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GENERATION OF RADICAL ANIONS
BY DECOMPOSITION OF AZO COMPOUNDS

by

RHONDA MICHELLE JENKINS

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
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APPROVED, THESIS COMMITTEE

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January, 1996
ABSTRACT

Generation of Radical Anions
by Decomposition of Azo Compounds

by

Rhonda Michelle Jenkins

A new method for the generation of radical anions has been developed. Homolytic cleavage of an azo compound bearing a negative charge \( \beta \) to the N=N linkage creates a radical anion intermediate. The radical anions so generated have been shown to undergo quantitatively the same chemical reactions as their neutral counterparts, namely disproportionation and recombination. The cage effects for anionic azo compounds are essentially the same as for their neutral counterparts. The negative charge causes a slight decrease in the overall stability of the azo compounds.
ACKNOWLEDGEMENTS

The research presented in this thesis is the cumulative effort of many hearts and minds, and to each person who offered his or hers, I am grateful.

My sincerest appreciation goes to my advisor, Dr. Paul Engel, for his wise and patient guidance throughout my graduate research. I would also like to acknowledge Drs. Shu-Lin He and Chuck Billera for the many hours they spent answering my questions and sharing their scientific expertise with me.

A few others deserve special recognition for their very personal contributions. Richard, my most treasured friend, has been my primary source of encouragement and laughter. Memories of my mom’s love have also been a great source of strength for me.

Finally, I would like to acknowledge the greatest influence in my life... my dad. It is a great privilege to dedicate this thesis and the work it represents to him.
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I. Introduction

A radical anion may be defined as a molecule which has both an unpaired electron and a net negative charge. Radical anions are usually prepared by either chemical reduction with alkali metals (Eq 1) or by electrolytic reduction (Eq 2).

\[ A + M \rightarrow A^- + M^+ \quad \text{Chemical reduction} \quad (1) \]
\[ A + e^- \rightarrow A^- \quad \text{Electrolytic reduction} \quad (2) \]

The reduction of molecules using an alkali metal was the first method used to generate radical ions. In 1891, Bechman observed that on addition of sodium metal to benzophenone, a strong blue color developed. This radical anion, now recognized as benzophenone ketyl, was probably the first to be observed.\(^1\),\(^2\) The chemical reduction method has been somewhat limited in its application due to the high reactivity of alkali metals toward many organic molecules.\(^1\)

\[ \text{C}_6\text{H}_5 \begin{array}{c} \text{C} \end{array} \begin{array}{c} \text{O} \end{array} \text{Na}^+ \begin{array}{c} \text{C}_6\text{H}_5 \end{array} \]

Fifty years later, it was discovered that electrochemical reduction could be used to prepare the radical anions of molecules such as anthracene, benzophenone, and anthraquinone.\(^3\) The intra muros method, whereby radical ions may be generated and observed in the
ESR cavity, was introduced by Maki and Geske in 1959 and has since developed into the most versatile method of radical ion production.\textsuperscript{4} The utility of this method may readily be seen by the wide range of solvents and the variety of types of functional groups which can be employed. For example, the radical anions of nitrobenzene and substituted nitrobenzenes may be formed electrolytically in acetonitrile, water, dimethyl sulfoxide, and dimethylformamide.\textsuperscript{5}

With the advent of the \textit{intra muros} ESR method, a large number of radical ions were identified and characterized before much interest was shown in their chemistry.\textsuperscript{1} This situation has changed, particularly with respect to radical anions.\textsuperscript{1,6} Researchers have become interested in understanding the various reactions that radical anions undergo once they are formed.

For many years, our laboratory has been involved in the study of azo compounds. As shown below, azoalkanes lose nitrogen either thermally or photochemically to cleanly and conveniently produce a pair of fragment radicals.\textsuperscript{7}

\[
\text{R} \quad \begin{array}{c} \text{N=N} \\ \text{R} \end{array} \quad \xrightarrow{h\nu \text{ or } \Delta} \quad 2\text{R}^* + \text{N}_2
\]

It occurred to us that a new route to radical ion intermediates would be simply to photolyze or thermolyze an azo compound bearing a negative charge $\beta$ to the N=N linkage.
Homolytic decomposition of such a compound would generate a radical center at the carbon α to the azo linkage, thereby creating a radical anion fragment. This novel approach would allow unimolecular generation of radical anions under a variety of conditions.

It was not obvious that this method would succeed; 1 might lose N₂ spontaneously to afford an olefin plus a carbanion. Huisgen and co-workers showed that the pyrazolin-4-yl anion 2 suffers a concerted nitrogen loss to form a highly stabilized anion.⁸

The observed reaction corresponds to a 1,3-dipolar cycloreversion and does not involve the formation of a radical anion. However, deazatization of 1 has no such pathway available, and, therefore, 1 might be thermally stable.

Additionally, Allred has shown that acetolysis of the azo compound 3 is accompanied by deazatization, indicating that the β-
azo cation is highly unstable.\textsuperscript{9,10} Earlier work in this laboratory showed that β-azo radicals had a short but finite lifetime.\textsuperscript{11}

![Chemical structure](image)

\[3\]

II. Purpose of this work

In general, the present study was concerned with examining the behavior of the radical anions produced by decomposition of the anionic form of specific azo compounds. Our choices of which compounds to study were determined by 1) our ability to make the azo compounds and 2) the estimated stability of their anionic forms.

The first compound we decided to study was the unsymmetrical azo diester 4\textbf{N}. This diester was chosen because the proton α to the two electron withdrawing groups could be easily removed, and the resulting anion, 4\textbf{A}, would be stabilized by the ester moieties.

![Chemical structures](image)

\[4\textbf{N} \quad 4\textbf{A}\]

We were interested to see whether the radical/radical anion pair generated by photolytic decomposition of compound 4\textbf{A} would recombine or disproportionate. The fact that little is known about
the reaction of radical ions with radicals is not surprising in view of
the difficulty of generating both reactive intermediates at the same
time.\textsuperscript{12}

The second molecule of interest for this study was the
symmetrical azoalkane, 5N. Treatment of this compound with two
equivalents of base would result in formation of a dianion, 5A.

\begin{center}
\includegraphics[width=0.8\textwidth]{5N_5A.png}
\end{center}

We were curious to see whether the two radical anions produced
upon homolytic cleavage of compound 5A would undergo slower
recombination than neutral radicals. A proposed mechanism for the
well-known acyloin condensation involves the dimerization of two
radical anions.\textsuperscript{13}

\section*{III. Synthesis Results and Discussion}

\subsection*{A. Synthesis of azo diester 4N}

The synthesis of 4N was achieved via two different approaches.
The first approach, shown below, utilized the pyrazolidinone
chemistry done previously in our laboratory.\textsuperscript{14} Heating of \(\beta,\beta\)-
dimethylacrylic acid and \textit{tert}-butyl hydrazine led to pyrazolidinone
6 which was subsequently hydrolyzed and oxidized with NaOH and
\(\text{NiO}_2\) to azo acid 7. Esterification of the acid using freshly prepared
diazomethane proceeded cleanly and in high yield. Finally, the monoester 8 was converted to 4N with LDA and methyl chloroformate.

\[
\begin{align*}
\text{6} & \xrightarrow{\text{NaOH, NiO}_2} \text{7} \\
\text{8} & \xrightarrow{\text{1) LDA, 2) CICOOME}} \text{4N}
\end{align*}
\]

The second approach to 4N was developed in response to the need for a more efficient, higher yield procedure than the one just described. In the new approach, compound 4N was obtained in two steps starting from acetone \textit{tert}-butylhydrazone (9). The \(\alpha\)-chloroaazoalkane 10 was easily prepared from the hydrazone and \textit{tert}-butyl hypochlorite.\(^\text{15}\) Nucleophilic displacement of chloride by dimethyl 2-bromomagnesiummalonate\(^\text{16}\) afforded the desired azo diester in good yield.
The advantages of the second approach over the first are:

1) The number of steps is reduced.

2) No purification is needed until the last step of this sequence.

   In the first approach, however, it is necessary to purify after each step.

3) The overall yield of the sequence is more than tripled (33% versus 10%).

B. Synthesis of azo diester anion 4A

Compound 4A was prepared by adding pure, dry 4N to an equimolar solution of NaOMe/MeOH. The anion was stable at room temperature as long as it was protected from moisture. The formation of the anion was confirmed by treating a solution of the salt with D$_2$O. The NMR of the resulting compound clearly showed loss of the methine proton [\(^1\)H NMR (250 MHz, C$_6$D$_6$) $\delta$ 1.17 (9H, s), 1.54 (6H, s), 3.29 (6H, s)].
C. Synthesis of azo tetraester 5N

Synthesis of the symmetrical azo compound 5N was achieved using Rüchardt's method as outlined below. The compound was prepared in good yield in two steps starting from acetone azine (11).

Chlorine gas was bubbled through a solution of the ketazine to produce pure, colorless crystals of 12. Nucleophilic displacement of chloride was then achieved with dimethyl 2-bromomagnesium malonate to yield compound 5N in 27% overall yield.

D. Synthesis of azo tetraester dianion 5A

The dianion 5A was prepared in a manner similar to the anion 4A using two equivalents of NaOMe. The dianion was also stable at
room temperature if protected from atmospheric moisture. Treating
the dianion with D$_2$O completely eliminated the NMR signal
characteristic of the methine protons ($\delta = 3.9$ ppm).

E. Independent synthesis of decomposition products

Several possible decomposition products of the azo esters and
their anions were synthesized independently. Methyl isopropylidene
malonate (13) was made using a modified Knoevenagel condensation.
In the presence of TiCl$_4$ and pyridine, dimethyl malonate condensed
with acetone to produce the $\alpha,\beta$-unsaturated compound in good
yield.$^{17}$ Compound 13 was then hydrogenated over a palladium
catalyst to make another possible decomposition product, methyl
isopropyl malonate (14). Compound 13 was also exposed to LDA and
HMPA in order to deconjugate the double bond, resulting in
formation of compound 15.$^{18}$ An attempt to deconjugate 13 by 254
nm irradiation gave no reaction.$^{14,19}$
F. Synthesis of azo monoester anion, 8A

In the first synthetic route to 4N, we had occasion to prepare the azo monoester 8. Treatment of the compound with freshly prepared LDA in THF produced the anion 8A. Although this anion was flanked by only one stabilizing ester group, it was stable at room temperature. Quenching of the anion with D₂O produced a compound whose NMR (250 MHz, C₆D₆) showed the following peaks: δ 1.17 (9H, s), 1.31 (6H, s), 2.53 (1H, t, J=2.1), 3.30 (3H, s)]. Clearly, one of the hydrogens adjacent to the ester group was replaced by deuterium.

IV. Photolysis Results and Discussion
A. Photolysis of 4N and 4A

1. Identification of photolysis products

Pure samples of 4N and 4A in freshly distilled methanol were degassed, sealed, and photolyzed in Pyrex tubes. UV spectroscopy was used to monitor the decomposition of the azoalkanes. The
decomposition products were identified either by comparison of GC retention times with authentic samples or by complete spectroscopic characterization of isolated samples. The photolysis products of the azo diester 4N are shown in Scheme I.

Scheme I.

\[
\begin{align*}
\text{4N} & \quad \xrightarrow{h\nu} \quad \text{366 nm} \\
& \quad \xrightarrow{\text{disproportionation}} \\
& \quad \xrightarrow{\text{recombination}} \\
& \quad \xrightarrow{14} \quad 40.4\% \\
& \quad \xrightarrow{16} \quad 7.9\% \\
& \quad \xrightarrow{15} \quad 39.7\%
\end{align*}
\]

Compound 4N undergoes the photochemical deazatization typical of azo-\textit{tert}-alkanes, generating the two alkyl radicals shown in Scheme I. These radicals subsequently disproportionate and
recombine to produce 14, 15, and 16. It is interesting to note that the \textit{tert}-butyl radical abstracts hydrogen only from the -CH$_3$ groups, never from the -CH group of the diester radical. Statistics predict that one of the six -CH$_3$ hydrogens will be abstracted more often than the single -CH hydrogen. The steric bulk of the two ester groups may further discourage abstraction of the -CH hydrogen.

The photolysis products of 4A were sodium salts. In order to work with and identify these compounds, it was necessary to protonate the salts. Commercially available Amberlite IR-120(plus), a high capacity ion exchange resin, was used to quantitatively exchange the sodium cations for hydrogen ions. Photolyzed solutions of 4A were passed through a small column containing the exchange resin (cf. Section VII.A). The neutralized photoproducts were subsequently identified by analyzing the collected column effluent.

The identified decomposition products of 4A and their absolute yields are shown in Scheme II. Compounds 14 and 16 were also produced in this photolysis; however, compound 15 was not detected. Instead, methyl isopropylidene malonate (13), a conjugated isomer of 15, was observed.
Scheme II.

\[
\begin{align*}
4A & \xrightarrow{\text{hv} \ 366 \text{ nm}} [ \cdot ] + \text{N}_2 + [ \cdot ] \\
\text{1. disproportionation} & \quad \text{1. recombination} \\
\text{2. work-up} & \quad \text{2. work-up} \\
\end{align*}
\]

14 \quad 38.8\% \\
16 \quad 10\% \\
13 \quad 35.1\%

We considered the possibility that 15 had initially formed in the decomposition but had rearranged to 13 under the basic conditions of the photolysis. The following control experiment was devised to test this hypothesis: an authentic sample of methyl isopropenyl malonate (15) was stirred into an equimolar solution of NaOMe/MeOH at room temperature. The resulting sodium salt of 15 was passed through the ion exchange column. The single product isolated after this work-up was 13. This experiment confirmed that
the presence of 13 in the anionic decomposition products can be attributed to base-induced rearrangement of 15 (Scheme III).

**Scheme III.**

\[ \text{COOMe} \quad \xrightarrow{\text{NaOMe, MeOH}} \quad \text{COOMe} \quad \xrightarrow{\text{Work-up}} \quad \text{COOMe} \]

15 \quad 17 \quad 13

Therefore, photolytic decomposition of 4A affords one molecule of nitrogen and two fragment radicals (tert-butyl radical and diester anion radical). Cross disproportionation of these fragment radicals generates either isobutene and the sodium salt of 14 or isobutane and a resonance stabilized carbanion, 17. Upon work-up, the allylic carbanion combines with a proton at the position that gives the more stable olefin. A tetrasubstituted double bond is thermodynamically favored over a disubstituted olefin by approximately 2 kcal/mol;\textsuperscript{20} moreover, 13 benefits from conjugation with the ester groups.

2. Yield (%) of photolysis products

The yield of each product detected in the photolysis experiments of 4A and 4N is listed below in Table I.
Table I. Product yields (%) from photolysis of 4N and 4A

<table>
<thead>
<tr>
<th></th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>Balance^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>4N</td>
<td>-</td>
<td>40.4</td>
<td>39.7</td>
<td>7.9</td>
<td>88.0</td>
</tr>
<tr>
<td>4A</td>
<td>35.1</td>
<td>38.8</td>
<td>-</td>
<td>10.0</td>
<td>83.9</td>
</tr>
</tbody>
</table>

^a analyzed on DB-5 capillary column using decane as internal standard
^b total yield of ester products

The factors governing the disproportionation to recombination ratio \( k_d/k_r \) of radical/radical pairs have been much discussed.\(^{21,22}\) Since the reaction of radical/radical ion pairs has been little studied,\(^{12}\) it is of interest to determine the effect of the radical anion partner on \( k_d/k_r \).

In the photolysis of 4A, we anticipated that allylic delocalization of the negative charge might favor disproportionation to isobutane and 13 over isobutene and 14. However, the yields of 13 and 14 were similar (35.1% versus 38.8%). The negative charge did not influence the disproportionation product distribution.

Typical values of \( k_d/k_r \) for tertiary radicals are in the range of 4.0-5.0.\(^{21}\) With the radical/radical pair generated from 4N, the calculated ratio of \( k_d/k_r \) was 5.1, which is only slightly higher than the 3.9 found for the radical/radical anion pair from 4A.\(^{23}\) Both of these values are close to the expected \( k_d/k_r \) values for tertiary radicals.

3. Cage Effect

In the solution phase photolysis of azo compounds, as in any homolytic scission reaction, two radicals are formed in the same
solvent cage. It has been shown previously that varying percentages of the radicals so formed react together in the solvent cage before they can escape and attack an external reagent.\textsuperscript{21,24} In an attempt to quantify the cage effect for 4N and 4A, it was decided to make use of a radical scavenger to count escaped radicals. The conditions of the photolysis experiments required that the scavenger be stable to both light (366 nm) and base (NaOMe) at room temperature. Cyclohexadiene, a commonly used scavenger, was initially considered for these studies; however, it would have been difficult to distinguish one of the cage products from the trapping product, both of which would be 14. A stable nitroxide radical, 2,2,6,6-tetramethyl piperidine-N-oxyl (TEMPO) was ultimately used as the scavenger. In a control experiment, several hours of irradiation of a solution of NaOMe and TEMPO was found to have no effect on the scavenger (cf. Section VII.C).

The "excess scavenger" technique\textsuperscript{25} was used to measure the cage effect for the azo diesters. In this technique, enough TEMPO is employed so that some remains after all the azo initiator has decomposed. The percentage of radicals escaping the cage is calculated using the following formula:

$$\text{% Escape} = 100\left(\frac{[S]_o - [S]_\infty}{[I]_o}\right)$$  \hspace{1cm} (3)

where $[I]_o$ is the initial concentration of the azo initiator, $[S]_o$ is the initial concentration of the scavenger, and $[S]_\infty$ is the concentration of
the scavenger after the initiator has fully decomposed. Table II lists the cage effects found for 4N and 4A.

<table>
<thead>
<tr>
<th>Radical</th>
<th>[I]₀ᵃ</th>
<th>[S]₀ᵃ</th>
<th>[S]∞ᵃ</th>
<th>Type of analysis</th>
<th>Cage effect, %ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>4N</td>
<td>0.057</td>
<td>0.16</td>
<td>0.101</td>
<td>GC</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>0.096</td>
<td></td>
<td></td>
<td>UV</td>
<td>44</td>
</tr>
<tr>
<td>4A</td>
<td>0.055</td>
<td>0.10</td>
<td>0.035</td>
<td>GC</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>0.038</td>
<td></td>
<td></td>
<td>UV</td>
<td>44</td>
</tr>
</tbody>
</table>

ᵃ concentration in mol/L
ᵇ % cage effect = 100 - % escape

The values obtained for the cage effect of 4N and 4A are typical for homolytic scission reactions. Slightly less than half of the radicals generated by decomposition of the compounds react together before they can escape the solvent cage. Some cage effects from the literature for various radicals are listed in Table III.

<table>
<thead>
<tr>
<th>Radical</th>
<th>Solvent</th>
<th>Cage effect %</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CH₂⁺</td>
<td>decalin</td>
<td>55</td>
<td>26</td>
</tr>
<tr>
<td>(CH₃)₂CH⁺</td>
<td>decalin</td>
<td>54</td>
<td>26</td>
</tr>
<tr>
<td>Cumyl</td>
<td>toluene</td>
<td>28</td>
<td>25</td>
</tr>
<tr>
<td>CH₃CO₂⁺</td>
<td>hexane</td>
<td>32</td>
<td>27</td>
</tr>
<tr>
<td>Cyclopropylmethyl</td>
<td>decalin</td>
<td>50</td>
<td>26</td>
</tr>
</tbody>
</table>

The 366-nm photolysis of 4N in the presence of TEMPO yielded only four compounds amenable to GC analysis (DB-5 capillary column with decane as internal standard). These compounds were identified as disproportionation products 14 and 15, recombination product 16,
and trapping product 18. No peak reasonably attributable to compound 19, the other trapping product, could be seen by GC.

\[
\text{18} \quad \text{MeOOC} \quad \text{MeOOC} \quad \text{19}
\]

Decomposition of 0.597 mmol of 4N, in the presence of decane as GC standard and TEMPO as scavenger, resulted in formation of 0.015 mmol 14, 0.011 mmol 15, and 0.0030 mmol 16. Assuming that all the 14 formed in the presence of scavenger came from disproportionation within the cage, then we can calculate \(k_d/k_r\) inside the solvent cage.\(^{23}\) The ratio was determined to be 5.0 for 4N. A similar experiment for 4A resulted in a \(k_d/k_r\) value of 3.8. These values agree well with those from photolysis runs without scavenger (cf. Section IV.A.2), indicating an approximate constancy of the ratio both inside and outside the cage.

Several others have observed similar \(k_d/k_r\) values for bulk and cage products.\(^{25,28}\) In the study of ethyl radicals in isooctane, Dixon, Stefani, and Szwarc\(^{29}\) found that \(k_d/k_r\) ratios were unchanged by adding or removing scavenger. Kochi\(^{26}\) also reached the same conclusion based on a lack of change in \(k_d/k_r\) for a number of alkyl radicals generated via photolysis of diacyl peroxides.
B. Photolysis of \( \text{5N and 5A} \)

1. Identification of photolysis products

Samples of azo tetraesters \( \text{5N and 5A} \) were photolyzed in the same manner as \( \text{4N and 4A} \). The photolysis products of \( \text{5N} \) are shown in Scheme IV.

**Scheme IV.**

\[
\text{MeCOOC} - \text{N} = \text{N} - \text{COOMe} \xrightarrow{h\nu, 366 \text{ nm}} [\text{N}_2 + 2 \text{COOMe}] \\
\text{5N}
\]

\[
\xrightarrow{\text{disproportionation}} \quad \xrightarrow{\text{recombination}}
\]

\[
\begin{align*}
\text{COOMe} + & \quad \text{COOMe} \\
\text{14} & \quad \text{36.2\%} \\
\text{COOMe} + & \quad \text{COOMe} \\
\text{15} & \quad \text{36.0\%} \\
\text{MeCOOC} - & \quad \text{MeCOOC} \\
\text{20} & \quad \text{7.1\%}
\end{align*}
\]

GC analysis of the photolysis mixture showed three product peaks. Two of the peaks, with retention times of 6.32 and 6.53 minutes, could be unambiguously assigned to the disproportionation partners \( \text{14 and 15} \). The third peak, which accounted for about 7% of the mixture, had a retention time of 17.8 minutes under HP-1 column conditions (cf. Section VII.A). The long retention time was
indicative of a large, polar compound and was tentatively assigned to recombination product 20. The ratio of disproportionation to recombination was typical for tertiary radicals ($k_d/k_r = 5.1$), further supporting our structure assignment for the peak. Attempts to isolate this compound using several different preparative GC columns met with failure because no peak corresponding to the compound could be seen.

The products of photolysis of 5A after work-up with an ion exchange column are shown in Scheme V.

**Scheme V.**

\[
\text{MeOOC} \begin{array}{c} \text{N} \cr \text{COOMe} \end{array} \begin{array}{c} \text{N} \cr \text{COOMe} \end{array} \begin{array}{c} \text{N} \cr \text{COOMe} \end{array} \begin{array}{c} \text{N} \cr \text{COOMe} \end{array} \xrightarrow{h\nu} \begin{array}{c} N_2 \cr \text{COOMe} \end{array} \begin{array}{c} \text{COOMe} \cr \text{COOMe} \end{array} \]

1. disproportionation
2. work-up

\[
\begin{array}{c} \text{COOMe} \cr \text{COOMe} \end{array} + \begin{array}{c} \text{COOMe} \cr \text{COOMe} \end{array}
\]

13 33.2%
14 37.5%

Under these experimental conditions, the tetrasubstituted olefin 13 was once again formed in preference to the less thermodynamically
stable olefin 15 (cf. Section IV.A.1). The GC peak assigned to the
recombination product in the photolysis of 5N was not present. Two
explanations for this result were considered plausible: 1) the
fragment radical anions did not combine with each other to form 20,
or 2) compound 20, once formed, did not survive the conditions of
the experiment.

The coupling reaction of radical anions has been little studied;\textsuperscript{13,30}
however, Garst proposes that most stable radical anions do indeed
undergo recombination to some extent.\textsuperscript{6} In our case, the coupling
product would be the dianion of compound 20. This dianion might
undergo a Dieckmann condensation to form the five-membered ring
compound 21 after work-up (Eq 4).

\[
\begin{align*}
\text{MeOOC} & \quad \text{work-up} \quad \text{MeOOC} \\
\text{O} & \quad \text{COOMe} \quad \text{O} \\
\text{OMe} & \quad \text{COOMe} \\
\end{align*}
\]

We devised an experiment to test the stability of 20 under basic
conditions. Sodium methoxide was added to the methanol solution
containing the photoproducts of 5N. This solution was first passed
through the ion exchange column as part of the usual work-up, then
injected into a gas chromatograph. The peak ascribed to the
recombination product 20, observable before exposure to base, was
no longer present. A new GC peak attributable to compound 21 was
not detected. We were, therefore, unable to determine whether compound 20 formed in the photolysis of 5A.

2. Yield (%) of photolysis products

The yield of each detected photoproduc of 5N and 5A is listed in Table IV.

<table>
<thead>
<tr>
<th></th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>20</th>
<th>Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>5N</td>
<td>-</td>
<td>36.2</td>
<td>36.0</td>
<td>7.1</td>
<td>79.3</td>
</tr>
<tr>
<td>5A</td>
<td>33.2</td>
<td>37.5</td>
<td>-</td>
<td>-</td>
<td>70.7</td>
</tr>
</tbody>
</table>

* a analyzed on HP-1 capillary column using dimethyl phthalate as internal standard
* b total yield of ester products

The total yield of photoproducts was lower for 5A than for 5N. Our inability to account for formation of a recombination product in the dianion system could explain the reduced product balance.

3. Cage effect

The cage effect for 5N and 5A was determined with TEMPO in a manner similar to the one used for 4N and 4A (cf. Section IV.A.3). Table V lists the values obtained. Though the cage effect for 5A appears to be slightly higher than that for 5N, this difference is probably due to experimental error since anions should repel one another.
Table V. Cage Effects for 5N and 5A Decomposition

<table>
<thead>
<tr>
<th></th>
<th>[I]₀ᵃ</th>
<th>[S]₀ᵇ</th>
<th>[S]wcᵇ</th>
<th>Type of analysis</th>
<th>Cage effect, %ᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>5N</td>
<td>0.077</td>
<td>0.225</td>
<td>0.145</td>
<td>GC</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.144</td>
<td>UV</td>
<td>47</td>
</tr>
<tr>
<td>5A</td>
<td>0.063</td>
<td>0.200</td>
<td>0.146</td>
<td>GC</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.143</td>
<td>UV</td>
<td>55</td>
</tr>
</tbody>
</table>

ᵃ [I] = azoalkane concentration in mol/L
ᵇ [S] = TEMPO concentration in mol/L
ᶜ % cage effect = 100 - % escape

4. cis-Azo tetraesters 5N and 5A

Engel³¹ and Rüchardt³² have shown that irradiation of most acyclic azoalkanes at sufficiently low temperatures will generate the cis isomer. The stability of a cis azo compound is dependent upon both its ground-state strain and incipient radical stability.⁷ For example, irradiation of trans-azo-2-methyl-2-propane, ATB(t), at -40 °C results in isomerization to the yellow cis isomer which loses nitrogen upon warming to 0 °C (Eq 5). The trans isomer of 22 photoisomerizes at temperatures as low as -150 °C and loses nitrogen upon warming to -120 °C (Eq 6). Since the steric bulk of the attached groups is approximately equal, the observed difference in decomposition temperature between ATB(c) and 22c can be ascribed to the greater stability of α,α-dimethylallyl radical than tert-butyl radical.

\[
\begin{align*}
\text{ATB}(t) \quad & \xrightarrow{hv \atop -40 \degree C} \quad \text{ATB}(c) \\
\end{align*}
\]

\[
\begin{align*}
\quad \xrightarrow{0 \degree C} \quad 2 + N_2
\end{align*}
\]
Taking this into account, it occurred to us that studying the stabilities of 5N(c) and 5A(c) might be informative. 5N and 5A were irradiated (at 366 nm) in methanol in sealed tubes at -78 °C for several hours. When the tubes were removed from the dry ice-acetone bath, both solutions were bright yellow in color, indicating formation of the cis isomers. This bright yellow color quickly disappeared and nitrogen bubbles were released as the solutions warmed to -25 °C. Visual inspection of the two solutions showed that the yellow color of 5A(c) faded more quickly than did that of 5N(c), indicating that 5A(c) was less stable than 5N(c). Perhaps repulsion of the negative charges in 5A(c) lowered its stability relative to its neutral counterpart.

5A(c)

Alternately, the lower stability of 5A(c) may reflect the influence of incipient radical stabilities on azoalkane thermolysis rates. The bond dissociation energy of the anion (BDE2) should be less than that of the neutral (BDE1). In the case of ethane versus ethyl anion, the
difference is 19 kcal/mol, according to MNDO calculations.\textsuperscript{33} In view of this large difference, it is interesting that 5A(c) is not far less stable than 5N(c).

\[
\begin{array}{c}
\text{COOMe} \\
\text{COOMe}
\end{array}
\rightarrow
\begin{array}{c}
\text{COOMe} \\
\text{COOMe}
\end{array}
+ \text{H}^* \\
\text{BDE 1}
\]

\[
\begin{array}{c}
\text{COOMe} \\
\text{COOMe}
\end{array}
\rightarrow
\begin{array}{c}
\text{COOMe} \\
\text{COOMe}
\end{array}
+ \text{H}^* \\
\text{BDE 2}
\]

In future work, the decomposition rates of 5N(c) and 5A(c) could be quantified by low temperature gas evolution kinetics, since UV monitoring would be obscured by window fogging.

V. Thermolysis Results and Discussion.

Thermolysis of the azo diesters 4N and 4A (generated by n-BuLi) was done in sealed UV cells with degassed diglyme as solvent. The compounds were subjected to thermolysis at 155 °C (428 K) for 280 minutes. The extent of decomposition was deduced from the UV absorbance at 364 nm.

Thermolysis of 4N and 4A without a radical scavenger led to an intractable mixture of products as judged by GC and TLC. Even with added 1,4-cyclohexadiene at a concentration of 1.03 M, the compounds gave complicated product mixtures; hence, no detailed product analyses were performed.
The rates of decomposition \( k_{\text{dec}} \) at 155 °C (428 K) were determined by UV spectroscopy, fitting the data to the following equation:

\[
\ln[A/A_0] = -k_{\text{dec}}t
\]  

(7)

where \( A_0 \) is the initial UV absorbance, \( A \) is the final absorbance, and \( t \) is the duration of the thermolysis in seconds.

Using these calculated rates of decomposition, we could determine an approximate half-life \( \tau_{1/2} \) and free energy of activation \( \Delta G^\ddagger \) for each of the azo diesters. The following equations were used:

\[
\Delta G^\ddagger = 23.76 + \ln T - 1.987T[\ln(k_{\text{dec}})]
\]  

(8)

\[
\tau_{1/2} = 0.693/k_{\text{dec}}
\]  

(9)

where \( T \) is the temperature of the thermolysis.

The parameters derived from the thermolysis data are listed in Table VI.

<table>
<thead>
<tr>
<th>Table VI. Thermolysis Parameters for 4N and 4A$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Azo], mol/L</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>4N</td>
</tr>
<tr>
<td>4A</td>
</tr>
</tbody>
</table>

$^a$ at 155 °C; diglyme as solvent
Our thermolysis experiments show that compound 4A decomposed approximately 8 times faster than 4N. As mentioned before, the thermal decomposition rate of azoalkanes depends strongly upon incipient radical stability and ground-state strain. Since compounds 4N and 4A differ only by the presence of an anion, any differences in their stabilities can be ascribed to the influence of that negative charge on the starting materials or radicals.

The value of $\Delta G^\ddagger$ for azo-2-methyl-2-propane (ATB) is 35.4 kcal/mol at 420 K. According to our thermolysis data, replacing one tert-butyl group in ATB by an isopropyl malonate group (to form compound 4N) lowers $\Delta G^\ddagger$ by 1.1 kcal/mol. Similar replacement of the other tert-butyl group (to form compound 5N) lowers $\Delta G^\ddagger$ by an additional 0.94 kcal/mol.

\[ \text{ATB} \quad \Delta G^\ddagger = 35.4 \text{ kcal/mol} \quad \text{4N} \quad \Delta G^\ddagger = 34.2 \text{ kcal/mol} \quad \text{5N} \quad \Delta G^\ddagger = 33.4 \text{ kcal/mol} \]

The calculated value of $\Delta G^\ddagger$ for thermolysis of 4N falls between that of its symmetrical counterparts. This trend has been observed in many other azoalkane systems.
VI. Attempted one-electron oxidation of 4A

A few anions are known to supply a single electron to sufficiently strong chemical oxidants.\(^6\) In the case of 4A, transfer of an electron to such an oxidant would generate a transient β azo radical. β azo radicals quickly decompose via loss of nitrogen to generate fragment radicals.\(^1\) We attempted to oxidize 4A using several one electron acceptors, namely CBr\(_4\), CCl\(_4\), TCNE, K\(_3\)Fe(CN)\(_6\), and chloranil. All our attempts were judged unsuccessful because none of these compounds reacted with the azo diester anion, 4A, according to GC and NMR.

Conclusions

In this research, we determined that azo compounds such as 4N and 5N can tolerate a negative charge β to the N=N linkage. Photolytic or thermal decomposition of the anionic azo compounds generates N\(_2\) and either a radical/radical anion pair or a pair of radical anions. The radical anions so generated undergo quantitatively the same reactions as their neutral counterparts, namely disproportionation and recombination. The cage effects calculated for the anionic azo compounds were similar to those determined for the neutral compounds. The cis form of compound 5A, generated at -78 °C, decomposed slightly faster than the cis form of 5N, and the same trend was seen in the trans isomers. Overall, the presence of the anion(s) seems to have little effect on the chemistry of the studied compounds.
VII. Experimental.

A. General Information

Ether and THF were distilled from Na/benzophenone; methanol was distilled from calcium hydride. Decane and dimethyl phthalate (used as internal GC standards) were also distilled. Cyclohexadiene was passed over neutral, Brockman activity grade I alumina just prior to use. The NMR solvents CDCl$_3$ and C$_6$D$_6$ from Cambridge Isotopes Laboratory were used without further purification. NMR spectra were recorded on a Bruker AF-250 spectrometer. Chemical shifts (δ, ppm) were determined using solvent signal (CDCl$_3$, $^1$H δ= 7.25, $^{13}$C δ=77.0; C$_6$D$_6$, $^1$H δ=7.15, $^{13}$C δ=128.5) as reference. Melting points were determined on a Mel-Temp apparatus. UV-VIS spectra were obtained on a Hewlett Packard 8452A diode array spectrophotometer. Each UV spectrum was acquired in either a quartz or pyrex cell with a path length of 1 cm.

Analytical GC analyses were carried out on a Hewlett Packard 5890A gas chromatograph using either a HP-1 or DB-5 capillary column. The GC data were collected, stored, and manipulated on an interfaced IBM-486 computer. Preparative GC was performed on an Antek 300 instrument with a TC detector. The operating conditions for each column used are listed in Table VII.

All samples for thermolysis or photolysis were freeze-thaw degassed three times and sealed on a vacuum line using dry ice-acetone (-78 °C) as a cooling bath. Samples for thermolysis were completely immersed in a well-stirred DC-200 silicone oil bath. The
Table VII. GC Conditions Used for Analyses

<table>
<thead>
<tr>
<th></th>
<th>HP-1&lt;sup&gt;a&lt;/sup&gt;</th>
<th>DB-5&lt;sup&gt;b&lt;/sup&gt;</th>
<th>FFAP&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injector temperature (°C)</td>
<td>170</td>
<td>250</td>
<td>180</td>
</tr>
<tr>
<td>Detector temperature (°C)</td>
<td>170</td>
<td>260</td>
<td>250</td>
</tr>
<tr>
<td>Initial oven temperature (°C)</td>
<td>40</td>
<td>80</td>
<td>190</td>
</tr>
<tr>
<td>Initial time (min)</td>
<td>2.5</td>
<td>2.5</td>
<td>0</td>
</tr>
<tr>
<td>Final oven temperature (°C)</td>
<td>250</td>
<td>250</td>
<td>190</td>
</tr>
<tr>
<td>Program rate (°C/min)</td>
<td>10</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>Final time (min)</td>
<td>10</td>
<td>15</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>a</sup> capillary column, 12m x 0.2mm I.D.

<sup>b</sup> capillary column, 30m x 0.25mm I.D.

<sup>c</sup> preparative column, 10% on Chromosorb W, 8ft x 0.25in I.D.

temperature was regulated with a Bayley Model 123 temperature controller and was measured with a Hewlett Packard Model 3456A digital voltmeter and a platinum thermometer. Photolysis experiments were carried out with an Oriel 500W high pressure mercury lamp employing a 7-60 Corning glass filter and a 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate (366 nm) filter solution.

Commercially available Amberlite IR-120(plus) was the resin used in all ion exchange experiments. A stock supply of the gel-type resin was prepared by allowing approximately 10 g of the resin to stand for at least 30 minutes in each of three 50-mL portions of 3 M hydrochloric acid. The resin was then washed free of the acid and stored in distilled water. A portion of this resin was slurried into a column as shown in Figure I. The resin was washed with several milliliters of dry methanol until the pH of the washings was about 4-5. The column was then ready for use.36
Figure I. Ion exchange column

B. Synthesis

2-tert-Butylazo-2-methyl-1,1-propanedicarboxylic acid dimethyl ester (4N). The synthesis of this compound was achieved by two different methods. The first method involved acylation of the methyl ester 8. A solution of LDA was prepared, in the usual fashion, by dropwise addition of n-butyllithium (5 mL, 12.5 mmol) to a cooled solution (-78 °C) of 1.75 mL diisopropylamine in 12.5 mL THF. The mixture was warmed to 0 °C, stirred for 15
minutes, then cooled to -78 °C again before introduction of compound 3 (0.30 g). This solution was allowed to stir at -78 °C for 45 minutes before 0.12 mL methyl chloroformate was added. The yellow solution was stirred for 10 minutes more then quenched with 1.6 mL of 5% NH₄Cl. After the reaction mixture warmed to room temperature, the aqueous layer was washed three times with 10 mL ether. The combined organic layers were dried with potassium carbonate and concentrated by rotary evaporation. The product, a yellow oil, was purified by column chromatography on silica gel, eluting with 25% ethyl acetate in hexanes. Yield 79%.

The second method to synthesize 4N used the basic procedure described by Rüchardt. A solution of 4.0 g alcohol-free dimethyl malonate in 19 mL dry benzene was placed in a 100 mL three neck flask equipped with a mechanical stirrer and a reflux condenser. Over the course of one hour a solution of ethylmagnesium bromide was added dropwise to the stirring malonate solution. This Grignard reagent was prepared from 0.71 g Mg turnings and 3.3 g bromoethane in 10 mL dry ether. The reaction mixture was warmed to 60 °C for 3 hours then cooled to 25 °C. A solution of 10 (3.8 g) in 12 mL benzene was dropped into the reaction mixture. The resulting yellow mixture was refluxed at 80 °C overnight. The reaction mixture was then hydrolyzed in the cold with 10 mL ethanol and 20 mL saturated aqueous NH₄Cl. After extraction with ether, the solution was dried with MgSO₄ and concentrated in vacuo. The residue was purified by column chromatography as described in the
first method. Yield 53%. $^1$H NMR (250 MHz, C$_6$D$_6$) δ 1.15 (9H, s), 1.55 (6H, s), 3.28 (6H, s), 4.14 (1H, s). $^{13}$C NMR (250 MHz, C$_6$D$_6$) δ 23.63, 26.65, 51.54, 58.82, 66.62, 70.18, 168.35. UV (methanol) $\lambda_{\text{max}}$ = 364, ε = 23. Anal. Calcd. for C$_{12}$H$_{22}$N$_2$O$_4$: C, 55.79; H, 8.58; N, 10.84. Found: C 55.80; H, 8.54; N, 10.85.

2-tert-Butylazo-2-methyl-1,1-propanedicarboxylic acid dimethyl ester anion (4A). A solution of sodium methoxide was prepared in a 25 mL flask by dissolving 0.10 g sodium metal in 10 mL dry methanol. The moisture-sensitive solution was protected from the atmosphere by positive N$_2$ pressure. A 0.5 mL aliquot of the NaOMe/MeOH mixture was added via syringe to a solution of 0.54 g 4N in 5 mL methanol. The reaction mixture was stirred for 15 minutes to allow complete formation of the azo anion. The anion solution was then immediately vacuum sealed in a pyrex tube and stored for no longer than 5 hours before use.

For use in thermolysis experiments, 4A was also prepared in 2-methoxyethyl ether (diglyme). This was accomplished by combining equimolar amounts of n-BuLi (2.5M solution in hexanes) and 4N in freshly distilled diglyme. The solution was stirred at -78 °C for approximately 20 minutes, warmed to room temperature, then sealed exactly as described above.

2,2'-Azo(2-methyl-1,1-propanedicarboxylic acid dimethyl ester) (5N) was prepared in the same manner as 4N from
2,2'-dichloro-2,2'-azopropane and dimethyl 2-bromomagnesium malonate. The pure compound was obtained by column chromatography on silica gel with 50% ether/petroleum ether as eluent. The resulting yellow crystals can be recrystallized from pentane to yield colorless crystals with mp 53-55 °C. Yield 42%. \( ^1\text{H} \) NMR (250 MHz, CDCl\(_3\)) \( \delta \) 1.34 (12H, s), 3.69 (12H, s), 3.86 (2H, s). \( ^{13}\text{C} \) NMR (250 MHz, CDCl\(_3\)) \( \delta \) 23.42, 52.36, 58.54, 70.60, 168.44. UV (methanol) \( \lambda_{\text{max}} = 360, \varepsilon = 27 \). Anal. Calcd. for C\(_{16}\)H\(_{26}\)N\(_2\)O\(_8\): C, 51.33; H, 6.99; N, 7.48. Found: C, 51.34; H, 6.97; N, 7.48.

2,2'-Azo(2-methyl-1,1-propanedicarboxylic acid dimethyl ester) dianion (5A) was prepared and stored exactly the same way as 4A. The amount of base used was adjusted to ensure formation of a dianion.

1-tert-Butyl-3,3-dimethyl-5-pyrazolidinone (6) was prepared by heating equimolar amounts of tert-butyl hydrazine and \( \beta,\beta \)-dimethyl acrylic acid to 120 °C for 4 hours. The crude product was purified by distillation; bp = 105 °C @ 10 mm Hg. Yield 58%. \( ^1\text{H} \) NMR (250 MHz, CDCl\(_3\)) \( \delta \) 1.19 (6H, s), 1.37 (9H, s), 2.32 (2H, s), 2.57 (1H, br).

3-tert-Butylazo-3-methyl butanoic acid (7) was made according to the procedure described by Aiyin Wu of this laboratory. Approximately one gram of freshly prepared NiO\(_2\)
was added to 0.64 g 6 in 15 mL ether. The black solution was stirred for 12 hours followed by addition of 8 mL 1 M NaOH. The black solid was removed by centrifugation. The aqueous layer was extracted several times with ether, acidified to pH 1 with 5 M HCl, then extracted again with ether. The combined ethereal layers were dried with MgSO₄ and concentrated by rotary evaporation. Pure 7 was obtained as a yellow oil. Yield 32%. ¹H NMR (250 MHz, C⁶D₆) δ 1.16 (9H, s), 1.24 (6H, s), 2.46 (2H, s).

Methyl-3-tert-butylazo-3-methylbutanoate (8). The acid 7 (0.26 g) was added dropwise to a solution of diazomethane (freshly prepared in about 50% excess). After addition of the acid, the solution remained intensely yellow in color, confirming the presence of excess diazomethane. The solution was stirred for several hours until the excess diazomethane decomposed. After removal of the solvent by evaporation, 0.25 g pure 8 was obtained. Yield 95%. ¹H NMR (250 MHz, C⁶D₆) δ 1.12 (9H, s), 1.26 (6H, s), 2.48 (2H, s) 3.25 (3H, s).“

Acetone tert-butyl hydrazone (9). A mixture of 8.7 g acetone and 8.6 g tert-butyl hydrazine hydrochloride in 17 mL ether was allowed to stir under nitrogen for a short time. Potassium hydroxide pellets (8.7 g) were then added to the mixture. After stirring at room temperature for four hours, the remaining solid KOH was filtered from the solution. The crude product isolated by solvent
removal was purified by distillation over barium oxide; bp 60-62° @ 72 mm Hg. 9 was a colorless, strong-smelling liquid. Yield 69%. ¹H NMR (250 MHz, CDCl₃) δ 1.17 (9H, s), 1.70 (3H, s), 1.91 (3H, s).

2-tert-Butylazo-2-chloropropane (10).¹⁵ A solution of 9.2 g acetone tert-butyl hydrazone (9) in 60 mL methylene chloride was cooled in a dry ice-acetone bath. tert-Butyl hypochlorite (8.1 mL) in 12 mL methylene chloride was added dropwise to the stirring solution. After the mixture was stirred at -78 °C for 6 h, the volatiles were removed by rotary evaporation in the dark. The NMR of the yellow residue was relatively clean, showing the following peaks: ¹H NMR (250 MHz, C₆D₆) δ 1.14 (9H, s), 1.62 (6H, s).

Acetone azine (11).¹⁴ Acetone (16 g), 85% hydrazine hydrate (4.7 g), and a few drops of concentrated HCl were refluxed for three hours. The cooled reaction mixture was neutralized to pH 7 with 1M NaOH then extracted three times with ether. The combined ethereal layers were dried with MgSO₄ and concentrated in vacuo. Ketazine 11 was purified by distilling and collecting the material at 49-50 °C @ 40 mm Hg. ¹H NMR (250 MHz, CDCl₃) δ 1.84 (6H, s), 2.02 (6H, s).

2,2'-Dichloro-2,2'-azopropane (12).¹⁴ A solution of 0.52 g acetone azine (11) in 60 mL petroleum ether was cooled to -78 °C in a dry ice-acetone bath. Chlorine gas was bubbled through the solution slowly until the yellow color persisted. The excess chlorine
was then rapidly removed by brief evacuation. The colorless dichloroazoalkane crystals that precipitated from the solution were filtered and recrystallized from petroleum ether. Yield 65%. \(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\) 1.85 (12H, s).

**Methyl isopropylidene malonate (13).**

Dry THF (200 mL) was placed in a three neck flask protected with N\(_2\) positive pressure and equipped with a mechanical stirrer. After the THF was cooled to 0 °C in an ice bath, a solution of 11 mL TiCl\(_4\) in 25 mL dry CCl\(_4\) was added by syringe. To the resulting yellow suspension was added 3.5 mL acetone and 5.7 mL dimethyl malonate. Under further ice cooling, a solution of 16 mL pyridine in 35 mL THF was then added dropwise over the course of an hour. The mixture was stirred at room temperature overnight. The solution was hydrolyzed in the cold with 50 mL water. After multiple extractions with ether, the organic layer was washed with 50 mL brine, 50 mL saturated aqueous NaHCO\(_3\), and again with 50 mL brine. The ethereal solution was dried with MgSO\(_4\) and then concentrated by rotary evaporation. Pure 13 was obtained as a colorless liquid by distillation; bp 70 °C @ 1.7 mm Hg. Yield 65%. \(^1\)H NMR (250 MHz, C\(_6\)D\(_6\)) \(\delta\) 1.76 (6H, s) 3.39 (6H, s). \(^13\)C NMR (250 MHz, C\(_6\)D\(_6\)) \(\delta\) 22.76, 51.44, 124.90, 155.14, 165.88. UV (hexane) \(\lambda\)\(_{\text{max}}\) = 216 nm, \(\epsilon\) = 12,400.

**Methyl isopropyl malonate (14).** Compound 13 (0.5061 g) in 10 mL of ethanol was hydrogenated at atmospheric pressure in
the presence of 50 mg 10% Pd/C. The reduction was carried out at room temperature in a 25 mL flask attached to a large gas buret. Under these conditions, the isopropylidenyl malonic ester absorbed 99.1% of the theoretical quantity of hydrogen in approximately one hour. The reduced ester was obtained in quantitative yield by filtering off the catalyst and evaporating the solvent. $^1$H NMR (250 MHz, C$_6$D$_6$) δ 0.91 (6H, d, J = 6.7), 2.49 (1H, octet, J= 6.8), 3.13 (1H, d, J= 8.4), 3.27 (6H, s). $^{13}$C NMR (250 MHz, C$_6$D$_6$) δ 20.33, 28.86, 51.63, 58.79, 168.95.

Methyl isopropenyl malonate (15). A freshly prepared solution of lithium diisopropylamide (0.5 M in THF) was cooled in a dry ice-acetone bath. Distilled hexamethylphosphoric triamide (1.6 mL) and compound 13 (0.435 g) were added to the solution. The mixture was stirred at -78 °C for 40 minutes then quenched with cold, dilute NH$_4$Cl. After warming to room temperature, the solution was extracted three times with ether. The combined ether extracts were dried over MgSO$_4$ and evaporated to yield a pure colorless liquid. $^1$H NMR (250 MHz, C$_6$D$_6$) δ 1.89 (3H, t, J= 1.1), 3.26 (6H, s), 4.09 (1H, s), 4.90 (2H, d, J=1.1).

Isolation of recombination product 16. A solution of 0.38 g 4A in 10 mL methanol was photolyzed at 366 nm. The resulting mixture of products was injected into a preparative GC column (cf. Section VII.A). Three photoproducts were isolated from the GC:
compounds 13, 14, and 16. A pure sample of the recombination product 16 was identified and characterized spectroscopically. $^1$H NMR (250 MHz, C$_6$D$_6$) δ 0.82 (9H, s), 1.24 (6H, s), 3.25 (6H, s), 3.85 (1H, s).

**Determination of cage effects.** Cage effects were determined using two methods of analysis: UV and GC. In the UV method, a solution was made by dissolving the azo compound and excess TEMPO scavenger in methanol. A UV spectrum of the well-mixed solution showed the azo maximum at 364 nm and the TEMPO maximum at 444 nm. The absorbances at these maxima were used to determine the initial concentration of the azo initiator ([I]$_0$) and the scavenger ([S]$_0$). The solution was photolyzed until all the azo compound had decomposed. The absorbance at 444 nm at this time was used to calculate the value for [S]$_\infty$.

In the GC method, a solution was made of known concentrations of the azo compound ([I]$_0$), an internal standard (cf. Tables I and IV), and excess TEMPO scavenger ([S]$_0$). The solution was photolyzed until a peak for the azo compound was no longer visible by gas chromatography. Then, using the peak area ratio for the internal standard and scavenger and their respective response factors (cf. Table VIII), the concentration of the remaining scavenger was determined. This value was used for [S]$_\infty$. 
Table VIII. Response Factors

<table>
<thead>
<tr>
<th>Compound</th>
<th>Response Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>decane</td>
<td>1.0</td>
</tr>
<tr>
<td>dimethyl phthalate</td>
<td>0.47</td>
</tr>
<tr>
<td>TEMPO</td>
<td>0.87</td>
</tr>
<tr>
<td>4 N</td>
<td>0.50</td>
</tr>
<tr>
<td>5 N</td>
<td>0.13</td>
</tr>
</tbody>
</table>

a peak area per unit weight; FID detector

Section IV.A.3 explains how these data were used to determine the cage effects for 4(N,A) and 5(N,A).

C. Control experiments

Ion exchange column reliability. A solution of 0.027 g 4 N and 0.011 g decane in 3 mL methanol was subjected to GC analysis (DB-5 capillary column). The resulting chromatograph showed two peaks whose area ratio was 1.27:1 ($A_{azo}:A_{decane}$). An appropriate amount of NaOMe was added to the solution to cause complete conversion from 4N→4A. The anionic solution was allowed to flow through the exchange column at not more than 2 to 3 mL per minute and was followed by two 2-mL washes. The resulting effluent was injected into the GC as before. The area ratio of the two peaks was again 1.27:1 ($A_{azo}:A_{decane}$). Since the ion exchange column allowed quantitative recovery of material, it could be used to work up the anionic solutions involved in this research.
TEMPO stability to base and light. A solution of NaOMe was prepared by adding 0.03 g sodium metal to 1.5 mL dry methanol. A UV spectrum of the solution showed no absorption in the range of 300-600 nm. A second solution was prepared by dissolving 0.031 g TEMPO ($\lambda_{\text{max}} = 444$ nm, $\varepsilon = 10$) in 0.5 mL methanol. Small aliquots (0.1 mL) of the TEMPO solution were stirred into the NaOMe solution. The absorbance of the solution at 444 nm was determined after each addition. Allowing the final solution to stand for two hours showed no change in absorbance. Figure II shows the linear relationship between absorbance and TEMPO concentration. The solution's adherence to Beer's law indicates that no changes were occurring in the properties of TEMPO on exposure to base. The solution was then subjected to three hours of irradiation at 366 nm. Periodic checks of the UV absorption of the solution showed no signs of instability (i.e., the absorption did not change). The scavenger was determined to be stable to light and base and could, therefore, be used in photolysis experiments.
Figure II. Beer's law plot for TEMPO
VIII. References


(23) This ratio was calculated using $k_d$ = relative yield (%) of disproportionation product 14 and $k_r$ = relative yield (%) of recombination product 16.


(33) Calculated using Hyperchem Version 2.0.


(35) In reference 16, Rührhardt gives the rate of decomposition of compound 5N at 453 K. The value of ΔG‡ (453 K) was then calculated using Equation 8. It was assumed that this value would change little over a 25° range, allowing comparison with the ΔG‡ values of ATB and 4N.


IX. Appendices

A. List of structures

1

2

3

4 N

4 A

5 N

5 A

6

7

8

9

10

11

12

13
B. UV and NMR spectra of various compounds

4N
Solvent: Methanol
Cell: Pyrex
$\lambda_{\text{max}} = 360 \text{ nm}$
$\varepsilon = 34$

4A
Solvent: Methanol
Cell: Pyrex
$\lambda_{\text{max}} = 364 \text{ nm}$
$\varepsilon = 23$
5 N
Solvent: Methanol
Cell: Pyrex
$\lambda_{\text{max}} = 360$ nm
$\varepsilon = 27$

5 A
Solvent: Methanol
Cell: Pyrex
$\lambda_{\text{max}} = 360$ nm
$\varepsilon = 32$
13
Solvent: Hexanes
Cell: Quartz
$\lambda_{\text{max}} = 216 \text{ nm}$
$\varepsilon = 12,400$