very often cited reason of a facile 1,2-hydrogen shift precluding carbene capture is not a valid statement. Our product analysis and Stern-Volmer results indicate that unhindered electron-rich alkenes may trap dimethylcarbene resulting in cyclopropanation (a common reaction of carbenes). As expected, dimethylcarbene derived from diazirines and oxadiazolines appear to exhibit similar reactivities for cycloaddition reactions. Due to the electrophilic nature of singlet dimethylcarbene, atoms with lone pairs of electrons (O, N, Cl) also react readily and give products detectable by GC-MS. Diazirines and oxadiazolines again exhibit similar reactivity profiles. Amine insertion which was found to be faster than reaction with pyridine results in a 60% yield of trapped carbene derived from the oxadiazoline. The product studies agree with Stern-Volmer quenching results in predicting which carbene quenchers yield carbene adducts upon photolysis of either the oxadiazoline or the diazirine precursor. To further strengthen our arguments for the rich bimolecular chemistry of dimethylcarbene, reactions involving insertions into Si-H bonds which were found to be non-competitive with pyridine ylide formation for both precursors although adducts are formed upon long-term photolysis of the precursor in neat silane. As a result, we may conclude that bimolecular chemistry may significantly contribute to carbene consumption in solvents with aromatic rings or with hetero atoms with available lone pairs and that oxadiazolines are equivalent to diazirines.
Laser flash photolysis (Nd/YAG laser, 355 nm, 35 mJ, 150 ps) of
dimethylidiazirine-\(\text{H}_2\), \textbf{18a} and dimethylidiazirine-\(d_2\), \textbf{18b} produces dimethylcarbene-\(\text{H}_2\), \textbf{13a}
and dimethylcarbene-\(d_2\), \textbf{13b} respectively. The carbenes were trapped with pyridine to
form ylides which absorb between 350 and 400 nm. It was possible to resolve the growth
of the ylides as a function of pyridine concentration in Freon-113, \(\alpha,\alpha,\alpha\)-
trifluoromethylbenzene and perfluorohexane as a function of temperature. The observed
rate constant \(k_{\text{obs}}\) to ylide formation was linearly dependent on the concentration of
pyridine. From plots of \(k_{\text{obs}}\) versus [pyridine] it was possible to extract values of \(k_{\text{pyr}}\)
(absolute rate constant of reaction of the carbene with pyridine) and \(\tau\), the carbene lifetime.
in the absence of pyridine, and their associated Arrhenius parameters. In Freon-113 and
\(\alpha,\alpha,\alpha\)-trifluoromethylbenzene the carbenes decay by rearrangement and by reaction with
solvent. In perfluorohexane the carbene decay appears to be predominantly unimolecular.
The Arrhenius parameters indicate that the rearrangement of hydrogen has a strong
tunneling component. The observed barrier to rearrangement of dimethylcarbene is much
smaller (2.5 kcal/mol) than that predicted by \textit{ab initio} theory (7.4 kcal/mol). This also
points to the involvement of tunneling in the rearrangement of \textbf{13a}. The barrier to
rearrangement of deuterium in \textbf{13b} in perfluorohexane (5.6 kcal/mol) is comparable to that
predicted by theory. Tunneling may not be important in the deuterated system.

Fluorescence lifetime measurements on \textbf{18a} and \textbf{18b} were performed by TCSPC.
Arrhenius treatment of the temperature dependence of the fluorescence shows no
discernible isotope effects on the fluorescence lifetime. Deuterium substitution alpha to the
carbene center increases the fluorescence quantum yield \((\Phi_F)\) and optical yields of the ylide
\textbf{40} \((\Phi_{y,3AT})\) by 20\%. The energy barrier of 3 kcal/mole for the fluorescence lifetime is
within the lower bounds for an \(S_1 (n\rightarrow\pi^*)\) to \(S_2 (n\rightarrow\sigma^*)\) surface crossing. We propose
that a biradicaloid structure is achieved upon traversing this barrier into the S₁ state. This biradical may undergo the intramolecular decay processes that we associate with the carbene. If 1,2-hydrogen migration occurs in this S₂ state, then a new pathway leading to the disappearance of the excited state (S₁) is set up and α-deuteration will affect the optical yield of ylide. Hydrogen migration can, in principle, also occur from the S₁ state producing a second biradical, hence the effect of α-deuteration of the fluorescence quantum yield. Loss of nitrogen from this second biradical gives propene. However, evidence for this pathway is not clearly demonstrated due to internal conversion effects.

The photochemistry of dimethyldiazirine is thus complicated by excited state reactions and pathways leading to free carbene may represent only a fraction of the yield expected from the absorption of radiation. Diazirines are thus inefficient precursors for carbenes. Oxadiazolines on the other hand appear to be more attractive alternative precursors to diazirines. Oxadiazolines are very good in duplicating the reactivity profile and lifetime measurements from diazirine precursors and thus provide a convenient alternate route to the carbene if the diazirine precursor is not available. On closer study, we believe that similar excited state reactions do occur in the oxadiazoline as with the diazirines. We are only able to obtain 60% carbene yield for amine trapping with the oxadiazoline precursor. This implies that ~40% of the quantum yield may result in propene derived from the excited state of the diazo compound produced on oxadiazoline photolysis. The similarities between Stern-Volmer analysis and bimolecular reactivities of both precursors also support this conclusion. The extent of excited state reactivity in oxadiazolines has yet to be studied. Future work in this area might entail the preparation of non-nitrogenous carbene precursors and comparative experiments on the ensuing chemistry.
CHAPTER 7

EXPERIMENTAL

7.1 General Methods

$^1$H NMR and $^3$H NMR spectra were obtained on a Bruker AC-200, 200 MHz NMR spectrometer. Chemical shifts are reported in $\delta$ (ppm) with tetramethylsilane or chloroform as an internal standard. Infrared spectra were taken 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. Fluorescence spectra were taken on a SPEX DM3000 Fluorescence Spectrometer.

All solvents and reagents were obtained from commercial sources and used without further purification, except where noted. Freon-113, $\alpha,\alpha,\alpha$-trifluoromethylbenzene, perfluorohexane, cyclopentene, cyclohexane and triethylsilane were purified by passing through a neutral alumina column immediately before use. Methanol and tert-butanol were dried by refluxing over calcium hydride followed by distillation. Diethyl ether and tetrahydrofuran were distilled over sodium and benzophenone. Pyridine was distilled over potassium hydroxide. All of the above distillation were performed under an atmosphere of nitrogen.
7.2 Product Analyses

3.3-dimethyl-3H-diazirine 18a was condensed into each solvent in Table 2.1 and the amount of diazirine adjusted to give \(-0.010\) mole of diazirine \((\varepsilon_{\text{mol}} = 180)\). For dimethyloxadiazoline 24a, a fixed amount corresponding to 0.010 mole was weighed out and placed in each of the solvents in Table 2.1. Photolysis was conducted in quartz cuvettes with the solutions degassed with Ar before photolysis using a Rayonet apparatus. The diazirine and oxadiazoline were photolyzed at 350 nm and 300 nm respectively for 24 hours at 5°C.

Product analyses were performed after photolysis of the diazirine 18a and oxadiazoline 24a using an HP-5890 Gas Chromatograph with a fused silica capillary column cross-linked with 5% phenyl methyl silicone (column i.d. 0.25 mm, column length 15 m). The gas chromatograph was linked to a HP-5970B Mass Spectrometer with a capillary direct interface allowing detection of photolysis products.

Yields were quantified by analytical GC with the appropriate external standard (methylcyclohexane and diisopropylamine). Analytical gas chromatography was performed on a Perkin-Elmer 8500 Gas Chromatograph equipped with a flame ionization detector, using a Supelco fused silica capillary column cross-linked with methyl silicone (column i.d. 0.32 mm; column length 30 m, phase film thickness 3 μm). The yields of products obtained upon decomposition of the oxadiazoline 24a were measured by integration of peaks in the gas chromatograms.
7.3 Laser Flash Photolysis Studies

7.3.1 Determination of Transient Absorption Spectra

Transient absorption spectra were obtained on an EG&G PARC 1460 Optical Multichannel Analyzer fitted with an EG&G PARC 1304 Pulse Amplifier, an EG&G PARC 1024 UV detector and a Jarrell-Ash 1234 Grating. The excitation sources used depended on the precursor being studied. For the diazirine 18a, a Lumonics TE-861-4 excimer laser (351 nm, 60 mJ, 17 ns) was used. The oxadiazoline 24a was excited with a Lambda Physik LPX-100 excimer laser (308 nm, 120 mJ, 17 ns).

7.3.2 Determination of Lifetimes and Absolute Rate Constants

Stock solutions of the 3,3-dimethyl-3H-diazirine and 3,3-bis-trideuteriomethyl-3H-diazirine were prepared in each solvent of interest with an optical density of 0.35 ± 0.20 at 355 nm for lifetime and kinetic experiments. The solvents utilized were Freon-113, \(\alpha,\alpha,\alpha\)-trifluoromethylbenzene and perfluorohexane. A constant volume (1.5 mL) of the stock solution was added to Suprasil<sup>®</sup> Quartz Fluorescence-free static cells and a varying amount of pyridine until the pyridine concentration reached approximately 1.12 M. A special sample holder for variable temperature work was used to avoid scattering the laser beam and the temperature of the set-up was regulated with a NESLAB RTE-110 variable temperature controller.

The LFP apparatus for the determination of kinetics consists of a Lumonics TE-861-4 excimer laser (350 or 249 nm, 60 mJ, 7 ns) and a Continuum PY62C-10 Nd/YAG laser (355 nm, 30 mJ, 2 ns). In dimethylidiazirine (18a and 18b) studies, samples were deoxygenated by bubbling with dry, oxygen free argon for two minutes. Each of the samples were placed in the appropriate sample cell fitted with rubber septum. The sample cells were irradiated with excimer or Nd/YAG laser pulses that impinged on the sample at a
right angle to a 150 W Xe arc lamp fitted with an aspherab beam collimator. The monitoring beam was focused on the slit of an Oriel monochromator, selected for the wavelength of interest, with both front and rear slits set between 0.2 to 0.4 mm. Signals were obtained with a photomultiplier tube detector and were digitized by a Tektronix 5815A A/D transient digitizer. The entire apparatus is controlled by a Macintosh IIx microcomputer which was also used for storage of the time resolved data. Data analysis was performed with IgorPro® PPC (version 3.02) by Wavemetrics.

Figure 7.1: Instrument for Laser Flash Photolysis experiments at The Ohio State University.
7.3.3 Stern-Volmer Quenching Methods

Stern-Volmer experiments of the reactions of dimethylcarbene 13a were performed similarly. Stock solutions consisted of diazirine 18a or oxadiazoline 24a were prepared in Freon-113 containing 1.37 M pyridine. The concentrations of the quenchers of interest were typically varied from 0 to between 2 and 4 M at constant pyridine concentration for a series of 8-10 cuvettes. Excitation sources for the diazirine 18a was a Lumonics TE-861-4 excimer laser (351 nm, 60 mJ, 17 ns) while in the case of the oxadiazoline 24a, a Lambda Physik LPX-100 excimer laser (308 nm, 120 mJ, 17 ns) was used.

7.3.4 Determination of Carbene Quantum Yields

Solutions of diazirines 18a, 41a, 42a and their deuterated isotopomers (18b, 41b, and 42b) were prepared in Freon-113 with an optical density of 0.35 ± 0.03 at 355 nm. Pyridine (0.200 mL) was added to 1.5 mL of each diazirine solution to give a final pyridine concentration of 1.45 M. The excitation source for the diazirines was a Lumonics TE-861-4 excimer laser (351 nm, 60 mJ, 17 ns). The transient growth curves were generated by photolysis at 351 nm and the maximum height of the signals obtained were determined using the MARQ 1.1 (for IICI) data analysis program.

7.4 Determination of Fluorescence Quantum Yields

Absorption spectra were collected on either a Milton-Roy Spectronic 3000 array spectrophotometer (accuracy <0.35 nm; precision ±0.0005 nm) or (in a few cases) a Hewlett-Packard HP8452A diode array spectrophotometer (accuracy 2.0 nm; precision 0.05 nm). Steady-state fluorescence excitation and emission spectra were measured on a SPEX Fluorolog-2. The excitation source was a 450-W xenon lamp (SPEX 1907-OFR),
passed through a single-grating monochromator (SPEX 1681B Minimate; 1200 groove/mm; 3.77 nm/mm). Fluorescence was detected in a T-box sampling module (SPEX 1692T) at 90° relative to the excitation through a double-grating monochromator (SPEX 168GB Spectramate; 1200 groove/mm; 1.70 nm/mm) with a SPEX 1911F detector. The slit widths were invariably 1.25 mm, so the excitation band-pass was 4.7 nm and the emission band-pass was 2.1 nm. Quantum yield calculations were performed by comparing the integrated emission intensities of diazirines (Scheme 5.2) to the intensity of a standard 9,10-diphenylanthracene solution in Freon-113 (Φ_{STD} = 1.00). The quantum yields were calculated using equation 5.3.

7.5 Time Correlated Single Photon Counting

All fluorescence lifetimes were determined using a time correlated single-photon counting (TCSPC) instrument (Figure 7.2). For experiments conducted at The Ohio State University, the pulse train of a synchronously-pumped cavity-dumped dye laser (Coherent 700 Series; Rhodamine 6-G or DCM) was directed to a beam splitter. A portion of the pulse train was routed to a fast photodiode that registered a "start" signal on a Time-to-Amplitude Converter (TAC; Tenaclex TC-864) after passing through a Constant Fraction Discriminator (CFD; Tennelec TCA55). This established the time position of each pulse with great precision. The "start" pulses initiated the charging of a capacitor in the TAC. The remainder of the pulse train was frequency doubled in an appropriate nonlinear crystal (Inrad, RDA) to generate UV excitation within the diazirine absorbance band.

Fluorescence was detected at 900 after having passed through a polarization analyzer (oriented at 54.7° relative to the polarization of the laser excitation), a depolarizer, and a subtractive double monochromator (American Holographic DB105). The detector was a Microchannel Plate Photomultiplier Tube (MCP-PMT: Hammamatsu R-2809U-07). The signals arising from single photons were amplified (Minicircuit ZHL-42) and passed
through a second CFD. The CFD output pulses then served as the "stop" signals for the capacitor in the TAC. The TAC capacitance was transferred to a Multichannel Analyzer (NICA: Tennelec PCA-II), where the data were binned and presented as a histogram. This histogram served as a representation of the fluorescence decay.

**Figure 7.2:** Instrument for TCSPC experiments at The Ohio State University.
7.6 Preparation of Diazirines and Oxadiazolines

7.6.1 Preparation of 3,3-Dimethyl-3H-diazirine

Ammonia was condensed in a solution of acetone (4.00 g, 0.07 mole) in methanol (20 mL) at -35°C. Hydroxylamine-O-sulfonic acid was added (slowly) over a period of 45 minutes and the reaction allowed to stir for 4 hours at -35°C. The temperature was slowly brought up to room temperature and the ammonia allowed to evaporate. The resulting solution was filtered and the undissolved ammonium salts washed with 2 x 50 mL of methanol. The methanol washes were collected and the solvent evaporated leaving a residue which was dissolved in chloroform (50 mL), filtered and dried over anhydrous sodium sulfate. Chloroform was evaporated yielding an oil which upon standing solidified (MP 38-40 °C). No further purification was attempted at this point.

Crude diaziridine (3.00 g, 0.04 mole) was dissolved in water (25 mL) in a modified 3-necked flask. A tube (~15 cm) containing KOH and Drierite is attached to the side port of the reaction flask and the other side connected to a trap pre-purged with argon containing trap solvent (Freon-113, α,α,α-trifluoromethylbenzene or perfluorohexane). Argon is circulated from the reaction flask exiting through the trap. The reaction flask is cooled to 0°C and a solution of potassium permanganate (6.48 g, 0.04 mole) in 75 mL 10% aqueous NaOH is added over a period of 30 minutes. The volatile diazirine is eluted with the carrier
gas into the trap cooled to -78°C and identified by its characteristic UV absorbance $\lambda_{\text{max}} =$ 350 nm, 364 nm in Freon-113; lit.$^{64} \lambda_{\text{max}} =$ 364 nm in pentane. $^1$H NMR (CDCl$_3$) $\delta$ ppm 0.99 (CH$_3$, s, 6H); lit$^50$ 0.99 (s, 6H).

7.6.2 Preparation of 3,3-bis-Trideuteriomethyl-3H-diazirine$^{64}$

A solution of acetone-$d_6$ (4.35 g, 0.068 mole, Cambridge Isotope Laboratories) and ammonia-$d_4$ (10 mL, 0.34 mole) was prepared at -35°C under an argon atmosphere in anhydrous methanol-$d$. To this solution was added tert-butylhypochlorite (14.80 g, 0.136 mole) over a period of 1.5 hours and stirred continuously for an additional 4 hours. The temperature was slowly brought up to room temperature and the ammonia allowed to evaporate. The resulting solution was filtered and the undissolved ammonium salts washed with 2 x 50 mL of methanol. The methanol washes were collected and the solvent evaporated leaving a residue which was dissolved in chloroform (50 mL), filtered and dried over anhydrous sodium sulfate. Chloroform was evaporated yielding an oil. No further purification was attempted at this point.

Crude diaziridine (1.50 g, 0.02 mole) was dissolved in D$_2$O (25 mL) in a modified 3-necked flask. A tube (~15 cm) containing KOH and Drierite is attached to the side port of the reaction flask and the other side connected to a trap pre-purged with argon containing trap solvent (Freon-113, $\alpha,\alpha,\alpha$-trifluoromethylbenzene or perfluorohexane). Argon is...
circulated from the reaction flask exiting through the trap. The reaction flask is cooled to 0°C and a solution of potassium permanganate (3.24 g, 0.02 mole) in 25 mL 10% aqueous NaOH is added over a period of 30 minutes. The volatile diazirine is eluted with the carrier gas into the trap cooled to -78°C and identified by its characteristic UV absorbance $\lambda_{max} = 350$ nm, 364 nm in Freon-113; lit.$^{64}$ $\lambda_{max} = 362$ in pentane. $^1H$ NMR (CDCl$_3$) $\delta$ ppm 1.033 (CD$_3$), with %D = 100.

![Diazirine Structure](image)

7.6.3 3H-Diazirine$^{46-48}$

Aqueous formaldehyde (37.47 mL, 0.50 mole) was added to tert-butylamine (52.54 mL, 0.50 mole) with stirring and the temperature was kept below reflux by external cooling. The mixture was stirred for one hour then solid KOH was added. The organic layer was separated from the aqueous and then dried with anhydrous sodium sulfate. This was then distilled at 760 torr with a pot temperature of 100°C and the fraction boiling at 65°C was collected yielding a clear oil.

A modified 3 necked round bottom flask equipped with 250 mL pressure equalizing addition funnel, magnetic stirrer and argon bubbler was connected as depicted in the figure. To the flask was added 75 mL of 4N ammonium chloride solution (0.300 mole) and 30 mL of dibutyl ether. The contents were cooled to 5°C with an ice-salt bath. tert-Butyl
azomethine (2.12 g, 0.025 mole) was added immediately followed by a 5.25% solution of commercial Clorox bleach (150 mL, 0.116 mole). The white gas formed was swept into the KOH/Drierite filter and into a trap held at -78°C. UV absorbance $\lambda_{max} = 310$ nm, 317 nm, 325 nm; lit. $\lambda_{max} = 308.5$ nm, 316 nm, 322 nm, 324.5 nm.

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

7.6.4 3,3-Dideuterio-3H-diazirine

Formaldehyde-$d_2$ (5.0 mL, 0.0312 mole) from Cambridge Isotope Laboratories was added to tert-butylamine (3.30 mL) and the solution stirred at room temperature for 3 hours under argon atmosphere. The aqueous phase was separated and the organic phase dried with anhydrous sodium sulfate. The organic residue was distilled on a short path apparatus under 20 mm of Hg yielding a clear liquid distillate.

A modified 3 necked 250 mL flask equipped with addition funnel, argon bubbler and stirrer was connected as depicted in Figure 7.3. To the flask was added 75 mL of a formate buffer solution (1N in formic acid and sodium formate) 75 mL of 4N ammonium chloride and the contents cooled to 0°C. tert-Butylazomethine was added to the reaction flask followed by 150 mL of sodium hypochlorite solution (5.25% Clorox Bleach) and the gaseous diazirine swept into a trap at -78°C. UV absorbance $\lambda_{max} = 308$ nm, 317 nm, 325 nm; lit. $\lambda_{max} = 322.4$ nm.
Figure 7.3: Apparatus for synthesis and trapping of gaseous diazirines.
A solution of cyclohexanone (36.75 g, 0.375 mole) in ammonium hydroxide (100 mL, 1.5 mole) was prepared and stirred at 0°C. Hydroxylamine-\( \text{-}\)sulfonic acid (31.0 g, 0.25 mole) was added in small portions keeping the temperature within 0-10°C. The resulting mixture was allowed to stir for another 5 minutes at 0°C and allowed to stand overnight in a -15°C refrigerator. The precipitated cake was filtered and washed with 15 mL portions of ether, toluene and finally ether. The product was boiled briefly in toluene (25 mL) and the solution decanted from the insoluble salts and cooled to 0°C for 2 hours to allow precipitation. The precipitate was filtered and washed with ice-cold petroleum ether. MP 98-100°C.

An aqueous solution of diaziridine (65 mmol in 15 mL) was added dropwise with stirring to a mixture of Ag\(_2\)O and ether (75 mL), over a period of 10 minutes at 0°C. Silver oxide was prepared from silver nitrate (197 mmol) and KOH (214 mmol) in water (75 mL). After one hour the mixture was filtered, and the ether separated, dried, and distilled off. The residual diazirine was then purified by eluting on a column of silica gel with pentane. Upon evaporation of the solvent, a colorless oil was obtained with a yield of 2.85 g (40%). The oil was immediately dissolved in Freon-113 and stored at 5°C in the dark. \(^1\)H NMR (CDCl\(_3\), \( \delta \) ppm): 1.10 (m, 4H), 1.60 (m, 6H); lit.\(^{132}\) 1.14 (4H), 1.63 (6H). UV absorbance \( \lambda_{\text{max}} = 349 \text{ nm}, 367 \text{ nm}; \) lit.\(^{133}\) \( \lambda_{\text{max}} = 338 \text{ nm}, 350 \text{ nm}, 363 \text{ nm} \) in gas phase.
7.6.6 1,2-Diaza-2,2,6,6-tetradecuterio-spiro[2.5]oct-1-ene

A solution of cyclohexanone-2,2,6,6-d$_4$ (2.55 g, 0.025 mole, Cambridge Isotope Laboratories) in ammonium hydroxide-d$_4$ (7 mL, 0.01 mole, Cambridge Isotope Laboratories) was prepared and stirred at 0°C. Hydroxylamine-O-sulfonic acid (2.10 g, 0.017 mole) was added in small portions maintaining the temperature between 0-10°C. The resulting mixture was allowed to stir for another 5 minutes at 0°C and allowed to stand for 1 hour in a -15°C refrigerator. The precipitated cake was filtered and washed with 2 x 5 mL portions of ice cold ether. No further purification of the diaziridine was performed.

A solution of diaziridine (1.14 g, 0.01 mole) in 5 mL D$_2$O was added dropwise with stirring to a mixture of Ag$_2$O and ether (10 mL), over a period of 10 minutes at 0°C. Silver oxide (Ag$_2$O) was prepared from silver nitrate (5.10 g, 0.03 mole) and KOH (2.17 g, 0.032 mole) in water (25 mL). After one hour the mixture was filtered and the ether separated. The aqueous solution was extracted with 2 x 15 mL of ether and all organic extracts were combined and dried with Na$_2$SO$_4$. Ether was evaporated in vacuo and the residual oil purified by eluting on a column of silica gel with pentane. Evaporation of pentane yielded 0.47 g (41%) of a colorless oil which was immediately dissolved in Freon-113. The diazirine was stored in solution at 5°C in the dark. $^1$HNMR (CDCl$_3$, $\delta$ ppm): 1.16 (s, 4H). UV absorbance $\lambda_{max}$ = 349 nm, 366 nm.
7.6.7 1-Adamantanecarboxaldehyde

Pyridinium chlorochromate (PCC) (3.234 g, 0.015 mole) was suspended in 25 mL of dichloromethane. Adamantane methanol (1.66 g, 0.010 mole, Aldrich) was dissolved in 25 mL of dichloromethane and added dropwise to the stirred PCC solution. The solution was stirred for 2 hours followed by addition of 200 mL of dry ether and the supernatant was decanted from the black gum. The insoluble residue was washed thoroughly with 3 x 50 mL of dry ether. The combined organic solution was passed through a pad of Florisil and the solvent removed by distillation. The residue was dissolved in methanol (5 mL) and the solution treated with a saturated solution of sodium bisulfite. The aldehyde was liberated by boiling in 20% sulfuric acid and extracting with 4 x 50 mL ether. The combined ether extracts were combined and dried with anhydrous sodium sulfate and the solvent evaporated. Purification by chromatography on silica gel with 10% ethyl acetate in hexanes as eluent yielded 1.15 g (70%) of a white solid MP 135-137°C; lit. 131-134°C. $^1$HNMR (CDCl$_3$, δ ppm): 1.65 (m, 12H), 2.15 (m, 3H), 11.45 (s, 1H); lit. 136 9.28 (s, 1H). MS m/e (rel intensity) M$^+$ 164 (3), 151 (5), 135 (100), 107 (15), 93 (20), 79 (30).
7.6.8 1-Adamantanecarboxaldehyde-α-d_1[^135]

1-Adamantanecarboxylic acid (3.32 g, 0.0184 mole) was reduced with LiAlD_4 (98%-d, Cambridge Isotope Laboratories) (0.772 g, 0.0184 mole) in boiling dry THF (51 mL) to give essentially pure (1-adamantyl)methanol-α,α-d_2 (AdCD_2OH) which was recrystallized from ligroin. Yield was 91%; MP. 116-117°C. ^1H NMR (CDCl_3, δ ppm): 3.15 (-CD_2-). MS m/e (rel intensity) M+ 168 (5), 135 (100), 107 (10), 93 (20), 79 (25).

The alcohol (2.77g, 0.0165 mole) was oxidized with pyridinium chlorochromate (5.43 g, 0.0252 mole) in dichloromethane (60 mL). The solution was stirred for 2 hours followed by addition of 100 mL of dry ether and the supernatant was decanted from the black gum. The insoluble residue was washed thoroughly with 3 x 50 mL of dry ether. The combined organic solution was passed through a pad of Florisil and the solvent removed by distillation. This yielded a yellow solid which was purified by chromatography on silica gel with 10% ethyl acetate in hexanes as eluent. A white solid was obtained upon evaporation of the eluent yielding 1.51 g (55%) MP 135-145°C.

^1H NMR (CDCl_3, δ ppm): 9.70 (s, 1H). MS m/e (rel intensity) M+ 165 (2), 151 (4), 135 (100), 107 (15), 93 (25), 79 (30).
7.6.9 3-Adamantan-1-yl-3\textit{H}-diazirine

1-Adamantane carboxaldehyde (0.931 g, 0.005 mole) was dissolved in benzene (20 mL) and \textit{tert}-butylamine (20 mL). The mixture was refluxed overnight with a Dean-Stark trap. Benzene and excess \textit{tert}-butylamine were removed by evaporation and the residual solid was dissolved in methanol (10 mL) containing triethylamine (5 mL). The solution was cooled to 0°C and hydroxylamine-O-sulfonic acid (2.00 g) was added in small portions with stirring. The reaction was maintained at 0°C for 3 hours. \textit{tert}-Butyl hypochlorite was added slowly over a period of 30 minutes while keeping the temperature within a 0-5°C range. After stirring for 30 minutes at 0°C, the mixture was poured into water (150 mL) and 15 g of sodium metabisulphite was added. The aqueous solution was extracted with methylene chloride (2 x 50 mL) and the extracts combined and dried with anhydrous sodium sulfate. The solvent was evaporated \textit{in vacuo} and the yellow oil obtained was purified on an alumina column with pentane as eluent. Evaporation of pentane yielded a colorless oil 89 mg (10%) which was immediately dissolved in Freon-113 and stored in the dark at 5°C. UV absorbance $\lambda_{\text{max}}$ = 325 nm, 335 nm, 350 nm.

$^1$HNMR (CDCl$_3$, $\delta$ ppm): 0.5 (s, 1H), 1.35 (d, 6H), 1.70 (m, 6H), 1.95 (s, 3H).
7.6.10 3-Adamantan-1-yl -3-deuterio-3H-diazirine

1-Adamantanecarbaldehyde-α-d_4 (1.00 g, 0.006 mole) was added to tert-butylamine (20 mL) and the solution stirred at room temperature for 3 hours under an argon atmosphere. Unreacted tert-butylamine was removed by evaporation leaving crude imine.

The tert-butylimine was dissolved in methanol-d (10 mL) and triethylamine (5 mL) with argon bubbled into the reaction mixture kept at 0°C. Hydroxylamine-O-sulfonic acid (2.00 g) was added in small portions with stirring and reaction was maintained at 0°C for 3 hours. tert-Butyl hypochlorite was added slowly via syringe over a period of 1 hour while maintaining the temperature at 0°C. The solution was stirred for an additional hour after addition and then poured into water (150 mL) with 15 g of sodium metabisulphite. The aqueous solution was extracted with methylene chloride (2 x 50 mL) and the extracts combined and dried with anhydrous sodium sulfate. The solvent was evaporated in vacuo and the yellow oil obtained was purified on an alumina column with pentane as eluent. Evaporation of pentane yielded a colorless oil 74 mg (7%) which was immediately dissolved in Freon-113 and stored in the dark at 5°C. UV absorbance λ_max = 325 nm, 340 nm, 350 nm. HNMR (CDCl_3, δ ppm): 0.55 (1D).
7.6.11 2-Methoxy-2,5,5-trimethyl-\(\Delta^1\)-1,3,4-oxadiazoline

Acetone (2.32 g, 0.04 mole) and acetic hydrazide (0.04 mole) were mixed in benzene (80 mL). The solution was refluxed overnight with a Dean-Stark trap for azeotropic removal of water. Benzene was removed by evaporation yielding a white solid which was recrystallized from ethyl acetate. Yield 80%. MP 138-140 °C; lit. 139-141 °C. \(^1\)HNMR (CDCl\(_3\), \(\delta\) ppm): 1.85 (s, 3H), 1.95 (s, 3H), 2.1 (s, 1H); lit. 1.87 (s, 3H), 1.97 (s, 3H), 2.20 (s, 3H). MS m/e (rel intensity) \(M^+\) 114 (30), 99 (60), 72 (65), 57 (80), 43 (100), 39 (35).

A solution of 1-acetyl-2-(2-propylidene)hydrazine (1.14 g, 0.010 mole) was prepared in dry methanol (70 mL) and cooled to 0°C. Lead tetraacetate (4.80 g, 0.010 mole) was added in small portions to the stirred solution and after complete addition was stirred under an argon atmosphere. When the brown color of the solution was discharged, a methanolic KOH (10 mmol) solution was added dropwise to the cooled reaction. The reaction was stirred at 0°C for two more hours and warmed to room temperature and stirred for an additional 24 hours. Methanol was then removed in vacuo and water (70 mL) was introduced to the residue. The mixture was extracted with dichloromethane (3 x 50 mL). All organic extracts were combined and dried over anhydrous sodium sulfate, evaporation of dichloromethane yielded the crude oxadiazoline which was purified by column chromatography on silica gel (petroleum ether: ethyl acetate 20:1) as eluent. The elution of the oxadiazoline was monitored by UV spectrometry. Fractions with absorption peaks...
within the 300-330 nm range were pooled and the solvent evaporated. This yielded 0.4355 g (30%) of a colorless liquid. \(^1\)HNMR (CDCl\(_3\), ppm): 1.45 (s, 3H), 1.57 (s, 3H), 2.95 (s, 3H); lit. \(^1\)HNMR (CDCl\(_3\), ppm): 1.43 (s, 3H), 1.55 (m, 6H), 3.06 (s, 3H).

\[
\begin{align*}
\text{CD}_3 & \quad \text{N} = \text{N} \\
\text{OCH}_3 & \quad \text{CD}_3
\end{align*}
\]

7.6.12 2-Methoxy-2-methyl-5,5-trideuteromethyl-\(\Delta^1\)-1,3,4-oxadiazoline

Acetone-\(d_6\) (3.44 g, 40.0 mmol) and acetylhydrazine (2.96 g, 40.0 mmol) were mixed in about 80 mL of benzene. The mixture was refluxed overnight using a Dean-Stark trap to separate the water formed during the process. After evaporation of the solvent the residue was recrystallized from ethyl acetate yielding white crystalline needles (73%) MP 139-140. \(^2\)HNMR (CDCl\(_3\), \(\delta\) ppm): 2.10 (s, 6H). MS \(m/e\) (rel. intensity) M\(^+\) 120 (20), 102 (50), 78 (50), 60 (100), 43 (70).

1-Acetyl-2-(2-propylidene)hydrazine-\(d_6\) (10.0 mmol) was dissolved in about 70 mL of anhydrous methanol-\(d_4\). Under an atmosphere of argon, equal molar amounts of lead tetraacetate (4.80 g, 10.0 mmol) was added at once, with stirring, to the above solution, which was pre-cooled with an ice-water bath. The brown reaction mixture was stirred in the ice-water bath until it turned pale yellow. About 10 mmol of methanolic potassium hydroxide-\(d_4\) solution was then added dropwise to the stirred, cooled reaction mixture, which was allowed to slowly warm up to room temperature and kept stirring under argon.
overnight. The methanol was then removed in vacuo and about 70 mL of water was
introduced to the residue. The resulting mixture was extracted with dichloromethane (3 × 50 mL). After the organic extract was dried over anhydrous Na₂SO₄, evaporation of
dichloromethane yielded the crude oxadiazoline which was purified by column
crromatography on silica gel (petroleum ether: ethyl acetate 20:1) as eluent. The elution of
the oxadiazoline was monitored by UV spectrometry. Fractions with absorption peaks
within the 300-330 nm range were pooled and the solvent evaporated. This yielded 0.3902
g (26%) of a colorless liquid. ¹HNMR (CDCl₃, δ ppm): 1.60 (s, 6H).
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APPENDIX A

GC/MS ANALYSIS OF THE PHOTOPRODUCTS FROM THE
PHOTOLYSIS OF 3,3-DIMETHYLDIAZIRINE IN VARIOUS SOLVENTS

The GC/MS analysis of the reaction mixtures obtained from the photolysis of 3,3-
dimethyldiazirine (18a) under the conditions specified in Chapter 2 are included in this
section. For brevity, only the products of mechanistic relevance are shown and the GC
chromatograms are provided if available. The structures are based solely on analysis of the
fragmentation patterns except in (4), (6) and (7) which are based on comparison with
authentic samples. The GC-MS analyses of the following reactions are presented:

(1) Photolysis of 18a in neat cyclopentene
(2) Photolysis of 18a in neat norbornene
(3) Photolysis of 18a in tetrahydrofuran
(4) Photolysis of 18a in isopropylamine
(5) Photolysis of 18a in triethylsilane
(6) Photolysis of 18a in cyclohexane
(7) Photolysis of 18a in benzene
(8) Photolysis of 18a in N,N-dimethylaniline
(9) Photolysis of 18a in α,α,α-trifluoromethylbenzene
(10) Photolysis of 18a in CCl₄

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(11) Photolysis of $18\text{a}$ in Freon-113

(12) Photolysis of $18\text{a}$ in perfluorohexane

(1) Photolysis of $18\text{a}$ in neat cyclopentene

(a) Total Ion Chromatogram

a - cyclopropane adduct 25 (r.t. = 4.21 min.); b - acetone azine (r.t. = 5.03 min.)
(b) Mass spectrum of the cyclopropane adduct 25

![Mass spectrum](image)

(c) Fragmentation pattern from the mass spectrum

![Fragmentation pattern](image)

25

\[ m/e = 110.20 \]

\[ m/e = 95.16 \]

\[ m/e = 67.11 \]
(2) Photolysis of 18a in neat norbornene

(a) Total Ion Chromatogram

a - cyclopropane adduct 26 (r.t. = 4.45 min.)

(b) Mass spectrum of the cyclopropane adduct 26
(c) Fragmentation pattern from the mass spectrum
(3) Photolysis of 18a in neat tetrahydrofuran

(a) Total Ion Chromatogram

a - acetone azine (r.t. = 4.60 min.); b - insertion product 36 (r.t. = 5.60 min.)

(b) Mass spectrum of the insertion product 36
(c) Fragmentation pattern from the mass spectrum

\[ \text{\textit{36}} \]

\[ m/e = 114.19 \]

\[ \text{\textit{36}} \]\n
\[ m/e = 71.10 \]

(4) Photolysis of 18a in neat isopropylamine

(a) Total Ion Chromatogram

a - C\textsubscript{4}H\textsubscript{11}N (r.t. = 3.56 min.); b - insertion product 34 (r.t. = 5.01 min.)
(b) Mass spectrum of the insertion product 34

(c) Fragmentation pattern from the mass spectrum

\[ \text{mass spectrum} \]

\[ \text{fragmentation pattern} \]

\[ m/e = 101.19 \]

\[ m/e = 99.18 \]

\[ m/e = 84.14 \]
(5) Photolysis of 18a in neat triethylsilane

(a) Total Ion Chromatogram

a - Et₃SiH (r.t. = 2.0 min.); b - acetone azine (r.t. = 2.80 min.); c - insertion adduct 33 (r.t. = 3.34 min.); d - CₓHᵧSiO (r.t. = 6.90 min.)
(b) Mass spectrum of the insertion adduct 33

(c) Fragmentation pattern from the mass spectrum
(6) Photolysis of 18a in neat cyclohexane

(a) Total Ion Chromatogram

a - insertion product 32 (r.t. = 3.49 min.); b - acetone azine (r.t. = 3.65 min.)

(b) Mass spectrum of the adduct 32
(c) Fragmentation pattern from the mass spectrum

\[ \text{ Fragmentation pattern from the mass spectrum } \]

\[ \begin{array}{c}
\text{[}\text{H}_8\text{C}_9\text{]}^+ \to \text{[}\text{H}_8\text{C}_9\text{]}^+ - \text{C}_3\text{H}_7^+ \to \text{[}\text{H}_8\text{C}_9\text{]}^+ - \text{H}^+ \to \text{[}\text{H}_8\text{C}_9\text{]}^+
\end{array} \]

\[ m/e = 83.15 \quad m/e = 82.14 \]

32

\[ m/e = 126.24 \]

(7) Photolysis of 18a in neat benzene

(a) Total Ion Chromatogram

a - adduct 27 (r.t. = 3.40 min.); b - acetone azine (r.t. = 3.90 min.); c - C_{12}H_{10} (r.t. = 8.40 min.); d - C_{14}H_{14} (r.t. = 9.4 min.)
(b) Mass spectrum of the product from electrophillic attack 27

(c) Fragmentation pattern from the mass spectrum

\[
\left[ \begin{array}{c}
\text{27}
\end{array} \right]^{+}
\rightarrow
\begin{array}{c}
\text{m/e} = 120.19
\end{array}
\rightarrow
\begin{array}{c}
\text{m/e} = 105.16
\end{array}
\]
(8) Photolysis of 18a in neat N,N-dimethylaniline

(a) Total Ion Chromatogram

a - electrophilic adduct 30 (r.t. = 5.91 min.); b - ylide product 28 (r.t. = 5.60 min.)

(b) Mass spectrum of the product from electrophilic attack 30
(c) Fragmentation pattern from the mass spectrum

\[
\text{Fragmentation pattern from the mass spectrum}
\]

\[
\begin{align*}
\text{Mass spectrum of the ylide product 28}
\end{align*}
\]
(e) Fragmentation pattern from the mass spectrum

\[
\begin{align*}
\text{m/e} &= 163.26 \\
\text{m/e} &= 161.25
\end{align*}
\]

(9) Photolysis of 18a in neat \(\alpha,\alpha,\alpha\)-trifluoromethylbenzene

(a) Total Ion Chromatogram

a - \(\text{C}_6\text{H}_5\) (r.t. = 4.90 min.); b - \(\text{C}_7\text{H}_7\) (r.t. = 7.60 min.); c - \(\text{C}_8\text{H}_8\) (r.t. = 9.60 min.); d - \(\text{C}_9\text{H}_{13}\) (r.t. = 14.7 min.); e - cycloadduct adduct 31 (r.t. = 15.1 min.)
(b) Mass spectrum of the cycloadduct adduct 31

(c) Fragmentation pattern from the mass spectrum

\[
\begin{align*}
\text{31} & \quad m/e = 188.19 \\
\text{m/e = 156.17}
\end{align*}
\]
(10) Photolysis of 18a in neat CCl₄

(a) Total Ion Chromatogram

a - acetone azine (r.t. = 7.90 min.); b - C₃H₅ClO (r.t. = 11.8 min.); c - C₄H₆Cl₁ (r.t. = 12.3 min.); insertion adduct 37 (r.t. = 13.5 min.); C₅H₇Cl₁ (r.t. = 14.0 min.); e - C₆H₈Cl₂O (r.t. = 18.0 min.)
(b) Mass spectrum of the insertion adduct 37

(c) Fragmentation pattern from the mass spectrum

\[
\begin{align*}
\text{37} & \quad \text{m/e} = 195.90 \\
\text{m/e} & \quad = 143.7
\end{align*}
\]
(11) Photolysis of 18a in neat Freon-113

(a) Total Ion Chromatogram

a - insertion adduct 38 (r.t. = 4.90 min.); b - acetone azine (r.t. = 10.0 min.).
(b) Mass spectrum of the insertion adduct 38

(c) Fragmentation pattern from the mass spectrum

\[ \text{m/e} = 107.5 \]

\[ \text{m/e} = 194.00 \]

\[ \text{m/e} = 157.6 \]

\[ \text{m/e} = 137.0 \]
(12) Photolysis of 18a in neat perfluorohexane
APPENDIX B

GC/MS ANALYSIS OF THE PHOTOPRODUCTS FROM THE
PHOTOLYSIS OF 2-METHOXY-2,5,5-TRIMETHYL-Δ1'-1,3,4-
OXADIAZOLINE IN VARIOUS SOLVENTS

The GC/MS analysis of the reaction mixtures obtained from the photolysis of 2-
methoxy-2,5,5-trimethyl-Δ1'-1,3,4-oxadiazoline (24a) under the conditions specified in
Chapter 2 are included in this section. For brevity, only the products of mechanistic
relevance are shown and the GC chromatograms are provided if available. The structures
are based solely on analysis of the fragmentation patterns except in (4), (6) and (7) which
are based on comparison with authentic samples. The GC-MS analyses of the following
reactions are presented:

(1) Photolysis of 24a in neat cyclopentene
(2) Photolysis of 24a in neat norbornene
(3) Photolysis of 24a in tetrahydrofuran
(4) Photolysis of 24a in isopropylamine
(5) Photolysis of 24a in triethylsilane
(6) Photolysis of 24a in cyclohexane

(7) Photolysis of 24a in neat N,N-dimethylamine

(1) Photolysis of 24a in neat cyclopentene

(a) Total Ion Chromatogram

a - acetone (r.t. = 3.70 min.); b - cyclopropane adduct 25 (r.t. = 4.52 min.)
(b) Mass spectrum of the cyclopropane adduct 25

(c) Fragmentation pattern from the mass spectrum

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{H}_3\text{C} \\
\text{H}_3\text{C} & \longrightarrow \quad \text{H}_3\text{C} \\
\text{H}_3\text{C} & \longrightarrow \quad \text{H}_3\text{C}
\end{align*}
\]

\[m/e = 110.20\]

\[m/e = 95.16\]

\[m/e = 67.11\]
(2) Photolysis of 24a in neat norbornene

(a) Total Ion Chromatogram

- cyclopropane adduct 26 (r.t. = 4.57 min.)

(b) Mass spectrum of the cyclopropane adduct 26
(c) Fragmentation pattern from the mass spectrum

\[
\text{m/e} = 136.24
\]
(3) **Photolysis of 24a in neat tetrahydrofuran**

(a) **Total Ion Chromatogram**

a - acetone azine (r.t. = 4.20 min.); b - insertion adduct 36 (r.t. = 4.62 min.)

![TIC of DATA: FCCF1.0](image-url)
(b) Mass spectrum of the insertion adduct 36

(c) Fragmentation pattern from the mass spectrum

\[
\begin{align*}
\text{Fragmentation:} & \\
\begin{array}{ccc}
\text{36} & \xrightarrow{\text{-H} \cdot} & \begin{array}{c}
\text{5/6} \\
\text{5/5} \\
\text{1/0} \\
\text{0/0}
\end{array} \\
\text{m/e} = 114.19 & & \text{m/e} = 71.10
\end{array}
\end{align*}
\]
(4) Photolysis of 24a in neat isopropylamine

(a) Total Ion Chromatogram

a - C₇H₁₁N (r.t. = 3.56 min.); b - insertion product 34 (r.t. = 4.93 min.)

(b) Mass spectrum of the insertion adduct 34
(c) Fragmentation pattern from the mass spectrum

\[
\begin{align*}
\ce{\text{H_3C-CH(NH_2)-CH_3}} & \quad m/e = 99.18 \\
\ce{\text{H_3C-CH(NH_2)-CH_3}} & \quad m/e = 84.14
\end{align*}
\]

(5) Photolysis of 24a in neat triethylsilane

(a) Total Ion Chromatogram

- acetone azine (r.t. = 2.85 min.);
- \( \text{C}_2\text{H}_5\text{Si} \) (r.t. = 2.95 min.);
- insertion adduct 33 (r.t. = 3.42 min.)

- TIC of DATA:FCGF.D
(b) Mass spectrum of the insertion adduct 33

(c) Fragmentation pattern from the mass spectrum

33

\[
m/e = 158.36
\]
(6) Photolysis of 24a in neat cyclohexane

(a) Total Ion Chromatogram
a - insertion product 32 (r.t. = 3.48 min.); b - acetone azine (r.t. = 3.58 min.)

(b) Mass spectrum of the insertion adduct 32
(c) Fragmentation pattern from the mass spectrum

\[
\begin{align*}
\text{m/e } &= 126.24 \\
\text{m/e } &= 83.15 \\
\text{m/e } &= 82.14
\end{align*}
\]

(7) Photolysis of 24a in neat N,N-dimethylaniline

(a) Total Ion Chromatogram

\text{a - electrophilic adduct 30 (r.t. } = 5.02 \text{ min.)}
(b) Mass spectrum of the electrophilic attack on ring 30

(c) Fragmentation pattern from the mass spectrum

\[ m/e = 163.26 \]