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The spectroscopy and mechanism of formation of \textit{m}-xylylene and related biradicals

Haider, Karl William, Ph.D.
The Ohio State University, 1989
THE SPECTROSCOPY AND MECHANISM OF FORMATION OF M-XYLYLENE AND RELATED BIRADICALS

DISSERTATION

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

By

Karl William Haider

The Ohio State University
1989

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Adviser
Department of Chemistry
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Karl William Haider
1989
To Mom, Dad, and Lainey
ACKNOWLEDGMENTS

First and foremost, I would like to thank my adviser Dr. Matthew Platz for his guidance, encouragement and friendship throughout my stay here. He has been an excellent and willing teacher (not only of chemistry), and for this I will always be grateful. I would also like to acknowledge the Platz group members, both past and present, for providing an enjoyable and fun atmosphere in which to work. Special mention is due to a friend and co-worker, Dr. N. Soundararajan, who prepared two precursors which played a key role in the completion of this thesis. It was a pleasure to collaborate with Dr. Eva Migirdicyan, both on the m-xylylene project as well as the fluorescence spectroscopy of diphenylcarbene. Her insight, persistence in lab (read Courage) and friendship are greatly appreciated. On a more personal note thanks to Joan Platz who offered not only her friendship but also many home cooked meals. Also, thanks are due to the entire Richey family who have "adopted" me and provided a much appreciated "home away from home". Thanks to Dr. Viresh Rawal, not only for many hours of good times over "lefty cuisine", but also for the assistance with the finer points of MacWrite and the emergency loan of his computer. The gang at Larry's has provided many hours of much needed recreation, and they will be remembered fondly. Finally, my parents and my sister Elaine have always had an unshakable faith in me, and it is to them that I dedicate this thesis.
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FIELD OF STUDY

Major Field : Organic Chemistry
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INTRODUCTION

Many of the efforts of chemists are aimed at gaining an understanding of the fundamental processes which occur during a chemical reaction. Based on product studies and trapping experiments, legions of chemists before us have postulated various unstable reactive intermediates. These molecules are believed to exist transiently during a variety of photochemically or thermally initiated reactions. They are familiar to us as the carbanions, carbocations, radicals, nitrenes, biradicals and carbenes which have been postulated as intermediates in innumerable reactions observed in the laboratory. It is currently a goal of experimentalists in our field to prepare these reactive molecules under conditions where they can be studied using the tools of spectroscopy. To date, two general techniques have been applied to this problem. In the first (flash photolysis), highly reactive species are observed by decreasing the requisite time for the spectroscopic observation. Using current technology, picosecond time resolution is readily achieved with UV-visible spectroscopic detection. Thus one can obtain absorption spectra of transient species, as well as monitor dynamic processes in solution by observing temporally resolved changes in the optical density of the bulk sample. In the second method, termed Matrix Isolation Spectroscopy (MIS), the desired "reactive intermediate" is generated in a rigid cryogenic environment (typically 4-77 K). The rigidity of the environment slows diffusion, thus bimolecular reactions are impeded.
while the low temperature prevents thermally activated decomposition pathways having an activation energy of ~5 kcal/mole or greater (assuming classical behavior with an Arrhenius A factor of $10^{12}$s$^{-1}$). Under these conditions, molecules which have lifetimes on the order of microseconds or less at ambient temperature in fluid solution, may be rendered stable for hours in the matrix. In this manner, ordinarily reactive molecules are characterized using standard spectroscopic tools, (primarily IR, UV-Vis, Fluorescence, EPR and NMR spectroscopy). Ideally, by employing a combination of these techniques, one would gain an understanding of the structure of highly reactive molecules to the same extent which is now enjoyed for shelf-stable organic compounds.

Specifically, in this work both of the aforementioned techniques were employed in order to prepare and investigate several biradicals of interest in organic chemistry. First, the photochemical reaction which led to the initial spectroscopic detection\(^3\) of the matrix isolated non-Kekule biradical \(m\)-xylylene is investigated. The biradical, produced from 77 K photolysis of matrices containing \(m\)-xylene, is shown to be formed from a thermal reaction of a photochemically generated \(m\)-methylbenzyl radical with a hydrogen atom, which was produced by initial bond scission of a benzylic C-H bond. A novel photochemical route, based on the photolysis of \(\alpha,\alpha'\)-(dichloro)-\(m\)-xylene which led to the formation of \(m\)-xylylene\(^4\) was developed and its mechanism investigated as well. This precursor was suitable not only for MIS, but also allowed the preparation and fluorescence detection of \(m\)-xylylene in fluid solution at ambient temperatures. An investigation of the mechanism of this photochemical reaction was
undertaken as well. Also, an interesting heteroatom analogue of the
m-xylylene biradical was prepared under matrix isolation conditions and
characterized by electron paramagnetic resonance spectroscopy. The zero
field splitting parameter $|D|/h\gamma = 0.019 \text{ cm}^{-1}$ was compared with that of a
calculation performed by Lahti.$^5$

As an extension of our work on the xylylene system, methodology for the
preparation of matrix isolated biradicals, based on electron transfer, was
developed. This procedure has proven to be applicable to the generation of
several matrix isolated biradicals including trimethylenemethane,
1,8-naphthaquinodimethane, m-xylylene, diphenylcarbene and
3,4-dimethylenethiophene.$^6$ In the course of these studies, it was observed
that the direct photolysis of cryogenic matrices containing the geminal
dihalide dichlordiphenylmethane led to the formation of matrix isolated
diphenylcarbene. This reaction was probed further and shown explicitly to
proceed via the intervention of a diphenylchloromethyl radical, which itself
photodissociates upon UV excitation, expelling a chlorine atom to form the
diarylcarbene.

Finally, the Laser Induced Fluorescence (LIF) spectra of several aryl and
diarylcarnes were examined. In particular, the effects of phase and
temperature on the LIF spectra of diphenylcarbene and its derivatives were
noted. During this investigation, it was observed that the combination of
Laser Induced Fluorescence spectroscopy, in concert with the matrix
isolation technique, was a powerful tool in collecting the fluorescence
emission spectra of highly reactive arylcarnes such as the parent
phenylmethylene and 2-naphthylmethylene.
Chapter I. The Mechanism of Formation of M-Xylylene and Its Derivatives From the Photolysis of Polymethyl Benzenes and Dihalides
HISTORICAL

Our efforts in the area of non-Kekule molecules have been focused on understanding the photochemical reactions which first led to the preparation and spectroscopic detection\(^3\) of the \(m\)-xyylene biradical (1). Many reactive molecules can be described as being atom deficient, i.e. they lack the sufficient number of atoms to satisfy the standard rules of valency (e.g. tetravalent carbon). Carbocations and radicals are ubiquitous examples of this type in organic chemistry. \(M\)-xyylene (1) on the other hand, is a highly reactive member of a class of molecules termed non-Kekule,\(^7\) which are distinguished by the fact that they are not atom deficient, but rather only bond deficient. Perhaps most simply stated, non-Kekule molecules are species in which all of the canonical resonance forms contain a minimum of two unpaired electrons. This concept is readily illustrated by example. \(M\)-xyylene (1) trimethylenemethane (2), and Schlenk's hydrocarbon (3) (Figure 1) are all non-Kekule molecules which have been investigated both by experimentalists\(^8\) and theoreticians\(^9\) alike.

![Figure 1. Illustration of non-Kekule molecules](image)
Although the first synthesis of a 3 was achieved 75 years ago,\textsuperscript{10} it is only within the last twenty years that a variety of non-Kekule species have been prepared and spectroscopically characterized.\textsuperscript{11}

Huckel $\pi$-electron theory,\textsuperscript{12} as well as perturbational molecular orbital theory\textsuperscript{13} predict that $m$-xylene contains a pair of degenerate singly occupied non-bonding molecular orbitals (NBMO's). Experimentally, ground state triplet multiplicity has been affirmed for a variety of non-Kekule molecules including those illustrated above.\textsuperscript{8} Theory and experiment are however, certainly not in universal agreement regarding predictions of electronic structure for all of the non-Kekule molecules which have been considered. In some cases, most notably tetramethylenethane, discrepancies between theory\textsuperscript{14} and experiment\textsuperscript{15} have led to vehement controversy which still awaits resolution. Hence, the study of non-Kekule molecules, both by theoreticians and experimentalists alike, actively continues.

The first spectroscopic detection of $m$-xylene (1) was accomplished in the mid 1970's by Migirdicyan and Baudet.\textsuperscript{3} These workers reported that photolysis of polycrystalline alkane solutions (77K) containing isomers of polymethylated benzene derivatives gave rise to two new fluorescence emission spectra, in addition to the previously reported fluorescence spectra of the substituted benzyl radicals. Photolysis of $o$-xylene (4) or 1,2,3-trimethylbenzene (5) led to a species exhibiting a broad, poorly resolved emission ($\lambda_{\text{emission}}$ 410-480 nm; Figure 2a). This species was assigned as being due to the $o$-xylylene derivatives (6) and (7) (Scheme 1). This assignment was supported by the work of Flynn and Michl,\textsuperscript{16} who
reported the generation and spectroscopic detection of the same spectrum from six independent precursors. The second emission spectrum (Figure 2b) observed by Migirdicyan, a well resolved band at 440-480 nm, was obtained upon photolysis of methylated benzene derivatives having two methyl groups in the \textit{meta} orientation, such as mesitylene (8) or \textit{m}-xylene (9). On the basis of this fact, along with analogy to the now secure assignment of the \textit{o}-xylylene structure, this second emission was attributed to the \textit{m}-xylylene biradicals (1) and (10).

\begin{center}
\begin{tikzpicture}
\node at (-2,0) {
\begin{tikzpicture}
\node at (0,0) (a) {
\begin{tikzpicture}
\node at (0,0) (b) {\includegraphics[width=0.8cm]{methylbenzene.png}};
\end{tikzpicture}
};
\node at (2,0) (c) {
\begin{tikzpicture}
\node at (0,0) (d) {\includegraphics[width=0.8cm]{phenyl.png}};
\end{tikzpicture}
};
\node at (0,-1) (e) {\textcolor{red}{\text{hv, 254 nm}}};
\node at (0,-2) (f) {\textcolor{blue}{\text{n-pentane, 77K}}};
\node at (0,-3) {4; \textcolor{red}{R = H} \textcolor{blue}{5; \textcolor{red}{R = CH}_3}};
\end{tikzpicture}
};
\node at (2,0) {
\begin{tikzpicture}
\node at (0,0) (g) {\includegraphics[width=0.8cm]{phenyl.png}};
\end{tikzpicture}
};
\node at (2,-1) (h) {\textcolor{red}{\text{hv, 254 nm}}};
\node at (2,-2) (i) {\textcolor{blue}{\text{n-pentane, 77K}}};
\node at (2,-3) {9; \textcolor{red}{R = H} \textcolor{blue}{8; \textcolor{red}{R = CH}_3}};
\end{tikzpicture}
\end{center}

\begin{center}
\textbf{Scheme 1}
\end{center}
Figure 2: a. Fluorescence Spectra of o-xyylene biradicals 6 and 7. b. Fluorescence Spectra of m-xyylene biradicals 1 and 10. Spectra were produced by photolysis (254 nm, 77K) of polycrystalline alkane matrices containing the corresponding methylated benzenes. (Reprinted from J. Am. Chem. Soc., 97, 7400, 1975.)
The vibronic analysis of the o-xylylenes (6) and (7) indicated that significant geometry changes had occurred upon relaxation from the photochemically excited state to the electronic ground state. The authors noted that this observation is most consistent with a polyene structure for the ortho-xylylenes, in which the aromatic character of the benzene ring has been disrupted. In contrast to the results obtained with the ortho isomers, m-xylylene biradicals 1 and 10 had vibronic structure very similar to that of the parent hydrocarbons m-xylene and mesitylene respectively, as well as with the corresponding monoradicals. These spectra were indicative of the fact that the aromatic character had remained intact in these diradicals.

Although we perceive the photochemical reaction which produced the matrix isolated xylylenes to be an interesting one, no mechanistic details regarding this photoreaction were reported by Migirdicyan at that time.

Platz and Wright17 subsequently succeeded in generating matrix isolated m-xylylene using an alternative approach. They were able to prepare the m-xylylene biradical by photolysis of cryogenic matrices containing the bis-diazo compound (11) (Scheme 2). It was demonstrated that photolysis of 11 resulted initially in the formation of the bis-carbene (12) which underwent a thermal reaction with the matrix, via double hydrogen atom abstraction, to form the m-xylylene biradical. The biradical was indefinitely stable (no observable decay over 5 days) at these temperatures (77K) in the absence of further photolysis.

In this manner, Platz was able to generate matrices which contained a sufficient concentration of the m-xylylene biradical to allow EPR detection of this paramagnetic species (|D/hc| = 0.011 cm⁻¹ ; |E/hc| ≤ 0.001 cm⁻¹). The
authors noted that the spectrum obeyed the simple form of the Curie law \((I-T=C)\) over the temperature regime of 30-77K, thus confirming that the triplet is either the ground electronic state, or within a few calories/mole of the ground state, congruent with theoretical predictions.\(^{12,13}\)

\[
\text{Scheme 2}
\]

Berson and Goodman\(^{18}\) subsequently reported that photolysis of 4-(benzoyloxy)-2,6-dimethylenebicyclo[3.1.0]hexane (13) in ethanolic matrices at 77K gave rise to the same six line EPR spectrum observed by Platz. They assigned the carrier of the spectrum to the triplet state of \(m\)-xylylene 1, which had been formed as a result of the Norrish type II fragmentation of benzoate 13, followed by ring opening to the
m-quinodimethane biradical 1 (Scheme 3). The reader should note, this sequence represents an independent synthesis of 1, confirming Platz and Wright's original EPR assignment.

The spectroscopic identification of m-xylylene as a reactive intermediate in solution, lags considerably behind the matrix isolation studies. Although well characterized by EPR and optical spectroscopy under matrix isolation conditions, m-xylylene has thus far eluded spectroscopic detection in solution. The strongest evidence supporting the existence of 1 or any of its derivatives, as a reaction intermediate in solution, comes from a number of ingenious chemical trapping experiments.
The first cyclophane synthesis was accomplished by allowing metallic sodium to react with \( \alpha,\alpha^\prime \)-dibromo-\( m \)-xylene (14).\(^{19} \) It is conceivable that the [2.2] metacyclopane (15) resulted from the dimerization of 1, which was produced from the action of sodium on the dibromide.

This work was later verified in the 1950's by Baker\(^ {20} \) who isolated the \( m \)-cyclophane (15) from a refluxing dioxane solution of dibromide 14 and metallic sodium.

\[
\begin{align*}
\text{CH}_2\text{Br} & \quad \text{Na, dioxane} \\
\text{CH}_2\text{Br} & \quad \Delta \\
14 & \quad \rightarrow \\
\text{CH}_2\text{Br} & \quad \text{CH}_2\text{Br} \\
15 &
\end{align*}
\]

**Scheme 4**

Although the cyclophane is formally a dimer of biradical 1, alternative pathways not involving the intervention of \( m \)-xylylene can be readily envisioned. Convincing chemical evidence for the existence of a \( m \)-xylylene derivative in solution would have to await the work of the Gajewski, Stang and Berson groups in the 1980's, who offered chemical evidence for the existence of \( m \)-xylylene derivatives in solution. Gajewski
and Stang demonstrated that the generation of dimethylvinylidene from (16) in solutions containing 6,6-dimethylfulvene (17), resulted in the formation of octamethyl-[2.2]-metacyclophane (18) (Scheme 5). The authors claimed that trapping of the vinylidene by the endocyclic π-bond of the fulvene resulted in the formation of the highly strained 4,6-diisopropylidenebicyclo[3.1.0]hex-2-ene (19).

![Scheme 5]

Subsequent thermal ring opening of the cyclopropane moiety gave the
tetramethyl-\textit{m}-xylylene derivative (20), which upon dimerization afforded the resultant octamethyl cyclophane (18) in 40\% yield based on consumed triflate. Attempts to trap the monomeric biradical 20 led only to intractable product mixtures.

Later, Berson\textsuperscript{18} succeeded in designing a clever experiment in which the parent \textit{m}-xylylene 1 was chemically trapped with a variety of olefins including methyl acrylate, methyl methacrylate and 1,3-butadiene. Based on Gajewski and Stang's work he reasoned that attempts to trap monomeric \textit{m}-xylylene by intermolecular reactions would be flawed if they involved a carbenic route to the xylylene, as the carbene would be intercepted by the external trapping agent, thus prohibiting formation of the desired biradical. Bearing this in mind, the workers sought entry into the xylylene system via a Norrish type II photochemical cleavage reaction (Scheme 6). In the laboratory, photolysis of 4-benzoyloxy-2,6-dimethylenebicyclo[3.1.0]hexane (13) in alkane solutions containing excess 1,3-butadiene, at ambient temperature, led to a 40-60\% yield of products which were formally 1:1 adducts of biradical 1 with butadiene. Berson demonstrated convincingly that photolysis of the methyl ketone 13 initiates a Norrish type II photoreaction to produce the highly strained 2,6-dimethylenebicyclo[3.1.0]hex-3-ene (21), which undergoes ring opening to generate biradical 1, which is subsequently trapped by the diene forming the adducts shown (Scheme 6). This work represents the first successful trapping experiment of the parent \textit{m}-quinodimethane 1.
Scheme 6
Berson\textsuperscript{22} has also considered heteroatomic derivatives of the \textit{m}-xylylene biradical. Before discussing this work in further detail, it is worthwhile to consider the motivation for such studies. Primarily, one is interested in the effect of heteroatom inclusion on the molecular orbital structure for the non-Kekule molecules. Does incorporation of heteroatoms alter significantly the theoretical and experimentally confirmed prediction of ground state triplet multiplicity in these non-Kekule molecules? This question represents an area in which experimentalists may make valuable contributions. Let us examine a simple molecular orbital energy diagram for the non-Kekule molecule \textit{m}-xylylene (Figure 3). There are in total eight molecular orbitals (considering only $\pi$ orbitals and ignoring the sigma framework). Three of the orbitals are bonding orbitals, three are anti-bonding. Hückel\textsuperscript{12} or PMO\textsuperscript{13} calculations predict a pair of degenerate non-bonding molecular orbitals (NBMO's) as well.

\begin{figure}[h]
\centering
\includegraphics[width=0.6\textwidth]{figure3.png}
\caption{Molecular Orbitals of the benzoquinodimethanes. (reprinted from Borden, W. T., "Diradicals", Wiley, p.197, 1982.)}
\end{figure}
Filling eight electrons into the available set of molecular orbitals, in accord with the aufbau principle, shows that the three bonding orbitals will be fully occupied, and the three antibonding orbitals will remain unoccupied in the electronic ground state. The remaining two electrons will occupy the two degenerate NBMO's. Based on Hund's rule, the molecule is therefore predicted to have triplet multiplicity in the ground electronic state.\textsuperscript{23} Strictly speaking, these predictions governing ground state multiplicity are only true for the planar hydrocarbons, as they are derived from PMO or Huckel theory based solely on the hydrocarbons. Recent theoretical approaches\textsuperscript{13b} have suggested that violation of Hund's rule may be expected in some cases, one important example being disjoint hydrocarbons. Perturbations such as distortion from planarity\textsuperscript{13b} or the inclusion of heteroatoms\textsuperscript{24} may also have significant effects on the molecular orbital energies. If, for example, a perturbation lifts the degeneracy of the NBMO's, does this in turn cause the molecule to adopt a ground state singlet electronic configuration? This question has been summarized in detail by Platz,\textsuperscript{11} and will be briefly reiterated here. The answer depends primarily on the magnitude of the HOMO-LUMO gap induced by the perturbation on the resultant orbital energy levels. The fundamental basis for Hund's rule is electron-electron repulsion. By occupying discrete molecular orbitals, this energetically unfavorable electrostatic interaction between the two electrons is minimized. If the HOMO-LUMO gap in the new set of MO's is larger than the term resulting from electron-electron repulsion, then the molecule would be predicted to possess a singlet ground state. If on the contrary, this splitting is not sufficient to override the electrostatic contribution associated with
placing both electrons in a single molecular orbital, then the molecule will be expected to retain the triplet configuration as the electronic ground state. An exact value for the mutual electrostatic repulsion of two electrons residing in the same molecular orbital is unknown, but the value of 2 eV has been suggested as a reasonable approximation. Thus, considering the case specifically for the substitution of a heteroatom into a non-Kekule hydrocarbon, if the incorporation of the heteroatom into the hydrocarbon causes a splitting of the formerly degenerate NBMO's by an amount greater than ca. 2 eV, then the heteroatom analogue is predicted to have a closed shell configuration in the lowest energy electronic state, otherwise it should retain the triplet ground state configuration as in the hydrocarbon case.

Consider the substitution of a single electronegative atom for carbon in a non-Kekule molecule like m-xylylene. One may reason that the substitution of the electronegative atom at one of the radical centers may favor a zwitterionic singlet form of the molecule, thus lowering the single electron energy of one of the NBMO's. The effects of electron-electron repulsion will, of course, oppose this tendency to pair both electrons into the orbital of lower energy. In an effort to determine which of these effects is overriding in the m-xylylene system, Berson wished to consider an oxygen atom substituted derivative of the parent m-xylylene. Toward this goal, Berson's group has prepared the highly strained α,β-unsaturated ketone (22). Thermolysis (150 °C) or photolysis (λ > 310 nm; 0 °C) of 6-methylenebicyclo[3.1.0]hex-3-ene-2-one 22 in alcohol solvents gave the ether shown as an isolable reaction product. (23) (Scheme 8). This product seems to indicate trapping of a zwitterionic singlet form of the
m-quinomethane biradical, 3-methyleneephenoxyl (24), rather than reaction of a triplet diradical structure, but this reaction could occur from an excited singlet state even if the triplet were the ground electronic state.

Scheme 8

In apparent contrast to the solution phase trapping experiments, photolysis
of 22 in the cavity of an ESR spectrometer at 11K generated the spectrum of a randomly oriented triplet biradical. The authors assigned this spectrum to the triplet state of the oxygen centered \textit{m}-quinomethane biradical (24). This assignment stands in agreement with a semiempirical calculation (CNDO wave functions, neglect of spin-orbit contribution to the D-value, the point charge approximation and application of a scaling factor of 0.5). The reliability of the computational approach was demonstrated by the calculation of the D value of 1,8-dimethylenenaphthalene, tetramethyleneethane and trimethylenemethane, for which the Zero Field Splitting parameters had previously been determined experimentally. Based on these values the scaling factor of 0.5 was applied to the results of the calculation. Unfortunately, Curie Law analysis of biradical 24 was unreliable due to technical constraints on the temperature regime over which the analysis could be performed. Only a twenty degree temperature range was available due to saturation of the signal at the low temperature end (<20 K) and thermal decay of the biradical at higher temperatures (> 40 K). Thus the ground state of the \textit{m}-quinomethane biradical 24 still remained in question.

In an extension of this methodology into the naphthalene system, Berson\textsuperscript{26} was able to prepare the \textit{m}-naphthoquinomethane, and demonstrate adherence to the Curie Law, by EPR, over a seventy degree temperature range in this system. Based on this data they concluded that in the\textit{m}-naphthoquinomethane system the triplet is either the electronic ground state or within 0.01 kcal/mole of the ground state.

Platz\textsuperscript{27} has prepared an interesting nitrogen containing analogoue of the 1,8-naphthaquinodimethane biradical (Scheme 9). These workers were able
to demonstrate the triplet nature of the ground state of aza-diyl (25), based on linear plots of the EPR signal intensity versus the reciprocal of the absolute temperature, over the range from 17 to 83.5K.

![Scheme 9](image)

Note the authors demonstrated that the nitrogen centered diradical was not formed by an intramolecular hydrogen atom abstraction by the 8-methylnaphthylnitrene (26), and that an abstraction of a hydrogen atom from the neighboring methyl group could not be induced thermally or photchemically.

At least in the examples presented above heteroatom substitution did not alter the ground state multiplicity from that observed with the hydrocarbon. Platz also prepared, the dinitrogen analogue (27) of the 1,8 dimethylene
naphthalene and demonstrated that this species as well had a triplet ground state.\textsuperscript{24}

Several groups have studied the problem of heteroatom substitution in the trimethylenemethane biradicals. Borden\textsuperscript{28} has considered the problem from a theoretical standpoint, and predicted that oxyallyl should be a triplet biradical, with the lowest lying singlet state within \( \sim 5 \text{ Kcal/mole} \) of the ground state. Attempts to prepare oxyallyl, which represents an oxygen containing trimethylenemethane, have thus far been unsuccessful.\textsuperscript{29} In search of a heteronuclear analogue of trimethylenemethane, Quast\textsuperscript{30} has synthesized 28, which is stable at liquid nitrogen temperatures. The species was characterized by EPR spectroscopy and interpreted as a randomly oriented triplet species having an axis of threefold or higher symmetry.

\[ \text{O} \begin{array}{c} \text{CH}_3 \text{N} \end{array} \text{NCH}_3 \]
There have been no reports to date of a successful preparation of a nitrogen containing analogue of the parent \textit{m}-xylylene biradical. Wright and Platz\textsuperscript{17} attempted to extend the methodology, which had been successfully used to prepare the parent \textit{m}-quinodimethane 1, to the synthesis of the nitrogen containing diaza-diyl (30) (Scheme 10). Unfortunately, photolysis of 1,3-diaziobenzene (29) under conditions which generated the parent biradical produced only "very complicated (ESR) spectra which defied analysis." The authors saw no evidence for the desired diaza-diyl 30.

\begin{center}
\includegraphics[width=0.8\textwidth]{scheme10}
\end{center}

\textbf{Scheme 10}

With the benefit of hindsight, this negative result is not at all unexpected. Unsubstituted aryl nitrenes are notoriously poor at undergoing photochemically initiated C-H abstraction reactions. For example photolysis of the parent phenyl azide in hydrocarbon solvents at room temperature gives only azobenzene, small amounts of aniline and an intractable polymeric material.\textsuperscript{31} No products derived from N-H insertion are detected.
Also, photolysis of phenyl azide at 77K in various hydrogen atom donor solvents produces phenyl nitrene, which is itself photolabile, but no radical pairs derived from reaction of the triplet nitrene with the solvent can be detected by EPR. Thus, based on these model reactions, it would have been rather surprising indeed if the dinitrene derived from 29 had been able to abstract two hydrogen atoms from the matrix to form the diaza-diyl 30. Interestingly, Reiser and Leyshon have shown that triplet aryl nitrenes substituted with electron withdrawing groups exhibit increased reactivity toward hydrogen atom abstraction. Young has also shown that aryl azides substituted with electron withdrawing groups give excellent yields of C-H insertion products, when photolyzed in frozen organic matrices at 77K. For example, photolysis of pentafluorophenyl azide in frozen toluene gave a 77% yield of formal C-H insertion adducts, N-benzylpentafluoroaniline being the major isomer. The origin of this enhanced yield of insertion adducts was disclosed by monitoring the course of the reaction during photolysis by EPR spectroscopy. Brief photolysis of the fluorinated azide in toluene matrices generated the EPR spectrum of a randomly oriented triplet aryl nitrene. This signal was indefinitely stable in the dark. However, upon further irradiation, the signal due to the nitrene decayed, with the concomitant formation of a new resonance pattern consistent with a pentafluoroanilino-benzyl radical pair. The coupling of this radical pair upon annealing of the matrix gave rise to the formal N-H insertion adduct. Thus Young has clearly shown that the incorporation of fluorine has enhanced the hydrogen atom abstraction reaction which would be required to form the m-xylylene biradical via a dinitrene route. We therefore set out to exploit this type of chemistry to
generate a heretofore unknown nitrogen analogue of biradical 1.
Results and Discussion

As mentioned earlier, we were intrigued by Migirdicyan's preparation\textsuperscript{3} of the \textit{m}-xylene biradical. Despite the recognition this work received, we were aware of no investigation of the mechanism of this rather unusual photochemical reaction. In order to perform a systematic investigation on the photolysis of matrix isolated polymethylbenzenes we have chosen first to study the photolysis of matrix isolated mesitylene. This choice was based on several factors. First, we were primarily interested in the xylylenes which have open shelled electronic configurations in the ground state, thus the two methyl groups need to reside in the \textit{meta} orientation to one another. We have selected mesitylene over the parent \textit{m}-xylene because photolysis of mesitylene gives a significantly higher ratio of biradical/monoradical (as determined by fluorescence spectroscopy) than does \textit{m}-xylene itself. Thus mesitylene proved to be experimentally more convenient for this investigation. Considering Migirdicyan's work,\textsuperscript{3} we were aware that two matrix isolated photoproducts could be spectroscopically detected following photolysis of matrices containing mesitylene at 77K, the \textit{m}-methyl substituted \textit{m}-xylene biradical (mesitylylene 31) and the 3,5-dimethylbenzyl radical 32. Several possible reaction pathways leading to the formation of the mixture of matrix isolated mono and biradicals could be envisioned. One
might imagine a stepwise mechanism (Scheme 11) leading to the observed mixture of matrix isolated radicals, in which photolysis of mesitylene 33 produces the methyl substituted benzyl radical 32, which is subsequently photolyzed to form the mesitylylene biradical 31 as a secondary photolysis product.

Scheme 11

This mechanism could be rapidly discarded because the relative yields of 32 and 31 are independent of light intensity (Table 1) or the duration of photolysis of the sample (Figure 4).
Figure 4. Growth of Monoradical (32) and Biradical (31) emission produced from Mesitylene as a Function of Photolysis Time. Photolyses were carried out at 77K using the 249 nm excimer laser at a pulse rate of ~5 Hz. Monoradical and Biradical were monitored by their fluorescence emission at 487 and 452 nm respectively, exciting at 296 nm.
Table 1. Ratio of Mesitylene biradical/monoradical (31/32) emission produced from matrix isolated mesitylene, as a function of light intensity. 

<table>
<thead>
<tr>
<th>Sample</th>
<th>Radiation Intensity</th>
<th>(31/32)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesitylene (1.6 x 10⁻²M)</td>
<td>100%</td>
<td>0.40</td>
</tr>
<tr>
<td>Mesitylene (1.6 x 10⁻²M)</td>
<td>60%</td>
<td>0.42</td>
</tr>
<tr>
<td>Mesitylene (1.6 x 10⁻²M)</td>
<td>29%</td>
<td>0.43</td>
</tr>
<tr>
<td>Mesitylene (1.6 x 10⁻²M)</td>
<td>9%</td>
<td>0.45</td>
</tr>
<tr>
<td>Mesitylene (3.0 x 10⁻³M)</td>
<td>100%</td>
<td>0.36</td>
</tr>
<tr>
<td>Mesitylene (3.0 x 10⁻³M)</td>
<td>9%</td>
<td>0.42</td>
</tr>
</tbody>
</table>

a. Samples were irradiated at 77K in 3-methylpentane using the 249 nm line of the excimer laser. The ratio was determined by monitoring the intensity of the fluorescence emission at the maxima for both the biradical (452 nm) and the monoradical (487 nm). The excitation wavelength was 296 nm throughout. The light intensity was modulated by means of neutral density filters.

These experiments demonstrate that the substituted benzyl radical 32 and the mesityllylene biradical 31 are both formed by processes requiring the same number of photons. This is clearly inconsistent with a stepwise mechanism where the biradical is formed only following secondary photolysis of the monoradical. One might assume that one bond cleavage to form a methylated benzyl radical would occur in a manner similar to the photochemical cleavage of the benzylic C-H bond in Durene as reported by Albrecht. The formation of the duryl radical from this reaction has been shown to proceed through an excited singlet state in a monophotonic process when irradiated at 254 nm. In any event, in our minds the cleavage of the second C-H bond is most intriguing. Any stepwise process would predict a higher relative yield of biradical at longer photolysis times or higher incident intensities, contradicting the results actually observed in the
laboratory. A stepwise mechanism is also inconsistent with the photochemistry of $m$-tolylacetylperoxide (34). Photolysis of 34 in 3-methylpentane with the unfiltered light of a medium pressure mercury arc lamp produces monoradical 35, but no trace of $m$-xylene 1 could be detected by fluorescence spectroscopy. (Scheme 12).

![Scheme 12](image-url)
Thus photolysis of 34 does not form 1, which is easily detected under identical conditions, when a glassy matrix containing meta-xylene is exposed to the same source. This indicates that there is an alternative route for the formation of the matrix isolated biradical 1 which does not involve secondary photolysis of the monoradical 35.

Similar to the results obtained with mesitylene, photolysis of matrices containing the parent m-xylene (9) indicate that the ratio of the fluorescence emission signal due to the biradical and the radical were independent of photolysis time as well (Table 2).

**Table 2. Ratio of m-xylene biradical/monoradical (1/35) emission produced from matrix isolated m-xylene as a function of photolysis time.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Irradiation time (minutes)</th>
<th>1/35</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-xylene (6.0 x 10^{-3}M)</td>
<td>0.25</td>
<td>0.094</td>
</tr>
<tr>
<td>m-xylene (6.0 x 10^{-3}M)</td>
<td>3.0</td>
<td>0.085</td>
</tr>
<tr>
<td>m-xylene (6.0 x 10^{-3}M)</td>
<td>10.0</td>
<td>0.070</td>
</tr>
<tr>
<td>m-xylene (6.0 x 10^{-3}M)</td>
<td>21.0</td>
<td>0.064</td>
</tr>
<tr>
<td>m-xylene (6.0 x 10^{-3}M)</td>
<td>30.0</td>
<td>0.064</td>
</tr>
</tbody>
</table>

a. Samples were irradiated at 77K in glassy 3-methylpentane using a rayonet reactor equipped with 5 RPR 2534 source bulbs. The ratio was determined by monitoring the intensity of the fluorescence emission at the maxima for both the biradical (440 nm) and the monoradical (470 nm). The excitation wavelength was 296 nm throughout.
In fact, in both cases, i.e. photolysis of glasses containing mesitylene or $m$-xylene, surprisingly the ratio of biradical/monoradical was slightly greater at very brief photolysis times, decreasing measurably as the photolysis continued. Clearly this result is inconsistent with any mechanism which postulates that the biradical results from secondary photolysis of the matrix isolated methylated benzyl radical 35, as the opposite dependence of the biradical/monoradical ratio on photolysis time must then be observed. This new, and rather surprising mechanistic fact, must also be addressed by any mechanistic proposal.

At this time, a plausible mechanism consistent with the data we had accumulated was suggested to us by Berson\textsuperscript{36}.

Scheme 13
In this proposal, the nascent hydrogen atom produced by photochemical scission of \textit{m}-xylene or mesitylene partitions between reaction with the matrix (MH) or reaction with the monoradical to produce the biradical. (see Scheme 13) Reaction of a hydrogen atom with 32 or MH is certainly exothermic\textsuperscript{37} and can proceed rapidly at 77K by quantum mechanical tunneling.\textsuperscript{38} The Berson mechanism predicts that decreasing the H atom donating ability of the matrix will increase the yield of biradical relative to monoradical. This expectation is borne out in Table 3 where the ratio of biradical/monoradical \textit{31}/\textit{32} as determined by fluorescence emission intensities of each species, is seen to be larger in hydrocarbon matrices than in methanol.

One could argue that this matrix dependence is a consequence of different packing arrangements however, perdeuteration of the matrix should not distort the packing of mesitylene within the host significantly. Furthermore, there should be large isotope effects on the reaction of hydrogen atoms with the glass.\textsuperscript{38} In fact a very dramatic increase in the ratio of biradical to monoradical was observed upon perdeuteration of the host matrix. With polycrystalline deuterated \textit{n}-hexane as the matrix material, one sees a particularly dramatic effect. For the first time the biradical/monoradical ratio monitored in the usual manner shows the signal due to the biradical to be larger than that of the monoradical (\textit{31}/\textit{32} = 1.26.) Compare this value with that observed in the excellent hydrogen atom donor methanol, where the relative yield of biradical has dropped considerably (\textit{31}/\textit{32} = 0.24).
Table 3. Ratio of Mesitylene biradical/monoradical (31/32) emission produced from matrix isolated mesitylene as a function of matrix.$^a$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Matrix</th>
<th>(31/32)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesitylene (3.0 x 10^-3M)</td>
<td>3-methylpentane</td>
<td>0.42</td>
</tr>
<tr>
<td>Mesitylene (4.7 x 10^-3M)</td>
<td>CH_3OH</td>
<td>0.24</td>
</tr>
<tr>
<td>Mesitylene (4.7 x 10^-3M)</td>
<td>CD_3OD</td>
<td>0.32</td>
</tr>
<tr>
<td>Mesitylene (5.0 x 10^-3M)</td>
<td>n-hexane</td>
<td>0.54</td>
</tr>
<tr>
<td>Mesitylene (5.0 x 10^-3M)</td>
<td>n-hexane (d-14)</td>
<td>1.26</td>
</tr>
<tr>
<td>Mesitylene (5.0 x 10^-3M)</td>
<td>methylcyclohexane</td>
<td>0.69</td>
</tr>
</tbody>
</table>

$^a$ Samples were irradiated at 77K in glassy 3-methylpentane using the 249 nm line of the Lumonics excimer laser. The ratio was determined by monitoring the intensity of the fluorescence emission at the maxima for both the biradical (452 nm) and the monoradical (487 nm). The excitation wavelength was 296 nm throughout.

Note also that the effect of increased substitution on the ratio of biradical to monoradical, can also be accommodated by this proposal. Comparing Table 2 and Table 3 we see that the ratio of the fluorescence signals due to the biradical/monoradical produced from photolysis of mesitylene is approximately a factor of four times greater than that produced from the parent m-xylene itself. This disparity was originally noted by Migirdicyan, but has remained an unexplained curiosity until the present study. Admittedly this ratio, which is based on fluorescent signal intensities, does not necessarily represent a direct measure of the relative yields of the matrix isolated biradicals in the two systems, since it may also be effected by differences in relative extinction coefficients or quantum yields for
fluorescence. We suggest however, that the Berson mechanism easily explains an increased yield of biradical from mesitylene relative to m-xylene as a consequence of the increased number of target methyl groups.

Since the biradical is formed in a thermal process from the mesitylene monoradical, the problem is now reduced to yet another question. What is the pathway by which the mesityl monoradical 32 is formed? Albrecht\textsuperscript{35} has reported that the photochemical conversion of durene into duryl radical at 77K is a biphotonic process when carried out at 275 nm but can be achieved monophotonically with 252 nm excitation. We initially examined the problem in a manner similar to that which Albrecht employed in his original work on Duryl radical formation. The signal intensity, as determined by fluorescence spectroscopy, of both the monoradical 32 and the biradical 31 was monitored as a function of the intensity of the 249 nm photolyzing laser beam. The intensity of the beam was attenuated using fine wire mesh of known optical density as a neutral density filter. A plot of the observed fluorescent signal intensity, following brief photolysis of matrices containing mesitylene at 77 K, versus light intensity was found to be linear for both the mesitylene monoradical and biradical (Figure 5).
Figure 5. Signal Intensity of monoradical (32) and Biradical (31) emission produced from Mesitylene as a Function of light intensity. Photolyses were carried out at 77K using the 249 nm excimer laser at a pulse rate of ~5 Hz. Monoradical and Biradical were monitored by their fluorescence, in the usual manner. Light intensity was attenuated by using neutral density filters.

This is indicative of a monophotonic process leading to the formation of both species in the matrix, as the rate of formation of products formed through secondary photochemical reactions usually do not have a first order dependence on the intensity of the source.39 Thus these data would seem to stand in agreement with those of Albrecht who found a linear relationship for the rate of growth of the duryl radical upon photolysis of matrix isolated durene.35 However, the observation of such a linear plot does not rigorously exclude the possibility that a two step biphotoic reaction is involved in producing the radicals, in both our own and Albrecht's
experiment. Consider for instance the general case of a two step photochemical reaction which forms product C through the intermediacy of the primary photochemical product B.

\[
\begin{align*}
A & \xrightarrow{hv} B & \xrightarrow{hv} C
\end{align*}
\]

**Scheme 14**

If the photolysis is carried out in such a manner so that the sample retains a high concentration of B throughout the experiment, so that sufficient B is present to absorb essentially all of the incident light, then the yield of product C will vary with the light intensity as if it were formed via a monophotonic process, i.e. linearly with light intensity.\textsuperscript{40} Thus, although our data are consistent with a mechanism in which a monophotonic process forms the mono and biradicals, bearing in mind the aforementioned caveat, the possibility that a biphotonic mechanism is operative could not be ruled out without further experiment. Thus, at this point, at least two equally reasonable mechanistic proposals seemed to be indicated by the data. Considering now the specific case for the photochemical bond cleavage in matrix isolated mesitylene, these two pathways are illustrated below. In the first possibility, (Scheme 15) a single 249 nm photon leads to the monophotonic dissociation of a benzylic C-H bond, presumably from an excited singlet electronic state of the hydrocarbon, in accord with Albrecht's work on the duryl radical formation.
In the second alternative, (Scheme 16) the first photon leads to formation of an excited singlet state of mesitylene, subsequent intersystem crossing to the lowest triplet electronic state of the hydrocarbon, followed by absorption of a second photon, produces a doubly excited triplet state $T_n$ which is dissociative, and results in the scission of the benzylic C-H bond. Thus this pathway represents a biphotonic alternative for the cleavage of the first C-H
Scheme 16

249, 337 or 405 nm

$\text{MH} + H^+$

$\text{MH} + H_2^+$

$H_2 + M^+ \rightarrow 32$

$32$

$31$

$33$

$S_0$

$S_1$

$T_1$

$T_a$
Regardless of the mechanism of the first C-H bond cleavage, the biradical is then formed in the thermal reaction as outlined in the Berson mechanism (Scheme 13).

An experiment was devised which can, in principle, distinguish these two possibilities. The experiment involves the use of a pulsed excimer laser to irradiate matrices containing mesitylene with a very short (~10 ns) highly monochromatic (249 nm) pulse. In this manner the effect of varying the pulse frequency, as well as the energy content of the excitation source, can be readily investigated. Excitation of mesitylene in glassy 3-methylpentane at 77K with a single pulse of an excimer laser at 249 nm produces the triplet state of the hydrocarbon, via ISC from an excited singlet state of mesitylene. The phosphorescence of $^3$33 is clearly visible to the unaided eye, and persists for several seconds after the photolysis is terminated. When the glass containing mesitylene is subjected to fifty laser pulses (249 nm) at a high pulse frequency (5 Hz) at 77K, the spectra of mono and biradical 32 and 31 as shown in figure 6 are produced. Under these conditions both mesitylene (33) and $^3$33 are present in the matrix and thus exposed to the 249 nm laser line. If instead mesitylene is irradiated with fifty laser pulses which are spaced far apart in time (0.05 Hz) so as not to irradiate $^3$33, which decays by phosphorescence prior to the onset of the following pulse, then the yield of mono and biradical decrease by greater than ten fold. (figure 6).
Figure 6. a. Fluorescence Emission Spectra recorded at 77 K of the Mesitylene Monoradical (32) (487 nm, 498 nm) and mesitylene biradical (31) (452 nm, 463 nm). The spectra were produced by the excimer laser irradiation (50 pulses 249 nm) of mesitylene (5 x 10^{-3} M) in glassy 3-methylpentane at 77K. The excitation wavelength was 296 nm. Upper trace indicates laser pulsed at 5 Hz, while the lower curve indicates a laser pulse frequency of 0.05 Hz.

Similar results were obtained when durene was employed as precursor as well. This experiment demonstrates that the photochemical cleavage of a benzylic C-H bond in matrix isolated methylated benzenes requires two photons, and that the second photon is absorbed by a long lived species (having a lifetime on the order of several seconds). We feel the most reasonable assignment for this long lived species is the triplet state of the
methylated benzene as illustrated in scheme 16. We point out that these results stand in contradiction to those of Albrecht who reported the monophotonic nature of the process leading to the duryl radical formation when matrix isolated durene was photolyzed at 252 nm.

Additional information was provided by a two laser experiment, performed once again using rigid glasses containing mesitylene. Joussot-Dubien has shown that polycyclic aromatic hydrocarbons (PAH's) undergo characteristic biphotonic photochemistry from an excited triplet state, in a photochemical reaction similar to that which we are proposing here with mesitylene. For example triphenylene was studied in a rigid organic glass at 77 K using a dual beam experiment. The first beam (265 nm; 3 ns pulse width) populated the lowest triplet state of the polycyclic aromatic hydrocarbon, following ISC. The lowest triplet state of the PAH was simultaneously irradiated in the visible region with an arc lamp. Individual laser pulses were spaced at 90 second intervals to ensure complete decay of the PAH triplet prior to the onset of the next pulse. Under these conditions Joussot-Dubien observed more than twice the yield of photoproducts formed by laser radiation alone. A similar experiment was employed in our work with mesitylene. In this experiment, mesitylene was subjected to fifty laser pulses spaced at relatively long intervals (~20 seconds) and simultaneously irradiated with a nitrogen laser (337.1 nm) operating at a repetition rate of ~50 Hz. These conditions produced the mono and biradicals (Figure 7), while photolysis of the glass with the nitrogen laser alone produced no detectible yield of either mono or biradicals. The yield of mono and biradical in the two laser experiment is at least ten fold larger than that
produced by a single 249 nm laser operating at 0.05 Hz. Thus clearly the combination of both the 337 nm and the excimer (at 0.05 Hz) was necessary to produce the C-H bond cleavage. This experiment indicates that a species formed by the first 249 nm excitation pulse, most likely $^333$ can be photolyzed with a second (337.1 nm) photon to produce monoradicals.

Figure 7. Two laser experiment (see text). Fluorescence Emission Spectra recorded at 77 K of the Mesitylene Monoradical (32) (487 nm, 498 nm) and mesitylylene biradical (31) (452 nm, 463 nm). The spectrum was produced by the simultaneous excimer laser irradiation (50 pulses 249 nm, 0.04 Hz) and N$_2$ laser (337 nm, 50 Hz) of mesitylene (5 x $10^{-3}$ M) in glassy 3-methylpentane at 77K. The excitation wavelength was 296 nm. The lower trace represents control experiment where the matrix was photolyzed with the nitrogen laser alone.

A simple argument based on thermodynamics proved to be informative at this point. The triplet energy of mesitylene is 80.3 kcal/mole, thus after absorption of a second photon, the doubly excited triplet state of mesitylene possesses a maximum of 165.3 kcal/mole, which is ample energy to
fragment to the monoradical 32 plus a hydrogen atom. However, 165.3 kcal/mole is insufficient to cleave 2 benzylic C-H bonds of mesitylene. This would require 170 kcal/mole assuming that the second C-H bond dissociation energy is the same as that of the first (the benzylic C-H bond dissociation energy of toluene is 85 kcal/mole). Furthermore, the ratio of 31/32 formed from this two laser experiment is identical with that formed when 33 is irradiated with 249 nm light alone. Admittedly, due to the necessarily approximate nature of the second C-H bond dissociation energy of m-xylylene this argument is rendered less than convincing. However, when the wavelength of the second beam in the double beam experiment is chosen to be 405 nm (isolated from a xenon arc lamp) similar results are observed. The sum of the triplet energy of mesitylene (80.5 kcal/mole) plus the energy provided by a 405 nm photon (70.7 kcal/mole) is clearly insufficient to break 2 C-H bonds in a purely photochemical process. Therefore, these data argue further in support of the Berson mechanism, in which the cleavage of the second benzylic C-H bond occurs in a dark reaction rather than through a photochemical process.

In order to confirm the conclusions drawn from the results of the dual beam experiments, we wished to consider the absorption spectrum of the triplet state of mesitylene. Recall, we have assigned the long lived species, which is demonstrated to undergo secondary photolysis forming the methylated benzyl radical 32, as the lowest triplet state of mesitylene. In order to secure this assignment, we wished to record the absorption spectrum of triplet mesitylene. This spectrum, which corresponds to the $(T_{1}-T_{n})$ absorption of mesitylene was recorded in a laser flash photolysis
experiment. The only detectable transient produced by 249 nm excitation of a dilute solution of mesitylene in methylcyclohexane was found to consist of a broad absorption (~ 100 nm in width) centered at 390 nm (figure 8).

![Absorption Spectrum](image)

**Figure 8.** $T_1-T_n$ absorption spectrum of mesitylene. Transient spectrum produced following laser (249 nm; KrF excimer laser) pulse of a solution of mesitylene 33 (O. D. 1.0 @ 249 nm) in methylcyclohexane. The spectrum was recorded 350 ns after the laser pulse.

This spectrum depicted in Figure 8 was recorded 350 ns after the laser pulse and demonstrated to be due to a transient species, as it could not be observed when a long delay time (50 µs.) was introduced prior to recording the absorption spectrum of the solution. We believe the assignment of this spectrum as the $(T_1-T_n)$ absorption of triplet mesitylene is the most reasonable one. The position of this absorption indicates that the second beam in both two laser experiments is of an appropriate wavelength to be absorbed efficiently by the triplet state of mesitylene. Recall, the wavelength
of the second beam was chosen to be either 337 or 405 nm, where the triplet does in fact have considerable absorption. Although not definitive, this represents permissive evidence that the triplet state of mesitylene is in fact the immediate precursor to the matrix isolated benzyl radical and a hydrogen atom.

A Laser Induced Fluorescence Experiment (LIF) using mesitylene as the precursor reveals results which are also in accord with the biphotonic mechanism detailed above. Laser (249 nm KrF line) excitation of an optically dilute solution of mesitylene in methylcyclohexane at room temperature leads to the fluorescence emission spectrum shown in figure 9.

![Figure 9. Room Temperature Laser Induced Fluorescence (LIF) spectrum of mesitylene (33). Spectrum produced from mesitylene (33). The spectrum was recorded in methylcyclohexane solution at room temperature. Fluorescence was collected beginning coincident with the laser pulse (249 nm KrF, 10 ns) for a total of 100 ns. (Optical density of the mesitylene was 1.0 at 249 nm).](image)
This strong emission, centered at 296 nm is due to the $S_1-S_0$ fluorescence emission of the mesitylene precursor. Note in particular the spectral region from 400-500 nm, in which there is no detectable emission characteristic of the dimethylated benzyl radical 32 (487 nm) or the m-xyylene type biradical 31 (452 nm). Conspicuous by their absence, the failure to detect any benzyl radical type products in this experiment is supportive of the mechanistic proposal of scheme 16, which predicts that neither the mono nor the biradical is formed within a single 249 nm laser pulse, but rather only by secondary excitation of the long lived lowest triplet state of the mesitylene. Although this is admittedly a "negative result", our ability to detect the emission of the m-xyylene biradical in a similar LIF experiment using an alternative precursor (vide infra) lends credence to the above argument. The failure to detect benzylic radicals or biradical in this LIF experiment supports our contention that the radicals simply are not formed from a single laser pulse.

Although systematic study was performed on the mesitylene system we feel the results are applicable to the photolysis of methylated benzenes in general. This is based on the excellent agreement observed when similar experiments to those performed on mesitylene, were extended to other methylated benzenes such as durene and m-xylene. For example, consider Table 2 which shows that when mesitylene is replaced with m-xylene the effect of varying photolysis time is very similar to that observed with the mesitylene system (Figure 4). Similarly the dramatic effect of laser pulse frequency on the yield of radicals can be reproduced when durene replaces...
mesitylene as the matrix isolated methylated benzene precursor. Furthermore, the two laser experiment discussed in detail for the mesitylene system, provides nearly identical results when durene replaces mesitylene as the precursor.

Dichlorides

A spectroscopic examination of the radical and biradical products formed by photolysis of $\alpha,\alpha'-(dichloro)-m$-xylene (36) in hydrocarbon matrices at 77 K gives significantly different results from those observed upon photolysis of the polymethyl benzenes under identical conditions. Photolysis of dihalide precursor 36 gives a much higher ratio of biradical/monoradical 1/35 than does photolysis of the methylated benzenes when the two precursors are irradiated under identical conditions. The lifetime of $^3$36 in glassy 3-methylpentane at 77K is much shorter than that of triplet mesitylene. This is readily apparent upon observing the phosphorescence of 36 and $m$-xylene with the unaided eye. We have investigated the photochemical reaction involving the formation of biradical 1 from the photolysis of dihalide 36 in a manner similar to that which was used to elucidate the predominant reaction mechanism with the hydrocarbon precursors. Based on the results of solution phase Laser Induced Fluorescence (LIF) and Laser Flash Photolysis (LFP) experiments (vide infra), as well as photolysis of 36 in matrices at 77 K, it is clear that 36 efficiently loses 2 Cl atoms upon photolysis to produce the $m$-xylene biradical. We wished to investigate this reaction further, with
hopes of understanding the mechanistic details. 

Photolysis of 36 at 77K with 350 laser pulses (KrF excimer laser; 249 nm) produces primarily the \textit{m}-xyylene biradical 1, as well as traces of the \textit{m}-methylbenzyl radical 35, which can be detected by fluorescence spectroscopy (figure 10).

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fluorescence_spectrum.png}
\caption{Fluorescence of the \textit{m}-xyylene biradical (1) (438 nm) and \textit{m}-methylbenzyl radical (35) (471 nm). Spectra produced by the photolysis of \textit{a,a'}-(dichloro)-\textit{m}-xylene (36) (8.0 \times 10^{-3} M) in glassy ethanol at 77 K using the excimer laser (249 nm, 5Hz) (\textit{\lambda}excitation throughout was 296 nm).}
\end{figure}

However, 350 laser pulses spaced 20 seconds apart are also effective in producing 1 and 35, in marked contrast to the results with mesitylene. The biradical 1 must be produced within the 10 ns width of a single excimer laser pulse. A 249 nm photon (115kcal/mole) has insufficient energy to fragment
two carbon-chlorine bonds, thus a species produced by absorption of a 249 nm pulse, must in turn absorb a second photon, within a single pulse, to form the biradical. A Berson type of mechanism appears unlikely in this system because the nascent chlorine atom is expected to abstract a hydrogen from the matrix or the monoradical rather than a chlorine atom. The latter reaction would produce 37 rather than m-xylylene 1.

\[ \text{CH}_2 \cdot 
\begin{array}{c}
\text{Cl} \\
. 
\end{array} 
\]

The biradical fluorescence emission and excitation spectra we observe from dichloride 36 are identical to those of m-xylylene 1, and we suspect quite different from 37. The two most reasonable candidates which could undergo secondary photolysis are the lowest triplet state of the dichloride (336), or alternatively the m-chloromethyl benzyl radical 38 formed by rapid fragmentation of 136. In either event, in contrast to the hydrocarbon precursors, the species which undergoes secondary photolysis to the biradical must be formed within the duration (≈10 ns) of the excimer laser pulse.

Varying the photolysis time or radiation intensity of matrices containing 36 (excimer laser; 249 nm) also shows significant departure from the trend
observed with the hydrocarbons. Monitoring the ratio of biradical/monoradical (31/32) as a function of time shows the yield of *monoradical* increasing dramatically relative to the biradical at long photolysis times. (Figure 11).

![Graph showing the ratio of monoradical to biradical vs. number of pulses](image)

**Figure 11.** Ratio of the monoradical/biradical (35/1) from the photolysis of dichloride (36) versus number of laser pulses delivered. Ratio calculated by measuring the emission intensities at the maxima for the monoradical and the biradical (471 and 438 nm respectively), with the λ excitation held constant at 296 nm.

Clearly the first species formed in the matrix under these conditions is the *m*-xylylene biradical, with only a small impurity of the monoradical at very
short photolysis times. At longer irradiation times, an appreciably higher ratio of monoradical/biradical (35/1) is produced in the matrix. Continued photolysis at this point leads to only small changes in the ratio of monoradical to biradical. We propose that there are two mechanistic possibilities which are equally consistent with the data for the dichloride precursor. In the first (scheme 17) we suggest that excitation of 36 and rapid intersystem crossing forms 336 within a single laser pulse. The triplet state of 36 absorbs a second photon, which leads to the simultaneous rupture of two carbon chlorine bonds and formation of m-xylylene from an excited triplet state of the dichloride. In the second possibility (Scheme 18), initial rapid bond cleavage of a C-Cl bond leads to the chlorine containing monoradical 38. This monoradical may then absorb a second photon, within a single laser pulse, which promotes it to a dissociative, non-fluorescent excited state, resulting in the formation of the m-xylylene biradical. Regardless of the mechanism forming the biradical, it is clear that secondary photolysis of the biradical leads to the slow photochemical hydrogen abstraction reaction of m-xylylene from the matrix to form the monoradical 35 along with a spectroscopically undetected matrix derived radical. Similar secondary photolysis of a biradical to form a monoradical via hydrogen atom abstraction from the matrix material has previously been observed by Closs in the 1,3-cyclopentanediyl system. In our system, as monoradical 35 accumulates in the matrix, it effectively screens the biradical from further photolysis, thus the ratio of biradical/monoradical (1/35) becomes relatively insensitive to continued photolysis. In the case of the hydrocarbon 33, even at very brief photolysis times, the monoradical was the primary light
absorbing species in the matrix, thus the relative yield of monoradical/biradical was essentially time independent throughout the experiment, showing only a slight change in this ratio as a function of photolysis time.
Scheme 17
It should also be pointed out that the photolysis of matrices containing the 
*ortho* substituted isomer $\alpha,\alpha'$-(dichloro)-$o$-xylene gave the 
*ortho*-quinodimethane, $o$-xylylene, which was detected by its known $^3$ 
fluorescence spectrum. (Figure 12).

![Fluorescence emission of the $o$-xylylene biradicaloid (6). Spectra produced by the photolysis of $\alpha,\alpha'$-(dichloro)-$o$-xylene (5.0 x $10^{-3}$ M) in glassy ethanol at 77 K using a rayonet photoreactor (RPR-2540) ($\lambda_{\text{excitation}}$ was 370 nm).](image)

**Figure 12.** Fluorescence emission of the $o$-xylylene biradicaloid (6). Spectra produced by the photolysis of $\alpha,\alpha'$-(dichloro)-$o$-xylene (5.0 x $10^{-3}$ M) in glassy ethanol at 77 K using a rayonet photoreactor (RPR-2540) ($\lambda_{\text{excitation}}$ was 370 nm).

The results obtained by ambient temperature solution phase laser 
induced fluorescence (LIF) experiments corroborate both mechanistic 
proposals discussed above. In these experiments, a single pulse from an 
excimer laser (249 nm, 10 ns.) was used to irradiate a solution of the 
dichloride (36). The laser pulse serves both to dissociate the precursor, as
well as to excite the nascent radicals or biradicals. The fluorescence emission from the electronically excited transient species is then collected, dispersed via a grating onto a photodiode array, and recorded. The (LIF) emission spectrum obtained in this manner from dichloride (36) (figure 13), has an origin band at 440 nm and the first vibronic band at 525 cm$^{-1}$, which is in excellent agreement with the triplet-triplet matrix fluorescence emission spectrum previously assigned to $m$-xylylene.
Figure 13. Room Temperature Laser Induced Fluorescence (LIF) spectrum of m-xyylene (1). a. Spectrum produced from α,α'- (dichloro)-m-xylene (36). The spectrum was recorded in isopentane solution at room temperature. Fluorescence was collected beginning coincident with the laser pulse for a total of 100 ns. (Optical density of the dihalide was 1.2 at 249 nm). b. Identical with a except employing α,α'- (dibromo)-m-xylene (39) as precursor.
An identical LIF spectrum was recorded using α,α'-dibromo-m-xylene (39) as the precursor (Figure 13). Regardless of precursor, only a very low intensity band which may correspond to the 0-0 transition of monoradical (35), or the chloromethylbenzyl radical 38, can be seen along with the solution phase emission spectrum of the m-xylene biradical. Clearly, the m-xylene biradical (1) produced by the cleavage of 2 C-Cl bonds is formed within a single 249 nm laser pulse. Laser flash photolysis of a dilute solution of dihalide 36 produces the transient spectrum shown in figure 14. This spectrum consists of a sharp band at 320 nm, which is very similar to the absorption spectrum of the m-methyl benzyl radical 35.3
Presumably, it is due to the chloromethyl benzyl radical 38 formed by rapid C-Cl bond cleavage of the dihalide (Scheme 18). This represents spectroscopic evidence supporting the stepwise nature of the biradical forming process. If we assume that 38 is only weakly or non-fluorescent, and its excited state efficiently dissociates to a chlorine atom and m-xylylene, the data are completely consistent with a stepwise pathway. We have observed no spectroscopic evidence (either in absorption or emission experiments) for the intermediacy of 336. Thus the stepwise mechanism leading to the formation of m-xylylene via the intermediacy of a chlorine containing monoradical is preferred at this time (scheme 18).

As described in the introductory section, the preparation of a nitrogen analogue of m-xylylene was also one of our goals. The strategy which would be used to prepare this nitrogen containing analogue of m-xylylene; double hydrogen atom abstraction from the matrix by a photochemically generated nitrene route is illustrated below (Scheme 19).
Recall, the motivation for fluorine incorporation was the dramatic effect of electron withdrawing groups on nitrene reactivity toward the desired hydrogen atom abstraction reactions. Broad-band photolysis of dilute (0.01-0.05 M) solutions of the fluorinated diazide 40 in 2-methyltetrahydrofuran at 77K produces initially the EPR spectrum of a triplet mono-nitrene 41 as well as the spectrum of dinitrene quintet 42 (figure 15).
Figure 15. EPR spectra produced following photolysis of diazide 40 at 77 K in 2-methyltetrahydrofuran. a. Spectrum recorded immediately following broad band photolysis at 77 K. b. Spectrum recorded following brief warming of 42 to 100 K and recouling to 77 K.
Figure 15. (cont.). EPR spectra produced upon irradiation of diazide 40 (0.05M) at 77 K. Spectrum recorded following brief warming of 42 to 100 K and recooling to 77 K. c. recorded in polycrystalline methanol. d. recorded in 3-methylpentane glass.
The spectrum of the dinitrene 42 is stable in the dark at 77K, as storage for 18 hours at liquid nitrogen temperatures led to no decrease of the quintet signal intensity within experimental error. However, upon brief warming of the sample to 100K followed by recooling to 77K, the quintet spectrum rapidly disappears and is replaced by that of a randomly oriented triplet biradical $|D/h\alpha| = 0.019$; $|E/h\alpha| \sim 0 \text{ cm}^{-1}$.

(Figure 13). Depicted below is a mechanistic summary of the proposed pathway leading to the formation of diaza-diyl 43 (Scheme 20)
The most reasonable assignment of the spectrum shown in figure 15 is, in our opinion, that of diaza-diyl 43, formed by the thermally activated double hydrogen atom abstraction from the matrix by the dinitrene 42. This assertion is based on several facts. First, the biradical spectral splitting is much too large to attribute to a solvent derived radical pair. Radical pairs such as 44

\[
\begin{align*}
\text{NH} & \cdot \\
\text{OH} & \\
\text{CH} & \\
\text{CH}_3 & \\
\end{align*}
\]

derived from the reaction of fluorinated triplet aryl nitrenes with matrices are known\(^{46}\) and they have zero field splitting parameters \(D/hc\) of approximately 1/3 the magnitude observed in this case. Also the observed zero field parameters were identical when 2-methyltetrahydrofuran, methanol, methanol (d\(_4\)) or 3-methylpentane (Figure 15) were chosen as the matrix material. If the triplet spectrum were due to a solvent derived radical pair, one would not expect a constant \(D\) value as the matrix is varied. This results from the different geometry and spin distribution that would occur upon variation of the matrix material.\(^{17}\) Furthermore, GC-MS analysis of the diazide solution in 2-MeTHF following photolysis at 77 K revealed traces of a species having an m/e and fragmentation pattern consistent with a dimer of the nitrogen centered biradical (See Appendix C). Significantly photolysis of diazide 40 in a perfluorinated matrix (perfluoro-2-\(n\)-butyltetrahydrofuran),
afforded the identical spectrum which we have assigned to the quintet state of the dinitrene, but the spectrum assigned to the biradical was not observed even upon warming the dinitrene sample to 100K in this matrix, which lacks donatable hydrogen atoms. Furthermore, photolysis of the parent diazide 1,3 diazidobenzene 29, under identical conditions with those of the fluorinated azide, leads to the formation of the dinitrene quintet 45 (scheme 21), whose spectrum is virtually identical with that of 42.
With this dinitrene, which is not substituted with electron withdrawing substituents, there is no evidence for the formation of a biradical even when the matrix is warmed to 100K.

Clearly, the substitution of fluorine for hydrogen on the aromatic ring of the diazide has had a dramatic effect on the chemistry of the resultant dinitrene, as was expected. The modification appears to have enhanced the ability of the dinitrene to undergo the desired hydrogen atom abstraction reaction from the matrix, in accord with our expectations. Our ability to detect the spectrum of the triplet biradical at 77 K indicates that the open shell triplet is either the ground state or lies with 1-2 kcal/mole of the ground state (assuming a detection limit of 10⁻⁶ M and 100 % conversion of the diazide into the biradical 43).

A calculated prediction for the D value of biradical 43 was determined by Lahti at the AM1 geometries using INDO/2 - UHF wave functions. The D value obtained in this manner for the fluorinated analogue is larger than our experimentally determined value by a factor of two ID/hcl_calculated = 0.035 cm⁻¹. When the fluorines are not entered into the calculation a value of 0.021 cm⁻¹ is obtained for the parent diaza-diyl 30, in reasonably good agreement with our experimental report for the fluorinated analogue. It must be stressed that the agreement between this value and the experimental value may be purely coincidental. One should recognize that in these calculations there is an empirically derived scaling factor²² which must be applied to the calculations in order to obtain agreement with the experimental data. This somewhat arbitrary scaling factor was obtained from a series of compounds containing only carbon, hydrogen and oxygen, by comparison of
Lahti stressed that the effect of inclusion of nitrogen and fluorine on the results of this calculation are unknown at this time. The scaling factor determined from the hydrocarbon series may be inappropriate for this heteroatom containing system resulting in large discrepancies between theoretical predictions and experiment. Thus the calculated values, must be regarded as somewhat dubious at this time.
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Chapter II: Double Dissociative Electron Capture; A Novel Route to Matrix Isolated Biradicals.
As previously described, the technique of Matrix Isolation Spectroscopy (MIS) has proven to be invaluable in rendering stability to ordinarily highly reactive molecules. Due to the long lifetime of "reactive intermediates" produced under matrix isolation conditions, they may be conveniently studied using the standard tools of spectroscopy. Obviously, in order to apply the MIS technique one requires a route which will efficiently produce the desired molecule under the conditions of the MIS experiment. One of the more common means of generating the desired "matrix isolated" reactive molecule is through the photolysis of a suitable precursor which produces the molecule of interest directly in the matrix. In this manner, the experimentalist has essentially a "switch" for initiating the production of the desired matrix isolated molecule simply by commencing photolysis of the sample. One of the major limitations of MIS spectroscopy as applied to date has been the paucity of chemical precursors which can be used to prepare the desired reactive molecule. We wished to address this problem by developing novel methodology which would hopefully represent a general route to matrix isolated biradicals.

A variety of photolabile precursors have been employed by various investigators to afford entry into a number of interesting systems. Specifically, the era of MIS spectroscopy of biradicals began in 1966 when
Dowd,\textsuperscript{1} reported the first spectroscopic detection of the 1,3-biradical, trimethylenemethane 2, using the MIS technique. The key step in Dowd's preparation of the biradical was the photolysis of a rigid low temperature glass containing the 4-methylene-pyrazoline 46, which had been prepared in one step by the reaction of diazomethane with allene. Extended photolysis led to the photo-extrusion of nitrogen, forming the trimethylenemethane biradical 2, which was characterized by electron paramagnetic resonance spectroscopy (Scheme 22).

Later, Dowd demonstrated that photolysis of 3-methylene cyclobutanone 47 also produced the same 4 line EPR spectrum which he had attributed to the trimethylenemethane biradical. This latter route was conceptually identical with the pyrazoline pathway, in that both molecules represent
precursors which in effect link the termini of the biradical with a fragment (either N₂ or CO), which could be photochemically removed to generate the desired biradical. A similar strategy has subsequently been reported by Closs² to generate the matrix isolated 1,3-cyclopentanediyl 49, which represents the first reported spectroscopic characterization of a localized 1,3-biradical (Scheme 23).

The parent o-quinodimethane, o-xylene 6, can also be generated by the use of this photochemical extrusion strategy.³

\[
\text{hv; 5.5 K cyclohexane} \xrightarrow{-N_2} \begin{array}{c}
\text{N} \\
\text{N}
\end{array} \quad \text{ID/hcl = 0.084 cm}^{-1} \\
\text{IE/hcl = 0.002 cm}^{-1}
\]

\[
\text{hv; 77 K; EPA Glass} \xrightarrow{-N_2} \begin{array}{c}
\text{N} \\
\text{N}
\end{array} \quad \text{6}
\]

Scheme 23

These examples should by no means be considered to be an exhaustive list, but rather a representative sampling of a commonly employed photochemical strategy which has led to the production of numerous interesting matrix isolated biradicals.

These traditional precursors possess several disadvantages. Many of
the precursor molecules themselves are difficult to handle due to their lack of thermal stability. For instance, consider Michl's precursor to o-xylylene, the 1,4-dihydrophthalazine 50; upon warming above -40 C 50 rapidly decomposed, resulting in the formation of o-xylylene dimers. Thus this compound had to be purified by column chromatography at -80 C. Furthermore, many of the requisite precursors to a desirable biradical require a complex synthesis, for example consider Berson's route to the m-xylylene precursors. A further limitation of the conventional precursors to matrix isolated biradicals is illustrated nicely by considering the m-xylylene biradical, the non-Kekule molecule which was the focal point of chapter one. Unlike the corresponding o-xylylene, a precursor which will generate the m-xylylene biradical via a simple photo-extrusion reaction has not yet been prepared. Hence, Berson, Platz and Migirdicyan all reported rather ingenious routes to the synthesis of this species. The reader should note that more conventional precursors to m-xylylene have not escaped scrutiny, for instance, Wright noted that the peroxide 51 and cyclophane 15 failed to produce detectible signals due to a biradical upon photolysis. In addition, attempts to prepare 52 and 53 (which may represent photochemical precursors to m-xylylene) by intramolecular cyclization strategies led only to polymerization.
The examples cited represent systems where the technical difficulties associated with the preparation and purification of the desired precursors have been surmounted. In other examples, which represent the most challenging cases from an experimentalists point of view, no suitable precursor has yet been prepared for many interesting systems. For example, this problem is described by Platz in "Diradicals" where the predictions of simple PMO theory for a variety of biradicals in the naphthalene system are considered. Platz notes "Simple PMO theory thus predicts that the 1,3-, 1,6-, 1,8-, and 2,7-naphthaquinodimethanes should be ground state triplets. Sadly enough, the simplicity of this method (PMO
theory) vastly outstrips our ability to verify its conclusions experimentally. Of
these NQM's, only the ground state multiplicity of the 1,8-NQM is known...."
The lack of spectroscopic data on these naphthaquinodimethanes results
from the fact that there simply are no known precursors which would be
suitable for the preparation of these species, neither in matrices, nor in
solution. Thus, clearly there is considerable need for alternative
approaches to the generation of matrix isolated biradicals.

Any newly developed methodology would address at least some of the
problems of conventional precursors described above. Ideally, the
precursors would be stable, readily prepared compounds, and any reagents
involved in the process should be commercially available at reasonable
cost, or easily synthesized. Ideally, the methodology would lead to the
desired biradical without the formation of significant amounts of deleterious
side products, which may complicate spectral analysis. The new
methodology should be experimentally convenient as well. Finally, the
method would be most significant if it were applicable to the generation of
biradicals which have been inaccessible by the more conventional routes
applied to date.

The paucity of precursors for the preparation of matrix isolated biradicals
has been recognized by other workers in the field as well. Michl has
addressed this problem by developing a procedure\textsuperscript{8} which was successful
in forming several matrix isolated biradicals via the gas-phase
dehalogenation of the corresponding organic dihalides. In this technique
the organic dihalides were subjected to alkali metal vapors, which had been
excited by the use of either microwave or ultrasound energy. The reactive
molecules formed by the gas phase dehalogenation were then condensed
onto a cold window along with excess solid argon, where they could be characterized by optical spectroscopy. Using this technique, Michl was able to prepare the matrix isolated parent ortho-, and para-xylylenes, the highly strained anti-Bredt olefin 1-adamantene, as well as benzocyclobutadiene. Michl's method, was clearly successful for the preparation of a variety of interesting systems. It is of note however, that Michl explicitly reports the failure of this method to produce simple alkyl biradicals of the trimethylene and tetramethylene series, as well as the failure to detect any species consistent with the structure of the meta-xyylene biradical. Nevertheless, the use of dihalides seemed attractive to us, since these precursors, if they could be converted to biradicals in matrices, would meet many of the criteria delineated above for a desirable precursor. They are generally stable compounds which are easily prepared. In fact, many dihalides, which would represent precursors to interesting systems, are commercially available compounds. Specifically, the 1,n-dihaloalkanes (n = 3,4,5,6 or 7) and α,α'-dihalo-xylenes can be purchased at reasonable cost. Thus we wished to design a strategy employing these dihalides as precursors to produce matrix isolated biradicals.

There is considerable literature precedence for the preparation of matrix isolated monoradicals through the use of a process known as Associative Electron Capture (DEC). In this reaction, transfer of an electron to a suitable acceptor, for instance an alkyl halide, results in the fragmentation of the molecule to a halide ion and the corresponding organic radical. For example Gallivan and Hamill have demonstrated that matrix isolated benzyl radicals could be formed by the application of ionizing radiation to non-polar hydrocarbon matrices containing benzyl halides. These workers
have reported the detection of broad charge transfer bands associated with the interaction of the halide ion with the neighboring benzyl radical, when benzyl iodides were used as precursors. The detection of the charge transfer bands due to the halide ion supports the dissociative electron capture interpretation, which predicts the formation of a neutral free radical plus a neighboring halide ion following electron transfer to the benzyl iodide. Yoshida\textsuperscript{12} has reproduced these results and confirmed the nature of the interaction as charge transfer. When polar matrices were utilized, the broad unstructured charge transfer bands due to the interaction of the radical with an iodide ion were not present, only the spectra of the "free" benzyl radical could be observed spectroscopically. The authors attributed this to the solvation of the halide ion by neighboring polar solvent molecules. Also, no charge transfer band could be observed in non-polar matrices when benzyl chlorides or bromides were used as the precursor, which the authors attributed to escape of the smaller chloride and bromide ions from the benzyl radical upon dissociation. Nearly identical results were observed with the parent diphenylmethyl radical,\textsuperscript{13} and explained once again in terms of the charge transfer interaction of the resultant halide ion with the neighboring radical. This provides support that the nature of this reaction is in fact dissociative electron capture. Clearly, DEC methodology is well preceded for the preparation of matrix isolated radicals.

DEC methodology has also been utilized by Meisel\textsuperscript{14} to prepare a series of arylmethyl radicals including diphenylmethyl (54) and triphenylmethyl radicals (55) in fluid solution at ambient temperature. In this work, exposure of dilute solutions of diphenylmethyl chloride (56) or diphenylmethanol to a 40 ns. pulse of electrons, accelerated to 15 MeV with
a linear accelerator (LINAC), produced the corresponding diphenylmethyl radicals 54, which were readily detected by optical spectroscopy. Once again, the production of the diarylmethyl radicals was proposed to result from a DEC process (Scheme 24).

![Scheme 24]

In a conceptually similar manner, Lappert\textsuperscript{15} made use of the exceptional reducing power of the electron rich olefin tetrakis(dimethylamino)-ethylene (57) to prepare several metal centered radicals in solution. This olefin is known to have an ionization potential of approximately 6 eV, exceedingly low for an organic compound.\textsuperscript{16} Photolysis of hexane solutions of this olefin with Group IV halides (Scheme 25) led to the production of Group IV centered radicals which were identified on the basis of their EPR spectra.
This method is conceptually identical to the dissociative electron capture experiments described above, however the source of electrons is now an electron rich organic compound rather than a beam of electrons from a LINAC. Experimentally, such methodology is of course much more convenient since the electron accelerator has in effect been replaced by a commercially available chemical source of electrons which can be trapped by suitable halides.

Despite the variety of experiments which have utilized this dissociative electron capture methodology to produce radicals, both in matrices and in fluid solution, prior to this work, DEC had not been successfully applied to the production of biradicals, in solution or matrices. We reasoned that DEC might provide an efficient, generally applicable entry into matrix isolated biradicals. This concept is illustrated below with a specific reaction scheme, which was designed to produce matrix isolated \textit{m}-xylene (Scheme 26) from the dihalo precursor 36.
This reaction can be thought of most simply as a *double* dissociative electron capture, similar to the examples provided above for the preparation of monoradicals. One can consider the transformation illustrated in Scheme 26 to be the prototype for our DEC route to matrix isolated biradicals. Our efforts have been aimed at determining the viability of this reaction, and the possibility of its extension into other systems.
Results and Discussion

One of the initial technical problems which needed to be resolved, dealt with the exact nature of the electron source which we were to apply. Initial experiments were conducted using the 3 MeV electron beam of the OSU LINAC facility to irradiate matrices containing the dihalide substrate. For example, exposure of 2-methyltetrahydrofuran matrices containing the commercially available dihalide α,α'-dichloro-m-xylene 36 (4.0 x 10^-4 M) to an electron beam at 77K produced a deep purple colored matrix; this color persisted for at least several hours at 77K. Examination of the matrix by fluorescence spectroscopy revealed the presence of a newly formed emitting species, which was not present in matrices prior to the radiolysis. The λ_max in the excitation spectrum of this species was centered at 295 nm. Excitation into this UV band gave rise to a highly structured emission in the visible region of the spectrum (λ 0.0 440 nm) (Figure 16). The species giving rise to the emission was demonstrated to be unstable in fluid solution at room temperature, as warming the sample to ambient temperature with subsequent recooling to 77 K, led to the disappearance of this emission band. Based on the agreement of the spectrum produced in this radiolysis experiment with the fluorescence spectrum of m-xylylene reported by Migirdicyan,6 it was concluded that the species giving rise to the emission at 77 K was in fact the desired m-xylylene biradical. The most reasonable explanation for the biradical formation is, in our minds, double dissociative
electron capture of the dihalide precursor 36, leading to the expulsion of two chloride ions and the formation of the matrix isolated biradical 1. It is interesting to note that the spectrum obtained in this experiment was much cleaner (i.e., free from monoradical impurities), as evidenced by emission spectroscopy, than that produced from 254 nm photolysis of polycrystalline matrices containing the hydrocarbon m-xylene (Figure 16).
Figure 16. Fluorescence emission spectrum of \textit{m}-xylene 1. a. Spectrum produced by 254 nm photolysis of \textit{m}-xylene (1.0 x 10^{-3} M) in ethanol at 77 K. b. Spectrum produced by exposure of \textit{\alpha,\alpha'}-dichloro-\textit{m}-xylene (4.0 x 10^{-4} M) in 2-methyltetrahydrofuran (77 K) to 3 MeV \textit{\beta}-particles (\textit{\lambda}_{\text{excitation}} throughout was 295 nm).
An attempt to obtain an EPR spectrum of $m$-xylylene from this sample proved to be unsuccessful. A very large broad signal (~350 Gauss in width) presumably due to a matrix derived paramagnetic species (2-methyltetrahydrofuran radical cation?) obscured the region of the spectrum which is characteristic for the $\Delta m = 1$ transition of the $m$-xylylene biradical. A weak transition at ~1600 G, characteristic of a triplet species, which corresponds to a quantum mechanically forbidden $\Delta m = 2$ transition, can sometimes be observed for biradicals under these conditions. This region of the spectrum was free from interference due to solvent derived radicals, nevertheless no $\Delta m = 2$ transition could be observed for $m$-xylylene from this sample. The inability to detect this spectral feature for $m$-xylylene is not unexpected, as it has not yet been observed for this biradical, regardless of the manner in which the $m$-xylylene was prepared. The inability to detect this transition is a common occurrence for triplet states with low $D$ values.4,5 Although the dissociative electron capture protocol produced matrices in which the biradical could be detected only by the sensitive technique of fluorescence spectroscopy, direct photolysis (254 nm; 77K) of matrices containing the dichloride 36 produced the $m$-xylylene biradical 1 which could be detected both by its fluorescence as well as its EPR spectra (Figure 17).
Figure 17. a. The fluorescence emission spectrum of \textit{m}-xylylene 1 produced by 254 nm photolysis of \(\alpha,\alpha^\prime\)-dichloro-\textit{m}-xylene 36 in ethanol at 77 K (\(\lambda_{\text{excitation}} = 295\) nm). b. The EPR spectrum of \textit{m}-xylylene 1 produced by photolysis (Hg lamp unfiltered) of dihalide 36 in ethanol at 77 K.
In this experiment, both the EPR as well as the fluorescence spectrum of m-xylylene were observed. Prior to this work, the EPR and fluorescence spectra of m-xylylene were obtained using different precursors. Recall, photolysis of matrices containing the hydrocarbon m-xylene produced the species detected by fluorescence spectroscopy,\(^6\) while the carbenic route developed by Platz\(^5\) was used to obtain the first EPR spectrum of the ground state triplet species which was assigned to the m-xylylene biradical. It is noteworthy that spectroscopic examination of matrices containing dihalide 36, following brief photolysis, revealed both the EPR and fluorescence spectra of m-xylylene. The ability to detect both spectra from a common sample strengthens each of these previous spectral assignments. Positive results were also realized upon 254 nm photolysis of cryogenic (77K) ethanolic matrices containing the o-chloromethyl compound 58 (Scheme 27) which yields the fluorescence spectrum of o-xylylene 6.

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{hv 254 nm} & \quad \text{hv 254 nm} \\
\text{77 K, EtOH} & \quad \text{77 K, EtOH} \\
36 & \quad 58 \\
\rightarrow & \quad \rightarrow \\
\text{Cl} & \quad \text{Cl} \\
\text{hv 254 nm} & \quad \text{hv 254 nm} \\
\text{77 K, EtOH} & \quad \text{77 K, EtOH} \\
1 & \quad 6 \\
+ 2 \text{Cl}^* & + 2 \text{Cl}^* \\
\end{align*}
\]

\textbf{Scheme 27}
Further radiolysis experiments were performed in which degassed 2-methyltetrahydrofuran matrices containing the commercially available dihalide precursor 2-chloromethyl-3-chloro-prop-1-ene (59) (3.8 x 10^{-4} M) were subjected to β-radiolysis using the linear accelerator. The larger D value of this biradical in comparison with m-xyylene manifests itself as a larger spectral envelope in the EPR spectrum. We had hoped that this would allow the observation of at least the outer portion of the spectrum due to the trimethylenemethane biradical 2, despite the broad interfering species which had totally obscured the EPR spectrum of the biradical in the m-xyylene system. Unfortunately no evidence for the trimethylenemethane biradical could be observed in this case. The only species detectable, other than the strong broad band at ~3200 Gauss, was a hydrogen atom, which is observed as two sharp bands symmetrically disposed about the central free radical region. The very large splitting of these two bands (~510 Gauss) indicates unmistakably that they are due to matrix isolated hydrogen atoms, whose nuclear coupling constant (a_H) is 510 Gauss.\(^{17}\) These hydrogen atoms presumably result from the decomposition of the 2-methyltetrahydrofuran radical cation (61), which had been formed by the ejection of an electron from the matrix material, following bombardment with the high energy electron beam at at 77 K (Scheme 28).

Two separate LINAC experiments indicate that although useful for producing matrix isolated biradicals which are to be detected by fluorescence spectroscopy, the LINAC procedure is not well suited to the production of biradicals to be detected by EPR. This is either due to the production of interfering paramagnetic species from the matrix material, the inability to form sufficient concentrations of the desired biradicals, or most
likely a combination of both of these problems.

\[
\begin{align*}
\text{CH}_3 & \quad \text{e}^- \quad (3 \text{ MeV}) \quad \text{CH} \quad + \quad 2\text{e}^- \\
\begin{array}{c}
\text{CH} \\
\text{O} \\
\text{CH}_3
\end{array} & \rightarrow \\
\begin{array}{c}
\text{CH} \\
\text{O} \\
\text{CH}_3
\end{array} & \quad + \\
\begin{array}{c}
\text{H} \\
\end{array}
\end{align*}
\]

Scheme 28

Based on Lappert's solution phase work,\textsuperscript{15} in which several metal centered radicals were produced by dissociative electron capture using the electron rich olefin tetrakis(dimethylamino)-ethylene 57, we reasoned that this olefin may also serve as a useful electron donor to produce matrix isolated biradicals. Photolysis (unfiltered Hg arc lamp; 77K) of degassed methylcyclohexane matrices containing olefin 57 (1.0 x 10\textsuperscript{-1} M) along with dichloride 59 (1.8 x 10\textsuperscript{-3} M) at 77K (Scheme 29) produced the EPR spectrum shown in Figure 18.
This spectrum, although weak, is reproducible and exhibits the spectral splitting consistent with a triplet biradical having the zero field parameters $|D/h\chi| = 0.025 \text{ cm}^{-1}$; $|E/h\chi| = 0 \text{ cm}^{-1}$, identical with those observed for trimethylenemethane by Dowd, when produced from the pyrazoline precursor 46 (Scheme 22). In this case the formally "forbidden" $\Delta m = 2$ half field transition is readily observed following irradiation. Attempts were made to optimize the EPR signal of biradical 2 by varying both the matrix material and the concentration of the dihalide precursor 59 in the matrix. The use of ethanol as the matrix material, instead of methylcyclohexane, led to an instantaneous thermal reaction, (evidenced by the formation of an orange colored solution) following addition of the donor olefin 57 to ethanol solutions. The reaction was independent of the substrate employed, in fact it was observed even in the absence of substrate, and apparently involves a thermal reaction between the olefin and the ethanol solvent itself. Alkane matrices are preferable, as this undesirable reaction was not observed upon syringing the olefin into alkane solutions of the dihalides. Variation of the dihalide concentration proved to be more successful in producing improved...
Figure 18. Epr Spectrum of trimethylenemethane biradical 2. a. Spectrum produced following broadband photolysis of a methylcyclohexane matrix (77K) containing olefin 57 (1.0 x 10^{-1} M) and dihalide 59 (1.8 x 10^{-3} M). b. Identical with a except concentration of dihalide 59 was increased to 1.8 x 10^{-2} M.
EPR signals of the trimethylenemethane biradical. Methylcyclohexane matrices were prepared having a dichloride concentration in the range of $1.8 \times 10^{-4} \text{ M} - 1.8 \times 10^{-2} \text{ M}$ with the olefin concentration being held constant at 0.1 M throughout. Clearly significantly increased signal/noise ratios were achieved with increased dihalide concentration (Figure 18). Using the optimum conditions derived from the trimethylenemethane system, an attempt was made to prepare the non-Kekule biradical 1,8-naphthaquinodimethane 63, using the dibromide 64 as precursor. Brief photolysis of matrices containing 64 ($1.7 \times 10^{-2} \text{ M}$) and the electron rich olefin 57 (0.1 M) (Scheme 30) gave rise to the EPR signal of a randomly oriented triplet biradical which showed spectral splitting consistent with that of the biradical produced from photolysis of Carpino's azo compound.¹⁸

![Scheme 30](image-url)
Once again the $\Delta m = 2$ transition as well as the spectral envelope due to the dipolar splitting in the $\Delta m = 1$ region are readily observed (Figure 19).

![EPR Spectrum](image)

**Figure 19.** EPR Spectrum of the 1,8-naphthaquinodimethane biradical 63. Spectrum produced following broadband photolysis of a methylcyclohexane matrix (77K) containing olefin 57 ($1.0 \times 10^{-1}$ M) and dihalide 64 ($1.7 \times 10^{-2}$ M).

Similarly photolysis under the standard electron transfer conditions as delineated above, produced diphenylcarbene (66), which was detected by EPR spectroscopy, when the geminal dichloride dichlorodiphenylmethane (65) was selected as the precursor (Scheme 30). For this carbene, the signal was much weaker than those observed with the other biradicals.
produced. It should be noted that appropriate control experiments show that photolysis of dihalides 59, 64 and 65 under identical conditions but in the absence of the electron donating olefin 57, do not form detectable yields of the corresponding biradicals, as determined by EPR spectroscopy. However, using the more sensitive technique of fluorescence spectroscopy, photolysis of the geminal dihalide 65 even in the absence of 57 gives rise to diphenylcarbene. This unusual photolysis reaction was subsequently investigated in detail; the results of this study are reported in the following chapter.

The photolysis of matrices (methylcyclohexane at 77 K) containing olefin 57 alone, results in the formation of a paramagnetic species, which gives rise to a fairly broad peak in the EPR spectrum (~3100-3300 G). Fortunately, in the biradicals discussed above, the dipolar interaction between the two unpaired electrons (which is usually expressed as a "D" value having units of energy in cm$^{-1}$) is large enough so that the resulting spectral envelope is several hundred gauss in width, allowing the spectral detection of the triplet biradical despite the interfering doublet species. In contrast, photolysis of olefin 57 in the presence of $\alpha,\alpha'$-dichloro-$m$-xylene 36 (the dihalide precursor to $m$-xylene) demonstrates the limitations of this methodology. In this case, the so called $z$ transitions, which are the outermost lines in the EPR spectral envelope, are barely discernible due to the broad doublet peak at 3200 G. Clearly, any species with a $D$ value on the order of 0.01 cm$^{-1}$ or less, will not be definitively detected using the electron transfer methodology, as it is currently employed. However, in defense of our method, species with small $D$ values are notoriously difficult to assign by EPR spectroscopy, regardless of the method of production
utilized. Solvent derived radical pairs\textsuperscript{19} often give rise to triplet EPR spectra having a $\Delta D/hc\ell$ Value on the order of 0.008 cm\textsuperscript{-1}, and photoysis of matrix isolated diazo compounds\textsuperscript{20} can give rise to species which have a $\Delta D/hc\ell$ value nearly identical with that of the triplet biradical $m$-xylene (0.011 cm\textsuperscript{-1}). Thus definitive assignment of an EPR signal with a small spectral splitting is difficult in any event. Olefin 57 proved not to be amenable to the production of biradicals which are to be detected by fluorescence spectroscopy, as its own strong fluorescence emission ($\lambda_{\text{max}} = 486$ nm)\textsuperscript{21} was the only luminescence which could be detected from the matrix which had given rise to EPR spectrum of $m$-xylene described above. This olefin will be problematic for optical spectroscopic experiments as it absorbs strongly below 350 nm (Figure 20).\textsuperscript{22}

![Figure 20. Absorption spectrum of tetrakis(dimethylamino)-ethylene 57 (9.0 x 10\textsuperscript{-5} M) in methylcyclohexane. ($\varepsilon_{249} = 1.4 \times 10^3$ M\textsuperscript{-1} cm\textsuperscript{-1}; $\varepsilon_{308} = 5.0 \times 10^3$ M\textsuperscript{-1} cm\textsuperscript{-1}; $\varepsilon_{337} = 1.6 \times 10^3$ M\textsuperscript{-1} cm\textsuperscript{-1}; $\varepsilon_{366} = 7.3 \times 10^2$ M\textsuperscript{-1} cm\textsuperscript{-1}.)]
Attempts to employ this DEC method for the production and spectroscopic detection of the simple polymethylene biradicals 68 shown below (Scheme 31) were unsuccessful.

\[
\begin{align*}
XCH_2(CH_2)_nCH_2X + & \quad \text{Me}_2N \quad \text{NMe}_2 \quad \xrightarrow{\text{hv (Hg lamp)}} \quad \text{CH}_2(CH_2)_nCH_2^* + 57^*(\text{Cl}_2) \\
n = 1, 2, 3 \text{ or } 4 & \quad X = \text{halogen}
\end{align*}
\]

Scheme 31

Even at 10 K, no evidence for a triplet biradical could be detected when olefin 57 was photolyzed in alkane matrices containing the corresponding dichlorides (67). The only observable peak in the EPR spectrum was a broad signal due to the doublet species which is produced by photolysis of tetrakis(dimethylamino)-ethylene alone under these conditions.

The failure to detect EPR signals diagnostic of a triplet species for any of the simple open chain polymethylene biradicals, could be rationalized in any number of ways. Although the electron transfer methodology was demonstrated originally at 77 K, we have demonstrated its utility for the preparation of trimethylenemethane at 10 K, thus the trivial question of temperature effects on the biradical producing reaction can be eliminated. The methodology, however, has not yet been demonstrated to be successful
for the preparation of localized biradicals, as all of the biradicals generated to date involve molecules in which the unpaired spin density can be delocalized over several atoms. The methodology may prove to be ineffective in preparing localized biradicals. Also, bear in mind that the ground state multiplicity of the localized polymethylene biradicals described above, remains as yet undetermined. Thus, the inability to detect them by EPR is not a conclusive answer as to whether such species can be formed using our methodology.

In an extension of the double dissociative electron capture methodology detailed above, Berson has demonstrated the applicability of the DEC procedure to an interesting heteroatom containing biradicaloid species (Scheme 32).
Berson²³ used the DEC strategy developed in our laboratory, to prepare matrix isolated 3,4-dimethylenethiophene (69), a non-Kekule molecule which is believed to have a singlet electronic configuration in the ground state. The spectra recorded for the biradicaloid (69) produced from the photolysis of tetrakis(dimethylamino)-ethylene in matrices containing 3,4-bis(chloromethyl)thiophene (70) were identical to those recorded when diazene precursor (71) was employed.²⁴ Furthermore, dihalide 70, proved to be much easier to handle than the thermally unstable diazine 71 (above -10 °C, 71 decomposes rapidly).

We first considered the possibility of a triradical such as 72 shortly after observing that direct photolysis of frozen solutions of dihalide 36 led to the formation of matrix isolated m-xylene. No experimental reports have appeared regarding this species, although the possibility of its existence has been considered in at least one theoretical report.²⁵ We reasoned that a triradical could be formed via the exhaustive photolysis of matrices containing 73. Toward this goal we prepared the tribromide shown below in Scheme 33, with the hope that it could be photolyzed to form 72.
The tribromide 73 has been previously prepared by an NBS bromination route, 26 which we followed without modification. Surprisingly, photolysis (254 nm at 77 K) of ethanolic matrices containing the tribromide 73 (2.3 x 10^{-2} M) produced no emission which could be detected by fluorescence spectroscopy. Even when the excitation wavelength was selected so as to correspond to the absorption maximum for the substituted benzyl radical 74.
or a m-xylylene type biradical like 75, emission could not be observed. Apparently carbon-halogen bond cleavage was not occurring in this system, although the possibility that each of these bromine containing radicals, as well as the triradical, were produced but non-fluorescent could not be ruled out at this time. Thus, we chose to investigate the matrix photochemistry of the dibromide 39, which should, in analogy to the dichloride 36 give a mixture of the m-xylylene biradical 1 and the m-methylbenzyl radical 35, which have strong, well characterized fluorescence spectra (Scheme 34).

Scheme 34

Consistent with the photochemistry of the tribromide, photolysis of matrices containing the dibromide 39, under conditions which produced the mixture of radicals from the dichloride precursor, led to no detectable yield of matrix isolated monoradicals or biradicals (1 or 35). Clearly, the matrix isolated radicals were simply not formed upon photolysis of the matrix isolated dibromides, although the reason remains unknown. Our failure to detect the biradical from the dibromide convinced us that our efforts to produce a matrix isolated triradical by photolysis of the tribromide 73 were futile. With this in
mind, the corresponding trichloride 1,3,5-trichloromethylbenzene 76 was prepared using the procedure of Cochrane\textsuperscript{27} which has been slightly modified, as described below (Scheme 35).

![Chemical formula of 77](image)

\[ \text{77} \xrightarrow{\text{CH}_3\text{OH, }\text{H}_2\text{SO}_4 \text{(cat)}} \text{78 (81% yield)} \]

Scheme 35

The initial esterification and reduction proceeded smoothly as described in the literature to produce the triol 79. In our hands, the final transformation of this sequence was carried out more successfully when triol 79 was converted to the desired trichloride 76 simply via stirring the triol at ambient temperature with concentrated HCL rather than through the thionyl
chloride/pyridine procedure as described by Cochrane. In any event, photolysis of the trichloride ( $8.0 \times 10^{-3}$ M) in ethanol at 77 K gave the emission spectrum characteristic of the mesitylyl biradicals along with a disubstituted benzyl radical (Figure 21). No evidence for the photochemical formation of a novel emitting species could be detected in the matrix.

Ambient temperature laser induced fluorescence experiments, which led to the detection of the $m$-xylylene biradical in fluid solution, were now applied to this triradical problem. Since, in this LIF experiment, the bromides were actually slightly better than the chlorides as precursors (based on fluorescence signal intensities in identical solutions of the dibromide vs the dichloride) to the $m$-xylylene type biradicals, a methyl cyclohexane solution of the tribromide 73 was prepared and subjected to LIF investigation. The ambient temperature emission spectrum recorded from this tribromide precursor 73, is very similar to the emission spectrum produced in the matrix isolation experiments from the trichloride 76 (Figure 21). Note, the apparent difference between the photochemistry of the arylmethyl bromides and chlorides appears to be matrix dependent, as solution photolysis of both precursors gave very similar results. A possible explanation is that photolysis of the arylmethyl halide leads to photochemical cleavage of the carbon-halogen bond regardless of precursor, in solution the nascent halogen atom quickly diffuses out of the initially formed radical pair cage to form the free radical. In the matrix however, the bromine atom behaves very differently from the chlorine. The reaction of the chlorine atom with the matrix by hydrogen atom abstraction is highly exothermic ($\Delta H_{\text{abs}} = -10$ Kcal.mole) and proceeds rapidly even at 77 K.
Figure 21. a. LIF emission spectrum produced following 249 nm laser photolysis of a 3-methylpentane solution of 1,3,5-tribromomethylbenzene at ambient temperature. b. Fluorescence emission produced following 254 nm photolysis of matrix isolated 1,3,5-trichloromethylbenzene ($\lambda_{exc} = 295$ nm).
In contrast, the reaction of the bromine atom with the matrix is endothermic by ~5 Kcal/mole, and would be expected to proceed much more slowly, if at all, at these temperatures. Thus recombination of the bromine atom with the benzyl type radical may be the major reaction channel of the bromine atom. This of course simply reforms the precursor in the matrix (Scheme 36).

Despite our failures to prepare a matrix isolated mesitylene derived triradical by photolysis of trihalides, we reasoned that the electron transfer methodology, as applied to the preparation of the parent m-xyylene
biradical may be useful in approaching the mesitylene triradical 72.

Preparation of a dilute 2-methyltetrahydrofuran solution of each of the trihalide precursors 73, and 76, and subsequent exposure to $\beta$-radiation at 77 K led to the now familiar purple colored matrices (Scheme 37). Examination of these matrices by fluorescence spectroscopy revealed the emission spectrum shown in Figure 22.

Scheme 37
Figure 22 a. Fluorescence emission spectrum produced following β-radiolysis of 1,3,5-trichloromethylbenzene 76 (1.0 x 10^{-3}M) in 2-methyltetrahydrofuran. b. same as a except precursor was 1,3,5-tribromomethylbenzene 73 (λ_{excitation} throughout was 295 nm).
In the spectra produced via radiolysis of the trihalides 73 and 76 (Figure 22) emission bands due to both the dihalomethyl substituted benzyl radical (74 or 80) (485 nm) and the halomethyl substituted biradicals (75 or 81) (458 nm) are present, although weak, in both cases, and their agreement with Migirdicyan's original assignment of the hydrocarbon radicals is reasonable. Presumably, the substitution of the halomethyl group for the methyl group of mesitylene has only a modest effect on the energy of the triplet-triplet fluorescence emission. Most interesting however is the small emission band centered at ~425 nm. This band, which is present in both of the trihalide samples following β radiolysis, is clearly absent when the dihalide precursor α,α'-dichloro-\textit{m}-xylene 36 was used as the precursor. This eliminates the possibility that the emission is due to a substrate independent process, and demonstrates the necessity of the third chloromethyl group to give rise to this emission. When identical matrices containing the trihalides are instead photolyzed with 254 nm light, no evidence for this emission band to the blue of the biradical can be seen.

Admittedly, the assignment of this weak band as being due to a triradical 72 is somewhat tenuous, especially in light of the fact that no chemical evidence for the existence of this species can be detected. Nevertheless the temptation remains to make an assignment, primarily due to the fact that the same band can be produced from two independent precursors. It is significant that these two precursors themselves were prepared by routes which do not involve common intermediates, thus an impurity common to both samples appears to be unlikely.

Our interest in biradicals in the naphthalene system was previously mentioned. Efforts were made to obtain the fluorescence emission spectrum
of the 1,8-napthaquinodimethane biradical 63 using the LIF experiment which was successful in the \textit{m}-xyylene system. Laser (249 nm) photolysis of a 3-methylpentane solution of dibromide 64, led to the emission spectrum shown in figure 23. Based on its similarities to the parent unsubstituted 1-naphthylmethyl radical\textsuperscript{28} the spectrum is assigned as being due to the 8-bromomethyl-1-naphthylmethyl radical. At first thought it appears that the double carbon-halogen bond cleavage photochemistry associated with the halogenated xylylenes does not occur in the corresponding dihalogenated naphthalene system.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure23.png}
\caption{Room temperature laser induced fluorescence (LIF spectrum produced from dibromide 64. Spectrum recorded in 3-methylpentane solution having an optical density of the dibromide of 1.4 at 249 nm.} 
\end{figure}
A possible explanation for this difference, which admittedly is no more than a post facto rationalization, is the substantially lower triplet energy of the substituted naphthalenes compared with the methylated benzenes (Compare $E_t = 82 \text{Kcal/mole vs 60 Kcal/mole for toluene vs. 1-methylnaphthalene})$.\textsuperscript{29}

The possibility that the biradical is formed, but not fluorescent must also be considered. Platz and Wirz\textsuperscript{30} have shown that upon photolysis, the 1,8-naphthaquinodimethane biradical efficiently cyclizes to form triplet acenaphthene and it seems that this process dominates the excited triplet state chemistry of the biradical, leading to a very low quantum yield of fluorescence. The question of whether other biradicals in the naphthalene system can be prepared and detected in this manner remains unanswered.

We briefly investigated a third possible electron donor for our matrix isolation work. During our studies on the photolysis of methylated benzenes, we observed that $n$-hexane matrices containing high concentrations of $m$-xylene (0.05-0.1 M) became pink colored following brief photolysis (249 or 254 nm) at 77 K. We speculated this may be due to the photoejection of an electron from the matrix isolated $m$-xylene (Scheme 38). In an attempt to trap the putative electrons, an $n$-hexane solution containing $m$-xylene (0.1 M) and chloromethylnaphthalene (83) (0.01 M) was prepared, degassed and cooled to 77 K. Photolysis of this matrix produced no visible color, and investigation of the matrix by fluorescence spectroscopy revealed no emission due to the 1-naphthylmethyl radical $\textsuperscript{28}$
In summary, the feasibility of electron transfer reactions as a means for the generation of matrix isolated biradicals has been demonstrated. Note that the biradicals produced are of varying structure, including the parent trimethylenemethane 2, m-xylene 1, a 1,8-naphthaquinodimethane 63, and the heteroatom containing 3,4-dimethylenethiophene 69 which was generated by Berson. We feel the variety of the species generated is significant, because it indicates that this approach may be applicable to many
systems, rather than a few isolated examples. Recall, since our goals were methodological in nature, general applicability is significant. In its current state, as noted, only biradicals with fairly large D values can be prepared using our strategy if they are to be observed by EPR spectroscopy. This is due to interfering paramagnetic species which result in the procedure. The requisite precursors are generally much more easily synthesized than those required by conventional methods. Unfortunately, unequivocal results on the preparation of a mesitylene triradical could not be obtained. All factors considered, the method has met some of the goals detailed at the outset, but certainly lends itself to improvement. The power of the method is illustrated by the fact that several known systems were prepared with ease, as well as the fact that some very interesting possibilities such as the desired triradical, for which a conventional precursor is not readily envisioned, may now be opened to consideration.
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Chapter III: The Double Photodissociation of a Geminal Dichloride; Evidence for the Stepwise Formation of a Diarylcarbene
HISTORICAL

It is well appreciated that the photolysis of arylmethyl halides can produce arylmethyl radicals, both in fluid solution and in rigid organic matrices at low temperature.\(^1\) As previously mentioned, direct photolysis of either the ortho or meta isomers of \(\alpha,\alpha'\) dichlorinated xylenes, serves as an efficient entry into the xylylene biradical system. The photoreaction which was operative in that particular case was investigated and reported in detail in chapter one. We have explored the possibility of extending this type of photoreaction, which represents the photochemical homolysis of two carbon-halogen bonds, into an additional system, that of the geminal dihalide dichlorodiphenylmethane \(65\) (Scheme 40). In our minds, this precursor represents an interesting one, in that homolysis of the two geminal carbon-halogen bonds, would lead to the formation of a 1,1-biradical or carbene \(66\).

![Scheme 40]

\(\text{Scheme 40}\)
Our goal was not only to examine the possibility of developing an alternative photochemically initiated route to carbenes for matrix isolation studies, but also to discern if a stepwise double dissociative mechanism similar to that which was observed with the dihalogenated xylenes, is operative in other systems as well.

Although there have been no reports in the literature on the photolysis of dihalides to produce biradicals, it may be helpful to consider the work of Rentzepis, who has recently investigated the mechanism of photodissociation of arylmethyl halides. Specifically with the 1- and 2-halomethylnaphthalenes, Rentzepis has suggested that excitation to the $S_2(\pi-\pi^*)$ of a chloromethyl- or bromomethylnaphthalene results in energy dissipation through two distinct pathways. In the first, internal conversion produces $S_1(\pi-\pi^*)$ which relaxes to the ground state ($S_0$) by fluorescence. In the second route, intersystem crossing forms an excited triplet state which is either dissociative itself, or alternatively crosses to a dissociative triplet state. This leads to homolysis of the carbon halogen bond to generate the naphthylmethyl radical. The evidence for this mechanism rests on the following results, which were determined from laser flash photolysis experiments employing two laser beams. Excitation of a solution of 1-chloromethylnaphthalene with a 266 nm laser, produces the 1-naphthylmethyl radical 84 within 15 ps of the laser pulse. The resultant radical can be detected by optical spectroscopy, most readily by probing the nascent radical with a 355 nm "excitation pulse" and monitoring the doublet-doublet fluorescence emission of the 1-naphthylmethyl radical (84).
By monitoring the intensity of this emission as a function of the time delay introduced between the 266 nm "synthesis" pulse and the 355 nm probe or "excitation" pulse, the yield of the parent 1-naphthylmethyl radical was found to be independent of the elapsed time between the two pulses - within the time regime ranging from 0 ps up to a 40 ns delay. In establishing a mechanism for the dissociation of the photochemically excited precursor, the authors advanced the following argument. The S\(_1\) state was excluded from being the dissociative level on the basis of two facts. First, the S\(_1\) is a (\(\pi-\pi^*\)) bound state; second, its lifetime, as determined by fluorescence emission spectroscopy (\(\tau_{II} = 2400\) ps),\(^3\) is much longer than the growth lifetime observed in this work for the 1-naphthylmethyl radical 84. Also, the bond homolysis must not occur from a vibrationally excited S\(_0\) state, because repopulation of the ground state is not detected within the 15 ps lifetime observed for the dissociation of the arylmethyl halide precursor. The lowest
triplet state of the halide can also be excluded as, as its lifetime is three orders of magnitude longer than the observed growth lifetime of the naphthylmethyl radicals (15 ps). The authors state that $S_2$ can be excluded because it is an associative state. There is no evidence of fluorescence from the $S_2$ state of the 1-chloromethylradical, as no unrelaxed fluorescence can be observed.

\[ \text{hv; 266nm} \quad S_0 \rightarrow S_2(\pi, \pi^*) \rightarrow T_n(\sigma, \sigma^*) \rightarrow \text{fragments} \]

\[ \text{Scheme 42} \]

Apparently, the $S_2$ state dissipates its energy via partitioning between ISC which leads to a dissociative triplet state and internal conversion to the $S_1$ state. The authors observe similar results with the
2-halomethyl napthalenes and propose that the mechanism which they have postulated (Scheme 42) is generally applicable to other benzylic haloaromatics. Bearing in mind the goals of this project, not only are we concerned with the photochemical reactions which lead to the formation of arylmethyl free radicals, but more importantly, we are concerned with the photochemistry, if any, that these radicals subsequently undergo. The closest analogy in the literature to our proposed carbene forming reaction is the solution phase work of Meisel\textsuperscript{4} in which the photochemistry and photophysics of the parent diphenylmethyl radical and several substituted derivatives were investigated. In this work, Meisel probed a series of diphenylmethyl radicals (86-90), using dual beam laser flash photolysis experiments.

\[ \text{Ph}_2\text{CH} \quad \text{86} \quad \text{Ph}_2\text{C} \quad \text{87} \quad \text{Ph}_3\text{C} \quad \text{88} \quad \text{Ph}_2\text{CH} \quad \text{89} \quad \text{Ph}_2\text{CCH}_3 \quad \text{90} \]

In Meisel's work the first beam was a 40 ns "synthesis" pulse of $\beta$-particles or electrons (15 MeV) from a linear accelerator (LINAC), which served to dissociate a diaryl halide or diarylcarbinol precursor therefore producing the diphenylmethyl radical of interest, in solution, by dissociative electron capture. The second "excitation" pulse, a frequency doubled ruby laser
beam (347 nm; 10 ns pulse), served to promote the nascent radicals to their electronically excited state. The delay between the two pulses was fixed at 4 μs throughout this work. At a ninety degree angle to the LINAC electron beam, a Xenon arc lamp passes through the sample cell which serves as an analyzing beam, and can essentially be thought of as a single beam spectrophotometer. In this manner, exposure of solutions of the diphenylmethyl halides to the LINAC "synthesis" beam, followed by the ruby laser excitation pulse, produced the arylmethyl radicals of interest, in their first excited doublet state. In the absence of the ruby laser excitation pulse, the UV-Vis absorption spectrum of the ground state of the radical could be collected. When the absorption of the ground state of the radical was monitored in this manner, the decay of the transient radical in solution could be observed as a decrease in the Δ O. D. at 320 nm (change in the optical density of the solution at 320 nm following the LINAC pulse). In this manner, any effect of the 347 nm laser "excitation" pulse on this transient can be monitored. Through this technique, the doublet-doublet absorption spectra of the excited radicals, as well as the fluorescence emission spectra of the transient radicals in solution were recorded. Meisel found that the diphenylmethyl radicals could be grouped into two categories. The unsubstituted diphenylmethyl radical (DPM) 89 and the bridged species 10,11-dihydro-5H-dibenzo[a,d]cyclohepten-5-yl (DBHP) 90 were found to be stable to photolysis. The second laser beam produced no detectable bleaching of the radical in non-hydroxylic solvents. However, these stable radicals were found to undergo significant bleaching when excited instead in alcohol solvents. The significance of this result will be discussed
momentarily. In contrast to the results observed for 89 and 90, when radicals 86-88 were studied, significant bleaching of the ground state could be readily observed following laser photolysis of these radicals in both acetonitrile and alcohol solvents. Thus, these species were classified as photochemically active radicals by Meisel. The bleaching reaction for these three radicals occurred with a quantum yield near unity at room temperature. Based primarily on the fact that the bleaching was independent of solvent, the authors proposed a unimolecular rearrangement reaction from an electronically excited state of the radical. The authors suggested that an intramolecular cyclization to produce a substituted fluorenyl type radical (91) led to the rapid unimolecular destruction of the substituted DPM radicals (Scheme 43). The results were interpreted in terms of the degree of twist or torsion angle of the phenyl groups out of the central molecular plane, introduced by the inclusion of a substituent. Thus, increasing this twist angle by the inclusion of bulky substituents appeared to enhance the cyclization reaction which led to the bleaching. In confirmation of this idea, production of the substituted DPM radicals in matrices led to significant enhancement of the quantum yield of fluorescence, presumably due to the inhibition of this competitive intramolecular cyclization process by matrix packing forces. The introduction of substituents also introduced blue shifts in the fluorescence excitation and emission spectra, consistent with the decreasing planarity of the system with increasing bulk of the substituent.
Most relevant to our study however, was the work on the parent diphenylmethyl radical (DPM). As noted above, the authors found no evidence for photochemical destruction of the DPM radical following 347 nm excitation in acetonitrile, observing only the fluorescence emission (quantum yield ~0.3) from the first excited doublet state of the radical. In striking contrast to the results obtained in acetonitrile, when the diphenylmethyl radical was generated in hydroxylic solvents, e.g. methanol or isopropanol, evidence for bleaching of up to 55 % of the signal of the DPM radical was observed following excitation of the DPM radical with the 347 nm laser line. Meisel measured the quantum yield of fluorescence in both acetonitrile and alcohols. If the bleaching involved photochemistry from a doubly excited state with the participation of the solvent, one would expect the quantum yield (of fluorescence) to vary dramatically with solvent. Interestingly, the yield of fluorescence remained unchanged upon going from acetonitrile to methanol.
Thus, they proposed a unimolecular reaction from the excited state of the DPM radical involving the homolysis of a C-H bond to produce diphenylcarbene (Scheme 44). In non-hydroxylic media, the DPM radical was rapidly reformed, either by a hydrogen atom abstraction reaction of the resultant diarylcarbene, or recombination of the hydrogen atom-DPM radical pair. Thus no bleaching of the radical signal could be observed. In the case of alcohol solvents, the carbene underwent an O-H insertion reaction, which resulted in trapping of the carbene prior to the hydrogen atom abstraction reaction, resulting in the permanent destruction of the radical, which is detected as photobleaching of the transient signal due to the DPM radical. If in fact this hypothesis is correct, this reaction represents the photolysis of a diarylmethyl radical to a diaryl carbene, which is a novel, and in our minds, a very interesting photochemical reaction. In Meisel's work, the existence of the carbene was inferred from the data as described above. The experiments presented by Meisel are elegant, but in our minds, the argument which claims the nature of the photobleaching reaction to be dissociation to diphenylcarbene and a hydrogen atom, is rendered less than convincing since direct spectroscopic detection of the resultant diphenylcarbene was not reported. Thus we set out to explore the possibility of this and similar reactions in low temperature organic glasses, with hopes of developing further understanding of this type of photodissociation.
Note that the reaction postulated by Meisel, is a two-step reaction explicitly involving the intermediacy of the DPM radical. One might intuit that a chlorinated DPM radical like 95 may exhibit an enhanced propensity...
toward this type of carbene forming reaction, as the bond dissociation energy of the C-Cl bond is substantially lower than that of the corresponding C-H bond. Thus we wished to investigate the photochemistry of matrix isolated dichlorodiphenylmethane, the results of this study are reported herein.

\[
\text{Cl} \\
\begin{array}{c}
\text{C} \\
\text{H} \\
\text{H}
\end{array}
\text{Cl}
\]
Results and Discussion

Photolysis of dichlorodiphenylmethane (65) in rigid low temperature glasses at 77 K produces diphenylcarbene (66) which is detected by its known fluorescence spectrum.\(^5\) One can envision that the diphenylcarbene is produced in a stepwise fashion in analogy with the reaction postulated by Meisel\(^4\) for the DPM radical in solution. Alternatively, secondary photolysis of a triplet state of the dihalide may also be a reasonable pathway to produce the carbene 66.
Recognize, this mechanistic problem is very similar to that raised in Chapter I, where the photodissociation of the dichlorinated xylenes was considered. These two alternative pathways for the dichlorodiphenylmethane system are illustrated in Scheme 45.

We sought to understand the details of this novel photoreaction which produces diphenylcarbene. This project involved, in a sense, two crucial experiments. First, since the matrix fluorescence spectra of the putative diphenylchloromethyl radical 95 has not yet been reported, an assignment of the fluorescence spectrum of this species must be made, if we are to claim its intervention or lack thereof in the photolysis reaction of the geminal dichloride. Second, if such a species can be detected in the matrix, it must be demonstrated to be an intermediate in the carbene forming reaction, as its detection alone does not implicate it as such in the carbene forming reaction.

Brief photolysis (254 nm, 5 seconds) of a 0.01M solution of dichlorodiphenylmethane 65 in 2-MeTHF at 77 K produces initially only a single fluorescent species (λ_{max} emission 522 nm; λ_{max} excitation 341 nm) whose emission and excitation spectra are shown in Figure 24.
Figure 24. a. Fluorescence Emission Spectrum of the diphenylchloromethyl radical (95) produced by 254 nm photolysis of 0.01M solution of 65 in glassy 2-MeTHF at 77K. (λ excitation = 340 nm).

b. Fluorescence Excitation Spectrum of the diphenylchloromethyl radical (95) produced by 254 nm photolysis of 0.01M solution of 65 in glassy 2-MeTHF at 77K. Emission was monitored at 520, 550, or 570 nm.
This spectrum is attributed to the diphenylchloromethyl radical 95, on the basis of several pieces of evidence. First, the carrier of the spectra of Figure 24 was readily demonstrated to be a thermally unstable intermediate. Photolysis at 77 K yields the emission assigned to chlorinated radical 95, but warming the sample to room temperature and recooling to 77 K led to the disappearance of this emission. Furthermore, the spectra of Figure 24 are not present in samples which have not been irradiated. This excludes the possibility that the species detected at 77 K is a stable reaction product or a fluorescent impurity present in the starting material. Together these two experiments indicate that the fluorescent species is a molecule produced photochemically, which is unstable in fluid solution at room temperature, but persistent in rigid matrices at 77 K. In addition to this, the fluorescence excitation and emission spectra of 95 are very similar in position and appearance to those previously reported for the parent diphenylmethyl radical 4a, and the excitation maximum agrees with the position of the absorption maximum of the diphenylchloromethyl radical 6. One disturbing point remains however; the fluorescence emission maximum of Figure 24 is blue shifted relative to that observed by Fessenden 7 who reported an emission originating between 560 and 600 nm (depending on the solvent) in a laser induced fluorescence experiment. It is important to note that Fessenden's spectrum was obtained in solution and ours in a rigid glass at 77K, a difference which in itself may be responsible for the discrepancy between the two observations. A very similar phase dependent shift in fluorescence maxima is well known for aromatic carbenes 8. However, due to the large matrix shift on the fluorescence emission spectrum of 95, we
searched for an additional precursor to generate the matrix isolated chlorinated radical in order to strengthen the assignment of the emission spectrum. 

Scaiano and Horn have independently demonstrated with laser flash photolysis experiments that an electronically excited state of diphenylcarbene \((366^+\) will abstract a Cl atom from carbon tetrachloride. We therefore attempted to generate the diphenylchloromethyl radical \(95\) in polycrystalline \(\text{CCI}_4\) by photolysis of the known diphenylcarbene precursor \(10\) oxirane \((96)\) at 77K (Scheme 46). Under these conditions, an emission spectrum very similar to that of figure 24 was produced. This independent generation of the diphenylchloromethyl radical confirms our assignment of chlorinated radical \(95\) as the species responsible for the emission spectrum observed following brief photolysis of dichloride \(65\) at 77 K. The \(\lambda_{\text{max}}\) of the excitation spectrum of \(95\), when formed from either precursor is slightly blue shifted (ca. 5 nm) relative to that of the unsubstituted diphenylmethyl radical. Similar blue shifts have been reported for various alkyl and aryl substituted diphenylmethyl radicals, as discussed in the introductory section. Our assignment of the fluorescent carrier as \(95\) is consistent with this trend. Furthermore, the vibrational structure of \(95\) is similar to that reported for the series of diphenylmethyl radicals investigated by Meisel. The first observable vibrational spacing in the spectrum of \(95\) is \(1041\text{cm}^{-1}\). Similar values were reported for 86-88 \((1049\text{cm}^{-1}, 1060\text{cm}^{-1}\) and \(1020\text{cm}^{-1}\) respectively) which the authors have attributed to a C-C stretching mode.
Furthermore radical 95 is photolabile (*vide infra*), producing diphenylcarbene upon photolysis. We find it difficult to envision a structure other than that of the diphenylchloromethyl radical (95) which could be consistent with all of these observed facts.

Confident of our assignment of the emission spectrum of the diphenylchloromethyl radical 95 as the only species produced following very brief irradiation of matrices containing dichloride 65, the second point must
now be addressed. Does the reaction pathway which leads to the photochemical formation of diphenylcarbene proceed through the intermediacy of radical 95, or do the two species merely result from two independent reaction pathways in the matrix photolysis of the dihalide?

Upon exposure of a rigid glass containing 65 and 95 to 254 nm light for extended time periods, the formation of a second emitting species in the matrix becomes evident. This second species is readily identified as diarylcarbene 66, as its fluorescence excitation and emission spectra agree with those previously reported for diphenylcarbene generated from diphenyldiazomethane.\textsuperscript{5} It is interesting to note that two independent precursors, possessing very different ground state geometries at the central carbon atom, give rise to similar matrix fluorescence spectra, both of which differ markedly from the solution phase spectrum obtained at room temperature.\textsuperscript{5,8} This observation precipitated an investigation into the effects of medium and precursor geometry on the fluorescence spectroscopy of diphenylcarbene and derivatives, which will be discussed in detail in chapter 4.

If one monitors the ratio of (95/66) as a function of photolysis time, an interesting trend is observed. Clearly, the data, given in Table 4, indicate that the yield of carbene 66 relative to that of radical 95, as determined by the intensity of the fluorescence emission bands of the two species, increases with increasing irradiation time.
Table 4. Ratio of diphenylchloromethyl radical/diphenyl carbene (95/66) as a function of irradiation time.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Photolysis time (minutes)</th>
<th>95/66</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td>0.5</td>
<td>13.2</td>
</tr>
<tr>
<td>65</td>
<td>1.5</td>
<td>4.50</td>
</tr>
<tr>
<td>65</td>
<td>3.0</td>
<td>2.43</td>
</tr>
<tr>
<td>65</td>
<td>5.0</td>
<td>2.41</td>
</tr>
<tr>
<td>65</td>
<td>10.0</td>
<td>2.20</td>
</tr>
</tbody>
</table>

a. Ratio determined by measuring absolute intensities of the fluorescence emission at the maxima for 95 and 66 (522 and 474 nm) while exciting at 340 and 300 nm respectively. Ratio determined following photolysis of 65 (0.01 M) in 2-MeTHF irradiated as indicated (Rayonet RPR 2534, 5 tubes) at 77 K.

Photolysis of 65 clearly leads to photodissociative expulsion of a Cl atom and formation of monoradical 95. However, as photolysis time increases, the concentration of radical 95 increases, at which point it too can undergo secondary photolysis to form 66 by a second fragmentation similar to that observed initially with dihalide 65 (Scheme 45). According to the stepwise alternative proposed in scheme 45 the ratio of 95/66 is expected to decrease with increasing photolysis time, as the chlorinated radical 95 becomes photolytically converted to diaryl carbene 66. In our hands the ratio of 95/66 could not be decreased below the value of 2.20 shown in Table
4 for a 10 minute photolysis time. Admittedly, longer irradiation times actually led to slight increases in this ratio. This result may at first seem inconsistent with the proposed pathway leading to diphenylcarbene (66), however, under the experimental conditions, 66 is both thermally and even more rapidly photochemically destroyed. Thus as 66 accumulates in the matrix it too is photochemically destroyed. A possible pathway for decomposition of 66 is via H atom abstraction from the 2Me-THF matrix. Such processes are well documented for diaryl carbenes\(^\text{11}\), and in this case would lead to the diphenylmethyl radical which could go undetected due to its overlapping absorption and fluorescence maxima with those of chlorinated radical 95. Thus, prolonged irradiation could lead to an increase in the apparent ratio of 95/66, consistent with the proposed mechanism.

The steps proposed in scheme 45 is neither unreasonable nor unprecedented. A single 254 nm photon does not have sufficient energy to cleave both C-Cl bonds of diphenyl dichloromethane, thus some intermediate species, at an energy higher than the dichlorodiphenylmethane, must be produced and subsequently photolyzed to form the diarylcarbene. As discussed in the introduction to this section, Meisel\(^\text{4}\) has demonstrated that the diphenylmethyl radical can be photochemically consumed and postulated that the radical photolytically fragments to form the diarylcarbene 66. But recall, this hypothesis was based on indirect evidence, as the carbene was not directly detected. To our knowledge the work presented here represents the first spectroscopic observation of a triplet carbene produced by photolysis of a radical.
We have tried without success to produce triplet diphenylcarbene by photolysis of the DPM radical 89 in organic glasses at 77 K; an experiment which would be the matrix analogue to the reaction observed by Meisel in solution. Photolysis (254 nm, 77K) of 1,1-diphenylacetone(97) in 3-methylpentane at 77K produces DPM 89, which is easily detected by its fluorescence (Figure 25). Prolonged photolysis of this radical (either 254 nm rayonet or Hg arc lamp), under conditions which led to the formation of the diphenylcarbene from the dihalide precursor, did not produce any evidence for the formation of diphenylcarbene in this case. (Scheme 47)

\[
\begin{align*}
\text{Ph} & \quad \text{H} \quad \text{CH}_3 \\
\text{Ph} & \quad \text{O} \quad \text{hv, 77K} \\
\text{97} & \quad \text{hv, 77 K} \\
\text{Ph} & \quad \text{Ph} \\
\text{66} & \quad \text{hv, 77 K} \\
\text{Ph} & \quad \text{Ph} \\
\text{hv, 77 K} & \quad \text{hv, 77 K} \\
\text{Ph} & \quad \text{Ph} \\
\end{align*}
\]

**Scheme 47**

Similarly, photolysis (254 nm) of chlorodiphenylmethane (65) in a rigid 3-methylpentane matrix at 77 K, produces a new emission band with a maximum at 525 nm (Figure 25). Because of the similarity in the spectra of
95 and the DPM radical, it is not immediately clear which radical (or if a mixture of radicals) has been produced (Scheme 48). We suspect that photolysis of 65 produces the DPM radical 89 because prolonged photolysis does not produce diphenylcarbene, as it must if chlorinated radical (95) were produced.

Intuitively, preferential cleavage of a C-Cl bond in 65 might be expected because this is the weakest bond in the molecule. The failure to produce diphenylcarbene from 97 or 65 demonstrates the uniqueness of the diphenylidichloromethane system.
Figure 25. a. Fluorescence Emission Spectrum of the diphenylmethyl radical (89). a. Spectrum produced by broadband (Hg lamp; unfiltered) photolysis of 0.01M solution of 1,1-diphenylacetone in glassy methylcyclohexane at 77 K (λ excitation = 340 nm). b. Spectrum of the diphenylmethyl radical (89) produced by 254 nm photolysis of 7.0 x 10^{-3} M solution of 56 in glassy 3-methylpentane at 77K (λ excitation = 340 nm).
The data presented to this point are consistent with, but do not require, the sequential nature of the double photodissociation as described in scheme 45. The data have not indubitably excluded the possibility that 66 is simply formed concurrently with 95, but by a lower quantum yield process which does not involve the intermediacy of 95 at all.

Highly monochromatic laser radiation can selectively excite one particular component in a mixture of compounds in solution or in a matrix, excluding all others which may be present but do not absorb significantly at the laser line. The monoradical 95 has a strong absorption band centered at 341 nm and the dihalide precursor 65 does not absorb significantly in this region. Thus by using the 337 nm line of a nitrogen laser one could hope to selectively excite 95, without depositing photochemical energy into dihalide 65. The results of this experiment are shown in Figure 26, where the fluorescence emission spectrum of both 95 and 66 are shown both before and after exposure to nitrogen laser radiation.
Figure 26. a. Fluorescence Emission Spectrum of the chlorodiphenylmethyl radical (95) produced by 254 nm photolysis of 0.01M solution of 65 in glassy 2-MeTHF at 77K. Following photolysis with a 337 nm line of a nitrogen laser, the intensity of the signal due to chlorinated radical 95 is shown to decrease. (λ excitation was 340 nm). b. Fluorescence Emission Spectrum of diphenylcarbene (66) produced by 254 nm photolysis of 0.01M solution of 65 in glassy 2-MeTHF at 77K, followed by 337.1 nm nitrogen laser photolysis of 95 (λ excitation was 300 nm).
Clearly, the intensity of the signal due to the carbene 66 has increased at the expense of the radical 95 following 337 nm photolysis. One is thus compelled to conclude that monoradical 95 is indeed a photochemical precursor to 66. This represents direct evidence supporting the stepwise nature of the double photodissociation of the geminal dichloride to a monochlororadical, with subsequent photolysis of the nascent monochlorodiaryl radical to a diarylcarbene.

Note, the fluorescent state of 95 can not be the state which fragments since the energy of this state (523 nm = 54.8 kcal/mole) is less than that of a typical C-Cl bond dissociation energy.12 Thus 254 or 337 nm (112.7 and 85 kcal/mole) excitation must lead to a higher energy dissociative state of 95; internal conversion to the first excited doublet state of 95 followed by fluorescence, must compete with dissociation of the chlorinated radical from the upper excited state. Of course, the exact nature of this dissociative state is unknown. The data are consistent with a mechanism similar to that which Rentzepis2 has postulated for dissociation of carbon-halogen bonds in monohalogenated naphthalenes, although we have not rigorously demonstrated agreement between the two systems.

In summary, 254 nm photolysis of 65 at 77K yields monoradical 95, which can be further photolyzed to 66 either by continued exposure to the same 254 nm source, or more efficiently by laser radiation. This represents the first case to our knowledge where a dihalide has been photolyzed to produce the corresponding carbene, and may serve as a viable route to other matrix isolated carbenes and biradicals.
References


Chapter IV: The Effects of Phase and Temperature on the Fluorescence Spectroscopy of Diarylcarbenes
Historical

The spectroscopic detection of species containing divalent carbon (i.e. 1,1 biradicals or carbenes) has been an active area of research over the last 30 years. The seminal experiment in this field, was Herzberg's spectroscopic detection of methylene, the simplest of all alkyl carbenes. Based on the electronic spectra of methylene, as determined by gas phase flash photolysis experiments of diazomethane, the authors indicated that there were two forms of CH₂ which gave rise to two distinct spectra. Initially, a species absorbing strongly in the red and having a weak band in the near UV was detected, and assigned to the bent singlet state of methylene (<HCH ~ 102°). The second species, which appears at somewhat later times after the flash and absorbs in the vacuum UV, has been assigned to the triplet-triplet transition of methylene. Herzberg claimed the simplest interpretation of the spectrum indicated a linear geometry in both the upper and lower states of the transition for triplet methylene. However, the authors were careful to note in their original publication, that a non-linear triplet CH₂ with an H-C-H angle of approximately 140° was also consistent with the data, assuming that several sub-bands escaped observation due to predissociation.

Definitive assignment of the ground electronic state of methylene as a triplet was later provided by EPR spectroscopy. The detection of an EPR signal for methylene at 4 K in a Xe matrix proved the ground state nature of
the simplest carbene was in fact a triplet, but determination of the geometry of matrix isolated methylene, from the EPR data, was leading to considerable confusion regarding the preferred H-C-H angle of triplet methylene. Briefly, Wasserman has described how the EPR of triplet states can be considered essentially as the resonance of a free radical perturbed by the magnetic field of the second unpaired electron. The triplet spectrum is characterized by two zero field splitting parameters usually termed D and E. Both of these parameters can be extracted from an EPR spectrum of a triplet species, and are usually expressed in the energy units of cm\(^{-1}\). The D value represents the magnitude of the dipolar interaction between the two unpaired electrons along the z-axis, and is related to \(1/z^3\) where z represents the magnitude of the vector between the two unpaired spins. The E parameter is a measure of the difference in the magnitude of the dipolar interaction along the other two molecular axes x and y. For a linear carbene with two degenerate p orbitals, this E value will necessarily be zero. The deviation from linearity at the divalent carbene carbon lifts the degeneracy of the dipolar interaction along the x and y axes, resulting in a non-zero value of E. The ratio of E/D has been correlated with the bond angle at the divalent carbon for a number of carbenes. However, these results must be regarded with skepticism since in some cases unrealistically large bond angles are obtained. Based on Skell's original EPR spectrum, he assigned a nearly linear structure for the triplet state of methylene, with only a slight degree of bending of the H-C-H angle. However, Wasserman's group arrived at a very different conclusion regarding the geometry of matrix isolated triplet methylene from an analysis of the EPR zero field splitting. These authors observed what appeared to be
methylene in two different matrix sites, one essentially linear, the other slightly bent. Through experiments involving deuterium for hydrogen substitution, the authors determined that geometric differences were not the cause of the different spectra, but rather the spectrum, which they had initially considered to be a slightly bent carbene, was due to a freely rotating species having an H-C-H angle of 137 °. As further confirmation of a significantly bent structure for ground state triplet methylene, Wasserman's group studied the matrix isolated 13C enriched methylene. Recall, the coupling constant of the 13C nucleus with an unpaired electron is dependent upon hybridization at the carbon containing the free electron. If the electron is in a purely p orbital, a node exists at the nucleus and coupling between the 13C and the free electron is minimized. As the degree of s character of the orbital containing the unpaired electron is increased, the magnitude of the 13C -electron coupling constant increases as well. Hence, the magnitude of this coupling constant provides a measure of hybridization. Based on calculations correlating hybridization and geometry6, an approximate bond angle for the carbene can be obtained. Wasserman7 observed spectra for methylene which had been isotopically enriched in 13C. In the site in which the carbene was held rather loosely, as well as a second site were the molecule was apparently locked in a rather rigid environment by the matrix, the carbene had an angle of ca. 140 ° as determined by the magnitude of the coupling constant with the carbon nucleus. The authors concluded that since the carbene assumed the same angle in different matrix sites, which varied significantly in their rigidity, that the matrix must not be distorting the carbene from its preferred ground state geometry. It is gratifying that the H-C-H angle
determined from the magnitude of the $^{13}$C coupling constant is in excellent agreement with the value based on an analysis of the zero field splitting parameters. Furthermore, both of these numbers are in accord with a value predicted by theory, as well as an experimentally determined angle in the gas phase. In the original report of the spectrum of methylene, Herzberg preferred the linear geometry for this carbene, but in light of compelling EPR and theoretical evidence for the bent structure of triplet CH$_2$, he demonstrated that the data could be reinterpreted in terms of a bent geometry, and deduced excellent agreement with the geometry derived from matrix EPR work. Thus there appears to be nearly universal agreement on an H-C-H angle of $\sim 137^\circ$ for methylene.

The current situation in the literature regarding the geometry of diphenyl carbene is highly reminiscent of the early confusion surrounding the geometry of the ground state of methylene. Despite a number of studies considering the problem, very little is known concerning the ground state structure of diphenylcarbene. The information which is known is derived from EPR and ENDOR experiments of the carbene in rigid matrices at low temperature. For instance, as was the case with methylene the ratio of the zero field splitting parameters E/D has been related to the deviation from linearity for the diarylcarbenes. Using this approach Wasserman and Trozzolo have estimated the value of the phenyl-carbon-phenyl bond angle in diphenylmethylene to be $\sim 145^\circ$. Thus, EPR evidence favored a substantially bent structure for the simplest diarylcarbene, as was the case with methylene. Using the technique of ENDOR spectroscopy, Anderson and Kohler have determined that the C-C-C bond angle about the divalent
atom of diphenyl carbene isolated in a single crystal of benzophenone at 4 K was approximately 140°, while each of the two phenyl rings was rotated approximately 30 degrees out of the plane defined by these same three atoms. Thus EPR data on diphenylcarbene would seem to indicate a geometry about the carbene carbon very similar to that for the unsubstituted methylene. However, the results of these ENDOR experiments must also be regarded with skepticism, as they are derived from correlations of bond angle with an estimated hybridization. This hybridization, in turn, is estimated from the magnitude of the various nuclear hyperfine coupling constants determined from the ENDOR experiment. Assuming that these approximations afford a reasonably accurate value for the structure of the carbene in the matrix EPR experiments, yet another uncertainty remains. A question which has plagued these results is whether the structure determined in rigid matrices at low temperature bears any resemblance to that of the preferred relaxed geometry of diphenylcarbene. In the case of methylene, this uncertainty was resolved by the excellent agreement between gas phase and matrix data, which were also supported by theoretical calculations. For diphenylcarbene, no corresponding gas phase determination exists and theory is much less reliable for the larger diarylcarbene. One can readily imagine that concern regarding a non-relaxed structure of diphenyl carbene in matrices is well founded, since the bulky phenyl groups may severely restrict motion in a rigid matrix. Thus, a great deal of experimental effort has been extended toward attempting to determine if the geometry of diarylcarbenes in rigid matrices is distorted by the matrix, or does in fact truly represent the "relaxed" geometry of the
Perhaps the strongest piece of evidence in support of a non-relaxed ground state geometry for a diarylcarbene in a rigid low temperature glass, is drawn from the work of Griller with dimesitylcarbene in various glasses at cryogenic temperatures. Upon generation of dimesitylcarbene (98) at 6 K from photolysis of the corresponding diazo compound (99) in an isopentane/ether mixture, the zero field splitting parameters of the triplet carbene indicated a structure which was intermediate between the substantially bent parent diphenylcarbene and the linear dianthrylcarbene (Table 5).

Scheme 49
**Table 5.** Values of D and E for Dimesitylcarbene in Various Matrices.\(^a\)

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Temp, (K)</th>
<th>D (cm(^{-1}))</th>
<th>E (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>before annealing</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>isopentane/ether</td>
<td>6</td>
<td>0.3558</td>
<td>0.0125</td>
</tr>
<tr>
<td>1,1-diphenyethylene</td>
<td>6</td>
<td>0.3533</td>
<td>0.0116</td>
</tr>
<tr>
<td>1,1-diphenylethylene</td>
<td>77</td>
<td>0.3513</td>
<td>0.0118</td>
</tr>
<tr>
<td>n-octane</td>
<td>77</td>
<td>0.3517</td>
<td>0.0115</td>
</tr>
<tr>
<td>after annealing</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>isopentane/ether</td>
<td>77</td>
<td>0.3460</td>
<td>0.0082</td>
</tr>
<tr>
<td>1,1-diphenylethylene</td>
<td>77</td>
<td>0.3493</td>
<td>0.0078</td>
</tr>
<tr>
<td>2- methyltetrahydrofuran</td>
<td>77</td>
<td>0.3486</td>
<td>0.00833</td>
</tr>
</tbody>
</table>


Most significantly, upon annealing the matrix to 77 K an irreversible change was induced upon the EPR spectra. The zero field parameters observed following this annealing were consistent with a structure which Griller described as "quite close to linear". One can see that the ratio E/D has decreased from ~0.033 to ~0.023 following annealing of the matrix. This experiment is suggestive that the dimesitylcarbene is originally generated in a non-relaxed geometry and that only when the rigid matrix is softened can the more linear, minimum-energy geometry of the carbene be achieved. No similar annealing experiment has been reported for the unsubstituted diphenylcarbene. Although not stated specifically, the authors imply that
similar results are not observed with the parent diphenylcarbene following annealing, as they state that the steric interactions of the ortho-methyl groups must force the molecule to adopt this structure which is nearly linear.

Hutchinson and Kohler\textsuperscript{15} have determined the value of the zero field splitting parameters for the parent unsubstituted diphenylcarbene in a variety of rigid matrix environments. The value of the zero field splitting parameters of diphenylcarbene (Table 6) show only a small dependence on the nature of the glass in which they are obtained, even when very different materials are employed as the matrix.

\begin{table}[h]
\centering
\caption{Values of $D$ and $E$ for Diphenylmethylene in Various Matrices.\textsuperscript{a}}
\begin{tabular}{lcc}
\hline
Matrix & $D$ (cm$^{-1}$) & $E$ (cm$^{-1}$) \\
\hline
Fluorolube & 0.4149 & 0.0197 \\
n-pentane & 0.4072 & 0.0188 \\
n-hexane & 0.4078 & 0.0188 \\
n-heptane & 0.4098 & 0.0189 \\
n-octane & 0.4085 & 0.0190 \\
n-nonane & 0.4081 & 0.0192 \\
diphenylether & 0.4020 & 0.0182 \\
benzophenone & 0.4055 & 0.0194 \\
diphenyldiazomethane & 0.4067 & 0.0188 \\
dibenzofuran & 0.4069 & 0.0189 \\
fluorene & 0.4085 & 0.0187 \\
1,1-diphenylethylene & 0.3960 & 0.0149 \\
\hline
\end{tabular}
\end{table}

One notable exception perhaps is the measurement employed in a single crystal of 1,1-diphenylethylene, where the D and E values are slightly smaller than in the other matrix materials. In general though, the effect of varying the matrix does not appear to have an overwhelming effect on the magnitude of these parameters. If the matrix were distorting the geometry of the diphenylcarbene from its preferred value by matrix packing forces, one would expect that the carbene would take on different geometries in different matrices, thus exhibiting a matrix dependence on the zero field splitting parameters.

An additional experiment which contraindicates the proposal of a non-relaxed diphenylcarbene in rigid glasses was offered over twenty years ago by Wasserman's group. These workers have demonstrated (Scheme 50) that the triplet sensitized photolysis of the geminal diazide 100 generated initially the azido-nitrene 101 which was detected by its EPR absorption spectrum. Continued irradiation led to the decay of this EPR signal which was accompanied by the growth of the absorptions characteristic of diphenylcarbene. Most relevant to our work, is the observation that the ZFS parameters of the carbene obtained in this manner were identical with those obtained when the carbene was generated from diphenyldiazomethane 102. This result was reproduced in a total of six different matrix environments differing from crystalline benzophenone to glassy 2-methyltetrahydrofuran at 77K. In each case, the carbene spectra were identical, regardless of the precursor utilized. Wasserman noted that the geometry about the central carbon atom in these two precursors varied from approximately 110° for the diazide 100 to nearly 120° for the diazo
precursor 102. The methylene angle in the carbene 75, while not known exactly is believed to lie near 145°. Although the corresponding angles in the precursors differ by ~10°, there is sufficient freedom in the matrix for both precursors to yield the same geometry for the carbene. Wasserman states that differences of 1-1.5° in final geometry of the carbene would be detectable as different zero field splitting parameters. Wasserman also notes that Griffin has shown that the carbene produced from 1,1,2,2-tetraphenylethylene oxide (103) also has the same EPR spectrum (and presumably the same geometry) as when produced from those precursors described above.

Scheme 50
The optical spectroscopy of diphenylcarbene affords in general much less information on the nature of the ground state structure of the carbene than can be derived from EPR. The absorption spectrum of diphenylcarbene (DPC) is characterized by a strong band near 300 nm and a weaker absorption near 470 nm. Closs has demonstrated through optical spectroscopy experiments of diphenylcarbene oriented in a single crystal of 1,1-diphenylethylene, that only light polarized parallel with a line bisecting the center of the two phenyl rings is absorbed by the oriented carbene. Based on this fact, the authors concluded this absorption could not be associated with the excitation of the electron which is essentially localized on the central carbon atom, but most likely involves the promotion of the delocalized $p_x$ electron to an excited $\pi^*$ state. The weak band in the visible region corresponds to the $n-\pi^*$ transition of the carbene. Trozzolo first reported the triplet-triplet fluorescence spectrum of diphenylcarbene (DPC) by irradiating diphenyldiazomethane in a variety of organic glasses at 77 K. The emission spectrum, which consists of a broad band extending from ~470-550 nm was qualitatively similar in appearance to that of the diphenylmethyl radical, but shifted to the blue by about 50 nm compared with the emission of the radical. The assignment was further strengthened by correlation of the emission intensity at 480 nm with the EPR absorption intensity of the DPC band near 1000 Gauss. The only other emitting species which could be detected in the photolyzed matrices, was a small band at 425 nm due to emission from the formal carbene dimer tetraphenylethylene. Unfortunately no phosphorescence of the diarylcarbene could be detected.
Recently with the advent of readily available laser flash photolysis equipment there has been somewhat of a renaissance in the area of the luminescence studies of aryl carbenes. Using the single pulse of an excimer laser (249 nm) to photolyze a solution of diphenyldiazomethane, a fluorescence emission band ($\lambda_{\text{max}} = 507$ nm) was obtained and assigned to the $T_1-T_0$ emission of diphenylcarbene in solution.\textsuperscript{20} Scaiano\textsuperscript{21} has reproduced these results and noted that the carbene fluorescence emission in solution is red shifted about 30 nm relative to the position of the fluorescence observed in rigid glasses at 77 K. Subsequently, Scaiano systematically investigated the fluorescence spectra of a series of substituted diarylcarbenes,\textsuperscript{22} and suggested that the discrepancy between the ambient temperature emission and that produced in matrices may result from fluorescence from a distorted geometry of the photochemically excited state of the carbene in the rigid matrices. They proposed that even if the ground state of the carbene were able to relax to its preferred "solution phase" geometry in the matrix, the shorter lived excited state (fluorescent lifetimes $120$ ns)\textsuperscript{22} may have a preferred geometry which differs significantly from the ground state but can not be achieved in the brief lifetime prior to fluorescence. We have investigated this possibility, and obtained additional results which further support Scaiano's hypothesis.
RESULTS AND DISCUSSION

Before undertaking a systematic study on this problem we briefly considered the very different manner in which the two fluorescence spectra (matrix vs. fluid solution) were recorded. Trozzolo's spectrum\textsuperscript{19} was obtained following irradiation of glasses containing diphenyl diazomethane at 77 K. He subsequently obtained the fluorescence of the photogenerated DPC using a commercial spectrofluorimeter employing a scanning monochromator. Turro\textsuperscript{20} and Scaiano\textsuperscript{21} independently obtained their spectra in a very different manner. They exposed solutions of the diphenyl diazomethane precursor\textsuperscript{102} to a brief, intense pulse of an excimer laser. The pulse was sufficiently intense both to decompose the diazo precursor as well as to excite the nascent triplet carbene. The emission from the excited state of the carbene was dispersed by a spectrograph and collected using an optical multichannel analyzer. In order to be certain that the different manner in which the spectra were recorded was not the cause of the observed spectral shift, we wished to record the emission spectrum of DPC in fluid solution and in the glassy matrix using the same experimental apparatus, and determine if the discrepancy between solution and matrix remains. The Laser Induced Fluorescence apparatus, and the manner in which the spectra were recorded are similar to Turro's apparatus\textsuperscript{20}, and are described in more detail in the experimental section. A solution of the
diphenyldiazomethane precursor having an optical density of ~1.0 at the 249 nm laser line was prepared in 3-methylpentane. The fluorescence emission spectrum of the carbene was recorded at 298 K, following a single pulse of the laser (249 nm KrF pulse; 10 ns pulse width). A fresh sample of the same stock solution was then cooled to 77 K and the emission spectrum was once again recorded following the laser pulse. As shown in Figure 27, the spectra of DPC generated in solution and in the low temperature glass are quite different even when measured with identical equipment.

Figure 27. Laser induced fluorescence emission spectrum of diphenylcarbene at 77 K and room temperature. The spectra were recorded following a 249 nm excimer laser pulse of a solution of diphenyldiazomethane (O. D. = 1.1 at 249 nm) in 3-methylpentane.
The position of the emission bands, both in solution and in the rigid glass, agree well with those previously reported by Turro and Trozzolo respectively. Similar results were obtained with the diphenylcarbene precursors 103 and 104 shown below.

In each case the $\lambda_{\text{max}}$ in the emission spectrum of DPC recorded at ambient temperature is shifted ~25 nm to the red of the spectrum observed at 77 K (Table 7). We have previously mentioned that diphenyldichloromethane 65 can also be photolyzed to DPC in matrices. Although ambient temperature LIF experiments employing 65 as the precursor did not produce a detectible signal due to DPC, the position of the emission in the rigid glass at 77 K is very similar to that observed with the other three precursors. Clearly, in each case, the emission maximum in the rigid glass is at substantially shorter wavelength than in the fluid solution, and this shift is not dependent on precursor or the details of the experiment. If the environmentally induced shift in the fluorescence spectrum of the carbene is due to significant changes in the carbene geometry between solution and the rigid matrix, this shift should disappear, or at least diminish, when a structurally more rigid carbene is examined.
Table 7 Low temperature glass and fluid solution fluorescence emission maxima of DPC in 3-methylpentane (see text).

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Emission 298 K (nm)</th>
<th>Emission 77 K (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diphenyldiazomethane</td>
<td>505</td>
<td>482</td>
</tr>
<tr>
<td>1,1,2,2-Tetraphenylethyleneoxide</td>
<td>505</td>
<td>482</td>
</tr>
<tr>
<td>2,2,4,4-Tetraphenyloxacyclobutan-3-one</td>
<td>504</td>
<td>478</td>
</tr>
<tr>
<td>Dichlorodiphenylmethane</td>
<td>...a</td>
<td>476</td>
</tr>
</tbody>
</table>

a. not observed in fluid solution

The diarylcarbene dibenzocycloheptadienylidene 105 or (DBC) represents an analogue of diphenylcarbene in which the two phenyl rings are linked via a two carbon ethano bridge, thus introducing the desired rigidity on the carbene structure.

Laser induced Fluorescence of 105 was obtained at 77 and 298 K as described with the parent diphenylcarbene above. As shown in Figure 28, the environmentally induced shift in the position of the fluorescence maximum for DBC is only a fraction of that observed with DPC.
Figure 28. Laser induced fluorescence emission spectrum of DBC 105 at 77 K and room temperature. The spectra were recorded following a 249 nm excimer laser pulse of a solution of the diazo compound 106 (O. D. = 0.67 at 249 nm) in 3-methylpentane.
In our minds, the most obvious interpretation of the data regarding the shift in the fluorescence spectra of DPC is that the rigid environment of the matrix prevents either ground state or the electronically excited state of diphenylcarbene from relaxing to its preferred, presumably solution phase like, geometry. It is conceivable that the geometry of the precursor predisposes the carbene to a matrix geometry which is very similar to that of the precursor. If the rigid matrix prevents the carbene from attaining its preferred geometry following formation, one might imagine the carbene could be permanently "locked" into a non-relaxed, precursor-like, geometry until the rigid matrix is softened by warming. This view is rendered unlikely if one notes that four different precursors, with significantly different geometries about the carbene carbon, give a very similar matrix fluorescence spectrum, which is dramatically different from the solution phase. When one considers that the precursor geometries vary from approximately 110 - 120° about the central carbon atom, yet all precursors lead to the formation of a carbene which has a very similar emission spectrum, it seems unlikely that the matrix is forcing the carbene to retain a precursor like geometry. One will recognize that this conclusion is based on an argument which is very similar to that advanced by Wasserman\(^1\) regarding the EPR spectra of diphenylcarbene, when the carbene was generated from a variety of precursors. Thus it appears that it is the shorter lived excited state (\(\tau_r \sim 120\) ns) which does not have the opportunity to relax to its equilibrium geometry. This interpretation of course requires that the geometry of the excited state be different from that of the ground electronic state.

It is interesting to note that a simple thought experiment may be as
helpful as any in distinguishing whether it is the ground state or the excited state of triplet DPC which is distorted in the matrix emission experiments. Consider first a triplet DPC which is hypothetically distorted in its ground electronic state by matrix packing forces, which do not distort the first excited state of DPC significantly. The energy gap between the lowest excited state and the ground state (which will of course correspond to the energy of the photon recorded in the T₁-T₀ emission spectrum) would be lower than if the DPC were in its relaxed form in the ground state as well. This is opposite to the actual experimental fact, where the emission occurs at higher energy in the matrix experiments than that observed in the fluid solution. Alternatively, a non-relaxed geometry of the first excited triplet state of DPC in the matrix experiment would lead to a higher energy emission in the matrix than that which would be produced in fluid solution. This second scenario correctly predicts the direction of the matrix shift which is observed in the laboratory.

During the course of these studies, we noted that the combination of low temperature and rigid glasses, along with the increased time resolution afforded by Laser Induced Fluorescence experiments, appeared to be a powerful method for obtaining fluorescence spectra of highly reactive carbenes.

Consider the parent 2-naphthylmethylene (2-NC) 109, whose fluorescence spectrum is unreported to date. In our hands, photolysis of 2-naphthyldiazo methane (107) (0.01 M in n-hexane) at 77 K failed to produce a species which could be detected by conventional fluorescence spectroscopy. At lower temperatures (22 K) the spectrum shown in Figure 29 was recorded following photolysis of Shpolski matrices containing diazo
compound 107. The species giving rise to this emission is both thermally and photochemically labile even at 22 K.

Figure 29. Conventional fluorescence emission spectrum recorded following photolysis of Shpolski matrices containing 2-naphthyl diazomethane 107. Species giving rise to this emission was labile under the conditions of this experiment. Spectrum recorded at 22 K: $\lambda_{\text{excitation}}$ was 385 nm.
When the diazo compound 107 is decomposed at ambient temperature in 3-methylpentane with the 249 nm line of a KrF excimer laser at ambient temperature, an emission spectrum of the 2-naphthylmethyl radical can be recorded from the excited solution (Scheme 51).

\[
\text{hv; 249 nm; 3-Methylpentane} \rightarrow \text{N}^* + \text{M}
\]

Scheme 52

This spectrum (figure 30), is consistent with the solution phase emission spectrum of the 2-naphthylmethyl radical obtained by Rentzepis following photolysis of the 2-chloromethylnaphthalene (110) (Figure 30).
Upon cooling an identical solution of the precursor 107 to 77 K and recording the LIF spectrum once again, a new emission at shorter wavelength can be observed along with the emission of the naphthylmethyl radical. The new emission (figure 31) originates at 566 nm, and can only be observed when the experiment is performed at cryogenic temperatures.

Figure 31. Laser Induced Fluorescence (LIF) spectrum of 2-naphthylmethylene (2-NC) 109. Spectrum produced following laser excitation (249 nm KrF excimer laser 10 ns pulse 100 mJ/pulse) of a solution of 2-naphthyldiazomethane 107 (O. D. 249 nm = 0.6 in 3-methylpentane) at 77 K.
Scaiano\textsuperscript{22} has reported an empirically derived relationship between the position of the onset of the emission spectra of various arylcarbenes and the $\lambda_{0-0}$ of the corresponding radicals. Upon applying this relationship to the 2-naphthylmethyl radical, one predicts an emission $\lambda_{0-0}$ for the 2-naphthylmethylene (2-NC) of 570 nm, in excellent agreement with the value of 566 nm observed in this work. Based on these results, the emission at 566 nm is assigned to the parent 2-naphthylmethylene (2-NC) \textsuperscript{109}.

Since 10,10-dimethylanthranylidene (DMA) \textsuperscript{111} represents a conformationally rigid diphenylcarbene analogue, we became interested in the fluorescence spectrum of this carbene in the context of the diphenylcarbene geometry problem. However, based on the previous work of Platz, this carbene is known to be highly reactive even at 77 K in rigid matrices. Platz has previously attempted to investigate the kinetics of \textsuperscript{111} along with a series of arylcarbenes in methanolic matrices at 77 K, by photolysis of diazo compound \textsuperscript{112}.\textsuperscript{25}

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figures/111_112.png}
\caption{Structures of DMA (111) and diazo compound (112).}
\end{figure}
Although the decay kinetics of several arylcarbenes including diphenylcarbene, fluorenylidene, dibenzocycloheptadienylidene and 1-naphthylcarbene were determined by EPR in this manner, 111 could not be detected following photolysis of 112 at 77 K under these conditions. Curie law analysis over the temperature regime (6-50 K) demonstrated the triplet nature of the ground state of this carbene, thus the authors attributed the failure to detect 111 at 77 K as being due to its high reactivity, compared with the other diarylcarbenes being investigated. The extremely high reactivity of DMA was rationalized in terms of a very small singlet-triplet energy gap, induced by the necessarily small divalent carbon angle. A decrease in this central carbon angle (introduced by incorporation of the divalent carbon into a 6-membered ring) tends to stabilize the singlet relative to the triplet electronic state of the carbene, due to the increased amount of s character in the doubly occupied in plane orbital. No reports on the fluorescence spectroscopy of DMA have been advanced to date. We reasoned that this molecule may lend itself well to LIF, where perhaps the highly reactive carbene can be visualized. LIF spectroscopy performed on an optically dilute solution of diazo precursor 112 in 3-methylpentane at ambient temperature gives the spectrum shown in figure 32. Assuming DBC to be a reasonable model system, there is no emission in the region which would be expected for the DMA 111. The only band which can be observed is a weak, poorly resolved emission at ~545 nm, which we believe to be due to the 10,10-dimethylanthranyl radical 113, derived from the hydrogen atom abstraction reaction of the carbene with the 3-methylpentane solvent.
Figure 32. a. Laser Induced Fluorescence (LIF) spectrum of 10,10-dimethylanthranyl radical 113. Spectrum produced following laser excitation (249 nm KrF excimer laser 10 ns pulse 100 mJ/pulse) of a solution of 112 (O.D. 249 nm = 1.2 in 3-methylpentane) at ambient temperature. b. Laser induced fluorescence spectrum of dimethylanthranlylidene 111; spectrum recorded identical with a except sample was cooled to 77 K.
Upon cooling an identical sample of 112 to 77 K and repeating the LIF experiment, the spectrum shown in figure 32 is obtained. Here one sees not only the band at 545 nm, which we have assigned to the radical 113, but also a new sharp band with a $\lambda_{0.0} = 508$ nm is observed. We assign this band to the $T_1-T_0$ emission of the dimethylanthranylidene 111, based primarily on the position and shape of the sharp emission band which are very similar to the unsubstituted diphenylcarbene and DBC.

Investigation of 1- and 2-naphthylphenylcarbenes (114 and 115) yields results which are similar to those observed with the parent 2-naphthylcarbene, except these carbenes, which are stabilized by an additional phenyl group, could be readily observed both at 77 K and in fluid solution at ambient temperature.

The 2-naphthylphenylcarbene (2-NPC) has been previously investigated by LIF spectroscopy at ambient temperature, and emits with an origin band at 587 nm and the first observable vibronic band at 635 nm. In this work, nearly identical results with those reported by Scaiano were realized when the 2-naphthylphenyldiazomethane was subjected to our typical LIF conditions at ambient temperature (figure 33).
Figure 33. a. Laser Induced Fluorescence (LIF) spectrum of 2-naphthylphenylcarbene (2-NPC) 114. Spectrum produced following laser excitation (249 nm KrF excimer laser 10 ns pulse 100 mJ/pulse) of a solution of 2-naphthylphenyldiazomethane (O. D. 249 nm = 1.1 in 3-methylpentane) at ambient temperature.; b. Laser induced fluorescence spectrum of 2-naphthylphenylcarbene 114 ; spectrum recorded identical with a except sample was cooled to 77 K.
Upon cooling the sample to 77 K, a nearly identical spectrum could be recorded; unlike diphenylcarbene, only a small spectral shift is observed upon increasing the rigidity of the matrix environment. In contrast to the more highly reactive carbenes (i.e. the parent 2-naphthylmethylene (2-NC) and the 10,10-dimethylantranylidene (DMA)) no evidence for emission due to the radical derived from reaction with the solvent, within the 10 ns pulse, could be observed with this carbene. The emission spectrum of this radical is known\(^\text{22}\) and is shifted about 30 nm to the red of the carbene emission which we have observed in this work. Similarly, we have investigated the emission spectrum of the 1-naphthylphenylcarbene and found results which were very similar with those reported above. LIF of 1-naphthylidazomethane at 77 K or ambient temperature in 3-methylpentane produced the emission spectrum shown in figure 34. This spectrum is due to the emission of the 1-naphthylphenylcarbene (1-NPC).\(^\text{26}\) Once again, no dramatic matrix shift is observed for this carbene and the spectrum of the carbene, free from interfering radical fluorescence can be easily recorded at both ambient temperatures and 77 K.
Figure 34. a. Laser Induced Fluorescence (LIF) spectrum of 1-naphthylphenylcarbene (1-NPC) 115. Spectrum produced following laser excitation (249 nm KrF excimer laser 10 ns pulse 100 mJ/pulse) of a solution of 1-naphthylphenyl diazomethane (O. D. 249 nm = 1.1 in 3-methylpentane) at ambient temperature. b. Laser induced fluorescence spectrum of 1-naphthylphenylcarbene (1-NPC) 115; spectrum recorded identical with a except sample was cooled to 77 K.
We have also considered the LIF emission spectrum from phenyldiazomethane 116 in 3-methylpentane at ambient temperatures and 77 K. Excitation (249 nm; KrF laser) of a solution of 116 at ambient temperature gives rise to a broad emission centered at 375 nm. The species responsible for this emission is unknown, but several possibilities can be readily excluded. The position and band shape of this spectrum are inconsistent with the emission spectrum of matrix isolated benzyl radical which has a strong blue-green emission band in the visible region. Furthermore, no emission has yet to be observed from the benzyl radical in fluid solution, hence this species can be eliminated from consideration.

The spectrum is also not due to the emission of cis or trans stilbene, which would be likely photoproducts and impurities in the diazo compound; the fluorescence emission of the stilbenes occurs at considerably higher energy than the unidentified emitting species in this experiment ($E_s$ cis and trans-stilbene = 332 and 329 nm respectively). Upon cooling an identical sample of diazo compound 116 and collecting the spectrum once again, one observes two sharp emission bands superimposed on the broad emission which is observed both at room temperature and in the matrix. This broad band can be subtracted from the 77 K emission spectrum to give the emission spectrum of the species ($\lambda_{emission} = 455$ and 476 nm) which is only observed at 77 K (figure 35). The fluorescence spectrum of the benzyl radical in the visible region is shown for comparison (figure 35). The band at 455 nm is clearly to the blue of the emission spectrum of the matrix isolated benzyl radical and is tentatively assigned as phenylcarbene (PC) (117).
We suggest, that in analogy to the work with the various diphenylcarbenes, the 1- and 2-naphthylphenylcarbenes and the parent 2-naphthylcarbene, that the emission observed at 77 K, may be due to the \( T_1 - T_0 \) fluorescence emission of the parent phenylmethylene (PC) \( 117 \), which is derived from nitrogen expulsion from the diazo compound \( 116 \) and subsequent excitation of the nascent carbene. The reader should note, that Griffin\(^{30} \) has observed emission bands at 390 and 414 nm from photolysis of matrix isolated cis-2,3-diphenyloxirane in a conventional 77 K fluorescence experiment. He has attributed these features to matrix isolated phenylmethylene \( 117 \). The EPR spectrum of the parent phenylmethylene (PC) can be observed by EPR in THF at 77 K, but it has a lifetime of only 4-5 minutes under these conditions.\(^{31} \) Thus, is difficult to detect in a conventional matrix fluorescence experiment. In any event, further work in this area is clearly necessary in order to explain the discrepancy between our work and Griffin’s result.

In summary, the spectra recorded in our LIF experiments are compiled in table 8 along with our assignments and literature references where available. The data obtained from various diphenylcarbene precursors suggest that the geometry of DPC in its lowest electronic excited state differs from that of the ground state of the carbene. The rigid matrix does not allow the first excited state of the triplet carbene to relax to its preferred geometry prior to fluorescence. The data do not demonstrate that the geometry of the ground state of DPC is significantly distorted from its solution phase geometry. Thus the results of ENDOR spectroscopy concerning the geometry of the carbene in the rigid matrix may be relevant in predicting the solution phase geometry of DPC. Also, we have demonstrated that the combination
of the increased time resolution achieved from LIF experiments, along with the longer lifetime imparted on carbenes by generating them in rigid matrices at 77 K, has led to the detection of fluorescence emission from highly reactive carbenes which are difficult to observe by more conventional means.
Table 8. Summary of (LIF) Experiments on Aryl and Diarylcarbenes.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Temp (K)</th>
<th>Emission ($\lambda_{0.0}$ nm)</th>
<th>Assignment</th>
<th>Lit.</th>
</tr>
</thead>
<tbody>
<tr>
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References

   b. Herzberg, G., "Electronic Spectra of Polyatomic Molecules", Van  


   409, 1970.


7. Wasserman, E., Kuck, V. J., Hutton, R. S., Anderson, E. D. and Yager,  

   1970.


Chapter V; Experimental Procedure
General Procedures

**Nuclear Magnetic Resonance Spectra**: $^1$H NMR and $^{19}$F NMR were recorded by Mr. Carl Engleman using either a Varian Am-250 (250 MHz) or an AM-250-2 (250 MHz) instrument. Chemical shifts for proton NMR are reported using tetramethylsilane (Aldrich) as the reference. For $^{19}$F NMR hexafluorobenzene was employed as the reference compound.

**Infrared Spectroscopy**: All spectra were recorded either on a Perkin-Elmer model 1710 Fourier Transform Infrared Spectrometer or a Beckman 4250 IR Spectrometer.

**UV-Visible Spectroscopy**: UV-Vis Spectra as well as optical densities of solutions for Laser induced fluorescence experiments were determined on a Perkin-Elmer Lambda 3 UV-Vis Spectrophotometer.

**Melting Points**: Melting points were obtained on an Electrothermal capillary melting point apparatus and are uncorrected.

**Mass Spectra**: Mass spectra were obtained by Mr. Richard Weisenberger of the OSU Campus Chemical Instrumentation Center using either a VG 70-250S or a Kratos MS-30 mass spectrometer.
Photolysis

Photolysis was carried out using one of five radiation sources indicated in the text as Hg Lamp, Xe arc Lamp, 254 nm, 249 nm or 337 nm. These sources are described in somewhat more detail below.

**Hg lamp**: 1000 Watt medium pressure mercury arc lamp manufactured by Schoeffel Instrument Corporation, powered by a Schoeffel 1000 Watt Universal arc lamp power supply, Model LPS 255 HR. Unless otherwise stated, the output was unfiltered.

**Xe arc lamp**: The output of a Schoeffel Xe arc lamp. The source was powered by an Electro Powerpacs universal power supply (1000 W). In the dual beam experiments, 405 nm light was isolated from this source with an Oriel Corporation 5654 interference filter (10 nm band-pass, transmittance at 405 nm was 35%).

**254 nm**: A rayonet photoreactor equipped with 5 RPR-2540 bulbs.

**249 nm**: The unfocused output of a Lumonics model TE-861M-4 excimer laser. The laser was charged with the mixture of Krypton, Fluorine and Helium as described in the manufacturers operations manual. The laser supplies a 15 ns 249 nm pulse (estimated power ~180 mJ/pulse).¹

**337 nm**: The unfocused output of a Molelectron UV-22 nitrogen laser (337.1
nm, 5-10 ns pulse up to 8 mJ/pulse). The repetition rate was typically 50 Hz, unless indicated otherwise.

**ESR Measurements**

All reported EPR experiments were recorded with a Varian E-112, X-band ESR spectrometer. The cavity of the instrument has been modified so that samples, within the cavity, can be photolyzed through a series of slits on one side of the cavity. All of the samples were prepared by transferring the appropriate precursor solution (typically 0.005 - 0.01 M substrate) into a 4 mm suprasil quartz tube equipped with a graded seal from quartz to pyrex. The solutions were subsequently degassed by a series of freeze-pump-thaw cycles (typically 4 or 5), and sealed under vacuum. The majority of the spectra were recorded at 77 K using the apparatus described by Wright.² Using this arrangement, the sample tube was immersed in a dewar flask and the entire flask placed into the cavity of the EPR spectrometer (Figure 36), where it was photolyzed.

![Figure 36. Apparatus used for EPR spectra at 77 K. Taken from Wright, B. B., "The Preparation and Characterization of m-Xylylene ", Ph. D. Thesis, Ohio State University, p. 136, 1983.](image-url)
EPR spectra recorded at 10 K were obtained using an Oxford Instruments Model ESR 400 liquid Helium cryostat. The sample is cooled in this system by a stream of boiling Helium, and the temperature monitored by the use of an Oxford DTCT/V30 digital temperature control unit.

*Fluorescence Spectroscopy*

Fluorescence Spectra were recorded in one of two different ways (termed "conventional" or "LIF" throughout the text). The instrumentation and procedure for recording fluorescence in both of these experiments is described below.

*Conventional Fluorescence Experiments*: In the first method, fluorescence spectra were recorded at 77 K using a Perkin-Elmer model LS-5 spectrofluorimeter. The sample compartment of the LS-5 has been modified so that fluorescence spectra can be recorded on samples immersed in a dewar flask of liquid N$_2$. Typically, the sample was prepared in a suprasil quartz tube, as per the EPR experiments. An emission spectrum of the sample (at 77 K) was recorded, to serve as a background. The dewar flask was subsequently removed from the fluorimeter and the sample photolyzed through the windows of the dewar using the source as indicated in the text. Finally, the dewar was repositioned in the sample compartment and the spectrum recorded once again. Absolute fluorescence signal intensities showed considerable variation depending on the positioning of the dewar in the sample compartment of the fluorimeter (~20-30 %). For this reason, in
general the *ratios* of fluorescence signal intensities were compared whenever possible. This ratio was determined by measuring the ratio of peak heights at the emission maxima of the two species being considered.

**Software for UV-Vis and Fluorescence Spectroscopy:** The UV-Vis instrument as well as the fluorimeter are command driven by an external Perkin-Elmer model 3700 data station. The software packages (PECUV) and (PECLS) were purchased from Perkin-Elmer and used for recording UV and fluorescence spectra respectively, as well as in data handling and storage. Fluorescence signal intensities were determined using this capability in PECLS, rather than manually measuring peak height or area.

**Laser Induced Fluorescence (LIF):** The LIF technique and apparatus was similar to that described by Turro and Scaiano.\(^3\) Solutions of the precursors having an optical density of ~1.0 at the 249 nm laser line were prepared in alkane solvents. Typically, spectral grade methylcyclohexane or 3-Methylpentane which had been stored over molecular sieves was used without further purification. Ambient temperature fluorescence spectra were recorded by decomposing the precursors and exciting the nascent carbene with a single pulse of the Lumonics model TE-861M-4 laser (249 nm as described above). The emission from the sample was directed onto an Allied Analytical Systems spectrograph through a fiber optics cable. The dispersed fluorescence spectrum was collected via a Princeton Applied Research Company (PARC) model 1303 optical multichannel analyzer (OMA). The 249
nm laser line was removed from this emission by the use of a glass filter (Oriel 295 nm long pass) positioned between the sample cell and the fiber optics inlet. The OMA was activated within 10 ns following the laser pulse, for a 100 ns time window. Initial LIF experiments at 77 K were recorded simply by immersing the sample cell in liquid N₂ prior to inserting into a precooled sample compartment. Some (indicated below) of the experiments at 77 K were later reproduced using a quartz walled dewar (2 cm x 2 cm) in which the sample cuvette could be immersed in liquid nitrogen. The diphenylcarbene precursors (diphenyldiazomethane 102 and 1,1,2,2-tetraphenylethylene oxide 103) as well as diazodibenzocycloheptadienylidene were studied at 77 K using both types of low temperature sample compartments. The position and shape of the emission spectra at 77 K were identical regardless of the sample compartment configuration. However, the use of the quartz walled dewar resulted in substantially diminished fluorescence signal intensity.

Glass Filter: Oriel long-pass glass filters were used to remove scattered excitation source light from the luminescence reaching the detector in the both the conventional and LIF experiments.

Transient Absorption Spectrum.

A laser flash photolysis system as described by Platz⁵ was used to record transient absorption spectra. In all cases the 249 nm laser was employed as the excitation source. Solutions of either mesitylene or α,α'-dichloro-m-xylene having an optical density of ~1.0 at 249 nm were
prepared in 3-methylpentane. Transient optical densities were recorded using the OMA, employing the Xe arc lamp as the monitoring beam. A delay of 250 ns was introduced following the laser flash, prior to recording the transient spectra.

**Growth of Fluorescence Signals as a function of Photolysis Time and Intensity.**

Quartz sample tubes were prepared (as described for EPR samples) containing solutions of the appropriate precursor (0.005 to 0.01 M). The sample tube, which is placed inside a quartz walled dewar filled with liquid nitrogen, is positioned in the path of 249 nm beam of the excimer laser. Reproducible positioning of the sample was achieved by mounting a holder onto an optical table into which the dewar flask could be inserted. The appropriate number of laser pulses was applied, the dewar removed from the holder, and the fluorescence of the sample measured on the conventional apparatus and stored to disk for subsequent analysis. The dewar flask containing the sample was then returned to the optical table, where an additional set of pulses was applied, and the fluorescence from the sample once again recorded on the fluorimeter. Alternatively, photolysis was affected using the rayonet reactor (5 bulbs RPR-2540). In this case, the dewar flask containing the sample to be photolyzed at 77 K, was clamped inside the Rayonet apparatus and photolyzed for the indicated length of time. In this manner the ratio of signal intensities of two species produced in the matrix was easily determined as a function of photolysis time. A similar approach
was used to determine the effect of light intensity on the ratio of signal intensities due to the matrix isolated monoradical and biradical from mesitylene. In this experiment, the sample of matrix isolated mesitylene (0.005 - 0.01 M) was prepared, cooled to 77 K, and placed in the path of the laser beam as with the preceding experiment. Fifty laser pulses were delivered to the sample. The fluorescence emission intensity of the mesitylene monoradical and biradical was recorded on the conventional fluorimeter. A fresh tube prepared from the same stock solution was then photolyzed once again, in the same manner, except a neutral density filter (wire mesh) was placed in the path of the laser beam. The sample was subsequently analyzed in the usual manner and the ratio of the mesitylene or m-xylene monoradical/biradical signal intensities produced from photolysis of mesitylene or m-xylene was determined as a function of light intensity. The optical density of the neutral density filter was measured both before and after the photolysis, and no difference in the transmission properties of the filter was caused by exposure to the laser beam. From this value, the transmittance of the filter was calculated.

In all experiments where a ratio of biradical/monoradical from α,α'-dichloro-m-xylene, mesitylene, or m-xylene is reported, the excitation wavelength was identical (295 nm). Thus, although the ratios determined in this manner do not represent actual ratios of the two species in the matrix in any given experiment, comparison of ratios obtained from different experiments accurately reflects changes in ratios of the mesitylene biradical/monoradical caused by different photolysis conditions, matrices, or precursors.
Double Dissociative Electron Capture Procedure

Linear Accelerator (LINAC) Procedure: The dissociative electron capture experiments employing the LINAC beam as the electron source were carried out in the following manner. The sample was prepared in 2-methyl-THF (refluxed over KMNO₄ and distilled), degassed and sealed in a 4 mm quartz tube, as per the ESR experiments. Typical concentrations of the dihalides were 0.005 M. The degassed sample (bathed in liquid nitrogen in a quartz walled dewar) was exposed to the pulsed output (400-700 pulses) of a Varian Model V-7715-A linear accelerator (LINAC). The pulse width was set to 1.4 µs, and the electrons possess an average energy of 3.5 MeV. The dewar flask containing the sample tube was subsequently transferred to the sample compartment of the Perkin-Elmer spectrofluorimeter and analyzed by fluorescence spectroscopy.

Tetrakis(dimethylamino)ethylene (57) Procedure: A solution of the dihalide (0.01 M) in methylcyclohexane (dried over sieves) is prepared. Olefin 57 is added to the dihalide solution by syringe, so that the final concentration of 57 is 0.1 M. This solution was immediately transferred to a 4 mm quartz tube, degassed by freeze-pump-thaw cycles, and stored at 77 K until it could be photolyzed. The sample was photolyzed (Hg lamp, unfiltered; 77 K) directly in the cavity of the EPR spectrometer (see general procedures). The EPR spectrum of the sample was then recorded. Typical spectra were recorded with the following instrument settings.
Source of Compounds Investigated

Mesitylene (8) (gold label), m-xylene (9), 2-methylbutane, methylcyclohexane (Spectral grade), n-hexane (HPLC grade), n-hexane (d14), ethanol, ethanol-d5-OD, 3-methylpentane, tetrakis(dimethyl amino)ethylene (57), \(\alpha,\alpha'-\text{dichloro-o-xylene}\) (58), diphenyldichloromethane (65), benzhydryl chloride (56), 1,1-diphenylacetone (97), 3-chloro-2-(chloromethyl)-propene (59) and 2,4,6-trifluoroaniline were purchased from Aldrich Chemical Co. and used as received.

Recrystallization of \(\alpha,\alpha'-\text{dichloro-m-xylene}\) (36) (Aldrich) and \(\alpha,\alpha'-\text{dibromo-m-xylene}\) (39) (Aldrich) from hexanes gave the crystalline dihalides which were used to prepare the solutions for photolysis studies.

Durene (technical grade) was purchased from Humble Oil and Refining Company and purified by elution through neutral alumina (hexanes as eluant) immediately prior to preparation of a sample tube.

2-Methyltetrahydrofuran (Aldrich) was refluxed over KMnO4, distilled and stored over molecular sieves prior to use. Professor G.W. Griffin kindly provided us with samples of the carbene precursors 1,1,2,2-tetraphenylethylene oxide (103) and 2,2,4,4-tetraphenyl-oxa-cyclobutan-3-one (104). Wright2 synthesized the following carbene
precursors; 9-diazodibenzocycloheptadiene (106) and
9-diazo-10,10-dimethyl-9,10-dihydroanthracene (112). Maloney\textsuperscript{14}
provided the diphenylcarbene precursor diphenyldiazomethane (102) as
well as both of the naphthylphenylcarbene precursors 1- and
2-naphthylphenyldiazomethaney.
Synthesis of 2,4,6-trifluoroacetanilide (119)

2,4,6-trifluoroaniline (5.0 g; 34.1 mmol) (Aldrich Chemical Co.) was dissolved in 10 ml of glacial acetic acid. Freshly distilled acetic anhydride (7 ml) was slowly added to the warm (steam bath) solution. The reaction mixture was heated with the steam bath for an additional 20 minutes following the addition of the anhydride. After allowing the mixture to reach ambient temperature, the products were precipitated by pouring the solution onto crushed ice. The precipitate was collected by filtration and recrystallized from benzene to yield 2,4,6-trifluoroacetanilide (119) (5.9 g; 91%). mp; 158-160 °C; ¹H NMR (CDCl₃ + DMSO-d₆, δ); 2.17 (s, 3H, acetyl CH₃), 6.70 (t, 2H, J = 7.6 Hz, aromatic H), 8.49 (s (broad), 1H, amide H); ¹⁹F NMR (CDCl₃ + DMSO-d₆); -118.37 (d, 2F, J = 5.3 Hz, 2 and 6 aromatic fluorines), -114.36 (t, 1F, J = 5.2 Hz, 4 aromatic F); MS (m/e); calculated for C₈H₆F₃NO = 189.0401, observed = 189.0421.
Synthesis of 3-nitro-2,4,6-trifluoroacetanilide (120)

2,4,6-trifluoroacetanilide (119) (5.8 g; 30.7 mmol) was dissolved in concentrated \( \text{H}_2\text{SO}_4 \) (25 ml). Fuming nitric acid (10 ml) was added to the cooled (0 - 10° C) stirred solution over a 30 minute period. The red colored solution was stirred an additional 1.0 hour at 0 - 10° C, and poured into crushed ice to precipitate the product. The precipitate was collected by filtration, washed with water, and dried under vacuum. Recrystallization from ethyl acetate afforded 3-nitro-2,4,6-trifluoroacetanilide (120) as colorless crystals (4.93 g; 69 %). MP; 183-185° C; \( ^1\text{H NMR} \) (\( \text{CDCl}_3 + \text{DMSO-d}_6 \)); 2.15 (s, 3H, acetyl \( \text{CH}_3 \)), 7.33 (m, 1H, aromatic H), 9.86 (s (broad), 1H, amide H); \( ^{19}\text{F NMR} \) (\( \text{CDCl}_3 + \text{DMSO-d}_6 \)); -126.19 (d of d, 1F, \( J = 3.15, 3.12 \) Hz, 2 F), -124.10 (d of d, 1F, \( J = 3.05, 2.09 \) Hz, 6 F), -110.34 (t, 1F, \( J = 8.23, 4 \) F); MS (m/e); calculated for \( \text{C}_8\text{H}_5\text{F}_3\text{N}_2\text{O}_3 \) = 234.0252, observed = 234.0275.
Synthesis of 3-acetamido-2,4,6-trifluoroacetanilide (121)

3-nitro-2,4,6-trifluoroacetanilide (120) (4.75 g; 20.3 mmol) was dissolved in fifty ml of a mixture of methanol/acetic acid (5:1 by volume). Hydrogenation (Pd/C at 20 psi H₂) for 12 hours was followed by in vacuo removal of the solvent. The residue was treated with freshly distilled acetic anhydride (7 ml) and heated over a steam bath for 0.5 hr. The product was precipitated by pouring the reaction mixture over crushed ice, collected by filtration, washed (water) and dried under vacuum. Recrystallization from methanol afforded 3-acetamido-2,4,6-trifluoroacetanilide (121) as colorless crystals (4.86 g; 97%). MP: 288-90° C; MS (m/e); calculated for C₁₀H₉F₃N₂O₂ = 246.0616, observed = 246.0625.
Synthesis of 2,4,6-trifluoro-1,3-diazidobenzene (122)

3-acetamido-2,4,6-trifluoroacetanilide (121) (2.86 g; 11.6 mmol) was dissolved in 30 ml of a mixture of ethanol/concentrated HCL (2:1). The solution was heated in a sealed high pressure reaction tube to 120 °C. After cooling, the solvent was removed by distillation under reduced pressure. The residue was taken up in 30 ml of con HCL/water (1:1), and cooled to 0-5 °C. Sodium nitrite (0.88 g; 12.8 mmol) was added to the solution over a period of 0.25 hr. The resulting solution was treated with sodium azide (1.13 g; 17.4 mmol) and stirred an additional 0.25 hr. The aqueous solution was extracted with ethyl acetate (3 x 50 ml), and the organic extracts were dried over anhydrous MgSO₄. Following gravity filtration, the solvent was removed by distillation at reduced pressure. The residue was purified by elution through neutral alumina (hexanes as eluant). Removal of the solvent gave 2,4,6-trifluoro-1,3-diazidobenzene (122) as a pale yellow oil (1.6 g; 64%). ¹H NMR (CDCl₃, δ) ; 6.80 (m, 1H, aromatic H); MS (m/e); calculated for C₆H₃F₃N₆ = 214.0215, observed = 214.0202 ; ¹⁹F NMR ; -129.5 (m, 2F, 4,6 aromatic fluorines), -136.2 (m, 1F, 2 aromatic fluorine); IR (cm⁻¹); 2110, 2200 (azide stretch).
Synthesis of \textit{m}-Tolylacetylperoxide (118)

\textit{m}-Tolylacetic acid (Aldrich) (3.0 g; 19.9 mmol) was treated with thionyl chloride (10 ml). The resulting solution was heated to reflux (4.5 hours). Removal of thionyl chloride by azeotropic distillation with benzene gave \textit{m}-tolylacetyl chloride which was used immediately without further purification. The acid chloride was taken up in 5 ml of tetrahydrofuran. A solution of sodium peroxide (1 g, 0.013 mol) in 10 ml of water was added to the cold stirred solution of the acid chloride. After 1.5 hr., the mixture was extracted with diethyl ether. The ether layer was washed with 10\% aqueous bicarbonate solution, dried and removed in vacuo to yield a pale yellow oil (2.1 g; 35\%) which tested positive for a peroxide (KI and starch paper) IR: 1800 cm\(^{-1}\) and 1730 cm\(^{-1}\) (peroxide doublet).
Synthesis of 1,3-diazidobenzene (29)\textsuperscript{6}

A solution of 1,3-phenylenediamine (2.16 g; 20.0 mmol) in concentrated HCl/H\textsubscript{2}O (3:1)(50 ml) was cooled to ice bath temperature. Sodium nitrite (2.8 g; 43.0 mmol) was added with stirring to the solution of the diamine hydrochloride. After stirring at 0 - 5 °C for 0.5 hr. sodium azide (2.97 g; 45.7 mmol) was added in portions over a 10 minute period. The resulting solution was allowed to stir for 1 h. at 0 - 5 °C. The aqueous mixture was extracted with diethylether (3 x 25 ml). The organic extracts were washed with saturated sodium bicarbonate solution and evaporated to afford a brown oil. Elution through silica gel (hexanes) gave 1,3-diazidobenzene (29) as a yellow oil. IR (cm\textsuperscript{-1}) ; 2100, 2110 (azide stretch).
Synthesis of 1,3,5-tri(bromomethyl)benzene (73)\textsuperscript{7}

Mesitylene (Aldrich) (6.0 g; 0.06 mol), N-Bromosuccinimide (28.5 g; 0.16 mol) and AIBN (13 mg) were combined in 130 ml of CCL\textsubscript{4}. The reaction mixture was heated to reflux (8.5 h.) while stirring vigorously. The solution was allowed to cool to room temperature and succinimide was removed by gravity filtration. The CCL\textsubscript{4} was washed with 5 % sodium bicarbonate (50 ml) followed by washing with water (2 x 50 ml). The CCL\textsubscript{4} was dried over anhydrous MgSO\textsubscript{4}, and concentrated to ~1/3 of its original volume. Ligroin (60-90 °C boiling range) was added dropwise until the solution became cloudy. Storage in a freezer (1.5 h.) initiated precipitation of a white solid. The precipitate was recovered by vacuum filtration, and recrystallized three times from CHCl\textsubscript{3}/ligroin to afford the tribromide 73 as a white crystalline material (2.0 g; 10 %); MP; 94-95 °C, lit. value\textsuperscript{7} 94 °C. $^1$H NMR (CDCL\textsubscript{3}, $\delta$); 4.45 (s, 6H, methylene), 7.35 (s, 3H, aromatic H).
Synthesis of 1,3,5-tri(chloromethyl)benzene (76)\(^8\)

1,3,5-tris(hydroxymethyl)benzene (79) (220 mg; 1.31 mmol) was dissolved in concentrated HCL (10 ml). Several drops of concentrated sulfuric acid were added, and the solution was allowed to stir at room temperature (40 hours). The aqueous acidic solution was extracted with benzene (3 x 10 ml), and the organic extracts were washed with 10 % sodium bicarbonate solution and dried over MgSO\(_4\) (anhydrous). Upon removal of the solvent (in vacuo) a viscous oil remained. Upon standing under vacuum, the residue crystallized affording trichloride 765 as a white crystalline material (235 mg; 81 %). MP: 52-56 °C. The trichloride was recrystallized from hexanes affording 190 mg (65%) of 1,3,5-tri(chloromethyl)benzene (76). MP: 61-62 °C, lit. value\(^8\) = 64 °C; \(^1\)H NMR (CDCL\(_3\), δ): 4.57 (s, 6H, methylene), 7.37 (s, 3H, aromatic H); MS (m/e); calculated for C\(_9\)H\(_9\)Cl\(_3\) = 221.9769, observed = 221.9729.
Synthesis of 1,3,5-tris(hydroxymethyl)benzene (79)

Lithium Aluminum Hydride (0.75 g; 19.7 mmol) was suspended in 100 ml of freshly dried THF under nitrogen. Addition of 1,3,5-benzenetricarboxylic acid-methylester (78) (2.0 g; 9.5 mmol) to the stirred solution of LAH at room temperature over a 0.25 h. period followed. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was quenched by addition of 1 ml water, followed by addition of 1 ml of a 15 % solution of sodium hydroxide. Finally, 3 ml of water were added, and the solution was stirred at room temperature for an additional 0.5 h. In vacuo removal of the THF left a pasty white residue which was extracted into hot methanol (100 ml). The methanol solution was saturated with dry ice, filtered, and evaporated to dryness to leave a white powdery solid. This solid was extracted with hot ethyl acetate (50 ml), upon cooling of the extracts, a white precipitate formed. The solid was collected by filtration, dried in vacuo to afford 1,3,5-tris(hydroxymethyl)benzene (79) (0.86 g; 54 %) as a white powdery solid. MP; 76-77 °C; lit. value8 77-78 °C.; MS (m/e) ; calculated for C9H12O3 = 168.0786, observed = 168.0786.
Synthesis of 1,3,5-benzenetricarboxylic acid-trimethylester (78)⁹

1,3,5-benzenetricarboxylic acid (77) (Aldrich) (5.0 g; 23.4 mmol) and con H₂SO₄ (5 ml) were heated to reflux in methanol (200 ml) for 3.5 h. The reaction mixture was concentrated to 1/3 of its original volume (rotary evaporator). The methanol solution was poured over crushed ice to precipitate the products. The white pasty precipitate was collected by vacuum filtration and recrystallized from methanol (125 ml) to give 1,3,5-benzenetricarboxylic acid-trimethylester (78) (4.8 g; 81%). MP; 144-144.5, lit. value¹⁰ 144 °C; MS (m/e) ; calculated for C₁₂H₁₂O₆ = 252.0634, observed = 252.0640.
Synthesis of 2-naphthylidazomethane (107) \(^{11}\)

A solution of 2-naphthaldehyde (3.0 g; 19.2 mmol) was dissolved in ethanol (100 ml). Toluenesulfonylhydrazide (3.93 g; 21.1 mmol) was added to the ethanol solution and the resulting reaction mixture was maintained at reflux temperature for 20 hours. The reaction mixture was allowed to cool, and the resulting slurry was filtered to yield a pale yellow powdery solid (5.1 g; 82 %). Recrystallization from ethanol gave the 2-naphthyltosylhydrazone \(^{12}\) (123) (3.0 g; 48 %) as pale yellow needles. MP; 170-171 °C, lit. value \(^{12}\); 174 °C.

Tosylhydrazone 123 (1.32 g; 4.1 mmol) was added to 15 ml of ethylene glycol (70 °C) to which 0.14 g of sodium metal had been dissolved. The solution was maintained at 70 °C for 20 minutes. After cooling to room temperature, diethyl ether (15 ml) was used to extract the diazo compound from the ethylene glycol solution. This procedure was repeated three times. The combined ether extracts were washed with 10 % sodium hydroxide solution (3 x 15 ml) and dried over anhydrous magnesium sulfate. Removal of solvent gave 2-naphthylidazomethane (107) (310 mg; 45 %). MP; 47-50 ; MS (m/e); calculated for C\(_{11}\)H\(_8\)N\(_2\) = 168.0699, observed = 168.0722; IR (pentane, cm\(^{-1}\)) 2064 (diazo stretch).
References

1. This value was not measured for our system with this gas mixture. Manufacturer reports maximum energy/pulse of 110 mJ/pulse at 308 nm; we have measured a value of ~ 80 mJ/pulse at 308. Lumonics specifications claim a maximum pulse energy of 250 mJ/pulse at 249 nm.


References

13. Berson, Jerome, Dept. of Chemistry Yale University, personal communication.


Appendix A;

GC-Trace of the Products of Photolysis of $\alpha,\alpha'$-dichloro-m-xylene in Ethanol at 77 K.
Figure 37. GC-Trace of the Products of Photolysis of $\alpha,\alpha'$-dichloro-$m$-xylene in Ethanol at 77 K.
Appendix B;

GC Trace of the Products of Photolysis of 2,4,6-Trifluoro-1,3-diazidobenzene (0.005 M in 2-MeTHF); solution was photolyzed (broadband Hg lamp) at 77 K.
Figure 38. GC Trace of the Products of Photolysis of 2,4,6-Trifluoro-1,3-diazidobenzene (0.005 M in 2-MeTHF); solution was photolyzed (broadband Hg lamp) at 77 K.
Appendix C:
Mass Spectrum of the Dimer of 2,4,6-Trifluoro-1,3-diaza-diyl.
Figure 39. Mass Spectrum of the Dimer of 2,4,6-Trifluoro-1,3-diaza-diy1.
GC-MS performed on a sample of 2,4,6-Trifluoro-1,3-diazidobenzene (0.005 M in 2-MeTHF) which had been photolyzed (broadband Hg lamp) at 77 K.