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Part I. Reduction of azoalkanes by benzhydryl radicals.
Part II. Thermolysis and photolysis of an α-aminoazoalkane,
2-tert-butylazo-2-dimethylaminopropane. Part III. A
reinvestigation of the photochemistry of trifluoromethylazocyclopropane

Wu, Wen-Xue, M.A.

Rice University, 1989
RICE UNIVERSITY

Part I
Reduction of Azoalkanes by Benzhydryl Radicals

Part II
Thermolysis and Photolysis of an α-Aminoazoalkane, 2-tert-butylazo-2-dimethylaminopropane

Part III
A Reinvestigation of the Photochemistry of Trifluoromethylazo-cyclopropane

by
WEN-XUE WU

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

APPROVED, THESIS COMMITTEE

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Houston, Texas
May, 1989
Abstract

by

Wen-Xue Wu

Part I

Benzhydryl radicals donate a hydrogen atom rapidly to the less hindered nitrogen atom of aliphatic and aromatic azo compounds, leading to the corresponding hydrazines. When the initially formed hydrazyl radical possesses a weak $\beta$ bond, it undergoes scission before receiving a second hydrogen atom. Thermolysis of benzpinacol with azocyclopropane causes a complex rearrangement to 1,5-diazaoct-5-ene-1-yne (21).

Part II

An unsymmetrical $\alpha$-aminoazoalkane, 2-$\text{tert}$-butylazo-2-dimethylaminopropane (3c) has been prepared by reaction of 2-$\text{tert}$-butylazo-2-chloropropane (4c) with dimethylamine. A photolysis and thermolysis study revealed that this azaalkane is unusual because it is sensitive to acid and protic solvents. A fast ionic reaction between cis 3c and methanol was postulated to explain the nature of the products. Normal homolysis of 3c in nonpolar solvents allows assessment of the radical stabilizing ability of the dimethylamino group. The activation parameters for thermolysis were measured in hexane: $\Delta H^\ddagger = 26.6 \pm 0.4$ kcal/mol, $\Delta S^\ddagger = -6.6 \pm 1.1$ eu. These figures would place the stabilizing ability of the $\text{NMe}_2$ group between that of CN and COC$_6$H$_5$.

Part III

The solution phase photolysis of trifluoromethylazocyclopropane(1) has been reinvestigated. The results showed that this azocyclopropane undergoes the same primary photoreactions as the other azocyclopropanes that have been studied. It is concluded that the original work on 1 is seriously in error.
Acknowledgement

I would like to thank my thesis adviser, Dr. Paul Engel, for his patience, understanding, and especially his brilliant guidance during my stay in his research laboratory. Special thanks are due to my labmates: Dr. Gregory Bodager for his wonderful work on the photochemistry of azocyclopropanes, Dr. Yan-Qiu Chen for stimulating discussions and her help both in the laboratory and in my everyday life, John Scholz for his masterful assistance in using the computer, and Anne Culotta for her helpful comments. I also thank CGP (a joint chemistry graduate program between the United States and the People’s Republic of China) which made my study here possible. Lastly and most importantly, I would like to thank my parents for their love and caring. This thesis is dedicated to them.
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Part I

Reduction of Azoalkanes by Benzhydryl Radicals
1.1. Introduction

Attempted triplet sensitization by aromatic ketones in the presence of a hydrogen donor can lead to complications due to the participation of ketyl radicals, a phenomenon commonly called chemical sensitization.\textsuperscript{1} Recently, it was discovered in this laboratory that irradiation of xanthone in the presence of azocyclopropane (ACP) and thiophenol afforded propanal cyclopropylhydrazone (6) and propanal azine (7).\textsuperscript{2} The mechanism in Scheme 1.1 involving hydrogen transfer from xanthydryl radical (1) to the ground state azo linkage was proposed to explain the formation of these products (s = syn, a = anti).

Scheme 1.1

Although the reducing properties of ketyl radicals are well known\textsuperscript{3-6} and the azo linkage is readily attacked by radicals,\textsuperscript{7} the only azo compounds reported
to react with ketyl radicals are azo dyes.\textsuperscript{8-11} In order to test the above mechanism, we studied the reduction of azoalkanes by thermally generated benzhydryl radicals.\textsuperscript{12}

1.2. Results

The photoreaction of benzophenone with triethylamine produces a near quantitative yield of benzhydryl radical,\textsuperscript{13} but irradiation of this solution in the presence of ACP caused rapid destruction of starting azoalkane and formation of a complex mixture. In contrast, azo-tert-butane (ATB) was reduced to 1,2-di-tert-butylhydrazine (8) under the same conditions. To confirm the participation of the benzhydryl radical, this species was produced independently in the presence of ATB by thermolysis of benzpinacol,\textsuperscript{14} leading cleanly to 8. Further investigation of the thermal reaction using the azoalkanes listed in Table I showed reduction to be general.

All of the aliphatic hydrazines were identified by comparing their \(^1\)H and/or \(^{13}\)C NMR spectra (cf. Table II) with those from the literature\textsuperscript{15} or from authentic samples made by catalytic hydrogenation\textsuperscript{16} of the corresponding azoalkane. The structures of the arylhydrazines are supported by the similarity of their \(^{13}\)C chemical shifts to those of hydrazobenzene. Products 21, 25, 27, and 29 were identified by comparison with independently synthesized samples.\textsuperscript{17} The reduction products of 36 were confirmed by NMR comparison with a mixture of acetone azine and acetic acid.
<table>
<thead>
<tr>
<th>Azoalkane</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>$\text{N} = \text{N}$</td>
</tr>
<tr>
<td>11</td>
<td>$\text{N} = \text{N} - \text{Me}$</td>
</tr>
<tr>
<td>ATB</td>
<td>$\text{N} = \text{N}$</td>
</tr>
<tr>
<td>13</td>
<td>$\text{N} = \text{N}$</td>
</tr>
<tr>
<td>15</td>
<td>$\text{N} = \text{N}$</td>
</tr>
<tr>
<td>17</td>
<td>$\text{N} = \text{N} - \text{Ph}$</td>
</tr>
<tr>
<td>19</td>
<td>$\text{N} = \text{N} - \text{Ph}$</td>
</tr>
<tr>
<td>ACP</td>
<td>$\text{N} = \text{N}$</td>
</tr>
<tr>
<td>22</td>
<td>$\text{Ph} - \text{N} = \text{N} - \text{Ph}$</td>
</tr>
<tr>
<td>24</td>
<td>$\text{Ph} - \text{N} = \text{N} - \text{Me}$</td>
</tr>
<tr>
<td>26</td>
<td>$\text{Me} - \text{N} = \text{N} - \text{Me}$</td>
</tr>
<tr>
<td>28</td>
<td>$\text{Ph} - \text{N} = \text{N} - \text{Ph}$</td>
</tr>
<tr>
<td>30</td>
<td>azo-1-adamantane</td>
</tr>
<tr>
<td>31</td>
<td>1,2-di-1-adamantylhydrazine</td>
</tr>
<tr>
<td>32</td>
<td>$\text{N} = \text{N}$</td>
</tr>
<tr>
<td>33</td>
<td>$\text{N} = \text{N}$</td>
</tr>
<tr>
<td>34</td>
<td>$\text{N} = \text{N} - \text{O}$</td>
</tr>
<tr>
<td>35</td>
<td>$\text{N} = \text{N}$</td>
</tr>
<tr>
<td>36</td>
<td>$\text{AcO} - \text{N} = \text{N} - \text{OAc}$</td>
</tr>
<tr>
<td>37</td>
<td>$\text{Me} - \text{N} = \text{N}$</td>
</tr>
<tr>
<td>38</td>
<td>$\text{Me} - \text{N} = \text{N}$</td>
</tr>
<tr>
<td>Product</td>
<td>Proton(^a)</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>8</td>
<td>2.2 (br s, 2 H), 1.04 (s, 18 H)</td>
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<td>10</td>
<td>2.57 (t, 4 H, J=7.04), 2.17 (br s, 2 H), 1.40 (m, 4 H)</td>
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<td>0.86 (t, 6 H, J=7.41)</td>
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<td>12</td>
<td>2.74 (sep, 2 H, J=6.21), 2.3 (br s, 2 H), 0.98 (d, 12 H, J=6.22)</td>
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<tr>
<td>14</td>
<td>3.14 (s, 2 H), 3.04 (br s, 2 H), 1.26 (s, 2 H), AB (1.23, 1.16, 4 H, J=9.32)</td>
</tr>
<tr>
<td>16</td>
<td>3.08 (br s, 2 H), 2.54 (s, 2 H), AB (1.55, 1.42, 8 H, J=7.8)</td>
</tr>
<tr>
<td>18</td>
<td>7.18 (m, 2 H, ar), 6.85 (d, 2 H, ar), 6.77 (t, 1 H, ar), 4.47 (br s, 1H), 2.75 (br s, 1 H), 2.63 (sep, 1H, J=6.22)</td>
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<td>0.83 (d, 6 H, J=6.22)</td>
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<td>20</td>
<td>7.22 (m, 2 H, ar), 6.96 (d, 2 H, ar), 6.79 (t, 1 H, ar), 4.58 (br s, 1 H), 2.52 (br s, 1 H), 0.88 (s, 9H)</td>
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</tr>
<tr>
<td>21</td>
<td>7.12 (t, 1 H, J=4.08), 2.84 (t, 2 H, J=6.45), 1.91 (dq, 2 H, J=4.21, 7.36(^d)), 1.76 (t, 2H, J=6.50), 0.87 (t, 3H, J=7.47)</td>
</tr>
<tr>
<td>23</td>
<td>7.08 (t, 4H, ar), 6.75 (t, 2 H, ar), 6.61 (d, 4 H, ar), 4.70 (br s, 2 H)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>7.10 (m, 5 H, ar), 6.44 (t, 1 H, J=5.04), 4.55 (br s, 1 H), 2.70 (t, 2 H, J=7.78), 2.46 (m, 5 H)(^e)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
27  3.90 (br s, 1H), 2.83 (s, 3 H), 1.77 (s, 3 H), 1.23 (s, 3H) 142.94, 25.02, 14.80

29  7.20 (m, 4 H, ar), 6.82 (m, 1 H, ar), 6.59 (br s, 1 H), 1.78 (s, 3 H), 1.13 (s, 3 H) 146.68, 142.34, 119.71, 129.40, 113.35, 24.98, 14.59

31  2.25 (br s, 2 H), 2.05 (br s, 6 H), 1.65 (br s, 24 H) 52.29, 41.87, 37.40, 30.02

33  3.49 (br s, 2 H), 1.30 (s, 2 H), 0.98 (s, 12 H) 63.58, 55.89, 28.36

35  2.38 (br s, 2 H), 1.21 (s, 4 H), 0.91 (s, 12 H) 48.75, 33.51f

38  5.71 (m, 1 H), 4.97 (m, 2 H), 3.07 (br s, 2 H), 2.40 (s, 3 H), 1.11 (s, 6 H) 146.09, 112.01, 56.94, 40.46, 25.50

39  3.27 (br s, 2 H), 3.22 (m, 2 H), 0.38 (m, 4 H), 0.28 (m, 4H) 31.69, 6.08

45  7.17 (m, 5 H, ar), 3.23 (br s, 2 H), 2.42 (m, 1 H), 2.11 (s, 3 H), 1.77 (m, 1 H), 0.75 (m, 2 H)

46  6.97 (m, 8H, ar), 4.80 (s, 2 H), 3.33 (br s, 2 H)

48  3.53 (s, 3 H), 2.40 (s, 3 H), 1.20 (s, 6 H), 1.18 (s, 6 H)

50  1.13 (s, 12 H), 1.11 (s, 4 H)

Note:  a. $^1$H chemical shifts are reported in ppm on the δ scale using either solvent signal (C$_6$D$_6$ δ 7.15) or internal hexamethyldisiloxane (δ 0.11) as reference.  b. C$_6$D$_6$ (δ 128.00) was used as internal standard.  c. all carbons except bridgehead.  d. Decoupling experiment clearly showed that this double quartet is coupled with the triplet at 7.12 and the triplet at 0.87.  e. NHCH$_3$ and CH$_2$CH=N.  f. methyl and methylene carbons.
Thermolysis of benzpinacol proceeds at low enough temperature (130 °C) that competing decomposition of the azoalkanes selected was generally not a problem. The observed overall rate constant (k = 1.1x10^-3 s^-1 at 130 °C), calculated from the time-dependent decrease of the ^1H NMR peak area of benzpinacol OH relative to that of internal reference hexamethyldisiloxane in the presence of 9 or 11, agrees very closely with the rate constant reported^{14} for thermolysis of benzpinacol in the presence of scavengers. Flash photolysis experiments indicated that ATB quenched benzhydryl radical with a rate constant greater than 10^8 M^-1 s^-1.

1.3. Discussion

Two possible mechanisms come to mind for the benzhydryl induced reduction of azoalkanes: hydrogen atom transfer, or single electron transfer (SET) followed by rapid protonation of the azoalkane radical anion. SET can be ruled out based on one electron redox potentials (versus sce) in acetonitrile, a solvent which favors electron transfer: benzhydryl radical, estimated E^0(ox)_{1/2} = -0.7 V,^{18} azobenzene, E^0(red)_{1/2} = -1.37 V.^{19} The free energy change for SET to azobenzene is substantially positive (ΔG^0=15.5 kcal/mol) and is expected to be still more endothermic for azoalkanes.^{20} Since it is impossible to reconcile the observed large interaction rate constant (> 10^8 M^-1 s^-1) with such endothermic electron transfer, we suggest that hydrogen transfer from benzhydryl radical to azo linkage is the first step of the reduction, as shown Scheme 1.2.
Scheme 1.2

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{C} & \quad \text{C} \\
\text{Ph} & \quad \text{Ph} \\
\text{OH} & \quad \text{OH} \\
\xrightarrow{\Delta} & \quad 2 \quad \text{Ph} \\
& \quad \text{OH} \\
\text{Ph}_2\text{CHOH} & + \text{Ph}_2\text{CO} \\
\text{RN} = \text{NR} & \\
\text{Ph}_2\text{CO} & + \text{RNH} \cdot \text{NR} \\
\xrightarrow{\text{Ph}_2\text{COH}} & \quad \text{RNHNHR} + \text{Ph}_2\text{CO} \\
\text{RNHNHR} & \\
\to & \quad \text{RNHNHR} + \text{RN} = \text{NR}
\end{align*}
\]

Many reducible organic compounds quench benzhydryl radicals by what is proposed to be the \textit{SET} mechanism.\textsuperscript{21} In the case of acridine, however, \textit{SET} is more endothermic than in azobenzene\textsuperscript{22} yet the interaction rate constant is still $2 \times 10^7$ M\textsuperscript{-1} s\textsuperscript{-1}.\textsuperscript{23} Initial hydrogen atom transfer is therefore the preferred mechanism for both acridine and azo compounds.

Once the hydrazyl radical has formed, another H\textsuperscript{-} is required to generate the product. The second hydrogen probably does not come from induced decomposition of benzpinacol since no rate acceleration is seen over that reported in the literature.\textsuperscript{14} Therefore this H\textsuperscript{-} must be transferred from a second benzhydryl radical or from a second hydrazyl radical, whose disproportionation is known.\textsuperscript{24}

The reaction of ACP with thermally produced benzhydryl radicals did not give 1,2-dicyclopropylhydrazine (39), as shown by NMR comparison with authentic 39 generated by diimide reduction\textsuperscript{25} of ACP. Instead the most prominent peaks in the complex NMR spectrum of the reaction mixture were
shown by comparison with independently synthesized material to arise from 21, a drastically rearranged isomer of ACP. This unusual product must derive from a scavangeable radical, for it was found among the products of irradiating benzophenone with triethylamine and ACP but was absent both in the xanthone-thiophenol-ACP photoreaction\(^2\) and in the benzpinacol-ACP thermolysis with added thiophenol. The major product ( > 80\% ) of the latter experiment was azine 7 but heating 0.10 M ACP with 0.24 M thiophenol in C\(_6\)D\(_6\) at 130\(^\circ\)C for 15 min gave no reaction. Since 7 must have arisen by scavenging of a radical on the pathway to 21, we propose that the reaction of ACP with benzhydryl radicals proceeds as shown in Scheme 1.3.

**Scheme 1.3**

\[\begin{align*}
&\text{ACP} \\
&\text{PhSH} \\
&\text{PhS}^- \\
&\text{FAST} \\
&\text{PhSH} \\
&\text{21}
\end{align*}\]
Rearrangement of 2 to 3s and of 4a to 5s (cf. Scheme 1.3) resembles the rapid ring opening of cyclopropylaminyl radicals\(^{26}\) while cyclization of 5s to 40 finds analogy in radical attack at imine nitrogen.\(^{27}\) The cyclization rate of 5s is apparently slow enough to allow scavenging so that 7 becomes the product when thiophenol is added. The absence of hydrazone 6 in the benzpinacol-thiophenol reaction is surprising since 2 should open to a high for such an explanation. Radical 3a may reclose to 2 faster than it is trapped or perhaps any 6 that forms is converted by phenylthiyl radicals to 4a. Similarly, 4a should open to both 5s and its anti isomer 5a. In the absence of PhSH, 5a must reclose to 4a and may also be responsible for some of the unidentified products of the unscaevaged reaction. The main route to 4a is proposed to be intramolecular hydrogen abstraction in 3s followed by facile isomerization of the initial syn-hydrazonyl radical to 4a.\(^{29}\) Conversion of 41 to product 21 requires disproportionation with another radical R'. Although recombination is the usual fate of dissubstituted iminyl radicals,\(^{30}\) an intramolecular analogy for our last step is found in the photolysis of pyrazoline 42.\(^{31}\)

\[
\begin{array}{c}
36 \\
\text{Ph} \\
\text{Me}^- \text{N=NN} \\
\text{H} \\
\text{Ph} \\
\text{Me}^- \text{N=NN} \\
\text{H} \\
\text{Ph} \\
\text{Me}^- \text{N=NN} \\
\text{C=NN} \\
\text{Me}^- \text{N=NN} \\
\end{array}
\]

Furthermore, phenylmethyleneimino (PhCH=\text{N}-.\text{-}) radicals disproportionate to benzonitrile,\(^{32,33}\) while the hydrazone H2C=\text{N-NH-CH}3 decomposes to HCN and CH3NH2 in the pyrolysis of (CH3)2N-N3.\(^{34}\)

Reaction of another azocyclopropane (24)\(^{31}\) with benzhydryl radicals
could lead initially to two hydrazyl radicals 43 or 44 (cf. Scheme 1.4).

Since 43 cannot undergo cyclopropylcarbinyl rearrangement, it should lead to hydrazine 45. However, 45 was not formed in this reduction, the observed product 25 arising exclusively from 44. The following control experiment showed that the absence of 45 was not due to its instability under the reaction conditions.

A mixture of 24, benzpinacol, and the anthracene adduct of diimide 46 in a 1:1:2 molar ratio was degassed and sealed in an NMR tube. This source of diimide, which undergoes thermolysis at 50-90 °C, was selected to avoid introduction of potentially reactive substances and to allow clean generation of the air-sensitive hydrazine. After the reduction of 24 to 45 was nearly complete, the temperature was raised to 130 °C to decompose benzpinacol. Hydrazine 45 was unchanged but the residual azoalkane 24 proceeded as usual to 25.
Another possible reason for the absence of 45 during benzhydryl radical reduction of 24 is that 43 transferred H• back to a benzhydryl radical, regenerating 24. However this process would lead to benzhydrol, which was not observed in the reaction. We conclude that 43 does not form and that hydrogen transfer to 24 occurs only at the least hindered nitrogen. Intermediate 44 then rearranges exactly as expected from the ACP results. Of course, the absence of a second cyclopropyl ring greatly simplifies the chemistry. The reaction of 24 and the initial steps for ACP are similar to the following reduction of cyclopropyl ketones reported by Neckers and Schaap\textsuperscript{36}

Bisazoalkanes 26 and 28 also behaved unusually upon prolonged exposure to benzhydryl radicals, giving only the hydrazones 27 and 29 (cf. Scheme 1.5). These products of central C-C bond cleavage were observed at a reaction time of 20 min as well; however, the early reduction mixture from 26 showed additional NMR peaks attributed to hydrazine 48. An authentic sample of 48 was generated for spectral comparison by catalytic half hydrogenation of 26. Based on the conclusions from 24 (see above), we suggest that hydrogen is delivered selectively to the less hindered end of the azo group of 26, 28 and not to the neopentyl-like nitrogen. The resulting hydrazyl radical 47 undergoes rapid β-scission when R = phenyl because the released radical has additional resonance stabilization\textsuperscript{37}. On the other hand, 47 (R = Me), which cleaves less readily, reacts as expected with benzhydryl radicals to give 48. Since 48 is still
Scheme 1.5

\[
\begin{align*}
R_\text{NNR} & \xrightarrow{\text{Ph}_2\text{COH}} R_\text{NNR} \\
26: & R = \text{Me} \\
28: & R = \text{Ph} \\
R_\text{NNRR} + R_\text{NNR} & \xrightarrow{\text{Ph}_2\text{COH}} R_\text{NNRR} \\
27: & R = \text{Me} \\
29: & R = \text{Ph} \\
\end{align*}
\]

an azoalkane, it can be reduced by benzhydryl radicals to 49, perhaps accounting for the absence of 48 at longer reaction times.

Despite the fact that thermolysis of 37 at 120 °C was only 2.4 times slower than that of benzpinacol, we were able to determine that the sole reduction product was the simple hydrazine 38. No evidence was found for delivery of H· to the olefin, intramolecular attack of the intermediate hydrazyl on the olefin, or free radical rearrangements.38

Reduction of azoxyalkane 34 by 2 equivalents of benzpinacol gave exclusively the expected hydrazine (35). According to NMR, the intermediate

\[
\begin{align*}
\text{34} & \xrightarrow{} \text{50} \xrightarrow{} \text{35} \\
\end{align*}
\]
azoalkane 50 reached a maximum concentration of about 10% of the mixture in 5 minutes, when 60% of 34 remained and 30% of 35 was formed. One equivalent of benzpinacol is known to reduce azoxybenzene to azobenzene but we did not try 34 with equimolar benzpinacol. Even if reduction of aliphatic azoxy compounds cannot be stopped cleanly at the azoalkane stage, the reaction is a potentially useful synthesis of azoalkanes from azoxyalkanes since hydrazines are easily reoxidized to azoalkanes.

Azoalkane 36 also behaved abnormally on reduction with benzhydryl radicals, the products being exclusively acetone azine and acetic acid. Following initial H- transfer to the azo linkage, loss of acetoxy radical probably generates a hydrazine that loses acetic acid.

By way of historical perspective, Monroe and Wamser obtained some secondary products from the reduction of azoxybenzene with photochemically produced acetophenone ketyl radical. Those products were postulated to arise from further reduction of azobenzenes by acetophenone ketyl radical. Hashimoto, et al. also noted the possibility of chemical sensitization in their work on photoreduction of azobenzene. Our reduction of azobenzene (22) nicely confirms their hypotheses.

In summary, we have found that thermolysis of benzpinacol in the presence of azoalkanes provides a clean method to generate air sensitive hydrazines. The mechanism begins with rapid hydrogen atom transfer from benzhydryl radical to the least hindered nitrogen of the azo linkage. When a
weak bond is situated $\beta$ to the initially formed hydrazyl radical as in azocyclopropanes or vicinal bisazoalkanes, cleavage of this bond leads to hydrazones by rational mechanisms.

1.4. Experimental

**General Procedures.** NMR spectra were obtained on an IBM AF-300 spectrometer in $\text{C}_6\text{D}_6$. Analytical GC was carried out on a Hewlett Packard 5890 instrument equipped with a data system while preparative GC employed an Antek 300 TC Chromatograph.

**Compounds.** Before use, $9^{43}, 11^{43}, 17^{44}$, and $29^{44}$ were purified from stock samples by preparative GC on an OV-17 column. Compounds $13^{45}$ and $15^{46}$ were purified by sublimation while $22$ was recrystallized from ethanol. Relatively pure $\text{ATB}^{43}, 19^{47}, \text{ACP}^2, 26^{44}, 28^{44}, 30^{48}, 32^{49}, 34^{50}$, and $36^{51}$ were used without further purification. A 0.1M solution of $24$ in $\text{C}_6\text{D}_6$ prepared by G.A. Bodager$^2$ was used without isolation. Benzpinacol was prepared by irradiating benzophenone in isopropanol.$^{52}$ The hexane solvent used for flash photolysis was B & J Chompure (American Scientific Products). Phenylbenzoin was prepared and purified as described in the literature,$^{53}$ benzophenone was recrystallized from methanol, and triethylamine was refluxed and distilled from potassium hydroxide pellets. Authentic samples of $8, 14, 16, 31, 33, 35$, and $48$ were prepared by catalytic hydrogenation of the appropriate azoalkanes at 1 atm in methanol or ether over 10% Pd/C.
1,5-Diazaoct-5-ene-1-yne (21). To 0.5 mL of C$_6$D$_6$ containing 14 mg (0.2 mmol) 3-aminopropanenitrile$^{54}$ in an ice bath was added dropwise with stirring a cold solution of 11.6 mg (0.2 mmol) distilled propionaldehyde in 0.5 mL C$_6$D$_6$. The mixture was stirred at room temperature for a few min and dried over anhydrous Na$_2$SO$_4$ for 2 h with frequent shaking. $^1$H and $^{13}$C NMR of the solution showed that the major peaks coincided with those found in the reduction of ACP. Attempted large scale preparation and purification were not successful due to the instability of the product. Thus the NMR solution described above decomposed to a complex mixture after standing for 26 days in the freezer.

3-Phenylpropanal-N-methyl hydrazone (25) was prepared according the literature procedure.$^{55}$ The pure hydrazone underwent air oxidation, presumably to the peroxide, on standing at room temperature for a few hours.

Benzhydryl reduction of azoalkanes. All reactions were run in sealed NMR tubes in C$_6$D$_6$ (Cambridge Isotope Laboratories, 99.6%) degassed by three freeze-thaw cycles. The concentrations of benzpinacol and azoalkane were typically 0.1 M. The tubes were immersed in an oil bath at 130±0.1 °C and were removed periodically for NMR analysis. GC analysis of the reduction mixture from ACP showed benzophenone, benzhydrol, and 21, whose retention times matched those of authentic materials. GC conditions: Supelcowax 30m capillary column (column: 150 °C, injector: 150 °C, detector: 250 °C). $^1$H and $^{13}$C NMR of the reduction of 24 showed that the major peaks coincided with those in the authentic sample of 25. Both the reduction product and the authentic
sample contained a small amount of Z isomer. The reduction mixture of 24 showed a GC peak with the same retention time as 25 on a 25m SE-54 capillary column (column: 160 °C, injector: 200 °C, detector: 250 °C). Anthracene-9,10-biimine (44) was prepared according to the published procedure except that hydrolysis of the dicarbamate required 7 days. The biimine was mixed in C₆D₆ with 24 and benzpinacol in a 1:1:2 ratio in an NMR tube. Reduction of 24 to 43 began even while the solution was being vacuum degassed and the remainder of 44 was decomposed by heating at 70 °C for 10 min. While the major product was 43, some azoalkane remained probably because the diimide was not consumed with 100% efficiency. After heating the sealed NMR tube at 130 °C for 10 min, all of the 24 had gone to 25 and the hydrazine 43 remained unchanged, even after additional 2 hours at 130 °C. Heating 26 with benzpinacol for 20 min afforded products 27 and 48 in a 5 : 1 ratio according to H NMR. The amount of 48 decreased on longer heating, reaching an undetectable level after 10 hours. In contrast, bisazoalkane 28 showed 29 as the only product, even when thermolysis was interrupted after 20 min.

Flash photolysis. The rate constant for quenching of benzhydryl radicals by ATB was determined by laser flash photolysis using 540nm light to monitor the radical. A nitrogen purged solution of 3.35x10⁻⁵ M benzophenone and 0.066 M triethylamine in hexane and a solution of 2.83x10⁻⁴ M phenylbenzoin was irradiated at 266nm. Similarly, a 5x10⁻³ M solution of phenylbenzoin was irradiated at 355 nm. Addition of ATB shortened the decay lifetime, although vaporization of the quencher during purging caused scatter in the calculated k_q values. It was clear however, that k_q was at least 10⁶ M⁻¹ s⁻¹.
1.5. References


(17) Authentic 27 and 29 were made by Y.-Q. Chen in this laboratory.


(24) For an example of this disproportionation, see Holt, P. F.; Hughes, B. P. *J. Chem. Soc.* 1955, 98.

(25) Although diimide has been used frequently to reduce azobenzene, we are unaware of its use in the aliphatic series. See Hünig, S.; Müller, H. R.; Thier, W. *Angew. Chem. Int. Ed. Engl.* 1965, 4, 271.


1985, p. 364


(37) Engel, P. S.; Chen, Y.-Q. manuscript in preparation.


(44) Chen, Y.-Q. Unpublished results from this laboratory.


Part II

Thermolysis and Photolysis of an $\alpha$-Aminoazoalkane,

$2$-tert-butylazo-2-dimethylaminopropane
2.1. Introduction

$\alpha$-Aminoalkyl radicals ($R_2N\dot{C}R_2'$) play an important role in photochemical, electrochemical, and enzymatic reactions.\(^1\) Most of the studies have been focused on their ESR spectra\(^2\) and reactions\(^3\) while a few dealt with aminoalkyl heats of formation.\(^4\)-\(^6\) The dimethylamino group is missing from two of the best scales of radical substituent constants\(^7\),\(^8\) and its resonance contribution is highly uncertain on the ER scale. This scale is based on an extended Hammett equation using hydrogen abstraction of nuclear-substituted cumenes by the polystyryl radical as the reference reaction.\(^9\) The few solution phase studies of the $\alpha$-aminoalkyl radical stabilization energy\(^{10}\) as well as gas phase pyrolysis,\(^4\) appearance potentials,\(^5\) and vinylcyclopropane rearrangement\(^{11}\) indicate a high stabilization for this species.

Azoalkane thermolysis rates depend on the ability of $\alpha$-substituents to

**Scheme 2.1**

\[ \text{Cl} \quad \text{N} = \text{N} \quad \text{Cl} \quad \xrightarrow{\text{HNMe}_2} \quad \text{Me}_2\text{N} \quad \text{N} = \text{N} \quad \text{NMe}_2 \]

\[ \downarrow \text{HNMe}_2 \]

\[ \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \]
stabilize a carbon centered radical.\textsuperscript{12} In order to quantify the stabilization by the Me\textsubscript{2}N group, it would be of interest to determine the decomposition rate of bis (2-dimethylamino-2-propyl) diazene (1). However, previous attempts to synthesize 1 from 2 gave only acetone azine\textsuperscript{13} (see Scheme 2.1). Our attention turned to the unsymmetrical analog 3 because the difference in activation free energies ($\Delta G^\ddagger$) between unsymmetrical azoalkanes and their less stable symmetrical counterpart is usually small.\textsuperscript{12} More importantly, 4 cannot form azine on treatment with dimethylamine.

\[
\begin{align*}
\text{HNMe}_2 & \quad \rightarrow \\
R & \quad \text{N=N}\quad \text{Cl} \\
\text{4} & \quad \text{3} \\
\text{a, } R & \quad \text{Ph} \\
\text{b, } R & \quad \text{Me} \\
\text{c, } R & \quad \text{tert-Bu}
\end{align*}
\]

2.2. Results

The original plan was to synthesize 3\textsubscript{a} from 4\textsubscript{a}. Although we made 3\textsubscript{a}, it proved inseparable from acetone phenylhydrazone by vacuum distillation or GC. 3\textsubscript{a} decomposed on silica, basic alumina, and Florisil and it formed a glassy solid on attempted low temperature recrystallization from ethanol. A preliminary thermolysis was done on the crude material in toluene-$d_8$ at 150\textdegree C. The identifiable products were acetone phenylhydrazone, dimethylamine, acetone, benzene-$d$, acetone N,N-dimethylenamine (5), condensed enamine
(6), and (o, m, p)-phenyltoluene-$d_7$. The phenyltoluenes and benzene-$d$ were identified by GC-MS. Irradiation of 3a in C$_6$D$_6$ at 435 nm gave acetone phenylhydrazone, biphenyl-$d_5$, dimethylamine, and 5. Since complete thermolysis of a 0.15 M solution at 150 °C required 100 min, the impurity acetone phenylhydrazone probably arises from photochemical C-NMe$_2$ cleavage.

Instead of trying other ways to purify 3a, we turned our attention to alternatives 3b and 3c. Cleavage of the C-NMe$_2$ bond should be slower when R is an alkyl group because of the lower stability of the resulting hydrazonyl radical.$^{14}$ While attempts to make 3b were thwarted by our failure to obtain appreciable amounts of the required α-chloroaquoalkane 4b, the synthesis of 3c turned out to be simple (cf Scheme 2.2). The use of tert-butyl hypochlorite with

**Scheme 2.2**

$$7 \xrightarrow{\text{t-BuOCl, -78 °C}} 4c$$

$$7 \xrightarrow{\text{HNMe$_2$/H$_2$O, r. t.}} 3c$$
7 deserves mention here since, to our knowledge, this reagent was used previously only with aryl hydrazones as a less reactive alternative to chlorine. Our experience was that tert-butyl hypochlorite is a very clean chlorination reagent.

It is well known that the long wavelength UV absorption of azoalkanes is due to an n-π* transition which is blue shifted and weakened in polar solvents. The λ\text{max} and ε of 3c displays the largest solvent dependence of any azoalkane but the bandwidth remains constant (cf Table 2.1).

<table>
<thead>
<tr>
<th>Table 2.1. Solvent Dependence of the UV Spectrum of 3c</th>
</tr>
</thead>
<tbody>
<tr>
<td>solvent</td>
</tr>
<tr>
<td>Hexane</td>
</tr>
<tr>
<td>Acetonitrile</td>
</tr>
<tr>
<td>Methanol</td>
</tr>
</tbody>
</table>

The thermolysis of 3c was monitored by the disappearance of the azoalkane UV absorption. Thermolysis kinetic data were obtained in hexane in sealed tubes at 111.60-130.35 °C (cf Table 2.2) and the activation parameters ΔH\text{\#} = 26.6 ± 0.4 kcal/mol, ΔS\text{\#} = -6.6 ± 1.1 eu were calculated from the Eyring Plot (see Figure 2.1).

<table>
<thead>
<tr>
<th>Table 2.2. Thermolysis Kinetic Data for 3c</th>
</tr>
</thead>
<tbody>
<tr>
<td>T(K)</td>
</tr>
<tr>
<td>10^4k, s\text{-1}</td>
</tr>
</tbody>
</table>
Figure 2.1

Eyring Plot for Thermolysis of 3c

The thermolysis rate of 3c was sensitive to solvent polarity and was slowed by the addition of base, as indicated in Table 2.3.

Table 2.3. Thermolysis of 3c in Various Solvents

<table>
<thead>
<tr>
<th>solvent</th>
<th>Temperature(°C)</th>
<th>$10^4 k$, s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>hexane</td>
<td>113.94</td>
<td>2.78</td>
</tr>
<tr>
<td>hexane</td>
<td>121.53</td>
<td>5.51</td>
</tr>
<tr>
<td>methanol</td>
<td>113.94</td>
<td>15.30</td>
</tr>
<tr>
<td>methanol(NaOH)</td>
<td>121.53</td>
<td>1.25</td>
</tr>
<tr>
<td>DMF</td>
<td>121.53</td>
<td>2.82</td>
</tr>
</tbody>
</table>

Product analysis was achieved by NMR and/or GC-MS (cf Table 2.4.)
while nitrogen yields were obtained using a Töpler pump and gas buret. In acetonitrile, the nature of the thermolysis products is very sensitive to water.

### Table 2.4. Products of Thermolysis and Photolysis of 3c (Relative Moles)

<table>
<thead>
<tr>
<th>reaction type&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Δ</th>
<th>Δ</th>
<th>Δ</th>
<th>Δ</th>
<th>Δ</th>
<th>Δ</th>
<th>Δ</th>
<th>Δ</th>
<th>Δ</th>
<th>Δ</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>solvent&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Bz</td>
<td>Aw</td>
<td>Ad</td>
<td>Me</td>
<td>MeB</td>
<td>BzA</td>
<td>Bz</td>
<td>Aw</td>
<td>Me</td>
<td>MeB</td>
<td></td>
</tr>
<tr>
<td>N&lt;sub&gt;2&lt;/sub&gt; yield, %</td>
<td>89.5</td>
<td>90.0</td>
<td>c</td>
<td>90.1</td>
<td>92.8</td>
<td>82.7</td>
<td>93.0</td>
<td>94.8</td>
<td>88.0</td>
<td>96.0</td>
<td></td>
</tr>
<tr>
<td>isobutane</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1</td>
<td>1&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>i-PrNMe&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.3</td>
<td>0.1</td>
<td>0.54</td>
<td>trace</td>
<td>2.2</td>
<td>0</td>
<td>2.5</td>
<td>2.3</td>
<td>0.3</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>t-heptylamine (9)</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
<td>0</td>
<td>0.4</td>
<td>0</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>enamine (5)</td>
<td>0.2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>isobutene</td>
<td>trace</td>
<td>trace</td>
<td>0.12</td>
<td>trace</td>
<td>0.34</td>
<td>0</td>
<td>1.6</td>
<td>1.3</td>
<td>0.1</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>acetone</td>
<td>0.2</td>
<td>1.4</td>
<td>0.16</td>
<td>e</td>
<td>e</td>
<td>0.26</td>
<td>0.8</td>
<td>0.7</td>
<td>e</td>
<td>e</td>
<td></td>
</tr>
<tr>
<td>dimethylamine</td>
<td>1</td>
<td>1.7</td>
<td>1.4</td>
<td>2.8</td>
<td>2.3</td>
<td>1.37</td>
<td>0.9</td>
<td>0.8</td>
<td>2.8</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>mesityl oxide</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.39</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>(t-BuNH)&lt;sub&gt;2&lt;/sub&gt; (8)</td>
<td>0.03</td>
<td>0.08</td>
<td>0.5</td>
<td>0.09</td>
<td>f</td>
<td>trace</td>
<td>0</td>
<td>0</td>
<td>0.15</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>t-BuNHNCMe&lt;sub&gt;2&lt;/sub&gt; (7)</td>
<td>0.06</td>
<td>0.05</td>
<td>0.39</td>
<td>0.07</td>
<td>0.26</td>
<td>trace</td>
<td>0.13</td>
<td>0.09</td>
<td>0.02</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>ATB</td>
<td>0</td>
<td>0</td>
<td>0.07</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

Note:  
- a. Δ: thermolysis, hν: photolysis.  
- b. solvent: Bz = C<sub>6</sub>D<sub>6</sub> as received from CIL, Aw = wet CD<sub>3</sub>CN as received from Aldrich, Ad = dried CD<sub>3</sub>CN solution of 3c, Me = CD<sub>3</sub>OD and CH<sub>3</sub>OD, MeB = CD<sub>3</sub>OD/NaOH and CH<sub>3</sub>OD/NaOH in thermolysis but CD<sub>3</sub>OD/NaOH only in photolysis, BzA = C<sub>6</sub>D<sub>6</sub>/HOAc.  
- c. not determined.  
- d. Isobutane-<sup>d</sup> was the major isobutane product.  
- e. acetone detected by GC-MS but not visible by NMR on account of H-D exchange with solvent.  
- f. NMR peak overlap obscured the product.
Thus thermolysis in wet acetonitrile gave only dimethylamine, acetone, isobutane, and a small amount of isobutene, isopropylamine, 7, and di-tert-butylhydrazine (8) while it gave mostly radical derived products in dried acetonitrile solution. In benzene, however, removal of residual water did not change the products except for decreasing the amount of acetone and dimethylamine, as expected if these products arise from hydrolysis of the enamine (5). Isobutane-$d$ reached a level detectable by NMR after a solution of 3c in D$_2$O/CD$_3$CN (1:1) stood in the dark for 36 h at room temperature.

Although 3c reacts slowly with methanol at room temperature in the dark, it is stable in basic methanol under these conditions. Thus a degassed solution of 3c in basic CD$_3$OD in a sealed tube did not show any isobutane-$d$ by NMR after 50 days in the dark at room temperature.

Except in methanol (see Discussion), photolysis products of 3c show less variation with solvent polarity than do the thermolysis products. The nitrogen quantum yield, 0.41, was determined at 366 nm in benzene using azo-tert-butane as actinometer$^{16}$. 
Finally, 3c forms complexes with Fe(II) and Cu(I). NMR of 3c in acetonitrile-$d_3$ with added FeSO$_4$ or CuCl showed two sets of three singlets in each case, one set of which was similar to that of the starting material. The Cu(I) solution was brick red colored, typical of azoalkane-CuCl complexes. No decomposition products were found in either experiment.

2.3 Discussion

\[ \text{Et-} \begin{array}{c} \text{N=} \\
\text{N} \\
\text{N} \\
\text{R} \end{array} \begin{array}{c} \text{NH} \\
\text{NR}_2' \end{array} \text{R} \]

\[ 10 \]

\[ R = \text{CH}_3, \text{C}_3\text{H}_7 \]

\[ R' = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \]

\[ (\text{CH}_2)_5, (\text{CH}_2)_6 \]

\[ \begin{array}{c} \text{Ph-} \\
\text{N=} \\
\text{N} \\
\text{NH} \\
\text{NH} \\
\text{N=} \\
\text{N-Ph} \end{array} \]

\[ 12 \]

\[ \begin{array}{c} \text{N=} \\
\text{N} \\
\text{N=} \\
\text{N} \\
\text{N=} \\
\text{N} \end{array} \]

\[ 13 \]

Although 3c was not known previously, a few azoalkanes with saturated nitrogen on the $\alpha$ carbon, 10$^{17}$, 11$^{14}$, 12$^{19}$, and 13$^{20}$, have been reported.
While thermolysis of 10 was mentioned and 11 was studied in depth, decomposition of 12 and 13 was not reported.

Nearly all azoalkanes decompose by a radical pathway. In fact, all but the last three compounds in Table 2.4 are expected from azoalkane homolysis while acetone, dimethylamine, 6, and mesityl oxide are secondary products of 5. Thermolysis is slowed down by polar solvents (e.g., DMF and basic methanol), suggesting that the rate determining step is not heterolysis. However, the rather unusual product 8 caught our attention. According to Kosower, this symmetrical hydrazine is formed along with isobutane from bimolecular reaction of tert-butyl diazene (14). At first, we hypothesized that 14 arose in our system when 2-dimethylaminopropyl radicals transferred an electron followed by a proton to tert-butyl diazenyl radicals in a solvent cage. Since α-aminoalkyl radicals are known to have very low oxidation potentials, electron transfer to the electron deficient diazenyl radical could be fast. In fact, cage electron transfer between two neutral radicals has been observed in a diacyl peroxide. However, we became disenchanted with this hypothesis on realizing that the estimated lifetime of tert-butyl diazenyl radicals was 4.6 ps at room temperature and is expected to be shorter at higher temperature. It seems highly unlikely that even caged electron transfer would compete with such a fast deazatation. Based on the assumed intermediacy of 14, we instead propose the purely radical mechanism shown in Scheme 2.3 to rationalize the observed products.

α-Aminoalkyl radicals are known to donate electrons or hydrogen atoms
Scheme 2.3

\[
\begin{align*}
3c & \quad \xrightarrow{k_1} \quad \text{[18]} \\
16 & \quad \xrightarrow{k_d} \quad \text{[15]} \quad \text{[16]} \\
5 \quad \xrightarrow{k_c} \quad \text{[18]} \quad \text{separated radicals}
\end{align*}
\]
to a variety of acceptors.\textsuperscript{3a} Loss of an electron from \textbf{16} affords an α-amino
cation but we were unable to detect any 2-dimethylamino-2-cyanopropane on
inclusion of the useful organic-soluble tetrabutylammonium cyanide\textsuperscript{26} in a
thermolysis of \textbf{3c} in acetonitrile. We demonstrated that this aminonitrile was
stable under the reaction conditions. Furthermore, electron transfer from \textbf{16} to
\textbf{3c} is expected to be endothermic based on one electron redox potentials
(versus sce) in acetonitrile: 2,4-dimethyl-3-dimethylamino-3-pentyl radical,
estimated $E^0(\text{ox})_{1/2} = -1.84$ $V$\textsuperscript{27}; 2-(1-adamantyl)azo-2-cyanopropane,
$E^0(\text{red})_{1/2} = -2.3$ $V$\textsuperscript{28}. Therefore, ordinary hydrogen transfer from \textbf{16} to \textbf{3c} is
more likely, by analogy to the reaction between benzhydryl radicals and
azoalkanes.\textsuperscript{29} The two radicals, \textbf{17} and \textbf{18}, thus formed undergo β-scission to
give \textbf{7} and \textbf{14}, respectively. Formation of dimethylamino radicals by β-scission
of \textbf{17} helps to explain the excess of dimethylamine over acetone when water is
carefully excluded.

In benzene, the fact that only small amounts of \textbf{7} and \textbf{8} are formed
implies that hydrogen transfer from \textbf{16} to \textbf{3c} is not important. Thus our kinetics
study in hexane should represent true carbon - azo homolysis ( $k_1$, Scheme
2.3 ). In basic methanol, deprotonation of radicals \textbf{17} and \textbf{18} may give the
radical anion of \textbf{3c} which then cleaves to a dimethylamino anion and an
acetone tert-butylhydrazonyl radical that ends up as \textbf{7}. We are not able to
explain why \textbf{16} is a better hydrogen atom donor in acetonitrile than in
benzene.

Except in methanol solvent, the photolysis products are indicative of a
purely radical process. In fact, considerably more of the typical radical products isobutene, N,N-dimethylisopropylamine, and 9 were found at the much lower temperature used for photolysis (25 °C) than thermolysis (130 °C), perhaps because the cage effect is greater at lower temperature. The temperature dependent cage effect contributes to the absence of 8 in photolysis because less 16 is available at 25 °C. Moreover, hydrogen transfer from 16 to 3c should be an activated process. The photolability of 14\textsuperscript{30} also decreases the yield of 8. Judging from the photolysis results, disproportionation of 15 and 16 to dimethylisopropylamine and isobutene is somewhat favored over the opposite direction, consistent with statistical and stereochemical factors.\textsuperscript{31} To our knowledge, only one solution phase study of disproportionation of two different radicals was reported previously.\textsuperscript{32} Formation of 5 was observed at early thermolysis times in dry acetonitrile but it later disappeared, probably due to polymerization. The absence of 5 in undried solvents suggests that it was hydrolyzed rapidly by adventitious water, producing the observed acetone.

1,4-Cyclohexadiene was found to be an ineffective scavenger of radicals 15 and 16. Thus thermolysis of 0.1 M 3c in toluene in the presence of 0.2 M cyclohexadiene did not change the product distribution significantly, although a small amount of benzene was detected by NMR. Thiophenol was found to react with 3c at room temperature. Alkyldiazenes are known to react with aldehydes under basic conditions to give α-azocarbinols which then tautomerize slowly to hydrazides.\textsuperscript{33} PhCONHNNH(t-Bu) was not detected by GC-MS when we attempted to trap 14 with benzaldehyde under acidic conditions in methanol and neutral conditions in benzene. In their work with α-azocarbinols, Schulz
and Missol suggested that alkyl diazenes react with benzaldehyde even under acidic and neutral conditions. However, while Chang, et al. raised doubt about the intermediacy of alkyl diazene in the reaction of α-azocarbinols with aldehydes under neutral conditions, one would not expect the same reaction under acidic conditions in view of the extreme instability of methyl diazene toward acid. The hypothesis that arises from diimide reduction of 3c followed by elimination of dimethylamine is ruled out based on the trapping experiment with norbornene. In this experiment, no norbornene was detected when norbornene was added to the dry thermolysis solution of 3c in acetonitrile. However, the GC-MS suggested the presence of 2-tert-butylnorbornane. This compound probably arises from tert-butyl radical additon to norbornene followed by hydrogen abstraction of the resulting radical.

**ATB** is another unusual product formed on thermolysis of 3c in acetonitrile. Addition of tert-butyl radical to the azo linkage of 3c and β-scission of the resulting radical would give acetone di-tert-butylhydrazone and **ATB** (cf. Scheme 2.4). This mechanism is also supported by the presence of a small GC-MS peak attributed to acetone di-tert-butylhydrazone.

Thermolysis in methanol without base is considered to be acid catalyzed decomposition since the addition of base drastically slowed the thermolysis rate and increased the amount of dimethyl isopropylamine and isobutene, both of which are radical derived. 3C reacts slowly with acetic acid in benzene at room temperature but rapidly at 100 °C. 3C reacts instantly with H2SO4 solution in CD3OD at room temperature giving 7-d, acetone-d6, dimethylamine-d,
isobutene, and $8\cdot d_2$. The sensitivity of 3c to water and acid is rationalized as acid catalyzed hydrolysis as shown in Scheme 2.5. This scheme correctly predicts isobutane-$d$ as the major isobutane product in MeOD. Although the amino nitrogen is more basic, protonation of the azo group is analogous to acid decomposition of $\alpha$-azocarbinols.\textsuperscript{38} Protonation of alkyldiazenes to give diimide is preceded\textsuperscript{36} and diimide reduction of azoalkanes was known previously.\textsuperscript{29} The presence of diimide in the system was proved by GC detection of norbornane when $H_2SO_4$ was added to a solution of 0.4 M
Scheme 2.5

\[ \text{HNMe}_2 \xrightarrow{H^+} \text{NHMe}_2 \]

\[ \text{HNMe}_2 \xrightarrow{H^+} \text{H} \xrightarrow{\text{H}_2\text{O}} \text{acetone + dimethylamine} \]

\[ \text{isobutene} \]

\[ \text{diimide} \xrightarrow{H^+} \text{HNMe}_2 \]

\[ \text{HNMe}_2 \xrightarrow{-\text{HNMe}_2} \text{H} \]

\[ \text{7} \]

\[ \text{8} \]

\[ \text{14} \]
norbornene and 0.1 M 3c in CD$_3$OD.

The similar deazatation quantum yield of ATB and 3c in benzene suggests that 3c probably photolyses by prior isomerization to the cis isomer, which then undergoes thermolysis. Since trans 3c is unstable in methanol at ambient temperature, the fact that photolysis under these conditions gives a similar product distribution to thermolysis (isobutane-d as major isobutane product when CH$_3$OD was used, much dimethylamine, presence of 7 but no isopropylamine, isobutene, or 9) suggests that cis 3c is readily protonated by methanol. Indeed, cis azoalkanes are much more polar than trans.$^{39}$ Since the product distribution hardly changes on addition of base, we propose that cis 3c is at least hydrogen bonded to and maybe protonated by methanol even in the presence of base. Although excited singlet cyclic azoalkanes are quenched by protic solvents,$^{40}$ the reactivity of cis 3c to methanol is remarkable in light of its thermolability, which can be estimated as follows. Assume that the internal steric strain of cis 3c is same as cis ATB (though it is surely greater). At 298 K, $\Delta G^{\neq}_{t-\text{ATB}} = 37.2$ kcal/mol in Ph$_2$O,$^{12}$ $\Delta G^{\neq}_{c-\text{ATB}} = 19.2$ kcal/mol in methanol,$^{41}$ $\Delta G(\text{strain}) = \Delta G^{\neq}_{t-\text{ATB}} - \Delta G^{\neq}_{c-\text{ATB}} = 37.2 - 19.2 = 18.0$ kcal/mol. Therefore, $\Delta G^{\neq}_{c-3c} = 28.6 - 18.0 = 10.6$ kcal/mol which corresponds to a maximum half life of 6.6 $\mu$s at 298 K for cis 3c.

Since 3c generates tert-butyl diazene in polar solvents at elevated temperature, we expect that 1 would do the same to give diimide at lower temperature in the presence of water. The diimide produced from 1 would then reduce 1 or more likely 2 to give acetone azine. This scheme explains the
previous failure\textsuperscript{13} to prepare 1 from 2.

Finally, if we assume that the activation free energy difference between 3\textit{c} and 1 is 2 kcal/mol as found in 19-20 and 21-22, respectively,\textsuperscript{12}

\[
\begin{array}{cc}
\text{19} & \text{20} \\
\text{21} & \text{22}
\end{array}
\]

the thermolysis rate constant of 1 at 100 °C would be $1.02 \times 10^{-3}$ sec\textsuperscript{-1}. At the same temperature, ATB decomposes with a rate constant of $2.42 \times 10^{-9}$ sec\textsuperscript{-1}.\textsuperscript{42} These figures place the stabilizing ability of the dimethylamino group between that of CN and COC\textsubscript{6}H\textsubscript{5} (cf. Table 2.5.) indicating high stabilization\textsuperscript{43} in accord with the earlier studies.\textsuperscript{4-6,10,11}

In summary, 3\textit{c} is an unusual azoalkane in its sensitivity to acid and protic solvents. Thermolysis in nonpolar, aprotic solvents gives nearly normal products, allowing the assessment of the radical stabilizing ability of the Me\textsubscript{2}N group.
Table 2.5. Relative Thermolysis Rates of Substituted Azoalkanes (100 °C)

<table>
<thead>
<tr>
<th>X</th>
<th>relative rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>1.0</td>
</tr>
<tr>
<td>OCH₃</td>
<td>1.0 x 10¹</td>
</tr>
<tr>
<td>Cl</td>
<td>1.1 x 10¹</td>
</tr>
<tr>
<td>CN</td>
<td>2.9 x 10⁵</td>
</tr>
<tr>
<td>NMe₂</td>
<td>4.2 x 10⁵</td>
</tr>
<tr>
<td>COC₆H₅</td>
<td>3.9 x 10⁶</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>3.9 x 10⁶</td>
</tr>
<tr>
<td>CH=CH₂</td>
<td>9.0 x 10⁶</td>
</tr>
</tbody>
</table>

Note: The table is adapted from that in ref. 43.

2.4. Experimental

**General.** NMR spectra were recorded on an IBM AF-300 spectrometer. Analytical GC was carried out on a Hewlett Packard 5890 instrument equipped with a data system. UV spectra were obtained on a Cary 17 spectrometer. GC-MS was carried out on a Finnigan 3300 GC-MS.

**Materials.** All the solvents were used without further purification unless otherwise specified. NMR solvents were obtained from Cambridge Isotope Laboratories (C₆D₆, C₇D₈: 99.6% D, CD₃OD: 99.8% D) or Aldrich (CD₃CN: 99% D, CH₃OD: 99.5% D). Hexane and methanol used for kinetic studies were Burdick & Jackson high purity solvent. The same brand of DMF
was dried with MgSO$_4$ and vacuum distilled. Authentic samples of 8 were made for NMR and GC comparison by reduction of ATB with benzpinacol in C$_6$D$_6$, CD$_3$CN, and CD$_3$OD.$^{29}$ Dimethylisopropylamine was synthesized by methylation of isopropylamine with formaldehyde and formic acid.

**2-phenylazo-2-dimethylaminopropane (3a).** Moon's attempt to chlorinate acetone phenylhydrazone with chlorine afforded a mixture of aromatic ring chlorinated 4a.$^{44}$ In our hands, tert-butyl hypochlorite chlorinated acetone phenylhydrazone cleanly. To a solution of acetone phenylhydrazone in 30 ml dichloromethane cooled with a dry ice acetone bath was added dropwise 4.9 g tert-butyl hypochlorite (18% excess) in 5 ml dichloromethane. The addition took 15 min. The mixture was then stirred at -78 °C for 5 h. After warming to room temperature, the yellow orange reaction mixture was washed with NaHSO$_3$ solution three times, then with water once. The organic layer was rotary evaporated, leaving 10 g of a wet, dark orange residue. The NMR spectrum of the K$_2$CO$_3$ dried residue in CDCl$_3$ was remarkably clean: 7.75 (ar, 2H), 7.48 (ar, 3H), 1.92 (s, 6H). Half of the above material was used for aminolysis without further purification. The aminolysis was done by stirring 4c with excess 40% aqueous dimethylamine solution at room temperature. After 14 h, the reaction mixture was extracted three times with ether. The extracts were then dried with K$_2$CO$_3$ and Na$_2$SO$_4$. After evaporation of the solvent, the product was distilled, giving 1g orange liquid, b.p. 74-78 °C/0.5-0.7 mm. $^1$H NMR (C$_6$D$_6$) δ 7.76 (ar, 2H), 7.14 (ar, 3H), 2.52 (s, 6H), 1.40 (s, 6H), minor peaks: 1.80 (s), 1.32(s), 1.14(s) which coincided with those of acetone phenylhydrazone and its hydroperoxide. $^{13}$C NMR δ 152.47, 130.38, 129.12,
122.65, 85.28, 39.08, 23.41 with a few minor peaks. UV (hexane) $\lambda_{\text{max}}$ 259 nm ($\varepsilon = 1.1 \times 10^4$), $\lambda_{\text{max}}$ 426 nm ($\varepsilon = 137$).

2-<i>tert</i>-butylazo-2-dimethylaminopropane (3c). The chloroazoalkane, 2-<i>tert</i>-butylazo-2-chloropropane was made from 5 g of acetone <i>tert</i>-butylhydrazone $^7$ by similar procedure to that used for 4a. If the reaction mixture was warmed to room temperature and stirred with aqueous NaHSO$_3$ for 1 h, gases were evolved and no 4c was obtained thereafter. To avoid the NaHSO$_3$ treatment, volatiles were removed from the yellow mixture by rotary evaporation in the dark. The NMR spectrum of the residue was relatively clean, showing the following peaks: $\delta$ 1.62 (s, 6H), 1.14 (s, 9H). Without further purification, excess 40% aqueous dimethylamine was added dropwise to the yellow residual liquid at 0 °C. After stirring at 0 °C for 5 min, the mixture was stirred with ether at room temperature for 2 h. The ether layer was separated and dried with K$_2$CO$_3$ and Na$_2$SO$_4$. After rotary evaporation of the solvent, the yellow residue (6 g) was relatively clean 3c as shown by NMR. Vacuum distillation gave the pure azoalkane, b. p. 66.5-67.5 °C/−25 mm.

NMR data in four solvents are listed in Table 2.5. MS (45 ev) 85(60), 70(100), 59(12), 57(17), 56(42), 55(25), 44(13), 43(13), 42(23), 41(37), 39(18), 28(25), 15(30).

<table>
<thead>
<tr>
<th>Table 2.5. NMR Data of 3c in Various Solvents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>C$_6$D$_6$</td>
</tr>
<tr>
<td>C$_7$D$_8$</td>
</tr>
<tr>
<td>CD$_3$CN</td>
</tr>
<tr>
<td>CD$_3$OD</td>
</tr>
</tbody>
</table>
**Acetone Dimethylenamine (5)** was prepared according to the literature procedure,\(^4^6\) NMR (C\(_6\)D\(_6\)) \(\delta\) 3.88 (br s, 1H), 3.73 (s, 1H), 2.38 (s, 6H), 1.72 (d, 3H, J = 0.6 Hz). Crude 5 polymerized on attempted distillation and even on storage in the freezer. Thus our stock 5 turned into a mixture in 4 days in the freezer under nitrogen. Attempts to purify 5 by GC gave 6 instead, NMR (C\(_6\)D\(_6\)) \(\delta\) 5.78 (m, 1H), 4.06 (s, 1H), 4.01 (d, 1H, J = 0.8 Hz), 2.45 (s, 6H), 1.79 (d, 3H, J = 1.1 Hz), 1.61 (d, 3H, J = 1.3 Hz); MS (70 ev) 125(17), 110(100), 95(30), 94(22), 42(27), 39(20), 15(43).

**N,N,1,1,2,2-hexamethylpropylamine (9)** was synthesized as described in the literature.\(^4^7\) The crude product was purified by GC. \(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 2.30 (s, 6H), 0.96 (s, 9H), 0.93 (s, 6H); \(^1^3\)C NMR (C\(_6\)D\(_6\)) \(\delta\) 59.96, 42.29, 40.49, 27.07, 21.09.

**Thermolysis Kinetics.** Thermolysis kinetics were done in a sealed 1 cm Pyrex UV cell in a constant temperature oil bath shielded from fluorescent lights. Solutions were degassed by at least three freeze and thaw cycles. The bath temperature was recorded by a platinum thermometer and a HP model 3456 6 1/2 digit voltmeter. The reaction was followed by the decay of the UV absorption maximum around 380 nm. In the kinetic data listed below, time is given in seconds. "A_{obs}" represents the observed absorbance while "A_{\infty}" means absorbance at infinite time ("t_{\infty}" min) except as noted. Rate constants were the slopes of the plot of ln (A_{obs}-A_{\infty}) versus time. "r" is the correlation coefficient of the plot. The zero points were discarded in the plot unless otherwise noted.
### Thermolysis of 3c at 111.60 °C in Hexane

<table>
<thead>
<tr>
<th>time</th>
<th>$A_{obs} - A_\infty$</th>
<th>$\ln (A_{obs} - A_\infty)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.856</td>
<td>-0.155</td>
</tr>
<tr>
<td>600</td>
<td>0.699</td>
<td>-0.358</td>
</tr>
<tr>
<td>1200</td>
<td>0.623</td>
<td>-0.473</td>
</tr>
<tr>
<td>2100</td>
<td>0.528</td>
<td>-0.639</td>
</tr>
<tr>
<td>3000</td>
<td>0.444</td>
<td>-0.812</td>
</tr>
<tr>
<td>3900</td>
<td>0.367</td>
<td>-1.002</td>
</tr>
<tr>
<td>4800</td>
<td>0.299</td>
<td>-1.207</td>
</tr>
<tr>
<td>6000</td>
<td>0.231</td>
<td>-1.465</td>
</tr>
<tr>
<td>7200</td>
<td>0.171</td>
<td>-1.766</td>
</tr>
<tr>
<td>9000</td>
<td>0.116</td>
<td>-2.154</td>
</tr>
<tr>
<td>13200</td>
<td>0.042</td>
<td>-3.170</td>
</tr>
</tbody>
</table>

$A_\infty = 0.003$, $t_\infty = 1132$ min, $r = 0.999$, zero point included.

### Thermolysis of 3c at 117.43 °C in Hexane

<table>
<thead>
<tr>
<th>time</th>
<th>$A_{obs} - A_\infty$</th>
<th>$\ln (A_{obs} - A_\infty)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.783</td>
<td>-0.245</td>
</tr>
<tr>
<td>480</td>
<td>0.503</td>
<td>-0.687</td>
</tr>
<tr>
<td>960</td>
<td>0.400</td>
<td>-0.916</td>
</tr>
<tr>
<td>1440</td>
<td>0.334</td>
<td>-1.097</td>
</tr>
<tr>
<td>2040</td>
<td>0.271</td>
<td>-1.306</td>
</tr>
<tr>
<td>2640</td>
<td>0.216</td>
<td>-1.532</td>
</tr>
<tr>
<td>3600</td>
<td>0.147</td>
<td>-1.917</td>
</tr>
<tr>
<td>4200</td>
<td>0.119</td>
<td>-2.129</td>
</tr>
<tr>
<td>5100</td>
<td>0.085</td>
<td>-2.465</td>
</tr>
<tr>
<td>6000</td>
<td>0.058</td>
<td>-2.847</td>
</tr>
<tr>
<td>7200</td>
<td>0.039</td>
<td>-3.244</td>
</tr>
</tbody>
</table>

$A_\infty = 0.017$, $t_\infty = 1353$ min, $r = 0.9997$. 
### Thermolysis of 3c at 121.65 °C in Hexane

<table>
<thead>
<tr>
<th>time</th>
<th>(A_{\text{obs}}-A_{\infty})</th>
<th>(\ln (A_{\text{obs}}-A_{\infty}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.927</td>
<td>-0.076</td>
</tr>
<tr>
<td>600</td>
<td>0.566</td>
<td>-0.569</td>
</tr>
<tr>
<td>1200</td>
<td>0.412</td>
<td>-0.887</td>
</tr>
<tr>
<td>1800</td>
<td>0.301</td>
<td>-1.201</td>
</tr>
<tr>
<td>2400</td>
<td>0.212</td>
<td>-1.551</td>
</tr>
<tr>
<td>3000</td>
<td>0.150</td>
<td>-1.897</td>
</tr>
<tr>
<td>3600</td>
<td>0.106</td>
<td>-2.244</td>
</tr>
<tr>
<td>4200</td>
<td>0.073</td>
<td>-2.617</td>
</tr>
<tr>
<td>4800</td>
<td>0.050</td>
<td>-2.996</td>
</tr>
<tr>
<td>6060</td>
<td>0.025</td>
<td>-3.689</td>
</tr>
</tbody>
</table>

\(A_{\infty} = 0.010, t_{\infty} = 650\text{ min}, r = 0.9997.\)

### Thermolysis of 3c at 127.08 °C in Hexane

<table>
<thead>
<tr>
<th>time</th>
<th>(A_{\text{obs}}-A_{\infty})</th>
<th>(\ln (A_{\text{obs}}-A_{\infty}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.952</td>
<td>-0.049</td>
</tr>
<tr>
<td>300</td>
<td>0.598</td>
<td>-0.514</td>
</tr>
<tr>
<td>600</td>
<td>0.458</td>
<td>-0.781</td>
</tr>
<tr>
<td>900</td>
<td>0.352</td>
<td>-1.044</td>
</tr>
<tr>
<td>1200</td>
<td>0.273</td>
<td>-1.298</td>
</tr>
<tr>
<td>1620</td>
<td>0.185</td>
<td>-1.687</td>
</tr>
<tr>
<td>2100</td>
<td>0.119</td>
<td>-2.129</td>
</tr>
<tr>
<td>2520</td>
<td>0.082</td>
<td>-2.501</td>
</tr>
<tr>
<td>3000</td>
<td>0.055</td>
<td>-2.900</td>
</tr>
</tbody>
</table>

\(A_{\infty} = 0.002, t_{\infty} = 210\text{ min}, r = 0.9999.\)

### Thermolysis of 3c at 130.35 °C in Hexane

<table>
<thead>
<tr>
<th>time</th>
<th>(A_{\text{obs}}-A_{\infty})</th>
<th>(\ln (A_{\text{obs}}-A_{\infty}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.865</td>
<td>-0.145</td>
</tr>
</tbody>
</table>
\[ A_{\infty} = 0.003, \ t_{\infty} = 285 \text{ min}, \ r = 0.9999. \]

<table>
<thead>
<tr>
<th>time</th>
<th>( A_{\text{obs}} - A_{\infty} )</th>
<th>( \ln (A_{\text{obs}} - A_{\infty}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.728</td>
<td>-0.317</td>
</tr>
<tr>
<td>420</td>
<td>0.356</td>
<td>-1.033</td>
</tr>
<tr>
<td>840</td>
<td>0.188</td>
<td>-1.671</td>
</tr>
<tr>
<td>1260</td>
<td>0.100</td>
<td>-2.303</td>
</tr>
<tr>
<td>1680</td>
<td>0.055</td>
<td>-2.900</td>
</tr>
<tr>
<td>2100</td>
<td>0.028</td>
<td>-3.576</td>
</tr>
</tbody>
</table>

\( A_{\infty} = 0.048, \) adjusted for highest correlation coefficient, \( r = 0.9997, \) zero point included.

<table>
<thead>
<tr>
<th>time</th>
<th>( A_{\text{obs}} - A_{\infty} )</th>
<th>( \ln (A_{\text{obs}} - A_{\infty}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.091</td>
<td>0.087</td>
</tr>
<tr>
<td>600</td>
<td>1.014</td>
<td>0.014</td>
</tr>
<tr>
<td>1800</td>
<td>0.859</td>
<td>-0.152</td>
</tr>
<tr>
<td>2700</td>
<td>0.773</td>
<td>-0.257</td>
</tr>
<tr>
<td>6900</td>
<td>0.458</td>
<td>-0.781</td>
</tr>
<tr>
<td>7800</td>
<td>0.407</td>
<td>-0.899</td>
</tr>
<tr>
<td>9000</td>
<td>0.345</td>
<td>-1.064</td>
</tr>
<tr>
<td>10800</td>
<td>0.286</td>
<td>-1.252</td>
</tr>
</tbody>
</table>
\[
\begin{array}{ccc}
12600 & 0.225 & -1.492 \\
16200 & 0.143 & -1.945 \\
\end{array}
\]

\[A_\infty = 0.020, \text{ adjusted for highest correlation coefficient, } r = 0.9999, \text{ zero point included.}\]

**Thermolysis of 3c at 121.53 °C in DMF**

<table>
<thead>
<tr>
<th>time</th>
<th>(A_{\text{obs}}-A_\infty)</th>
<th>(\ln (A_{\text{obs}}-A_\infty))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.189</td>
<td>0.173</td>
</tr>
<tr>
<td>600</td>
<td>1.006</td>
<td>0.006</td>
</tr>
<tr>
<td>1500</td>
<td>0.770</td>
<td>-0.261</td>
</tr>
<tr>
<td>2100</td>
<td>0.653</td>
<td>-0.426</td>
</tr>
<tr>
<td>2700</td>
<td>0.555</td>
<td>-0.589</td>
</tr>
<tr>
<td>3600</td>
<td>0.445</td>
<td>-0.810</td>
</tr>
<tr>
<td>4200</td>
<td>0.369</td>
<td>-0.997</td>
</tr>
<tr>
<td>4800</td>
<td>0.312</td>
<td>-1.165</td>
</tr>
<tr>
<td>6000</td>
<td>0.220</td>
<td>-1.514</td>
</tr>
<tr>
<td>7800</td>
<td>0.129</td>
<td>-2.048</td>
</tr>
</tbody>
</table>

\[A_\infty = 0.007, t_\infty = 830 \text{ min, } r = 0.9998, \text{ zero point included.}\]

**Thermolysis Product Study.** All solutions for thermolysis were degassed by at least three freeze and thaw cycles. Product analysis was done in sealed NMR tubes heated at an appropriate temperature (110-130 °C) in the same bath as used for kinetics. A dry solution of 3c in CD\(_3\)CN was obtained by stirring the wet solution with CaH\(_2\) followed by trap to trap distillation on the vacuum line into an NMR tube. In the trapping experiment, tetrabutylammonium cyanide was first placed in the NMR tube and pumped to dryness. Dried 3c solution (see above) in CD\(_3\)CN was then distilled into the NMR tube and the reaction was followed by NMR. In the reaction of 3c with
acetic acid, the HOAc-C₆D₆ solution and the solution of 3c-C₆D₆ were
degassed separately. This solution was first allowed to react at room
temperature for 30 h in the dark and was then heated at 100 °C for 20 min to
complete the reaction. The acetic acid solution was then distilled into the frozen
3c solution at -196 °C. For GC-MS analysis, the tube was usually opened after
thermolysis and the reaction mixture was analyzed immediately to avoid air
oxidation of the products and escape of volatile components. Products were
identified by ¹H and ¹³C NMR, or by GC-MS comparison with authentic
material. The product ratio was estimated from NMR peak area or peak height.
Nitrogen volumes were obtained on a Töpler pump and the gas purity was
checked by GC on a 5 Å molecular sieves column. An NMR tube sealed to a
7/25 standard taper joint was used for the nitrogen yields.

**Photolysis of 3c.** All photolyses were done in degassed solution in
sealed NMR tubes using an Oriel 500 W high pressure mercury lamp with a 366
nm light filter without visible light filter. Products were identified and quantified
by the same methods used in thermolysis.

**Quantum Yield.** A Hanovia 450 W medium pressure mercury lamp
with 366 nm light filter was used this purpose. The quantum yield was obtained
from the nitrogen volume ratio of 3c relative to ATB standard with NMR tubes
on a merry-go-around apparatus at an average temperature of 20 °C. 0.3 M
3c-C₆D₆ and 0.82 M ATB-C₆D₆ solution were used. The tubes were
frequently removed for NMR analysis. Caution was exercised to make sure that
all light was absorbed by the samples during the photolysis. Thus after the
photolysis, about 25% of ATB and 63% of 3c were decomposed.

2.5. References


(13) Timberlake, J. W., private communication.

(14) Engel, P. S.; Chen, Y.-Q. manuscript in preparation.


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    4912.


Part III

A Reinvestigation of the Photochemistry of
Trifluoromethylazocyclopropane
3.1. Introduction

There had been two reports\textsuperscript{1,2} on the photochemistry of azocyclopropanes before we became interested in their chemistry. While a careful investigation\textsuperscript{3} revealed the first one to contain serious errors, our photochemical study of azocyclopropane\textsuperscript{4} raised doubts about the second one. In that work,\textsuperscript{2} Chakravorty, Pearson, and Szwarc (CPS) claimed that vapor phase trifluoromethylazocyclopropane (1) gave the molar ratios of products shown in Scheme 3.1.

**Scheme 3.1**

\[
\text{N=N}_\text{CF}_3 \xrightarrow{h\nu, 65^\circ C} \begin{array}{c} \text{CF}_3\text{H} + \text{F}_3\text{C} - \text{C} = \text{C} \quad \text{0.25} \\ \text{vapor} + \text{N}_2\text{H} + \text{NHC} = \text{CF}_3 \quad \text{0.25} \\ \text{N}_2 \quad \text{0.15} \quad \text{0} \quad \text{trace} \end{array}
\]

In solution, photolysis of 1 supposedly afforded the products shown in Scheme 3.2.

Although 2-pyrazoline was not among the solution phase products, CPS noted that the sum of the products involving CF\textsubscript{3} moieties exceeded the total amount of N\textsubscript{2} formed in the reaction. The diazenyl radical rearrangement presented in this paper\textsuperscript{2} to explain the formation of 2-pyrazoline has long been
Scheme 3.2

\[
\begin{array}{c}
\text{N} \equiv \text{N} \quad \text{CF}_3 \quad \text{hv, 32}^\circ\text{C} \\
\text{1} \\
\text{CF}_3\text{H} \quad \text{0.15} \\
\text{CF}_3 \\
\text{0.1} \\
\text{very small}
\end{array}
\]

cited as an example of stepwise decomposition of an azoalkane\(^5\). Our work reported here proves the results of CPS to be incorrect.

3.2. Results and Discussion

Trifluoromethylazocyclopropane was prepared by the same procedure used by CPS, reaction of cyclopropylamine with nitrosotrifluoromethane\(^2\), affording material with similar spectral properties. Products were identified by comparing their NMR spectra and/or GC retention times with those of authentic samples. Trifluoromethylcyclopropane\(^6\) and trifluoromethane\(^7\) were identified by their \(^{19}\text{F}\) NMR chemical shift and coupling constant. 1-Trifluoromethyl-2-pyrazoline (2) was isolated by preparative GC from the photolysis mixture and was characterized by NMR and GC-MS.

We found that 1 is rather photo-stable. Thus photolysis of a 0.1 M solution ( \(\sim 0.8 \text{ ml}\) ) at 366 nm generally required 100 h. Photolyses were done at 366 nm in benzene, toluene, 2,3-dimethylbutane, decane, and cyclohexane as well as at 254 nm in benzene. In every case, we found a large amount of ethylene and 2, products that were not noted by CPS, while we found and only
small amounts of trifluoromethane, CPS's major product. No 2-pyrazoline was
detected by NMR. We also observed cis-trans isomerization, another process
expected but not mentioned in CPS's report. The nitrogen yield, 27.7%, was
obtained from 366 nm photolysis of 1 in decane and the reaction was followed
by UV. This number should be regarded as a lower limit since GC-MS showed
the presence of a small amount of residual 1. According to UV however, at
least 78% of 1 was converted. The product ratios (cf Table 3.1) were
estimated by \(^1\)H and \(^{19}\)F NMR peak area or, when necessary, by peak height.

<table>
<thead>
<tr>
<th>Table 3.1. Photolysis Products of 1 (Relative Moles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>wavelength (nm)</td>
</tr>
<tr>
<td>solvent</td>
</tr>
<tr>
<td>ethene</td>
</tr>
<tr>
<td>residual 1</td>
</tr>
<tr>
<td>cyclopropane</td>
</tr>
<tr>
<td>(CF_3H)</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>c-(C_3H_5CF_3)</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>(C_6D_5CF_3)</td>
</tr>
</tbody>
</table>

Note: a. Estimated from peak area of low temperature (-80 °C) \(^1\)H and \(^{19}\)F
NMR. Because the cyclopropane peak superimposed on that of the reference,
hexamethyldisiloxane, at low temperature, the same sample was run at room
temperature where these peaks separated. The cyclopropane yield was
calculated from its peak height ratio over that of ethene in room temperature
NMR. b. \(^1\)H NMR was messy probably due to extensive polymerization. Ratios
were estimated from the peak area of room temperature \(^1\)H and \(^{19}\)F NMR. c. Ratios
were estimated from the peak area of room temperature \(^1\)H and \(^{19}\)F
NMR. d. The ratio of 3 over 2 calculated from \(^1\)H NMR was equal to that from
\(^{19}\)F NMR.
In the photolysis of 1 at 254 nm in benzene-$d_6$, azine 3 appeared at late irradiation times. Although the proposed structure of 3 is consistent with the observed $^1$H and $^{19}$F NMR, we were unable to find a suitable way to prepare an authentic sample.

![Chemical Structure](image)

Unlike azocyclopropane, 1 did not rearrange to 2 at high temperature (200 °C). Thus heating a 0.1 M solution of 1 in benzene at 200 °C for 453 min resulted in polymerization and unreacted starting material.

As one would expect from the behavior of azocyclopropane, irradiation of 1 at 254 nm in benzene gave a higher concentration of 1c due to singlet energy transfer from the solvent. Indeed 1c reached a maximum concentration equal to half that of 1, according to NMR of a 0.3 M solution of 1 in C$_6$D$_6$ at 254 nm after 270 min photolysis.

Since the photolysis product distribution from 1 resembles that of azocyclopropane, it is likely that both compounds follow a similar mechanistic pathway (see Scheme 3.3). Like azocyclopropane, the primary photolysis processes include cis trans isomerization, cyclopropyl ring C-C cleavage, C-N cleavage, and fragmentation to ethylene and a carbene. The transformation of 4 to 3 is preceded.\textsuperscript{8}
Scheme 3.3.

Based on our results and other reasons\textsuperscript{4} we consider CPS's report to be completely in error.
3.3. Experimental

**General.** All the room temperature $^1$H and $^{13}$C NMR spectra were recorded on an IBM AF300 spectrometer. $^{19}$F and low temperature NMR spectra were obtained on a JOEL FX-90 Q spectrometer. GC-MS was carried out on a Finnigan 3300 GC-MS while GC analyses were done on a Hewlett Packard 5980 instrument equipped with a data system or on an Antek 300TC Chromatograph.

**Material.** CF$_3$NO was purchased from SCM Specialty Chemicals (PCR) while cyclopropylamine was from Chemical Dynamics Corporation. The deuterated solvents were from Cambridge Isotope Laboratories ($C_6D_6$, $C_7D_8$: 99.6% D, $C_6D_{12}$: 99.5% D). All the solvents were used as received except for decane which was distilled from the laboratory stock.

**Trifluoromethylazocyclopropane** (1) was prepared in a specially constructed glass apparatus according to CPS's method. The reaction vessel was built to allow ready estimation of CF$_3$NO gas volume. The reaction was exothermic. Impurity cyclopropylamine was removed from the yellow product by shaking with solid oxalic acid. The sample was stored in the freezer over molecular sieves. $^1$H NMR ($C_6D_6$) $\delta$ 3.20 (m, 1H), 1.10 (m, 2H), 0.60 (m, 2H); $^{13}$C NMR ($C_6D_6$) $\delta$ 121.06 (q, J = 272.2 Hz), 51.94, 12.30; $^{19}$F NMR ($C_6D_6$, $\delta_{PhCF_3}$ = -63.90) $\delta$ -74.15; UV (hexane) $\lambda_{max}$ 346 nm ($\varepsilon$ = 26); MS (45 ev) 138(4), 137(7), 110(25), 91(17), 69(100), 41(57), 39(45), 28(18).
Photolysis of 1 at 366 nm was carried out using a Hanovia 450 W medium pressure mercury lamp with 366 nm light filter. The whole system was immersed in a tap water bath to keep the temperature below 35 °C. Solutions for photolysis were degassed by at least three freeze and thaw cycles using liquid nitrogen as coolant, and were then sealed into tubes. The photolyses were followed by UV or NMR. After photolysis, the tubes were opened and analyzed immediately by GC and GC-MS. NMR data for the photolysis products are listed in Table 3.2. The structure of 1c was supported by the similarity of its \(^1\)H and \(^{13}\)C NMR to that of 1. The NMR data for 1c were clearest at early photolysis times when the only other products were ethylene, trifluoromethylcyclopropane, and 2. 1-Trifluoromethyl-2-pyrazoline (2) was isolated from a 366 nm photolysate in C\(_7\)D\(_8\) by preparative GC on an 1/8 inch, 10 feet, 10% FFAP column (flow: 22.5 ml/min, column: 75 °C, injector: 160 °C, detector: 170 °C). Attempts on 1/4 inch columns were unsuccessful.) from 366 nm photolysate in C\(_7\)D\(_8\). MS (70 ev) 138(93), 137(67), 117(68), 97(21), 78(27), 69(100), 41(95), 40(26), 39(63), 27(30).

| Table 2.3. NMR Data for Photolysis Products of 1 in C\(_6\)D\(_6\) |
|------------------|---------------|---------------|---------------|
|                  | \(^1\)H a     | \(^{13}\)C b  | \(^{19}\)F c  |
| \(1\)c           | 3.20 (m, 1H)\(^d\), 1.28 (m, 2H), 0.65 (m, 2H) | 121.04 (q, J = 305.2 Hz), 51.19, 14.13 | -69.43 (d, J = 4.9 Hz)\(^e\) |
|                  | 6.18 (br s, 1H), 2.68 (t, 2H, J = 9.5 Hz), 1.58 (dt, 2H, J = 9.5, 1.5 Hz) | | -68.79 |
| \(2\)            | 6.02 (t, 1H, J = 5.0 Hz), 1.75 (dq, 2H, J = 5.0, 7.5 Hz) 0.72 (t, 3H, J = 7.5 Hz) | | -67.66\(^f\) |
| \(3\)            | 6.02 (t, 1H, J = 5.0 Hz), 1.75 (dq, 2H, J = 5.0, 7.5 Hz) 0.72 (t, 3H, J = 7.5 Hz) | | |
Note: a. $^1$H chemical shifts are reported in ppm on the $\delta$ scale using solvent signal ($\delta$ 7.15) as reference. b. C$_6$D$_6$ ($\delta$ 128) was used as internal reference. c. PhCF$_3$ ($\delta$ -63.90) was used as external reference. d. Decoupling experiments suggested that the signal of 1c was buried in that of 1. e. in C$_7$D$_8$. f. distorted quartet.

Photolysis at 254 nm. Three 15 W GE low pressure mercury lamps in a cylindrical reactor were used for this purpose. Quartz NMR tubes were placed inside a vycor sleeve to prevent penetration of 185 nm light. The photolysis was stopped frequently for NMR analysis. During the photolysis of 1 in C$_6$D$_6$, an unknown, light brown, crystalline solid formed on the wall of the upper part of the NMR tube. It was dissolved in the solvent by shaking before final analysis. Propanal difluoroformyl azine (3) was observed only in 254 nm photolysis of 1 in C$_6$D$_6$ at later times ( see Table 3.2 for NMR data ).

3.4. References
