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STUDIES OF THE TRIPLET SEN SITIZED DECOMPOSITION OF AZOALKANES AND OF THE THERMOLYSIS OF STABLE CIS ALKYLDIAZENES

Rice University

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Studies of the Triplet Sensitized Decomposition of Azoalkanes
and of the
Thermolysis of Stable Cis Alkyldiazenes

by

Matthew A. Page

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

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Edward S. Lewis, Professor of Chemistry

HOUSTON, TEXAS
April, 1980
ABSTRACT

Studies of the Triplet Sensitized Decomposition of Azoalkanes
and of the
Thermolysis of Stable Cis Alkyldiazenes

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Matthew A. Page

The triplet sensitized photolysis of methylazo-(1,1-dimethyl-2-propene) (3) and azo-bis-(1,1-dimethyl-2-propene) (4) have been examined due to their unique ability to decompose under those conditions. The cis isomer was found by two independent experiments not to lie on the triplet sensitized decomposition pathway. Instead, the azo triplet decomposes directly to radicals plus N₂. This result encouraged an attempt to observe a SCE (spin correlation effect). By means of a crossover experiment, it was established that the cage effect was substantially lower for triplet sensitized decomposition than for direct irradiation, which is consistent with a SCE. However, the data are also "consistent" with a number of other hypotheses as well. These alternate proposals are discussed in some detail; from this discussion emerges a hybrid postulate that incorporates an SCE and a long-lived diazenyl radical in the triplet sensitized decomposition of these azo compounds.

Two stable cis azoalkanes were isolated (azoadamantane and azo-norbornane). The activation parameters for the disappearance of the
cis isomer of both compounds were determined. These activation parameters for cis-azoadamantane disappearance were compared to those obtained by others. The postulate that decomposition of azoalkanes is sensitive to the nature of the incipient radical is borne out by our results. Finally, an interesting discrepancy was noted in which the 1-adamantyl radical is estimated as unfavorable due to the reluctance of azoadamantane to decompose thermally. On the other hand, the 1-adamantyl radical is judged as similar to the t-butyl radical by other means.
Acknowledgments

I would like to express my gratitude:

-To Paul S. Engel, for his patient and skillful direction of my graduate study. For each immovable problem, he provided an irresistible solution.

-To all of my friends and acquaintances at Rice during these years, whose good advice, good companionship and occasional laughs lightened the load.

-To the Robert A. Welch Foundation and the National Science Foundation for their generous financial assistance.

-To my parents, who put up with this gag much longer than they should have.

-To Ellie Biebers for her assistance in typing the thesis.

-To Linda Connell for preparing the drawings contained herein.
To my parents,
Reavis and Patricia
and to the memory of
Michael Vaughan Dollar
"Or set upon a golden bough to sing
To lords and ladies of Byzantium
Of what is past, or passing, or to come."

William Butler Yeats
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INTRODUCTION

Alkyldiazenes (azoalkanes) have the general structure shown in Figure 1. The R group can either be alkyl or aryl, and either a cis or trans configuration about the double bond is possible. In addition, the azo linkage can be incorporated into a ring, forming a cyclic azo compound.

\[
\begin{align*}
\text{trans} & \quad R-N=N-R \\
\text{cis} & \quad R-N=N-R \\
\text{cyclic} & \quad (CH_2)_n \quad N \quad N
\end{align*}
\]

Figure 1. Various types of azoalkanes

A basic illustration of the chemistry of these compounds is shown in Figure 2. When the azoalkane is represented by the linear form, this implies that the geometry of the alkyldiazene is left unspecified.

\[
\begin{align*}
R-N=N-R & \overset{h\nu \text{ or } \Delta}{\longrightarrow} R^\cdot + N_2 + R^\cdot \\
R-N=N-R & \overset{h\nu}{\underset{(\Delta)}{\longrightarrow}} R-N=N-R \\
RCH_2-N=N-R' & \longrightarrow RCH=NNHR'
\end{align*}
\]

Figure 2. Basic chemistry of azoalkanes
The most important reaction of alkyl diazenes is thermal decomposition to alkyl radicals plus N₂. This homolysis is used on an industrial scale to initiate free radical polymerizations which form products of commercial interest.² Academically, this reaction is valuable as it generally produces free radicals cleanly without the complications caused by induced decomposition and polar effects.³ Because of this and the fact that the radicals are partly developed in the transition state, azoalkane activation parameters are useful as gauges for the relative stability of the incipient radicals formed.⁴

Another important reaction is the photochemical interconversion between the cis and trans isomers.⁵ When the R groups are tertiary alkyl, and especially when the incipient radicals are resonance stabilized, the cis isomer instantaneously thermolyses to radicals plus N₂. In these cases, therefore, the cis isomer is much less stable than the trans. However, sometimes the cis isomer is stable at room temperature and can be converted partially back to the trans by irradiation.

One particular reaction which is very troublesome for azoalkanes possessing an α-hydrogen is tautomerization.⁶ As the resulting hydrazone is thermodynamically more stable than the azoalkane, tautomerization can compete, in the presence of an adventitious acid catalyst, with decomposition or photochemistry. The more reactive cis isomer is particularly sensitive to tautomerization. As a consequence, the most easily studied azo compounds usually contain fully substituted alpha carbons (i.e., no α-hydrogens) to eliminate potential tautomerization.

Implicit in any mention of azo compounds is the assumption that one is referring to the trans isomer. This bias is due to the fact that the cis diazenes are more reactive toward decomposition as noted above.
However, the cis isomers of some azo compounds are known to exist. Cis aromatic diazenes have been known for quite some time. On the other hand, cis aliphatic azo compounds were discovered only about 15 years ago, probably for the reason cited above.

The behavior of a "typical" cis isomer (see Figure 3) is best illustrated by work done by Mill and Stringham on the irradiation of azo-t-butane (ATB).

\[ \text{N} \equiv \text{N} \quad \xrightarrow{h\nu} \quad \left[ \begin{array}{c} \text{N} \equiv \text{N} \\ \downarrow \end{array} \right] \]

\[ 2 \text{N} \equiv \text{N} + \text{N}_2 \]

Figure 3. Irradiation of azo-t-butane (ATB)

Irradiation of ATB at ambient temperatures produced \( \text{N}_2 \) and the characteristic products of t-butyl radicals. Irradiation below -50°C produced an intensely yellow solution, but virtually no \( \text{N}_2 \) was generated. However, upon warming the solution, \( \text{N}_2 \) was evolved concurrent with the disappearance of the yellow color. Mill and Stringham deduced that cis-ATB was produced upon irradiation. If the solution was kept cold, the cis remained stable until the solution was warmed above its decompo-
sition temperature. Irradiation at ambient temperature, on the other hand, generated the cis isomer which instantaneously decomposed.

As mentioned before, activation parameters for decomposition of azoalkanes seem to be determined by the relative stability (or instability) of the incipient radicals. Although thermal studies have been almost exclusively on the trans isomer, this correlation should hold also for the cis compounds. The range of decomposition temperatures, however, needs to be shifted downward to account for the added reactivity of the cis isomer. This has been verified experimentally. 4

Another area of long standing interest for free radical chemists has been the problem of cage effects and radical efficiency. In the early days of studying azonitriles (for the purpose of using them as initiators of free radical reactions and oxidations), it was noticed that there was a substantial inefficiency in the production of radicals. 10 This was rationalized as a recombination of geminate pairs of radicals inside the solvent cage before they could escape and become "free radicals". The radical efficiency represents the fraction of radicals which escape the cage and are therefore available for radical chain reactions. That fraction (α) which recombines with geminate partners is called the cage effect. The phenomena of cage effects are based on the fact that solvent molecules are able to restrict the diffusion of the geminate pair of radicals from one another. The pair remains together for a finite amount of time, during which the recombination step can take place.
Figure 4. Scheme showing genesis of cage and non-cage products

One method for determining $\alpha$ is called a crossover experiment. The technique for doing this might be best described by using as an example the work by Lyon and Levy.\textsuperscript{11,12} These workers conclusively demonstrated the presence of a cage effect in the photolytic dissociation of azomethane. The photolysis of a 50-50 mixture of azomethane-$h_6$ and azomethane-$d_6$ resulted in a mixture of isotopically labeled ethanes ($h_6$, $h_3d_3$ and $d_6$), which was analyzed by mass spectrometry. Consideration of the limiting cases might facilitate understanding of the technique. These limiting cases would of course be a 0% cage effect and that of a 100% cage effect. In a situation with a 0% cage effect, one would expect a statistical mixture of products consisting in the azomethane work of a 1:2:1 mixture of the $C_2H_6:CH_4CD_3:C_2D_6$ products. On
the other hand, a cage effect of 100% implies that no radicals can ever escape from the cage so that no crossover product is ever seen. Con-

\[
\begin{bmatrix}
\text{CH}_3 \cdot & \text{CH}_3 \cdot \\
\end{bmatrix}
\rightarrow \text{CH}_3 \cdot \text{CD}_3 \rightarrow \text{CH}_3 \text{CD}_3
\]

\[
\begin{bmatrix}
\text{CD}_3 \cdot & \text{CD}_3 \cdot \\
\end{bmatrix}
\rightarrow \text{CH}_3 \cdot \text{CH}_3 \rightarrow \text{C}_2 \text{D}_6
\]

Figure 5. Outline of possibilities for caged methyl radical

sequently, the ratio of \( \text{C}_2 \text{H}_6 : \text{CH}_3 \text{CD}_3 : \text{C}_2 \text{D}_6 \) ought to be 1:0:1. In the work of Lyon and Levy, the limiting cases nicely fit the experimental results. They concluded that the cage effect in the gas phase was 0% and the cage effect of photolysis in isooctane solution was nearly 100%. It has been pointed out that methyl radicals that escape the cage should abstract hydrogen atoms from isooctane instead of recombining. Since the methane formation was not considered in calculating the cage effects, it is likely that the "actual" cage effect is lower than 100%. In fact, it is about 70% (see p. 49).
An interesting question in this area concerns the effect of spin multiplicity on the cage effect. The central question is whether or not a triplet radical pair, on account of its parallel spins, would result in a lower cage effect than a singlet radical pair with antiparallel spins. The term spin correlation effect (SCE) which was coined by

![Diagram](image)

Figure 6. Effect of spin multiplicity on the cage effect

Bartlett,\textsuperscript{13,14} describes this situation in which the chemical behavior of a radical pair is determined solely on the basis of its spin orientation.

An illustration of why this might be the case can be seen in Figure 6. The singlet radical pair can either recombine or diffuse apart. On the other hand, the triplet radical pair cannot recombine, but can separate by diffusion. A spin inversion step prior to recombination is required for the geminate partners of the triplet radical pair to be able to recombine. This implies that diffusion will become relatively more important due to the increased amount of time before re-
combination can occur for the triplet radical pair; hence, more triplet radical pairs will be separated by diffusion than in the singlet radical pair case. Of course, the magnitude of this effect depends upon the rate of spin inversion. The lower the rate of spin inversion, the lower the triplet sensitized cage effect (the more radical pairs will be separated by diffusion).

With this in mind, Fox and Hammond\textsuperscript{15} attempted to determine whether or not an SCE could be observed. Their basic strategy was to irradiate a solution containing a triplet sensitizer and an appropriate azoalkane. The sensitizer was expected to absorb the light, intersystem cross to the triplet manifold and transfer triplet energy to the azo compound. The excited azoalkane would then decompose to a triplet radical pair plus $N_2$. By determining the cage effect of this process, and by comparing it to the cage effect of direct irradiation (which presumably goes through the singlet radical pair), they hoped to see whether a SCE could be observed.

Fox and Hammond used the scavenger method to determine the cage effects. In its simplest form, a substance is placed in the solution that reacts quantitatively with all non-cage (free) radicals. The cage effect ($\alpha$) is the amount of dimer recovered divided by the total number of radical pairs generated.

Fox and Hammond irradiated triphenylene in the presence of azo-1-cyanocyclohexane (ACC), using cumene to scavenge the free radicals. Their results, shown in Table 1, indicate that in their system there is no difference between singlet and triplet decomposition.
Table 1. Dimer Yields from the Decomposition of ACC

<table>
<thead>
<tr>
<th>Direct Photolysis</th>
<th>Sensitized Photolysis</th>
<th>Thermolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.9%</td>
<td>17.7%</td>
<td>9.4%</td>
</tr>
</tbody>
</table>

a. Mean value determined with cumene as the solvent at 28°C.
   b. Mean value determined with cumene as the solvent and triphenylene as the sensitizer at 28°C.
   c. Mean value determined in chlorobenzene at 80°C using Br₂ or I₂ as a scavenger.

Nelsen and Bartlett\textsuperscript{16} were also interested in the effect of spin on the apparent cage effect. Along with some work on thermal cage effects, they decided to reinvestigate the hypothesized dependence of cage effect on spin multiplicity. They irradiated triphenylene in the presence of azocumene using a nitrooxide as a radical scavenger. Their results, shown in Table 2, matched those of Fox and Hammond; namely, there was no difference in the cage effect between direct irradiation and triplet sensitized decomposition (singlet radical pairs vs triplet radical pairs). The conclusion arrived at by both groups was that spin inversion
Table 2. Cage Effect Values of Photosensitized Decomposition of Azocumene in Toluene

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>% Cage Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>35-45(^b)</td>
</tr>
<tr>
<td>triphenylene</td>
<td>35.7(^c)</td>
</tr>
<tr>
<td>pyrene</td>
<td>42.2(^d)</td>
</tr>
<tr>
<td>pyrene</td>
<td>38.8(^e)</td>
</tr>
<tr>
<td>pyrene</td>
<td>35.6(^f)</td>
</tr>
<tr>
<td>pyrene</td>
<td>35.1(^f)</td>
</tr>
</tbody>
</table>

\(^a\) Using nitroxide as a scavenger. \(^b\) Temperature not specified; a range of values. \(^c\) 20.3°C. \(^d\) 16.0°C. \(^e\) 16.8°C. \(^f\) 29.3°C.

is much faster than diffusion, and therefore is not an important factor in the amount of cage recombination observed.

However, an alternate explanation was soon forthcoming. Engel and Bartlett\(^{14}\) demonstrated convincingly that the so-called "triplet sensitizers" that had been used in both experiments were actually singlet sensitizers. That is, the azo compounds were actually intercepting the singlets of the aromatic hydrocarbons before intersystem crossing could occur. This, in turn, produced azoalkane singlets which decomposed to singlet radical pairs, not to triplet radical pairs. It is small wonder, then, that the results for the singlet and "triplet sensitized" reactions were the same.

Unfortunately, this discovery did not completely explain the problem. Using the equation given below\(^{17}\) (where \(\phi_o\) is the quantum yield in the absence of quencher, \(\phi\) is the quantum yield in the presence...
of quencher, \( k_q \) is the quenching rate constant and \( \tau_s \) is the singlet lifetime), one can calculate that the singlets should still have been

\[
\frac{\phi_o}{\phi} = 1 + k_q \cdot \tau_s [Q]
\]

(1)

able to intersystem cross to their triplet states almost completely in the Fox and Hammond case (99%) and partially in the Nelsen and Bartlett case (36%), so that some cage effect differences should have been seen. Nelsen and Bartlett's results can be explained by postulating that the nitrooxide scavengers also quench the triphenylene triplets that are formed. However, no such simple explanation can be forwarded for the Fox and Hammond results. One alternative is to postulate that the rather complicated analytical procedure buried the difference in the cage effect between the two modes of decomposition.

Although the situation concerning SCEs in acyclic azoalkanes was very obscure, the situation involving cyclic azo compounds,\(^{18}\) like compound \( \text{I} \), was much more straightforward. Porter and Barlett attempted

\[
\text{I}
\]

to observe an SCE with compound \( \text{I} \) by monitoring the stereochemistry of direct irradiation and triplet sensitized decomposition. It is clear
from Figure 7 that if a singlet biradical is formed, immediate recombination will result in stereospecific product formation. On the other hand, rotation of some bonds will racemize the asymmetric centers. Therefore, the product ratio should depend critically upon the rates of closure vs rotation. In a triplet biradical, the recombination process is inhibited by the parallel nature of the respective spins. Recombination can therefore not occur until after spin inversion at one of the two radical sites. This increases the lifetime of that biradical and allows more time for the rotations to occur. As a result, one expects to see greater scrambling of the stereochemical label.

The results (see Table 3) show that an SCE is indeed observed in this system. Cyclic and acyclic azoalkanes appeared to differ in their ability to exhibit an SCE.\textsuperscript{18a}

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Mode of Decomposition</th>
<th>%A</th>
<th>%B</th>
<th>%C</th>
<th>% retn of confign in B and C</th>
</tr>
</thead>
<tbody>
<tr>
<td>meso</td>
<td>thermal</td>
<td>49</td>
<td>43</td>
<td>2.5</td>
<td>98</td>
</tr>
<tr>
<td>d,l</td>
<td>thermal</td>
<td>51</td>
<td>3.5</td>
<td>42</td>
<td>98</td>
</tr>
<tr>
<td>meso</td>
<td>direct photolysis</td>
<td>61</td>
<td>35</td>
<td>3.5</td>
<td>95</td>
</tr>
<tr>
<td>d,l</td>
<td>direct photolysis</td>
<td>60</td>
<td>4</td>
<td>33</td>
<td>97</td>
</tr>
<tr>
<td>meso</td>
<td>thioxanthone sensitized</td>
<td>77</td>
<td>11.5</td>
<td>8</td>
<td>61</td>
</tr>
<tr>
<td>d,l</td>
<td>thioxanthone sensitized</td>
<td>75</td>
<td>8</td>
<td>12</td>
<td>65</td>
</tr>
</tbody>
</table>

\textsuperscript{a} 1 was 0.05-0.1 M in benzene with the results in cyclohexane being the same. \textsuperscript{b} Decompositions were carried out in thoroughly degassed, sealed tubes.
Figure 7. Products obtained from the decomposition of 1.
It should be pointed out that in the case of \textsuperscript{1}, aromatic ketones were used as sensitizers as opposed to aromatic hydrocarbons. Since the rate of intersystem crossing is much faster for aromatic ketones than for aromatic hydrocarbons, one expects that the singlets of the ketones would be quenched to a lesser degree.\textsuperscript{19} In fact, Engel and Bartlett\textsuperscript{14} showed that ATB quenches the photoreduction of benzophenone and also quenches the phosphorescence of biacetyl, two lines of evidence demonstrating that azo compounds are able to quench the triplets, not the singlets, of aromatic ketones. However, the ATB did not decompose after receiving the triplet energy from benzophenone (whereas the cyclic azoalkanes did), frustrating attempts to observe an SCE in acyclic systems.

Later, Wamsler et al\textsuperscript{20} showed that aromatic ketones transferred triplet energy to azoalkanes. In addition, they determined that the energy of the azoalkane lowest triplet (T\textsubscript{1}) was about 53 kcal, in good agreement with earlier work.\textsuperscript{22} Furthermore, they showed that the maximum k\textsubscript{q}, the rate constant for quenching of an excited state by another compound (quencher), for any particular compound depended on the steric hindrance of the azoalkane to energy transfer.
EARLIER WORK ON THIS PROJECT

While working on a project concerning the effects of allylic resonance on thermal decomposition of azo compounds, Engel and Bishop\textsuperscript{21,4}\makebox[0pt][r]{\(3\)} made several compounds with the general structure of 2. For exploratory purposes, they tested the possibility that these compounds might decompose on irradiation in the presence of a triplet sensitizer. To their surprise, the quantum yields for the decomposition of these azo compounds were not zero, but in fact, very high (about 0.5). Their results, shown in Table 4, suggested that a SCE should be observed with this series of compounds.
Table 4. Quantum Yields of Triplet Sensitized Decomposition of Various Azoalkanes

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>$E_T$</th>
<th>3</th>
<th>4</th>
<th>AIBN$^b$</th>
<th>ATB$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetophenone</td>
<td>73.6</td>
<td>0.18</td>
<td>0.18</td>
<td>0.13</td>
<td>0.16</td>
</tr>
<tr>
<td>p-methoxy acetophenone</td>
<td>71.5</td>
<td>0.22</td>
<td>0.57</td>
<td>0.11</td>
<td>0.22</td>
</tr>
<tr>
<td>benzophenone</td>
<td>68.5</td>
<td>0.16</td>
<td>0.54</td>
<td>0.11</td>
<td>0.17</td>
</tr>
<tr>
<td>thioxanthone</td>
<td>65.5</td>
<td>--</td>
<td>0.35</td>
<td>0.017</td>
<td>0.12</td>
</tr>
<tr>
<td>anthraquinone</td>
<td>62.4</td>
<td>--</td>
<td>0.35</td>
<td>0.017</td>
<td>0.12</td>
</tr>
<tr>
<td>Michler's ketone</td>
<td>61.0</td>
<td>0.24</td>
<td>0.27</td>
<td>0.06</td>
<td>0.13</td>
</tr>
<tr>
<td>β-acetonaphthone</td>
<td>59.3</td>
<td>0.15</td>
<td>0.50</td>
<td>0.045</td>
<td>0.08</td>
</tr>
<tr>
<td>9-fluorenone</td>
<td>53.3</td>
<td>0.09</td>
<td>0.09</td>
<td>0.055</td>
<td>0.015</td>
</tr>
</tbody>
</table>

a. Quantum yields were determined at 6-11°C using benzene as a solvent. b. Azoisobutyronitrile. c. Azo-t-butane.

Implicit in all discussion heretofore$^{15,16}$ has been the assumption that the azoalkane triplet, if it decomposes, would give $N_2$ plus two alkyl radicals with parallel spins. A priori, however, it was impossible to distinguish this mechanism from one in which the azo triplet yields a ground state cis isomer, which subsequently thermolyzes, producing a singlet radical pair. This pair is obviously the same as that derived from direct irradiation, and therefore, if the latter mechanism described the actual chemistry, it would have been ridiculous to attempt to observe an SCE. As a result, it was imperative to determine the mechanism of the triplet sensitized decomposition of azoalkanes before other studies were considered.
Figure 8. Two possible pathways for triplet sensitized decomposition

The two possible pathways for decomposition are illustrated in Figure 8. A salient feature is that one pathway has a thermally labile intermediate, whereas the other does not. Therefore, if an experiment were done at a temperature at which the azoalkane cis isomer is stable, and if one were armed with an analytical method for cis azoalkanes, then the two pathways could be distinguished.

A cursory examination of Table 4 reveals that the quantum yields for the various azoalkanes seem to be about the same regardless of the R group (see compound 2). Therefore, the compound most favorable (compound 3) for the low temperature experiment (the one with the most thermally stable cis isomer) was selected. Since concurrent thermolysis of cis azoalkanes would ruin the experiment, it was necessary to determine that the cis isomer had sufficient lifetime at the temperature of the experiment. A calculation based upon the activation parameters determined previously showed that the half-life of the cis 3 should be
about three centuries.\textsuperscript{76}

The two analytical methods used to distinguish the cis azoalkane isomer from the decomposition products (seen below in Figure 9) were \(N_2\) evolution and NMR. These methods complement one another since one follows mainly the cis isomer, whereas the other monitors the decomposition products (i.e. \(N_2\)).

\[ \begin{align*}
\text{\(5\)} & & \begin{align*} 
\text{\(6\)} 
\end{align*}
\end{align*} \]

Figure 9. Hydrocarbon products from the decomposition of \(3\)

The NMR method is based on the fact that the shift of the hydrogens on the N-methyl group is different for the cis and trans isomers. Consequently, the presence of the cis isomer can easily be determined at low temperature. In addition, the aliphatic H shifts of the decomposition hydrocarbons lie upfield in the range of \(\delta 1-2\) where only the azoalkane gem-dimethyl shift is. Therefore, the peaks due to hydrocarbons are easily distinguished from those of the azoalkanes.

The strategy of this experiment was fairly simple. The NMR tubes were prepared and a spectrum was run before irradiation on each tube (the "before spectrum"). The tube was then cooled and irradiated for a preset length of time. Another spectrum was obtained on each tube (the "during spectrum") at about \(-40^\circ\)C without the tube having been warmed. It is at this point that one determines whether the cis isomer or the decomposition products are present in the cold solution. The tubes
were then warmed to ambient temperature, and after enough time had elapsed for any thermally labile intermediates to decompose, a final spectrum was taken on both tubes (the "after spectrum").

The strategy of the low temperature N₂ evolution experiment was similar to that of the NMR experiment. The solution was cooled to -80°C (in earlier experiments, -40°C was the temperature used), and the solution was then irradiated. While the solution was still cold, all of the gases that had been evolved were collected and measured. The solution was then warmed to room temperature and all gases were again collected and measured. After each gas measurement, the composition of the gases collected was determined by vpc, using a method developed by Charlier and Obermiller.²³

If isomerization were the exclusive pathway, no gas would be evolved at low temperature. On the other hand, decomposition of trans would be indicated if the N₂ was evolved before the solution was warmed. The results of these experiments are shown in Tables 5 and 6.²⁴ As one can readily see, the general trend indicates photolytic decomposition of trans, not isomerization to cis followed by thermolysis. However, in the case of the acetone sensitized experiment, it is not clear as to the pathway it takes, resulting in an ambiguous conclusion.
Table 5. Low Temperature $N_2$ Evolution Experiment With 3

<table>
<thead>
<tr>
<th>Method of Photolysis</th>
<th>Before Warming</th>
<th>After Warming</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetone sensitized, photolysis$^b$</td>
<td>0.062</td>
<td>0.086</td>
</tr>
<tr>
<td>p-methoxy acetophenone sensitized$^c$</td>
<td>0.0615</td>
<td>0.0009</td>
</tr>
</tbody>
</table>


Table 6. Quantum Yield for the Formation of cis-3 at Low Temperatures

<table>
<thead>
<tr>
<th>Method of Photolysis</th>
<th>Cis Formation</th>
<th>Disappearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetone sensitized</td>
<td>0.23-0.34$^b$</td>
<td>$\sim$ 0.00</td>
</tr>
<tr>
<td>p-methoxy acetophenone sensitized$^c$</td>
<td>$\sim$ 0.00</td>
<td>0.11</td>
</tr>
</tbody>
</table>

a. Singlet reaction. b. Depended upon the time of irradiation. c. Triplet reaction. d. Experiments performed at -40°C.

After it had been determined that the cis isomer was not on the decomposition pathway, it seemed likely that triplet radical pairs were being formed; hence, the next step was to attempt to observe a spin correlation effect. Scavenger methods, used by both Hammond$^{15}$
and by Bartlett,\textsuperscript{16} were judged clearly unsatisfactory for this purpose. According to Bishop,\textsuperscript{25} "Use of stable free radicals as scavengers is not advisable because they usually absorb in the visible region and more importantly, they are known to be efficient quenchers of the triplet states of both aryl ketones and aromatic hydrocarbons. Hydrogen donating scavengers were not considered suitable either. Abstraction of hydrogen from cumene by the dimethylallyl radical is probably not efficient, due to the similar stabilities of the two radicals involved. Thiophenol forms diphenyl disulfide, which is yellow."\textsuperscript{25}

As a consequence, an alternate method for determining the cage effects was needed.

The method resorted to was the crossover experiment.\textsuperscript{26} \textit{4-d\textsubscript{2}} was prepared, along with \textit{4}, by methods that will be discussed later. A 1:1 mixture of the labeled and unlabelled azo compounds was photolyzed both with and without a triplet sensitizer producing dienes \textit{7(hh)}, \textit{8(ht)} and \textit{9(tt)} (head\textsubscript{=}h, tail\textsubscript{=}t), compounds referred to collectively as the \textit{C\textsubscript{10}} dimers, shown in Figure 10. Each isomer, of course, should contain

\begin{center}
\begin{tabular}{ccc}
\includegraphics[width=0.3\textwidth]{7(hh).pdf} & \includegraphics[width=0.3\textwidth]{8(ht).pdf} & \includegraphics[width=0.3\textwidth]{9(tt).pdf} \\
\textit{7(hh)} & \textit{8(ht)} & \textit{9(tt)}
\end{tabular}
\end{center}

\textbf{Figure 10. Products from decomposition of \textit{4}}
the same isotope distribution. The isomers were separated by preparative vpc, then analyzed by mass spectrometry. The l:m:h (low:medium: high peak) were calculated from the respective intensities of the 138, 139 and 140 peaks. With this ratio, the fraction of crossover product could be determined. Using equations that will be discussed later, the results shown in Table 7 were obtained.27

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>λ, nm</th>
<th>hh</th>
<th>ht</th>
<th>tt</th>
<th>avg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>366</td>
<td>---b</td>
<td>0.55</td>
<td>0.54</td>
<td>0.54</td>
</tr>
<tr>
<td>p-methoxy acetophenone</td>
<td>313</td>
<td>---b</td>
<td>0.16</td>
<td>0.15</td>
<td>0.16</td>
</tr>
<tr>
<td>thioxanthone</td>
<td>366</td>
<td>0.17</td>
<td>0.16</td>
<td>---b</td>
<td>0.16</td>
</tr>
<tr>
<td>benzophenone</td>
<td>313</td>
<td>---b</td>
<td>0.20</td>
<td>0.26</td>
<td>0.23</td>
</tr>
</tbody>
</table>

a. Photolyses carried out in benzene at 6-11°C. b. Raw data unacceptable upon inspection.
RESULTS AND DISCUSSION

Synthesis. The early synthesis used by D. J. Bishop to prepare compounds 3 and 4 was improved to reduce saturated and alkynyl impurities. These impurities made the analysis more difficult because peaks of a less reduced but more heavily deuterated dimer had the same molecular weight as a more reduced but less deuterated dimer molecule. The new syntheses of 3 and 4 are shown in Figure 11.

Quantum Yields. Although the earlier results were fairly convincing, some of the experiments needed to be improved. First of all, the quantum yield curve, which is a plot of quantum yield vs $E_T$ (triplet energy of the sensitizer), looked a bit peculiar. In addition, the use of acetonitrile as the solvent in the low temperature NMR experiment may have affected the results. Finally, the low temperature $N_2$ evolution experiment results seemed to be a bit ambiguous as noted before.

The most serious problem with the older work, and one that played havoc with all the experiments including the quantum yield determinations, was the "light leak" in the filter solution train. Consequently, a great deal of 405 nm light was transmitted by the filter into the azo solutions. This, in turn, affected several things. The actinometer does not absorb 405 nm light, but the azo does, so that all quantum yields tend to be anomalously high. In addition, the efficiency of direct irradiation is much higher than that of triplet sensitized decomposition (vide infra). Therefore, a small amount of stray light absorbed by the azo compound could cause an appreciable amount of decomposition. Also, the sensitizers absorb differing amounts at 405 nm, causing the fraction of stray light absorbed by the azos to vary as well. Wild variations in the
Figure 11. Improved syntheses of compounds 3 and 4
apparent quantum yield resulted due to the sensitivity of the quantum yield to the amount of absorbed stray light.

The sensitivity of quantum yields to stray light absorption is based upon the fact that the quantum yield of decomposition for direct irradiation is at least a factor of 4 greater than that of triplet sensitized decomposition. A simple calculation using Equation 3 (see p 40) demonstrates that 5% of stray light will produce about 20% of the total decomposition. Therefore, it is obviously desirable to reduce stray light as much as possible. Unfortunately, practical considerations dictate that some stray light absorption will be occurring. There is a minimum concentration of the azoalkane that must be present for the experiments to be successful. Therefore, a correction is needed to compensate for the unavoidable stray light absorption.

In order to rectify this problem, a solution of NiSO₄ was added to the filter solution train to remove the unwanted 405 nm light. Quantum yields for decomposition were then redetermined for several of the compounds used previously (though not all). The results are given in Table 8. Although the curve still does not conform to the shape predicted by classical energy transfer theory, it is improved over what it was previously. For example, the wild variations in quantum yield were eliminated and replaced by a gradual downward sloping curve (with decreasing $E_T$), which is at least qualitatively correct. In addition, all non-zero quantum yields for ATB were redetermined to be essentially zero, in agreement with other work.¹⁴

Finally, an explanation for a rather unusual concentration effect noted by Dr. Engel,⁷⁸ can be provided. While determining the quantum yield for the β-acetonaphthone sensitized decomposition of 4, it was
Table 8. Nitrogen Quantum Yields for Azoalkane Photolysis\textsuperscript{a}

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>$E_T^b$</th>
<th>$\lambda^c$</th>
<th>$\phi^d$</th>
<th>EAB\textsuperscript{e}</th>
<th>AIBN\textsuperscript{f}</th>
<th>ATB\textsuperscript{g}</th>
</tr>
</thead>
<tbody>
<tr>
<td>none\textsuperscript{h}</td>
<td>0.57</td>
<td>0.47\textsuperscript{i}</td>
<td>0.42</td>
<td>0.44</td>
<td>0.46</td>
<td></td>
</tr>
<tr>
<td>acetophenone</td>
<td>73.6</td>
<td>0.14</td>
<td>0.12</td>
<td>-</td>
<td>0.14</td>
<td>0.018</td>
</tr>
<tr>
<td>p-MAP\textsuperscript{j}</td>
<td>71.5</td>
<td>0.13</td>
<td>0.12</td>
<td>-</td>
<td>0.14</td>
<td>0.021</td>
</tr>
<tr>
<td>benzophenone</td>
<td>68.5</td>
<td>0.11</td>
<td>0.10</td>
<td>0.06</td>
<td>0.10</td>
<td>0.02</td>
</tr>
<tr>
<td>thioxanthone</td>
<td>65.5</td>
<td>0.12</td>
<td>0.10</td>
<td>-</td>
<td>0.07</td>
<td>0.017</td>
</tr>
<tr>
<td>anthraquinone</td>
<td>62.8</td>
<td>0.11</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
<td>0.017</td>
</tr>
<tr>
<td>Michler's ketone</td>
<td>61.0</td>
<td>0.086</td>
<td>-</td>
<td>-</td>
<td>0.06</td>
<td>0.018</td>
</tr>
<tr>
<td>$\beta$-acetonaphthone</td>
<td>59.3</td>
<td>0.068</td>
<td>-</td>
<td>0.10</td>
<td>0.04</td>
<td>0.017</td>
</tr>
<tr>
<td>1-naphthyl phenyl ketone</td>
<td>57.5</td>
<td>-</td>
<td>-</td>
<td>0.06</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9-fluorenone</td>
<td>53.3</td>
<td>0.049</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
<td>0.015</td>
</tr>
</tbody>
</table>

\textsuperscript{a} In benzene by nitrogen evolution with 313 nm irradiation. \textsuperscript{b} Triplet energy, kcal mol\textsuperscript{-1}. \textsuperscript{c} At 10°. \textsuperscript{d} At 23°. \textsuperscript{e} Ethylazoisobutyrate; quantum yield for disappearance of starting material at 25°; ref. 16. \textsuperscript{f} Azoisobutyronitrile at 13.5°. \textsuperscript{g} Azo-tert-butane. \textsuperscript{h} At 366 nm. \textsuperscript{i} In toluene at 313 nm. \textsuperscript{j} p-Methoxyacetophenone.

discovered that reducing the concentration of the sensitizer by a factor of 10 increased the quantum yield by about 20% (from 0.18 to 0.21).

Previously, one would have thought that a decrease in the concentration of the sensitizer would either reduce the quantum yield or cause no change. After discovery of the "light leak", however, it was obvious that the source of this curious effect was stray light absorption.

Examination of the table reveals several noteworthy points. First of all, electron transfer does not appear to be a viable alternative to
energy transfer as a mechanism to decomposition. The quantum yields for 4 and AIBN (shown below) seem to be roughly the same, in spite of the fact that the electronegativity of the vinyl group differs greatly from that of the cyano group. If electron transfer were responsible for the decomposition, one would expect a variation in quantum yield with varying electronegativity of the substituents. In addition, the sensitizers employed possessed substituents of varying electronegativity, yet no particular dependence of the quantum yield on the substituents can be discerned.

Another point observed in Table 8 is that decomposition seems to depend upon having a group on one side of the azoalkane that can form a resonance stabilized radical. If this condition is met, the R group on the other side does not seem to have much bearing on the ability of the azo triplet to decompose. Note particularly that the quantum yield of decomposition for 3 and 4 are about the same despite the fact that the relative stabilities of the methyl and dimethylallyl radicals are grossly different. This constancy suggests that only one bond is cleaved when the azo triplet decomposes (see below).

**Low Temperature NMR Experiment.** A problem already mentioned was that acetonitrile did not appear to be a good solvent for doing low temperature experiments. This conclusion is based on results of a low temperature NMR experiment repeated by Engel in which he used
acetonitrile as the solvent in the direct irradiation tube. None of the expected cis appeared. This experiment was therefore rerun substituting toluene-d₈ for acetonitrile. This time the cis isomer did appear in the direct irradiation tube (cf. Figure 12). No cis appeared in the tube containing the triplet sensitizer, confirming the previous result. Although the previous conclusions remain unchanged, the results are much more credible because it was demonstrated that the cis isomer could form and be detected under the photolysis conditions employed.

**Low Temperature N₂ Evolution Experiment.** As in the low temperature NMR experiment, the solvent was changed from acetonitrile to toluene-d₈. In addition, a new apparatus was constructed to facilitate the experiment (cf. Figure 13). A stirrer was incorporated to obtain more uniform irradiation and to prevent a local "hot spot" from developing which would cause the thermolysis of the cis.

The results of the experiment, shown in Table 9, confirms those obtained in the low temperature NMR experiment. Since most of the N₂ was obtained after warming the directly irradiated tube, it is clear that cis-ζ is able to survive at low temperatures in toluene.

To calculate the N₂ evolution quantum yield, it was necessary to determine the percentage of N₂ in the N₂-CH₄ mixture. The gas analyses, included in Table 9, were determined by gc as described in the experimental section.

An unexpected bonus was obtained in determining the CH₄/N₂ ratio. It is evident from the table that there is a difference between the CH₄/N₂ ratio of the direct and of triplet sensitized irradiations. This in itself is an encouraging indication that a SCE will be
Figure 12a. Low temperature NMR spectra of 3 in toluene-d₈ at -80°C. a. Before irradiation; b. After irradiation, but before the tube has been warmed; c. After irradiation and after the tube has been warmed. Each successive spectrum has been shifted in order to prevent superimposition of the taller peaks.
Figure 12b. Low temperature NMR spectra of 3 and p-methoxyacetophenone in toluene-d$_8$ at -80°C.  
a. Before irradiation; b. After irradiation, but before the tube has been warmed; c. After irradiation and after the tube has been warmed.
Figure 13. Low temperature photolysis apparatus
Table 9. Determination of the Quantum Yields of Decomposition for 3 at Low Temperature

<table>
<thead>
<tr>
<th>Method of Photolysis</th>
<th>Quantum Yields</th>
<th>CH₄/N₂</th>
<th>CH₄/N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before Warming</td>
<td>After Warming</td>
<td></td>
</tr>
<tr>
<td>direct irradiation</td>
<td>0.08</td>
<td>0.40</td>
<td>0.12±0.03</td>
</tr>
<tr>
<td>triplet sensitization</td>
<td>0.034</td>
<td>0.007</td>
<td>0.28±0.03</td>
</tr>
</tbody>
</table>

a. Of nitrogen evolution. b. The experiments were performed at -80°C. c. The methane/nitrogen ratio in the gas obtained while the irradiated solution was kept at -80°C. d. The sensitizer employed was p-methoxyacetophenone.

observable. A scheme for explaining the results in Table 9 is diagrammed in Figure 14.

![Diagram](image)

Figure 14. Scheme demonstrating genesis of cage and non-cage products

In this scheme, it is assumed that the only non-cage products
are methane and the C\textsubscript{10} dimers, whereas all cage products are assumed to be one of the two C\textsubscript{6} recombination products. If these assumptions are correct, the CH\textsubscript{4}/N\textsubscript{2} ratio provides a quantitative measure of the cage effect. Since neither the methyl and dimethylallyl radicals have much of a tendency toward disproportionation,\textsuperscript{86} and also since escaped methyl radicals would abstract a hydrogen from toluene as opposed to recombining with another radical, these assumptions are pretty sound. (With regards to the recombination of a methyl radical with another radical, it must be pointed out that the intensity of the light was low, and therefore, the steady state concentration of radicals would consequently also be low. The probability that a methyl radical would encounter another radical of any sort would be reduced, allowing hydrogen abstraction to become the predominant reaction).

The existence of this quantitative measure of the cage effect allows a consideration of the effect of spin multiplicity in this system. If our original hypothesis about the SCE is correct, a lower cage effect for the triplet sensitized photolysis would be expected compared to that for direct irradiation. Since a higher CH\textsubscript{4}/N\textsubscript{2} ratio implies a lower cage effect, the CH\textsubscript{4}/N\textsubscript{2} ratio should be higher for the triplet sensitized decomposition. In fact, this is what is observed experimentally.

If one compares the quantum yield for triplet sensitized decomposition of 3 at room temperature (Table 8) to that at -80°C, a temperature dependence is readily seen. A rough E\textsubscript{a} for the photoreaction can be calculated by fitting to the Arrhenius equation assuming that:
a) the quantum yield is directly related to the temperature dependent rate constant,

\[ \phi_1 = Ae^{-E_R/RT_1} \]

\[ \phi_2 = Ae^{-E_R/RT_2} \]

b) no other temperature dependent processes are taking place.

\[ \frac{\phi_1}{\phi_2} = e^{\frac{-E_R}{R_1} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)} \]

The equation used to calculate the \( E_a \) is given below.

\[ \frac{\phi_1}{\phi_2} = e^{\frac{E_a}{R \cdot T}} \]

The \( E_a \) calculated for the quantum yield for the triplet sensitized decomposition of 3 was 1.3 kcal/mole. One possible source for this dependence may be a barrier on the azoalkane triplet excited state surface which hinders the decomposition. There would then be a competition between decomposition and radiationless decay. On the other hand, the temperature dependence may be due to viscosity changes in the solvent (toluene) over the 100°C range. For example, if the solvent viscosity became high enough to drastically effect diffusion control, some of the sensitizer triplets might decay before the triplet energy is transferred
to the azoalkane. In any event, it is a little risky to interpret the presence of the temperature dependence, although the observation may turn out to be very important.

Finally, there does seem to be some N₂ produced in the direct irradiation even before the solution is warmed to room temperature. This implies that the N₂ is produced without the intermediacy of a cis isomer. This small amount of gas, henceforth referred to as residual direct photolysis, seems to appear in other compounds as well. Residual direct photolysis does not seem to occur via the (same) triplet state that the sensitized reaction goes through. This follows from the fact that the products of residual photolysis and triplet sensitized decomposition differ substantially. A discussion of the remaining possibilities can be found in Engel, et al. 28

**Cage Effect Determinations.** Cage effects in direct and sensitized irradiation of 4 were rerun because several improvements in this experiment had been made since the earlier work of Bishop. 79 The elimination of stray 405 nm light was not the only improvement that had been made. A Finnigan gc/ms system was acquired after the set of cage effect determinations obtained by Bishop had been run. This instrument facilitates the experiment because the C₁₀ dimers no longer have to be separated by preparative gc. Instead, the entire reaction mixture can be separated and analyzed with a minimum of handling, improving the reproducibility of the experiment.

The first set of determinations were done with 4 and 4-d₂, identical to those compounds used in the previous work. The synthesis of 4-d₂ is given in Figure 15. 4 was synthesized in the same manner, except for the omission of the deuterium exchange step.
Figure 15. Synthesis of 4-\textsubscript{d\textsubscript{2}}

The determinations were run exactly as they had been previously except for the use of the Finnigan system (as stated above). The relative intensities were determined for m/e = 138, 139 and 140 and these were used to calculate the values of $\alpha$ shown in Table 10.

Certain experimental problems plagued this system, however. In the first place, a sizable $^{13}$\textsubscript{C} correction was needed because the peaks only differed by one mass unit. In addition, the hydrogen and deuterium atoms were being partially scrambled during the hydrogenation. Finally, a substantial amount of saturated or alkynyl impurity was
Table 10. Cage Effect Determinations with 4 and 4-d₂

<table>
<thead>
<tr>
<th>Mode of Photolysis</th>
<th>Cage Effect Values (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>direct irradiation</td>
<td>0.60</td>
</tr>
<tr>
<td>p-methoxy acetophenone sensitized</td>
<td>0.12</td>
</tr>
<tr>
<td>thioxanthone sensitized</td>
<td>0.10</td>
</tr>
</tbody>
</table>

a. In benzene at 6-11°C.

present in the starting azo (and, as a result, in the decomposition products), which makes the analysis more difficult as previously noted.

In order to lessen the need for correction, 4-d₆ was prepared according to the synthetic scheme shown in Figure 16. The improved

![Chemical Reaction Diagram]

Figure 16. Synthesis of 4-d₆
hydrogenation step was a modification of a procedure suggested by Freifulder.\textsuperscript{29}

Although the synthesis of 4 was more difficult than previously, analysis of the mass spectral data was simplified. In addition, the results needed fewer corrections and tended to be much more internally consistent. For example, the $^{13}$C correction was no longer required because three mass units now separated the molecular ions of the recombination hydrocarbons as opposed to the one before. In addition, under- and overreduction resulted in mass differentials of even numbers (2 for H$_2$; 4 for D$_2$), whereas the peaks were separated by an odd (3) number of mass units. As a consequence, the peaks representing molecules with under- or overreduced fragments would not coincide with those of the C$_{10}$ dimers, even if they eluted at the same time.

Although some corrections were eliminated, corrections for underdeuteration and stray light absorption were still necessary. The first correction was required because about 40% of the azos were d$_5$, with the remaining azos being d$_6$. The presence of an appreciable amount of d$_5$ azoalkane would tend to lower the intensity of the 144 peak of the
analyzed products below what it should be. The lost intensity appears at \( \text{m/e} = 143 \). Adding the intensity of the 143 and 144 peaks together results in a value corresponding to the "actual intensity". If we define the intensity of the 143 peak as 2c times the intensity of the peak at 144, the observed value of c was usually about 0.2. Likewise, \( \text{m/e} = 140 \) had an intensity of c times that of the peak at 141 (because only one of the sides contained deuterium). As a consequence, a new correction factor was needed in order to obtain the "actual intensity" for every set of runs. This factor served the above-mentioned function of adding the intensities of \( \text{m/e} = 143 \) and \( \text{m/e} = 144 \) together.

After the peak heights were corrected for underdeuteration, the raw cage effect values were calculated using equation 1. Here l, m and h

\[
\alpha = \frac{2.2}{2.2 + m} - \frac{m}{2.2 + m}
\]  

(1)

represent the relative peak intensities of the low, medium and high molecular weight peaks, respectively. In this case, the values of l, m and h equal the 138, 141 and 144 "actual intensities".

After raw cage effect values (\( \alpha \)) were calculated, a correction was still needed for stray light. Keeping in mind that even a small amount of stray light can cause an appreciable amount of singlet decomposition, it is necessary to determine how much stray light the azo had absorbed to make the required correction. An estimate of the fractional amount

\[
F = 1 - \frac{1}{2} \cdot \frac{a(\text{azo})}{a(\text{azo}) + a(\text{sens})}
\]  

(2)

of light absorbed by the sensitizer (F) is obtained by using equation 2. The average amount of light absorbed by the azo compound was approximated
as being one half the original (initial) absorbance value (hence the factor of one half in the equation). This fraction was in turn inserted into equation 3 (seen below). \( Q \) represents that fraction of the decomposition which proceeds via a triplet radical pair. Finally, the value of \( Q \) was used to determine the corrected cage effect values. It should be noted here that an analogous approach was employed to correct the raw quantum yield data seen before in Table 8.

The cage effect values, \( \alpha \), were calculated from the raw data given in Table 11. Table 12 includes important parameters used in these determinations and also contains \( F \) and \( Q \) values used. Table 13 contains the average cage effect values obtained in the decomposition of \( \frac{Q}{F} \) by various means.

Examination of Table 13 reveals a substantial difference in the cage effect of singlet and triplet radical pairs, in accordance with the less exact results obtained previously. All of these results support the hypothesis that spin multiplicity has a substantial effect on the behavior of the radical pair; in other words, a SCE has been observed. It is encouraging that the results of the experiments are affected only marginally by changes in the method, mass spectrometer, student, etc.

One troublesome problem was that of reduced hydrocarbon yield when \( n, \pi^* \) sensitizers were used as opposed to the \( \pi, \pi^* \) sensitizers. This re-
Table 11. Mass Spectral Peak Intensities and Uncorrected Cage Effects from Decomposition of an Equimolar Solution of 4 and 4-d₆ in Benzene at 12°

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Mode of Decomposition</th>
<th>Hydrocarbon &amp; Monitored</th>
<th>Intensity at M/e</th>
<th>(a_{\text{obs}})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>138</td>
<td>141</td>
<td>144</td>
</tr>
<tr>
<td>1ᵃ</td>
<td>thermolysis at 51°</td>
<td>ht</td>
<td>148.5</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>tt</td>
<td>159.0</td>
<td>100.0</td>
</tr>
<tr>
<td>2ᵃ</td>
<td>direct photolysis</td>
<td>ht</td>
<td>235.3</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>tt</td>
<td>214.1</td>
<td>100.0</td>
</tr>
<tr>
<td>3ᵃ</td>
<td>acetophenone sensitized</td>
<td>ht</td>
<td>58.6</td>
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</tr>
<tr>
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<td>tt</td>
<td>59.9</td>
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<tr>
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<td>p-MAP sensitized</td>
<td>tt</td>
<td>74.3</td>
<td>100.0</td>
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<tr>
<td>5ᵇ</td>
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<td>ht</td>
<td>1280</td>
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<td>tt</td>
<td>6816</td>
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<td>thermolysis at 65°</td>
<td>ht</td>
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<td>672</td>
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<td></td>
<td></td>
<td>tt</td>
<td>6880</td>
<td>4448</td>
</tr>
<tr>
<td>7ᵇ</td>
<td>direct photolysis</td>
<td>ht</td>
<td>1344</td>
<td>416</td>
</tr>
<tr>
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<td></td>
<td>tt</td>
<td>6976</td>
<td>2784</td>
</tr>
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<td></td>
<td>ttᶜ</td>
<td>960</td>
<td>320</td>
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<td>8ᵇ</td>
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<td>ht</td>
<td>800</td>
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<td>tt</td>
<td>3040</td>
<td>3200</td>
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<tr>
<td></td>
<td></td>
<td>ttᶜ</td>
<td>416</td>
<td>480</td>
</tr>
<tr>
<td>9ᵇ</td>
<td>p-MAP sensitized</td>
<td>ht</td>
<td>1120</td>
<td>1216</td>
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<td>7648</td>
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<td></td>
<td>ttᶜ</td>
<td>832</td>
<td>896</td>
</tr>
<tr>
<td>10ᵇ</td>
<td>thioxanthone sensitized</td>
<td>ht</td>
<td>1120</td>
<td>1216</td>
</tr>
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<td></td>
<td></td>
<td>tt</td>
<td>5792</td>
<td>7328</td>
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<tr>
<td></td>
<td></td>
<td>ttᶜ</td>
<td>672</td>
<td>832</td>
</tr>
</tbody>
</table>

a. Correction factors for runs 1-4 are 1.19 and 1.38 for the 141 and 144 peaks.  b. Correction factors for runs 5-10 are 1.21 and 1.42.  c. Run one month after photolysis on the same solutions; correction factors are 1.167 and 1.333.
Table 12. Parameters for Triplet Sensitized Cage Effect Measurements.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>[sens], M</th>
<th>$P^b$</th>
<th>$Q^c$</th>
<th>$a_{corr.}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.0646</td>
<td>0.975</td>
<td>0.916</td>
<td>0.02</td>
</tr>
<tr>
<td>4</td>
<td>0.0216</td>
<td>0.973</td>
<td>0.904</td>
<td>0.07</td>
</tr>
<tr>
<td>8</td>
<td>0.0750</td>
<td>0.979</td>
<td>0.928</td>
<td>0.16</td>
</tr>
<tr>
<td>9</td>
<td>0.0258</td>
<td>0.978</td>
<td>0.919</td>
<td>0.15</td>
</tr>
<tr>
<td>10</td>
<td>0.0145</td>
<td>0.976</td>
<td>0.909</td>
<td>0.07</td>
</tr>
</tbody>
</table>

a. Concentration of $4 + 4$-$d_2$ was 0.0441 M. b. See eq. (2). c. See eq. (3).

Table 13. Average Cage Effects for Decomposition of $4$.

<table>
<thead>
<tr>
<th>Decomposition</th>
<th>Runs</th>
<th>$a_{corr.}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>thermolysis at 54°</td>
<td>1,5,6</td>
<td>0.44</td>
</tr>
<tr>
<td>direct photolysis</td>
<td>2,7</td>
<td>0.61</td>
</tr>
<tr>
<td>acetophenone sensitized</td>
<td>3,8</td>
<td>0.09</td>
</tr>
<tr>
<td>p-MAP sensitized</td>
<td>4,9</td>
<td>0.13</td>
</tr>
<tr>
<td>thioxanthone sensitized</td>
<td>10</td>
<td>0.07</td>
</tr>
</tbody>
</table>
duction in hydrocarbon recovery manifests itself as a lower intensity of the ions of interest in the mass spectrometer. As a consequence, the values of $\alpha$ obtained with the $\pi,\pi^*$ sensitizers were often less reproducible. The cause of this problem undoubtedly lies in the fact that $\pi,\pi^*$ sensitizers have a tendency to add in a [2+2] manner to olefins or abstract hydrogen atoms from hydrocarbons.$^{30}$ Therefore, the usual triplet sensitized azoalkane decomposition probably occurs, followed by a subsequent reaction of sensitizer with the $C_{10}$ dimers.

Control experiments were run in order to insure that the results in Table 13 were not simply an artifact of the reaction. We were especially concerned that the labels were being scrambled after the two alkyl fragments had recombined, for example, by the mechanism in Figure 17.

![Figure 17. Mechanism for scrambling of deuterium label](image)

In the control experiment, 1:1 mixtures of $h_6$ and $d_6$ hydrocarbons (produced by thermalyzing small amounts of the respective stock solutions separately so that concentrations of the hydrocarbons would approximate that of the real experiment) were combined and the amount of sensitizer
comparable to that in the real experiment was added to the solution. The solutions were degassed as usual, and irradiated for slightly less time than in the azoalkane experiment in the same apparatus. The solution was then analyzed by gc/ms as usual. No crossover product was observed in any of the solutions, demonstrating that no scrambling took place.

The argument for a mechanism involving triplet sensitization is bolstered by the observation that 4 quenches the phosphorescence of benzophenone. The quenching rate constant \( k_q \) was calculated to be about \( 1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \), which compares to Wamser's determination for the \( k_q \) of azo-t-butane \( (8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}) \). It is unfortunate that our \( k_q \) is not in as good agreement as one would like with the values obtained previously for analogous compounds. However, the important point here is that triplet energy transfer does indeed appear to take place.

**Alternative Explanations for the Cage Effect Data.** Thus far, the cage effect results have been interpreted in the context of a spin multiplicity effect. That is, it is solely the spin multiplicity of the radical pair that governs the cage effect. However, two alternate hypotheses exist that also could explain the data: a "hot radical" postulate and diazenyl radical formation solely in the triplet sensitized decomposition.

There are actually two "hot radical" postulates that need to be mentioned. The first of these concerns the excess kinetic energy that the newly formed radicals might possess. Since uv irradiation provides the azoalkanes with a large excess of energy above that needed for dissociation, it seems plausible that the derived radicals could have excess kinetic energy which could enable them to diffuse more rapidly
than a vibrationally equilibrated radical.\textsuperscript{31} However, a study of azo-
methane demonstrated that the cage effect is about 70\% regardless of
the wavelength used to irradiate the azoalkane (254, 313 and 366 nm).\textsuperscript{32,14}
If excess energy were contributing to a decrease in cage effect, it
seems reasonable that the more excess energy available, the lower would
be the cage effect. However, this is not observed experimentally.

Another "hot radical" postulate was developed in order to explain
the "anomalous" work of Porter and Bartlett\textsuperscript{33} (cf. Figure 7). By using
rates of rotation and the activation energy for closure (7.4 kcal/mole)
determined from the pyrolysis work on dimethyl cyclobutane and applying
this information to the work of Porter and Bartlett, Stephensen and
Brauman\textsuperscript{34} deduced that a surprisingly low rate of spin inversion was re-
quired to explain the loss of stereochemistry in triplet sensitized
decomposition of 1. As a consequence, they felt an alternative hypoth-
esis was needed. The alternate proposal was that spin inversion was
fast in both cases, but in the singlet case, one had a vibrationally
"hot radical", whereas in the triplet case, the radical was vibrationally
equilibrated. The result of this excess energy of the hot diradical was
that the diradical was able to overcome any barrier on the potential
surface and quickly relax to a cyclobutane. On the other hand, the
vibrationally equilibrated radical would require more time to overcome
the barrier; as a result, closure would be slower and rotation would have
more of a chance to compete. The result would be that the "hot diradical"
would have greater stereospecificity because of greater rates of ring
closure.

This mechanism could also explain our cage effect results. One
would assume that radical pairs from triplet sensitized decomposition
of 4 were thermally equilibrated while direct irradiation (with the subsequent thermolysis of the cis isomer) resulted in a "hot radical" pair. The spin inversion is assumed here to be so fast that it would not be a factor. The vibrationally cool radical pair generated from the triplet sensitized decomposition would have to cross a barrier to recombination, whereas the vibrationally excited radical pair could more easily relax to a C\textsubscript{10} dimer.

Unfortunately, this attractive hypothesis was based originally on the assumption that secondary and tertiary radicals have the same rate constant of rotation. In fact, even prior to this publication, it had been estimated that rotation of a secondary radical is ten times faster than that of a tertiary radical.\textsuperscript{35} Recently, studies of the decomposition of 10\textsuperscript{36,37} demonstrated that stereochemistry is essentially scrambled. The diradical intermediate behaves identically to one derived from the pyrolysis of dimethylcyclobutane.\textsuperscript{34} On the other hand, the diradical of Porter and Bartlett\textsuperscript{33} is not similar to either of the other two diradicals because the diradical of Porter and Bartlett is tertiary, whereas the diradicals of Dervan and of Waters are secondary. Since all precursors to diradicals with analogous structures (similar substitution on the α-carbons of each of the radical centers) give similar product ratios, there are no experimental results which require the "hot
radical" explanation. The slower rotation rate of tertiary radicals allowed the stereospecificity to be greater than Stephensen and Brauman expected. It is interesting to note that the earlier estimates of secondary radicals rotating more rapidly than tertiary radicals is qualitatively supported by a comparison of 1 and 19.

In addition to the criticisms above, this explanation for our data would fail on a number of other points. First of all, quenching of the vibrationally excited radicals should be extremely fast in solution. It has been previously shown that collisional deactivation is extremely rapid in the gas phase even down to pressures around 7 torr. Therefore, it seems unreasonable that the hot radicals could have an appreciable lifetime in solution. In addition, the barrier to recombination for two free radicals is thought to be small. Surmounting the barrier should not be the problem that it is with the diradicals mentioned in the previous paragraph.

The other hypothesis available to explain the experimental results is that a diazenyl radical (R-N=N-) is formed in the triplet sensitized photolysis of the azo compounds. The diazenyl radical would have to live

\[ \text{Diazenyl Radical} \]

long enough for it to escape from the cage, whereupon the diazenyl radical could decompose to the alkyl radical plus N\(_2\). A crossover ex-
periment could not distinguish between this mechanism and an SCE.

Although the diazenyl radical looks too unstable to be an intermediate, there is actually a reasonable amount of evidence supporting its existence. In the first place, it has been shown above that triplet sensitized photolysis appears to proceed through one-bond cleavage, implying the transient existence of a diazenyl radical. Also, theoretical work by Baird has indicated that a 3 electron bond (such as a diazenyl radical) has some stabilization. He points out that although R-N=\(\text{N}^-\) decomposition to hydrogen atom plus \(\text{N}_2\) is probably an exothermic process (consequently, R-N=\(\text{N}^-\) is certainly exothermic), theoretical calculations indicate that the diazenyl radical has some kinetic stability. The question remains as to how much kinetic stability these radicals actually have.

There is also more concrete evidence that diazenyl radicals can have a finite lifetime if they decompose to \(\text{N}_2\) plus particularly unfavorable alkyl radicals (methyl, 1-norbornyl). Seltzer's work on azo compounds using secondary isotope effects renders a diazenyl radical intermediate plausible (though not absolutely necessary) to explain the results in the thermal decomposition of methylazo-\(\alpha\)-phenylethane (II).

![Diagram of methylazo-\(\alpha\)-phenylethane](image)

Furthermore, when one of the two possible optical isomers of this azo-alkane was thermally decomposed at 162°C, "the rate of optical loss was greater than the rate of \(\text{N}_2\) evolution." This observation requires the
intermediacy of a diazenyl radical or tautomer formation.\textsuperscript{44} However, there was no mention of tautomer formation.

![Diazenyl radical]

Other evidence supporting the existence of a diazenyl radical is an experiment performed by Porter, et al., in which the 1-norbornyldiazenyl radical was actually trapped.\textsuperscript{45} In addition, I2 was observed by 15N CIDNP.

![Norbornyl azocumene]

Porter and coworkers studied the thermal decomposition of cis-norbornyl azocumene produced by irradiation of the trans compound.

![Azocumene with 15N]

When theazo was labeled with 15N and the thermolysisc was effected in an 15N spectrometer, a strongly enhanced absorption was noted in the spectrum.
This implied the recombinaiton of cumyl and 12.

It is possible that 12 could exist while the methyldiazenyl radical (13) does not. 13 would be an intermediate in the triplet sensitized

\[ \text{CH}_3-\text{N}=\text{N}. \]

\[ 13 \sim \]

decomposition of 3 if one-bond cleavage were the true mechanism. A hypothetical reaction, illustrated in Figure 18, reveals that the

\[ \text{[Chemical Structure]} + \text{CH}_4 \xrightarrow{\text{graphical representation}} \text{[Chemical Structure]} + \text{CH}_3. \]

Figure 18. Hypothetical reaction to determine relative stabilities of the methyl and 1-norbornyl radicals

existence of 12 implies the existence of 13. Calculations indicate that the left side of the chemical equation is favored by about 7 kcal/mole over the right side.47,48 This, in turn, implies that the methyl radical is somewhat less favored than the 1-norbornyl radical.49 Therefore, since 12 has been trapped and the decomposition of 13 produces even more thermodynamically unfavorable alkyl radicals, it is entirely reasonable that 13 should exist as a discrete intermediate.
It could be argued that this analysis applies to 13, but not to the dimethylallyldiazenyl radical (14), which could decompose to a much more favorable radical. In view of its potential for supplying information on this particular point, the decomposition of 4 achieved by heating, direct irradiation and triplet sensitized decomposition was studied using the CIDNP technique. The results were kindly obtained for use by Professor G. L. Closs (University of Chicago). Thermolysis of 4 in DMSO at 108°C and direct irradiation produced no CIDNP peaks of interest. However, thioxanthane-sensitized photolysis in CDCl₃ or in benzene-d₆ resulted in greatly enhanced absorption for the methyl protons of the hydrocarbon recombination products with the emission peaks seen in emission. Applying Kaptein's rule⁹³ for the net effect to a radical pair from 14 and a dimethylallyl radical fragment, we obtain

\[ \Gamma_{ne} = \mu \in \Delta g A_i = + + + + = + \]

where \( \mu \) is + for a triplet precursor, \( \epsilon \) is + for recombination product, \( \Delta g \) is + because \( g \) (dimethylallyl) > \( g \) (diazenyl), and \( A_i \) is + for the methyl groups on the \( \alpha \) carbon of an alkyl radical.⁹⁷ This leads to \( \Gamma_{ne} \) being +, meaning that the methyl protons should show enhanced absorption while the emission is expected. Closs explained, "Most likely we have a (radical) pair with a triplet precursor consisting of the (dimethyl) allyl radical and another radical with a smaller \( g \)-factor. The most
likely candidate would be the (dimethyl)allyldiazenyl radical which is expected to have a g-factor smaller than the free electron value.

However, a second possibility involves a pair generated from a singlet precursor which consists of the (dimethyl)allyl radical and another species with a g-factor larger than the free electron value... I prefer by far the first explanation.\textsuperscript{50,51} The diazenyl radical intermediate can be viewed as a viable intermediate.

In order to understand how this diazenyl radical hypothesis applies to 4, it is helpful to examine the scheme seen in Figure 19. First of all, the triplet of the azoalkane probably decomposes to the diazenyl-alkyl radical pair A (see above). If the diazenyl radical loses N\textsubscript{2}, intermediate B of a triplet alkyl radical pair will be formed. Spin inversion to form a diazenyl-alkyl singlet radical pair is though to be unlikely. No CIDNP was ever seen in the starting material and C is able to recombine to starting material. The two radicals can diffuse apart to form the free (uncaged) radical pair (intermediate E). Diffusion back together of a geminate pair is highly unlikely.\textsuperscript{83} Recombination to form the starting azo is unlikely again because there was no CIDNP effect in the starting azo compound and also because the lifetime of the diazenyl radical is probably limited severely. Intermediate E will therefore automatically become intermediate F. The radical pair of intermediate B can diffuse apart to become the uncaged pair (intermediate F) or spin inversion can occur in one of the two radicals to form a caged singlet radical pair (intermediate D). Since the triplet sensitized cage effect is not zero, we know that intermediate D must form to some extent. In fact, using 0.1 as an average for the observed \alpha of triplet sensitized decompositions, and using as an average value
Figure 19. Scheme illustrating possible pathways for the decomposition of 4.
0.6 for direct irradiation decompositions (singlet radical pair), one can estimate that 15-20% of the triplet radical pairs generated end up as the singlet alkyl radical pair D, whereas the remainder go via intermediate F.

If pathway i is followed, one is really dealing with a spin correlation effect, whereas, if pathway ii is followed, then one is observing the effect of a long-lived diazenyl radical. It is important to note that we have considered the limiting cases, and the real situation probably incorporates both pathways. The mechanism could be easily changed by a modification of the R group. For example, changing the R group from a dimethylallyl group to a methyl group might cause a shift in the decomposition pathway away from pathway i to ii.

It is not possible at this time to do this sort of analysis on the photochemical decomposition of 3. Since no CIDNP experiments have been done on this compound, little can be said about the mode of decomposition. A set of CIDNP experiments analogous to those performed on compound 4 would be helpful in determining in more detail the decomposition pathway for 3. An experiment in which the methyl diazenyl radical is trapped chemically would also be useful.
Summary of the Work on Triplet Sensitized Decomposition of 3 and 4.

Moderate quantum yields were obtained for the triplet sensitized decomposition of acyclic azo compounds where the resultant free radicals are stabilized by resonance. Low temperature N₂ evolution and NMR experiments clearly demonstrate that excited (T₁) alkyl diazenes decompose directly to radicals, without the intermediacy of the cis-azoalkane. This suggests that it might be possible to observe a spin correlation effect. Analysis of the products of the low temperature N₂ evolution experiment demonstrated that excited singlets of azoalkanes in solution do not intersystem cross to any significant degree prior to decomposition and further encouraged work on observing an SCE. Indeed, cage effects for triplet sensitized decomposition were found to be significantly lower than those of direct irradiation. While it is very tempting to ascribe this observation to an SCE, formation of diazenyl radicals in only the triplet sensitized decomposition remains a reasonable alternative hypothesis. In fact, a hybrid postulate incorporating both mechanisms probably represents the most complete and reasonable explanation of the data.
Kinetic Study of the Thermally Induced Disappearance of Two Stable Cis Azoalkanes.

In the introduction, it was noted that there is some interest in the chemistry of cis azoalkanes. However, as seen above, many cis isomers decompose rapidly either to the tautomer (if possible) or to N₂ plus radicals.⁹ As a consequence, only cis azomethane and cis azo-isopropyl had received much attention. Unlike their aliphatic analogs, cis azobenzenes only isomerize to the trans isomer.⁵³ Their failure to decompose is due to the high energy of phenyl radicals. As a result, the isomerization pathway is favored over the decomposition pathway.

The steric strain caused by Van der Waal's interaction of the two R groups is an important factor to consider in cis azo compounds. This strain destabilizes the ground state relative to the transition state, lowering ΔH° for disappearance. Therefore, a large amount of steric bulk would increase the lability of the cis isomer, regardless of the ultimate products.

It was decided that it would be interesting to see if stable cis compounds could be made which, on mild heating, would isomerize to the trans isomer. The two compounds as subjects for study were azo-adamantane (15) and azonorbornane (16). Their structures are shown in Figure 20.

It is of passing interest to mention the products of the decomposition of the cis isomer. Isomerization, of course, produces the respective trans isomer. Decomposition produces either biadamantane or binorbornane from 15c or 16c respectively.
Figure 20. Structures for cis and trans azoadamantane (15) and azonorbornane (16)

These compounds contain a number of features which make them useful for a study of this sort. First of all, they are fully saturated at the \( \alpha \)-carbon, and therefore, are not subject to tautomerization. Also, the incipient radicals are either not too good (15) or extremely unfavorable (16); in this regard, they are like arylazo compounds. The compounds should be reluctant to decompose to radicals plus \( \text{N}_2 \), increasing the possibility that the trans isomer will be the reaction. On the other hand, the large amount of steric bulk does destabilize the ground state as mentioned before. As it turned out, this allowed the kinetics of the disappearance of the cis isomer to be observed without resorting to excessively high temperatures (< 100°C).
An interesting effect of the steric strain caused by interaction of the R groups is seen in the \( \lambda_{\text{max}} \) of the two respective compounds. It has been proposed that the \( \lambda_{\text{max}} \) is a function of the NNC bond angle.\(^{54}\) This, in turn, is related to the strain energy.\(^{55,56}\) The \( \lambda_{\text{max}} \) of the compound represents the energy difference between the ground state and the \( S_1 \) state. If the ground state level is raised relative to the \( S_1 \) state, the \( \lambda_{\text{max}} \) will shift to longer wavelength. This effect is indeed observed in these compounds. One might also assume that the shift in \( \lambda_{\text{max}} \) is proportional to the amount of strain present. If this is so, one could use the equation below to calculate the strain present in \( 15\alpha \)

\[
\Delta E_{\text{strain}} = 2.86 \times 10^7 \text{ cal/mole} \left( \frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right)
\]

and \( 16\alpha \)^\(^{57,58}\) Substituted into the equation are the \( \lambda_{\text{max}} \) of the trans and the \( \lambda_{\text{max}} \) of the cis. It has been seen in less strained cis isomers that the \( \lambda_{\text{max}} \) of the cis and trans isomers are almost the same. The strain calculated by this method for \( 15\alpha \) was 14.9 kcal/mole, while the strain for \( 16\alpha \) was calculated to be 11.0 kcal/mole. The strain in \( 16\alpha \) has been measured as 12.6 kcal/mole,\(^{55}\) in good agreement with this crude calculation. However, the strain in cis-azoadamantane (\( 15\alpha \)) has been estimated at 24 kcal/mole,\(^{55}\) which is much higher than the number calculated here. Therefore, it appears that this sort of calculation is of limited value.

The ability of these compounds to isomerize from the cis to trans isomers was of some interest. Rate constants for the disappearance of the cis isomer were determined by monitoring its uv-visible absorption
spectrum, especially the $\lambda_{\text{max}}$. The rate constants and the resulting activation parameters are listed in Table 14. Included are some results from other workers in our group and other groups. Table 15 lists the activation parameters for the thermal decomposition of $\mathbf{15t}$ and $\mathbf{16t}$, along with azo-t-butane.

It is obvious from examining the table that azo-t-butane decomposes with greater facility than $\mathbf{15t}$, which implies that the t-butyl radical is more stable than the 1-adamantyl radical. The source of this disparity is somewhat puzzling, since other studies\textsuperscript{85} have shown that there is not much difference between t-butyl and 1-adamantyl radical stabilities. However, since azoalkanes are usually considered to be the most reliable gauge of incipient radical stability, these results ought to carry more weight. In any event, it does seem that a direct determination of the $\Delta H_f$ for the 1-adamantyl radical is necessary for this issue to really be resolved.

On the other hand, the stability of $\mathbf{16t}$ is hardly surprising. As shown before, the 1-norbornyl radical is almost as "bad" as the methyl radical, which in turn is much "worse" than the t-butyl radical. A discussion of the thermochemistry of $\mathbf{16}$, as well as azo-t-butane, can be found in Engel, Timberlake, et al.\textsuperscript{55}

In summary, two cis azoalkanes were prepared. One is stable at ambient ($\mathbf{16c}$), while the other compound decomposes slowly at room temperature ($\mathbf{15c}$). The activation parameters demonstrate once again that azo compound thermolysis (or isomerization) is sensitive to the relative stability of the incipient radical. The ground state of the cis isomers appears to be destabilized by the steric strain of the two bulky cis $R$
Table 14. Kinetics of Cis Azoalkane Disappearance.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k \times 10^4$ s$^{-1}$</th>
<th>Temp., °C</th>
<th>$\Delta H^#_a$</th>
<th>$\Delta S^#_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15c$^c$</td>
<td>1.97</td>
<td>18.42</td>
<td>25.9±0.5</td>
<td>13.3±1.6</td>
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<tr>
<td></td>
<td>2.82</td>
<td>21.01</td>
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<tr>
<td></td>
<td>4.07</td>
<td>23.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.03</td>
<td>25.98</td>
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</tr>
<tr>
<td></td>
<td>9.16</td>
<td>28.41</td>
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</tr>
<tr>
<td></td>
<td>13.3</td>
<td>31.38</td>
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</tr>
<tr>
<td>16c$^d$</td>
<td>0.857</td>
<td>79.50</td>
<td>31.8±0.4</td>
<td>12.8±1.2</td>
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<tr>
<td></td>
<td>1.648</td>
<td>84.58</td>
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<td>3.875</td>
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<td>4.388</td>
<td>92.10</td>
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</tr>
<tr>
<td></td>
<td>8.015</td>
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</tr>
<tr>
<td>16c$^{e84}$</td>
<td>1.640</td>
<td>83.2</td>
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<td>4.897</td>
<td>93.1</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>14.165</td>
<td>103.4</td>
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<tr>
<td>16c$^f$</td>
<td>0.818</td>
<td>81.2</td>
<td>30.0 0.5</td>
<td>11.2 1.4</td>
</tr>
<tr>
<td></td>
<td>0.885</td>
<td>81.5</td>
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<td></td>
<td>2.933</td>
<td>91.5</td>
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<td></td>
<td>3.167</td>
<td>91.8</td>
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<td></td>
<td>9.983</td>
<td>102.0</td>
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<td></td>
<td>9.150</td>
<td>102.3</td>
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<td></td>
<td>9.167</td>
<td>101.8</td>
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</tbody>
</table>

Table 15. Activation Parameters for the Thermolysis of Trans Azoalkanes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H^+$</th>
<th>$\Delta S^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15t$^{87}$</td>
<td>60.7</td>
<td>31.4</td>
</tr>
<tr>
<td>16t$^{88}$</td>
<td>53.8</td>
<td>99.0</td>
</tr>
<tr>
<td>azo-t-butane$^{89}$</td>
<td>42.2</td>
<td>16.2</td>
</tr>
</tbody>
</table>


groups; as a result, isomerization appears to be more facile than it ordinarily would. From this it was deduced that more stable cis isomers could be prepared with relative unstable incipient radicals as R groups and less bulky R groups. Again, this is supported by the fact that the cis isomers of azomethane and azoisopropyl are both known.
EXPERIMENTAL

Material and Equipment

Melting points and boiling points are uncorrected; melting points were obtained with a Mel-Temp apparatus. NMR spectra were obtained on a Varian XL-100, A-56/100 or EM-390 spectrometer using 10% solutions of material in CDCl₃ with TMS as an internal standard unless otherwise indicated. IR spectra were obtained on a Beckman IR-8, UV spectra on a Cary 17 spectrophotometer, and mass spectra on a Finnigan Model 3300 Mass Spectrometer. VPC was carried out on a Hewlett-Packard Model 700 Chromatograph and on a Barber-Coleman Electra Series 5000 flame ionization chromatograph. Hydrogenations were run both in a standard Parr apparatus and in a microhydrogenator. Photochemical experiments were carried out on a merry-go-round using as a light source a 450 W Hanovia lamp with an inner NiSO₄ filter solution and an outer K₂CrO₄ filter solution to isolate 313 light. Other experiments employed a 500 W point source mercury lamp with the same type of filter solutions.

Reagent quality benzene and toluene were dried over LiAlH₄ overnight, then distilled from LiAlH₄ through a 6" glass helices packed column. 3-Amino-3-methyl-1-butyne (Aldrich Chemical Co.) was swirled with solid KOH until an aqueous layer separated, whereupon the aqueous layer was discarded. After this process was repeated several times, the amine was distilled from KOH pellets through a 6" glass helices column. Methylamine hydrochloride was dried overnight under vacuum with P₂O₅; SO₂Cl₂ was used without purification. Toluene-d₈ was distilled from LiAlH₄ and AIBN was recrystallized from diethyl ether and ethanol.
Purification and Synthesis of Compounds

Cis-azonorbornane. Trans-azonorbornane was kindly supplied by Dr. Jack W. Timberlake (University of New Orleans). As the material had been used in previous kinetic runs, all of those various solutions were combined and the solvents removed by rotoevaporation. The resultant off-white crystals were taken up in hexane, whereupon a small portion of ethyl acetate was added to aid in the dissolution of the solid. In addition, a few drops of triethylamine were added to prevent acid-catalyzed isomerization of cis-azonorbornane back to the trans isomer. The entire solution was syringed into a tube and degassed (using a freeze-thaw cycle), after which the tube was sealed with a torch.

The tube was placed into an ice-water bath and irradiated by a 450 W lamp with a uv filter for about 2 hr. After the irradiation was completed the components were separated on an alumina column using ethyl acetate-hexane (4:96 v/v) as eluent. The cis-azonorbornane band could be easily followed by observing its distinctive yellow color. The first 20% of the azo band was discarded as was the last 10%. The solvent of the collected fraction was removed by rotoevaporation, yielding yellow crystals.

Cis-azoadamantane solutions. Azoadamantane (306 mg) was dissolved in toluene containing a few drops of triethylamine (total volume = 15 ml). Two ml of the stock solution was syringed into square tubes which were then sealed with a torch. The tubes were irradiated for about 5 min with a 450 W mercury arc lamp at -78°C (Dry Ice-isopropanol). The tubes were then stored in Dry Ice until used.
Purification of sensitizers. Anthraquinone was successively recrystallized from benzene and CHCl₃ (40 ml/g). Benzophenone was recrystallized from hexane. Michler's ketone was recrystallized three times from ethanol. β-Acetonaphthone was recrystallized from ethanol-H₂O and then from hexane. Acetophenone was dried over CaSO₄, then distilled twice. p-Methoxyacetophenone was distilled through a Vigreux column, then recrystallized from ether-pentane. Thioxanthone was purified by dry column chromatography with chloroform as eluent followed by recrystallization from ethanol. 9-Fluorenone was recrystallized from ethanol.

**NaOD in D₂O solution.** D₂O (100 g, 5.0 mol) in a dry 250 ml RB3N flask, equipped with N₂ inlet and mechanical stirrer, was cooled with an ice-salt bath under a brisk N₂ flow. Sodium (13.3 g, 0.578 mol), previously cleaned by the method of Newman, was added carefully in small chunks. The resulting NaOD-D₂O solution was allowed to stir for 5 min, then transferred to a bottle and stored under N₂.

**D₃PO₄ in D₂O solution.** To a dry 250 ml RB3N flask, equipped with a N₂ inlet, drying tube and a magnetic stirrer, was added D₂O (100 g, 5.0 mol). After cooling the solution with an ice-salt bath, P₂O₅ (3 g, 27 mmol) was added with rapid stirring under a brisk N₂ flow. A pressure equalizing addition funnel with a plug of glass wool in the bottom was placed on a 125 ml erlenmeyer flask with a standard taper joint. The system was flushed with N₂ and the D₃PO₄-D₂O solution was filtered through the glass wool into the erlenmeyer flask. The solution was stored under N₂.
N,N'Dideutero-N,N'-bis-3-(1-deutero-3-methyl-1-butynyl)sulfonimide.

N,N'-bis-3-(3-methyl-1-butynyl)sulfonimide (20.0 g, 87.5 mmol) was dissolved in 150 ml of dioxane. NaOD-D₂O solution was added until the pH was about 12, then the mixture was stirred for 1.0 hr. About half of the dioxane was then removed by rotary evaporation, and D₃PO₄-D₂O solution was added until the pH was about 7. The rest of the dioxane was evaporated and the remaining D₂O was removed from the precipitate by suction filtration. The process was repeated, yielding 17.8 g (88%) of white crystals, which were dried over P₂O₅ under vacuum. The NMR showed no acetylenic hydrogen even when the spectrum was amplified by a factor of 20. It was found convenient to carry out the first exchange with used NaOD-D₂O solution, so as to conserve D₂O.

N,N'bis-(1-deutero-3-methyl-1-butenyl)sulfonimide. In a 100 ml RBSN flask was placed, in order, 5% Pd/BaSO₄ (39.1 mg), 40 ml of THF, and quinoline (807.6 mg, 20 times catalyst weight). A 10 ml portion of THF was used to wash the quinoline into the flask. After the suspension had been stirred under H₂ for 2.0 hrs on a microhydrogenator, N,N'-dideutero-N,N'-bis-3-(1-deutero-3-methyl-1-butynyl)sulfonimide (2.65 g, 11.4 mmol) was added to the reaction flask. Hydrogenation was allowed to proceed at 1 atm at 25°C, until 515 ml of H₂ had been taken up (93% of theoretical). The catalyst was removed by filtration and then the THF was removed by rotary evaporation. The solid was dissolved in ether, and the ethereal solution was washed twice with dilute H₂SO₄ to remove quinoline, and once with NaCl solution. The procedure with Tollen's reagent and successive washings was repeated, the solution was dried over Na₂SO₄, and finally, the ether was removed by rotary evaporation. Although an NMR spectrum showed very little acetylenic compound present, there was some saturated
material. It was also readily seen in the NMR that the deuterium originally incorporated on nitrogen had been back-exchanged for hydrogen. Yield 2.5 g (93%): NMR δ 1.44 (s, 12H), 4.26 (br s, 2H); 5.05 (br d, J=10, 2H), 5.97 (sextet, J=1, 10, 2H).

Lindlar catalyst. The method was essentially that of Lindlar and Dubuis except that the catalyst was dried after the Pb(OAc)$_2$ poisoning in a 250 ml RBSN flask at 60°C under 1 mm pressure instead of in an oven.

3-Amino-3-methyl-1-butene. 3-Amino-3-methyl-1-butyne (10.0 g, 120 mmol) was hydrogenated using Lindlar catalyst as described by Frei-felder, except that the hydrogenation was carried out at 1 atm in a mic hydrogenator at 0°C. The reaction was monitored by vpc on a 250 ft capillary SF-96 column and was stopped after the 3-amino-3-methyl-1-butyne peak disappeared. The catalyst was removed by filtration and the reaction mixture was distilled through a 4" glass helices column (bp 72-74°C), yield 5.2 g (51%): NMR δ 0.99 (s, 2H), 1.15 (s, 6H), 4.95 (m, 2H), 5.95 (m, 1H). It was found on similar compounds that distillation under N$_2$ dramatically improved yields.

N,N'-Bis-3-(3-methyl-1-butenyl)sulfonimide and related compounds.

A 250 ml RB3N flask, equipped with a mechanical stirrer, addition funnel with a drying tube and a tube extending one inch into the flask, and a N$_2$ inlet was placed under a brisk flow of N$_2$ and warmed thoroughly with a heat gun. The system was then allowed to cool under the N$_2$ flow. A solution of 3-amino-3-methyl-1-butene (5.00 g, 58.7 mmol) and tri-ethylamine (6.5 g, 64.2 mmol) in 20 ml of CH$_2$Cl$_2$ was placed in the flask. After the RB flask was cooled with a dry ice-acetone bath and vigorous stirring was commenced, a solution of sulfuryl chloride (3.80 g, 28.2
mmol) in 20 ml of CH₂Cl₂ was added dropwise to the solution. After 15 min, the addition was complete, and the solution was stirred an additional 2-3 hr at -78°C. The cooling bath was removed and the solution was stirred overnight.

50 ml of a 2M HCl solution was added to the reaction flask and the solution was allowed to stir for 0.5 hr, then the two layers were separated. The organic layer was washed one more time with 2N HCl, then once with H₂O and with NaCl solution. After each separation, the aqueous layer was always washed with a small portion of CH₂Cl₂ which was then combined with the main organic layer. The organic layer was dried over K₂CO₃, then the CH₂Cl₂ was removed by rotary evaporation. The resultant white solid was dried in a vacuum dessicator to remove the last traces of CH₂Cl₂ or H₂O, yield 5.6 g (85%); mp 84.2-86.2°C; NMR δ 1.43 (s, 12H), 4.42 (br s, 2H), 5.10 (m, 4H), 6.04 (m, 2H).

1,N,N-Trideutero-3-amino-3-methyl-1-butyne. To a 100 ml RBSN flask, that had been previously heated in an oven and flushed thoroughly with N₂, was added a saturated K₂CO₃-D₂O solution (37 ml) and 3-amino-3-methyl-1-butyne (15.1 g, 181.5 mmol). This solution was stirred rapidly under N₂ for 15 hr. The layers were separated and the whole process repeated for 3.0 hr. The layers were separated again and the organic material was then distilled through a 2" glass helices packed column: bp 80-81°C; yield 11.5 g (73%); NMR δ 1.43 (s).

1,1,2,N,N-Pentadeutero-3-amino-3-methyl-1-butene was prepared from 1,N,N-trideutero-3-amino-3-methyl-1-butyne as described for the h₅ analog substituting D₂ for H₂: yield 7.7 g (64%); bp 73.0-74.5°C; NMR δ 1.23 (s); other small peaks due to a small amount of back exchange appeared at δ 4.50, 5.10 and 6.03.
N,N'-Bis-3-(1,1,2-trideutero-3-methyl-1-butenyl)sulfonimide was prepared from the deuterated amine (1.5 g, 16.7 mmol) as described above for the h₆ analog. The deuteriums on the nitrogens were lost during the workup: yield 1.6 g (81%); mp 83.8-85.0°C; NMR δ 1.44 (s, 12H), 4.42 (broad s, 2H) plus small peaks at δ 5.10 and 6.05 due to incomplete deuteration.

Azo-bis-3-(3-methyl-1-butene) (4) was prepared as described previously⁴: yield 1.4 g (79%); NMR δ 1.22 (s, 12H), 5.02 (m, 4H), 5.98 (m, 2H); UV (hexane) λmax 366 (є 29.6).

Methylsulfamylchloride was prepared according to Weiss and Schulz.⁶⁴ bp 73-78°C (0.1 mm) (lit. bp 67°C (0.03 mm)); NMR δ 3.03 (d, J=5, 3H), 5.78 (br s, 1H).

N-Methyl-N'-3-(3-methyl-1-butenyl)sulfonimide was prepared according to Engel and Bishop:⁴ mp 66.3-69.0°C; NMR (CDCl₃) δ 1.40 (s, 6H), 2.62 (br s or d, J=6, 3H), 4.67 (br, 2H), 5.07 (m, 2H), 5.90 (m, 1H).

Methyldazo-1,1-dimethyl-2-propene (3) was prepared by the method of Ohme⁶² and also by the method of Baldwin.⁶³ The azo compound was purified by preparative vpc on a 1/4" x 20' 8% OV-17 on Chromasorb W 70/80 Mesh column, followed by a short path distillation: yield 0.487 g (19%); bp 45-50°C (30 mm); NMR δ 1.22 (s, 6H), 3.63 (s, 2H), 4.90 (m, 2H), 5.90 (m, 1H); UV (hexane) λmax 363 nm (є 17.0).

2,3-Diazabicyclo-(2.2.1)-hept-2-ene was prepared by the method of Gassman.⁶⁵ Purification was effected by sublimation: NMR δ 0.89 (m, 2H), 1.10 (br s, 2H), 1.50 (m, 2H), 5.07 (br s, 2H); UV (benzene) λmax 342 (є 360).

Azo-t-butane was prepared via the sulfonimide⁶² and was spinning band distilled (bp 109°C). The purity of the compound was checked by
vpc and NMR (§ 1.16, s).
PROCEDURES

Kinetic Runs on Azoadamantane and Azonorbornane Disappearance

Rate constants for the disappearance of azoadamantane and azonorbornane, given in Table 14, were determined in an apparatus illustrated in the appendix. In a typical kinetic run, the apparatus was allowed to equilibrate at the selected temperature. A tube of azoalkane solution was then warmed up to room temperature (to prevent a drastic disruption of the thermal equilibrium of the kinetic bath). The tube was placed in the oil bath and the temperature monitored by a thermistor-Wheatstone bridge-strip chart recorder apparatus. When the temperature fluctuations dropped to an acceptable level, the chart trace was marked in order to insure that data were taken only when the temperature was well known and stable. The run was continued through ten half-lives in order to obtain an infinity point. The resultant data were plotted analytically using the POLYTWO computer program (see appendix 2), yielding the rate constants.

Quantum Yields

The azoalkanes were photolyzed in solution using a merry-go-round apparatus in an insulated, cooled water bath. A Hanovia 450 W lamp in a quartz immersion well with a dual filter train of NiSO$_4$-K$_2$CrO$_4$ was used to irradiate the solutions. Quantum yields were determined by measuring the amount of N$_2$ evolved with a Töpler pump-gas burette system. In the case of 3, the total amount of N$_2$ and methane was measured. The relative amount of each gas was then determined by vpc according to the method of Obermiller and Charlier. In general, this involved chroma-
to graphing the gases on two Poropak Q columns in series, one being at 
-78°C and one being at ambient temperature. Solutions of 2,3-diaza-
bicyclo[2.2.1]hept-2-ene (DBH) in benzene with absorbance between 2.0 
and 3.0 at 313 nm were employed as the actinometer.

For the determination of a set of quantum yields, a stock azoalkane 
solution was prepared (usually in benzene) such that the azo absorbance 
at 313 nm was below about 0.15. The appropriate amounts of sensitizer 
absorbance at 313 nm was about 2.9, thus making the total absorbance 
about 3. Twenty ml portions of these solution and of the actinometer 
solutions were then syringed into their respective irradiation tubes and 
degassed four times before being sealed with a torch. The tubes were 
irradiated for a preset amount of time in the merry-go-round apparatus 
and the amount and composition of the gases were determined by the 
Topler-burette-vpc system. Values of $\phi_{N_2}$ were based upon $\phi_{N_2} = 1.0$ for 
DBH.

Cage Effect Determinations.

The sulfonimides of 4-$h_6$ and 4-$d_6$ were oxidized separately using 
conditions similar to that for the synthesis of the isolated with the 
following exceptions: 1) no pentane was added to the oxidation mixture; 
the reaction mixture was washed instead with benzene to extract the azo-
alkane from the aqueous layer and 2) the temperature of the reaction 
was constantly monitored to ensure that 4 did not decompose during its 
preparation.

After benzene solutions of 4-$h_6$ and 4-$d_6$ were obtained, their 
absorbance was reduced by dilution to a value between 0.10 and 0.15. 
The absorbance of the two solutions was equalized by addition of small
amounts of benzene, then equal amounts of the two solutions were mixed together to make the stock solution for the cage effect determinations experiment. In each experiment, a small portion of the $4-h_6$ and $4-d_6$ solutions were kept separate to be photolyzed as a reference standard. Sensitizers were weighted into volumetric flasks and made up to the mark with the azoalkane stock solution. A 3.0 ml portion of each solution was introduced into irradiation tubes by syringe, degassed five times and sealed with a torch. The tubes were then exhaustively irradiated (5-7 hr) on the photochemical merry-go-round. As in the case of the quantum yields, the tubes were kept cool (11-15°C) to prevent complications from concomitant thermolysis. After irradiation, the solutions were stored in vials at −20°C. In early experiment, the amount of gas evolved from each tube was measured; 95-100% of the expected $N_2$ was collected.

Analysis of the hydrocarbon mixtures was performed on a Finnigan mass spectrometer (as mentioned before) using a 250' SF-96 capillary column to separate all products. Conditions were adjusted to maximize the molecular ions. At least two runs were performed for each tube. After the raw data were obtained, corrections and calculations were made as described in the results section.

A control experiment consisted of thermolyzing separate equimolar solutions of $4-h_6$ and $4-d_6$ at 60°C overnight. Equal amounts of the resultant solutions of $C_{10}$ and hexadeuterated $C_{10}$ dimers were then mixed together and to portions of this mixture was added the appropriate amount of sensitizer. The resultant sensitizer-hydrocarbon solutions were then introduced into an irradiation tube by syringe, degassed five times, sealed with a torch and irradiated for about 6 hr. Analysis of these
solutions on the gc/ms demonstrated the absence of any label scrambling
during the photoreaction.

Low Temperature $\phi_{N_2}$ Determination.

The apparatus used to determine the quantum yield for $N_2$ appearance
at low temperatures is shown in Figure 13. The square cell was con-
ected to the Topler-burette-vpc system previously described via a cold
trap with a sidearm for convenient addition and withdrawal of solutions.
The cell was cooled by refluxing Freon-13 (bp ~80°C) in the dewar; the
pressure above the Freon was controlled by a 29 cent party balloon.

Direct and triplet-sensitized quantum yields at low temperature
were determined as follows. A solution of $3$ in dry toluene was made at
the concentration appropriate to the experiment (direct photolysis:
202.3 mg/3.1 ml toluene; triplet sensitized photolysis: 15 mg/3.1 ml
toluene), whereupon $3.0$ ml of solution was syringed into the trap through
the sidearm. For the triplet sensitized reaction, the p-methoxyaceto-
phenone ($12.2$ mg) was introduced into the cell. The solution in the
trap was degassed five times. Freon 13 was condensed into the low tem-
perature apparatus using liquid $N_2$ as a cooling medium; the solution
was then distilled into the cell. After the system had equilibrated,
it was irradiated by a $500$ W lamp mercury arc lamp through a $\text{NiSO}_4$
$\cdot K_2\text{CrO}_4$ dual filter train for a known amount of time. The product gases
were then collected with the Töpler pump, a process which required
about $3$ hr. The total amount of gas was measured in the burette, and
it was then analyzed by vpc as described above. The burette was evacu-
ated, the Freon removed by distillation, and the contents of the cell
allowed to warm up. After the thermally labile intermediates had de-
composed, the contents of the cell were distilled back into the trap and the resultant gases were measured and analyzed by vpc.

Low Temperature NMR Experiment

A 10.1 mg portion of 3 was weighed into a 1.00 ml volumetric flask, which was made up to the mark with toluene-d₈ plus a few drops of TMS. A 0.50 ml portion of the solution was syringed into an NMR tube attached to a 7/22 standard taper joint. To the remaining solution was added p-methoxyacetophenone (29.8 mg) and the mixture was diluted to the 1.00 ml mark. 0.5 ml of the sensitizer-azoalkane solution was syringed into an NMR tube like the first. Both tubes were degassed five times and sealed with a torch. NMR spectra were taken on the tubes, which were then irradiated at -78°C in a dry ice-isopropanol bath for about 1 hr; then NMR spectra were again run at about -50°C. The tubes were warmed to room temperature and allowed to stand for a few minutes to thermolyze any labile intermediates, especially cis-3. Warm spectra were then run on the tubes.

Low Temperature Product Study

Two NMR tubes with solutions similar to those in the previous experiments were made. Both tubes were irradiated for 2-3 hr, whereupon NMR spectra at -50°C demonstrated the absence of any 3 (cis or trans). The contents of the tube were analyzed by vpc using a 250' SF-96 capillary column and a temperature program (30 min isothermal at 40°C; 0.5°C rise/min up to 120°C). Peaks were identified by injection of authentic samples of various compounds and by obtaining mass spectra of the various compounds as they eluted from a Finnigan gc/ms system under similar gc conditions.
REFERENCES


18. P. D. Bartlett and N. A. Porter, J. Am. Chem. Soc., 90, 5317 (1968); other SCEs have been reported in (a) P. S. Engel, D. J. Bishop and M. A. Page, J. Am. Chem. Soc., 100, 7009 (1978) and references cited therein.


27. Ref. 6, p. 51.

28. Ref. 18a, pp. 7012-7013.


31. Ref. 6, p. 3.


39. For R=Me, the decomposition to the methyl radical plus N₂ would be slightly favored (about 2 kcal/mole) over H-N=N⁺ decomposing to H⁺ plus N₂. All other R groups would consequently have even more favorable decompositions.


47. Calculated by using techniques found in ref. 40a.

48. $\Delta H_f$ values for the two radicals are found in ref. 40b, p. 284-286.

49. *ibid.*

50. G. Closs, personal communication to P. S. Engel.

51. Ref. 6, pp. 42-46.

52. For a discussion of other related topics, see ref. 18a.


57. This calculation can be found in appendix 3.

58. Ref. 17, p. 6.


61. See ref. 29, p. 103.


76. Ref. 4, p. 7012.

77. Ref. 6, pp. 67-76.

78. P. S. Engel, unpublished work.

79. Ref. 6, pp. 46-51.

80. See ref. 20, p. 4864.


84. A. Schulz and C. Rüchardt, personal communication.
90. P. S. Engel, private communication.
94. Dimethylallyl radical is assumed to have a g-value similar to that of all allyl radicals for which g = 2.00025495. It has been suggested that g of phenyl diazenyl is less than 2.0012.
97. A_i for the methylene protons of dimethylallyl radical should be negative by analogy with the results for allyl radical.95,98 Sign alternation in conjugated systems predicts a positive A_i for the methyl protons.98
APPENDIX
Appendix 1. Do Alkyl Peroxides Quench the Triplet States of Aromatic Hydrocarbons?

The thermal chemistry of peroxides has been exhaustively studied. This is due in part to interest in their chemistry as free radical polymerization initiators. In contrast, not so much is known about the photochemistry of organic peroxides. However, due to a recent upsurge in interest in electron transfer photochemistry, bioluminescence, etc., renewed interest in peroxide photochemistry has been spurred. In spite of this renewed interest, however, little systematic work has been done on their sensitized decomposition. This is somewhat surprising in light of the fact that there is no mechanism that can explain the scattered results satisfactorily.

The first systematic study on this topic appears to be that of Walling and Gibian. They demonstrated that sensitizers with triplet energies greater than 59 kcal/mole were able to effect decomposition of benzoyl peroxide (1). However, sensitizers with triplet energies below 55 kcal/mole were ineffective. In contrast, even benzophenone ($E_T = 68$ kcal/mole) was unable to sensitize decomposition of t-butyl peroxide (2).

\[
\text{[Diagram]} \quad \text{[Diagram]}
\]

In a related paper, Elad and coworkers used biacetyl ($E_T = 55-56$ kcal/mole) as a triplet sensitizer for 2. This is surprising in light of the fact that Walling and Gibian were unable to do this with benzo-
phenone, the higher energy sensitizer. Elad hypothesized that "the reactions proceed through energy transfer from the photoexcited triplet \( \alpha \)-diketone to the peroxide leading subsequently to fragmentation of the latter". However, it was also mentioned that electron transfer processes may as well be responsible for the decomposition.

Fahrenholtz and Trozzolo\textsuperscript{70} determined, using DICNP as a probe, that no decomposition of benzoyl peroxide ensued with sensitizers with an \( E_T \) of less than 59 kcal/mole, but if \( E_T \) was greater than 59 kcal, then the decomposition did proceed. This result is in good agreement with the work of Walling and Gibian. The results implied that acetophenone, Michler's ketone and 2-acetonaphthone transferred triplet energy, whereas biacetyl, benzophenone and xanthone did not. Neither \( n,\pi^* \) or \( \pi,\pi^* \) sensitizers seem to be especially effective in this experiment; in fact, no particular trend emerges from this data.

Although it is far from clear how the decomposition of these peroxides proceeds, several plausible mechanisms can be postulated. First of all, one could hypothesize energy transfer as the function of the sensitizer. This would not explain why biacetyl can sensitize the decomposition of 2 but benzophenone, with a triplet energy 10 kcal/mole higher, cannot. One could also suggest non-vertical energy transfer as a mechanism. Unfortunately, this would not explain why ascaridole (3)

\[
\text{\includegraphics{ascaridole.png}}
\]
is such a good quencher (see below). Electron transfer is an attractive alternative mechanism. Finally, one could propose an induced decomposition pathway but this mechanism would require the n,π* sensitizers to be more efficient. The results of Fahrenholtz and Trozzolo demonstrate that this is not the case. Although each of these postulates has some merit, each also has a number of problems which need to be resolved.

To distinguish among these possibilities, one needs information concerning the relative ability of a selected set of peroxides to quench a specific set of sensitizers. The method used quite often to determine relative quenching rate constants is kinetic spectroscopy. This involves observing the effect of quencher concentration on the triplet lifetime of the sensitizer. By using the equation below (where τ is the observed lifetime with quencher added, τ₀ is the observed lifetime without quencher and [Q] is the concentration of the quencher), k_q for various peroxides and sensitizers can be determined. This information should provide some insight into the relationships between peroxide structure, ionization potential, reduction potential, etc., and its ability to quench the triplets of various sensitizers. The mechanism of photosensitized peroxide decomposition may be elucidated by an approach of this sort.

In order to do kinetic spectroscopy, however, an appropriate instrument needed to be constructed. The circuits and plans for the construction of the apparatus can be found in later appendices. A block diagram of the apparatus is given in Figure 1.
Figure 1. Block diagram of the kinetic spectroscopy instrument.
After the apparatus was constructed, it was necessary to determine that the rate constants obtained would be correct. Therefore, $k_q$ of the triphenylene triplet state by trans-stilbene was redetermined. This rate constant had been determined in two important studies, so that it was considered to be a well established number. The $k_q$ from our apparatus ($4.5 \times 10^9$) was slightly smaller than the values previously determined by Herkstroeter and Hammond ($7.6 \times 10^9$)\textsuperscript{71} and also by Wamser,\textsuperscript{20} et al ($6 \times 10^9$).

Some very sketchy data were obtained on two peroxides, namely 3,3,6,6-tetramethyl-1,2-dioxacyclohexane (4)\textsuperscript{73} and 3. The $k_q$ values for quenching of triphenylene triplets by these peroxides were obtained. The results (seen in Table 1) show that aliphatic peroxides do indeed quench the triplet states of aromatic hydrocarbons.

\begin{table}[h]
\centering
\caption{Rates of Quenching of Triphenylene Triplets by Selected Alkyl Peroxides}
\begin{tabular}{|c|c|c|}
\hline
\textbf{Compound} & \textbf{0.0} & \textbf{72} & \textbf{2.4x10^8} \\
\hline
3 & $2.62 \times 10^{-4}$ & 17 & \\
& $6.60 \times 10^{-4}$ & 7.3 & \\
\hline
4 & 0.0 & 44.1 & $6.5 \times 10^6$ \\
& $5.54 \times 10^{-4}$ & 18.0 & \\
\hline
\end{tabular}
\end{table}
Although these data are insufficient to discern any trend, non-vertical transfer does not seem to be the pathway of sensitized decomposition. Otherwise, the efficiency of ascaridole as a quencher would have been much reduced due to its rigidity. In addition, quenching seems to be facilitated by the ability of the peroxide to donate electrons, as the better quencher is the one with the lower ionization potential. Based on the known chemistry of peroxides, one would actually expect the peroxide to be an electron acceptor, however, so that it is not clear whether this observation has any value.
3,3,6,6-Tetramethyl-1,2-dioxacyclohexane. A solution of H$_2$SO$_4$ (70%, 17.4 ml) and H$_2$O$_2$ (50%, 12.4 ml) was placed into a 100 ml RB3N flask, equipped with a magnetic stirrer, a thermometer and an addition funnel. The flask was heated in a water bath to 55-65°C, and a solution of 2,5-dimethyl-2,5-hexanediol (5.8 g, 39.7 mmole) dissolved in H$_2$O$_2$ (50%, 12.4 ml) was slowly added so that the reaction would not become too exothermic. After addition of the diol was complete, the reaction mixture was heated at 55°C for 0.5 hr. The solution was then cooled in an ice-water bath in order to check for the presence of a precipitate, which would imply the presence of the mono- or dihydroperoxide. The reaction mixture was then poured into 180 ml of deionized H$_2$O (approximately three times the volume of the reaction mixture), extracted several times with petroleum ether. The organic fraction was stored until the reaction was repeated four times, whereupon all organic fractions were combined and distilled, yielding 4.1 g (14% of theoretical yield) of a clear water-white liquid: NMR 1.25 (s, 3H), 1.62 (s, 1H).

Purification of benzene. The benzene used as a solvent for kinetic spectroscopy was purified by the method of Herkstroeter and Hammond.71

Kinetic spectroscopy. In a typical kinetic run, the tubes used were first exhaustively rinsed with reagent quality acetone and "flash benzene". The tubes were then annealed in the glassblowers oven. The tubes were finally checked for leaks on the vacuum line with a Tesla coil.

All glassware used in these experiments was painstakingly cleaned with reagent-grade acetone and "flash benzene". Stock solutions were
then made up with the appropriate hydrocarbon and quencher. The solutions were then syringed into the flash tubes and degassed through five freeze-thaw cycles, after which the tubes were sealed with a torch.

In preparation for a run, the intensity of the monitoring beam was maximized by adjusting the height, angle, etc. of the various components of the system: the monitoring lamp, the shutter, the housing, and the monochrometer. Several trial traces were obtained on a dummy tube. When it appeared that the entire apparatus was working properly, the "real" tubes replaced the dummy tubes and the kinetic runs were performed. Points were read off the trace from the strip chart recorder, and the various lifetimes and rate constants were obtained from these points by means of the FOFA computer program (see appendix 2).
Appendix 2. Computer programs used to analyze kinetic data.

```
\$FOFA[]\$
\$ FOFA;A;B;C;D;E;F
[1] TIMECALC
[2] 'ENTER A'
[3] A++
[4] 'ENTER B'
[5] B++
[6] 'ENTER I OF TIME ZERO'
[7] C++
[8] 'ENTER I VECTOR OF POINTS AFTER TIME ZERO'
[9] D++
[10] D
[13] Y++(E+F)
[14] 'Y IS'
[15] Y
[16] POLYTWO
[17] 'THE RATE CONSTANT IN INVERSE SECONDS IS'
[19] 'THE LIFETIME IN SECONDS IS'
```

```
\$TIMECALC[]\$
\$ TIMECALC;K;L;M;N
[1] K++256\div16.9
[2] 'HOW MANY MICROSECS PER WORD?'
[3] L++
[4] 'WHAT FRACTION OF CM INTERVAL USED?'
[5] M++
[6] 'HOW MANY POINTS AFTER TIME ZERO?'
[7] N++
[8] X++K\timesLMX\timesN
[9] 'THE X VECTOR IS'
[10] X
```
\*POLYTWOD[]\*
\*POLYTWOD;B;LB;S;YOB;SIGMA;AN
\*INPUT X VECTOR\*
X+0
\*INPUT Y VECTOR\*
Y+0
\*INPUT POLYNOMIAL ORDER\*
M+0
E=E+(QA)+,XA*XO,0,M
L=E+(QA)+,XY
(+'COEFFICIENTS FOR DEGREE '),(+M),('+ POLYNOMIAL'
'
'
'
'
'
'
'
'
'
'
'
'
'
'
'
'
'
'
'

SIGMAA+((1(1 QA))*0.5)X5+(S=((FX)-(M+1)))*0.5
\*STAND. DEV. OF COEFFICIENTS'
'
'
'
'
'
'
'
'
'

(X' STAND. DEV. OF FIT'),+S
\*CORRELATION COEFFICIENT'
R1=((FX)x(+/XXY))-((+/X)x(+/Y))
R2=((FX)x(+/X2))-((+/X)x2)*0.5x((((FY)x(+/Y2))-((+/Y)x2))*0.5)
R1=R2
\*X,Y,Y-CALC., Y-CALC. MINUS Y-DBS.'
'
'
'
'

X((4),(FX))F(X,Y,YOB,(YOB-Y)))
END;0
Sample of Kinetic Trace Demonstrating Origin of Variables in Computer Program
Shutter close and disable

TR

IN4004

110 V AC

yel

relay

CHIPS ARE TWO NE556's

reset

20 K

1 M

R

TR

DIS

0.1 mfd

trigger of Biomation

DELAYED PULSE GENERATOR
Appendix 4. Plans for Construction of the Flash Photolysis Instrument

6 SPACES @ 1.667" = 10"

14.5"

10"

2.25"

BODY

holes for nylon 2-56 screws
holes for nylon 2-56 screws

\[ \text{LID} \]

\[ \text{4 SPACES} \]

\[ \text{(1.82" - 1.667" = 0.668")} \]
Appendix 5. Kinetic Bath Used for Azoadamantane and Azonorbornane Kinetic Studies.