THE CHEMISTRY OF 1,2,3-Δ²-TRIAZOLINES

by

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Abstract

The 1,3-dipolar cycloaddition of azides to olefins proceeds most readily for strained double bonds, for double bonds that are polarized by substituents, and for azides which have electron-withdrawing substituents.

Phenyl azide has been observed to form two isomeric 1,2,3-Δ²-triazolines upon the reaction of the strained double bond of a series of nonconjugated bicyclic dienes. The major isomer formed in each case is that resulting from stabilization of the dipolar transition state by the neighbouring unreactive double bond.

A modified mechanism for the 1,3-dipolar cycloaddition of azides to alkenes has been suggested.

The thermal decomposition of the phenyl azide adduct of bicyclo (2.2.1) hept-2-ene resulted in the elimination of nitrogen and the formation of isomeric products. The major products were exo-aziridine and imine, which are considered to be formed by loss of N₂ from the triazole and ring closure or hydrogen shift to form...
products respectively. In addition the presence of endo-
aziridine suggested that C-G bond cleavage of the triazoline
ring had taken place.

The thermal decomposition of the 1,5-diaryl
triazolines has been observed to give aziridine and
imine products with the p-substituted styrenes giving a
greater amount of imine. In the p-methyl substituted
styrenes the major aziridine component produced was observed
to have the same relative geometry about the ring carbons
as the triazoline. This implied some form of steric
control of the transition state.

A mechanism has been proposed which can account
for the observed products on the basis of orbital
symmetry considerations.

The photodecomposition of the 1,5-diaryl
triazolines gives mainly aziridines. A concerted mechanism
for the photodecomposition is suggested which is similar
to that suggested for the thermal decomposition.

A kinetic investigation of the thermal
decomposition of some 1,2,3-\Delta^2-triazolines indicated that
the thermal decomposition may proceed by a mechanism
which does not necessarily involve ionic intermediates, contrary to the currently held theory.

A number of $1,2,3-\Delta^2$-triazolines were synthesized by the cycloaddition of phenyl azide and substituted styrenes. A detailed structure analysis has been carried out by N.M.R. to determine the conformations of the triazoline ring in some of these adducts. They were found to have essentially the same conformation.

Generalized mass spectral cracking patterns are suggested for the triazolines of norbornylene and for the phenyl azide adducts of para-substituted styrenes. Some correlation of the pattern with substituent is observed.

Some experiments have been proposed which should allow the concertedness or non-concertedness of the decomposition mechanism to be more definitely assayed.
TO MY WIFE

FOR HER UNDERSTANDING

AND

TO DR. D. E. MCGREER

FOR STARTING ME OFF

CORRECTLY IN CHEMISTRY
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I wish to express my thanks to my Research Director, Dr. Allan C. Oehlschlager, for his guidance and advice during the course of this work.

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Introduction

The chemistry of 1,2,3-$\Delta^2$-triazolines has been studied from several different points of view over the past few decades. The major aspects receiving attention have been synthesis, thermal decomposition, and photodecomposition.

Part 1: Synthesis

The synthesis of 1,2,3-$\Delta^2$-triazolines may be carried out by three major routes.

The first involves the isomerization of 1-arylazoaziridines by sodium iodide in acetone solution $^1$-$^3$. (Figure 1). A mechanism involving initial cleavage of the aziridine ring, 1, to give the intermediate, 2, followed by a backside displacement of iodide ion by the nitrogen adjacent to the aryl group to give the triazoline, 2, has been proposed by Heine $^2$.

The second synthetic route to triazolines is the 1,3-dipolar cycloaddition of diazoalkanes, 4, to Schiff bases (imines), 5 $^4$-$^7$. (Figure 2). Kinetic investigation of this reaction $^5$-$^6$ revealed the lack of any general
Figure 1: The Formation of 1-Aryl-
1,2,3-$\Delta^2$-triazolines from 1-Arylazoaziridines.
Figure 2: The 1,3-Dipolar cycloaddition of diazoalkanes with Schiff bases.
dependence of the rate of addition on the dielectric constant of the solvent and a definite dependence of the rate on substituents attached to the participating atoms. These effects suggest that the 1,3-dipolar cycloaddition proceeds via an activated complex with partial dipolar character rather than a discrete zwitterion intermediate.

A third route to 1,2,3-Δ²-triazolines of particular interest in this study was the 1,3-dipolar cycloaddition of azides to alkenes. This reaction was first reported by Wolff in 1912.

The addition of azides to alkenes is a stereospecific cis cycloaddition. For example, Scheiner added phenyl azide, 6, to cis (Z) and trans (E)-γ-methylstyrenes. The products formed were 2 and 10 respectively. (Figure 3). The relative geometry of the substituents in the alkenes was maintained in the triazolines.

The more recent work of Aratani and coworkers using 85% optically pure (-)(R)-trans-cyclooctene, 11, and 6 to give an optically active triazole, 12, is further proof of the cis nature of the cycloaddition of azides to alkenes. (Figure 4).
Figure 3: Stereospecific cis addition of Phenyl Azide to cis and trans-β-Methylstyrenes.
Figure 4: The 1,3-Dipolar cycloaddition of phenyl azide to cyclooctene.
Large negative entropies of activation, $\Delta S^\pm$, have been measured for the addition of azides to bicyclo (2.2.1) hept-2-ene, 13, to give exo-triazolines, 14. This indicates that the cycloaddition reaction proceeds via an highly ordered transition state.

Scheiner 16 and Zalkow 17 have measured $\Delta S^\circ$ values in the range -29 to -35 e.u. Bailey 18 has reported $\Delta S^\pm$ values in the range -26 to -36 e.u. for a comprehensive series of alkenes reacting with picryl azide. These results are completely analogous to those obtained in similar studies.
of the Diels-Alder reactions 19.

Strain \(^{10b}\) on the double bond of an alkene has been shown to enhance the rate of cycloaddition of azides. Scheiner's work \(^{15}\) with simple alkyl alkenes, Henery-Logan's \(^{20}\) work with monocyclic alkenes, and Bailey's \(^{18}\) work with cyclic and bicyclic alkenes has shown that highly strained bicyclic alkenes are more reactive than monocyclic alkenes which are in turn more reactive than acyclic alkenes. The rate of phenyl azide addition to alkenes indeed parallels their heat of hydrogenation. This latter thermodynamic parameter is a measure of the degree of strain associated with the \(\pi\)-bonds \(^{10c}\).

The orientation of azide addition to alkenes depends on both steric and electronic factors \(^{21-43}\).

Steric effects have some importance in determining the orientation of azide addition to alkenes in triazoline formation. They may block the approach of an azide to an alkene bond \(^{21,22}\). Typical examples of this are found in the bicyclic alkenes. Studies \(^{22-27}\) have been carried out in which azides were added to \(^{13}\). Invariably the adducts formed are exo triazolines, e.g. \(^{14}\). Where steric blocking
is reduced in bicyclic systems the formation of adducts
by attack of azide from both the exo and endo sides of the
double bond is possible. This point is exemplified by
McLean's work with norbornadiene, 15. For the monoadducts
of 6 and 15 McLean detected an exo:endo ratio of 11:1.
(Figure 5). The endo-adduct, 17, when treated with 6
yielded only endo-exo adducts 20 and 21. The steric effects
are straightforward, i.e. 15 is relatively unhindered for
exo or endo attack; whereas, the endo species, 17, is
severely hindered for attack from the endo side. This is
analogous to the situation in dicyclopentadiene where only
the exo adduct is formed 22.

In addition to studies concerned with the
orientation of azide addition with respect to which "face"
of the double bond is attacked, studies have been carried
out to determine which orientation, of two possible, occurs
on a single face of a reacting double bond. Except in
cases where overriding steric effects operate, azide
addition to alkenes has always been observed to take place
in a Markownikoff fashion. If the cycloaddition were
initiated by electrophilic attack of the terminal azide
Figure 5: Adducts of Phenyl Azide and Norbornadiene.
nitrogen on the alkene, one would expect the substituted nitrogen of the azide to become attached to the carbon of the reacting double bond, best able to support a positive charge. In fact, numerous observations indicate that azides add in this preferred direction to alkenes.

Substituents capable of stabilizing a positive charge on C_5 of the alkene direct the terminal nitrogen of the azide to C_4. The synthesis of triazoline adducts \(26a, 26b\) from enol ethers \(30(24a, 24b)\) and para-nitrophenyl azide, \(25\), is typical of this electronic directive effect. (Figure 6).

Substituents capable of destabilizing a positive charge direct the azide terminus to the C_4 carbon. The addition of \(6\) to acrylonitrile \(12, 27\), to give the triazoline, \(28\), is a typical case. (Figure 6).

The investigations cited above point to a transition state for the cycloaddition which possesses some dipolar character. Substituents on N_1 of the azide have a large effect on the rate of cycloaddition as Scheiner \(16\) has shown in the reactions of substituted aryl azides and \(13\). He observed a \(\rho\) value of +0.84 at 25°C.
ENOL ETHERS

\[ \begin{align*}
R_1 &= H; \quad R_2 = CH_3 \\
R_1 &= CH_3; \quad R_2 = H
\end{align*} \]

PARA-NITROPHENYL AZIDE

\[ \begin{align*}
26 a: \quad R_1 &= H; \quad R_2 = CH_3 \\
26 b: \quad R_1 &= CH_3; \quad R_2 = H
\end{align*} \]

PHENYL AZIDE

\[ \begin{align*}
27 & \quad 1\text{-PHENYL-4-CYANO-} \\
& \quad 1,2,3-\Delta^2\text{-TRIAZOLINE}
\end{align*} \]

Figure 6: The directive electronic effects of alkene substituents.
which indicates a rate enhancement for the addition of the more electronegative azide substituents. He explains this in terms of a stabilization of negative charge on the substituted nitrogen in the transition state.

One notices that the substitution of strong inductive electron-withdrawing substituents on alkenes, as for example fluorinated alkenes, decreases the rate of azide addition to the alkene. A comparison of the rates of addition of benzyl azide to bicyclo (2.2.1) hept-2-ene, hexafluoropropene, and octafluorobutene-2 shows a decrease in the rate with increasing fluorine substitution. This may be explained from two points of view: first, that the inductive effect of the fluorine reduces the nucleophilicity of the alkene bond so that it is relatively unreactive; or second, the transition state for cycloaddition is raised in energy because the fluorinated alkene lacks the ability to stabilize a positive charge.

The promoting effect of conjugation on the activity of alkenes toward azides (Table 1) has been clearly established. Thus, electron deficient alkenes
TABLE I. RATE CONSTANTS FOR 1,3-ADDITIONS OF ORGANIC AZIDES ONTO OLEFINIC DIPOLAROPHILES IN BENZENE AT 25°C (10b).

<table>
<thead>
<tr>
<th>R-N-N=N</th>
<th>k_2 \times 10^7 \text{ (liters/mole/sec)} for</th>
<th>maleic anhydride (31)</th>
<th>N-phenylmaleimide (32)</th>
<th>norbornene (13)</th>
<th>pyrrol-1,2-dinocyclopentadiene (33)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pNO_2-C_6H_4^-</td>
<td>(25)</td>
<td>1.3</td>
<td>11</td>
<td>1530</td>
<td>1480000</td>
</tr>
<tr>
<td>C_6H_5^-</td>
<td>(6)</td>
<td>7.2</td>
<td>28</td>
<td>254</td>
<td>9930</td>
</tr>
<tr>
<td>pCH_2O-C_6H_4^- (Hammett)</td>
<td>(29)</td>
<td>21</td>
<td>67</td>
<td>187</td>
<td>3400</td>
</tr>
<tr>
<td>C_6H_5-CH_2^-</td>
<td>(30)</td>
<td>53</td>
<td>95</td>
<td>22</td>
<td>25</td>
</tr>
</tbody>
</table>
react more easily with azides carrying electron-releasing substituents and electron-rich alkenes react more easily with azides carrying electron-withdrawing substituents. Huisgen has attributed these trends to the stabilization of partial negative or positive charge on N1 in the transition state.

Electron withdrawing groups tend to reduce the electron density of the azide making it more electrophilic. The shift in electron density from the azide to the aryl substituent (Figure 7) is indicated by the observation that para-chlorophenyl azide has a dipole moment of 0.33 Debye whereas phenyl azide has a dipole moment of 1.55 Debye. The evidence presented supports a concerted mechanism for 1,3-dipolar cycloaddition of azides to alkenes involving an electronically unsymmetrical transition state such as $35^{15,16,18}$. The electronic substituent effects support the dipolar nature of the transition state, $35$, however, the lack of any general solvent effect has been interpreted in terms of only partial dipolar character $15,16,18$. In $35$, bond formation occurs simultaneously at $C_4$ and $C_5$ but has proceeded further.
Figure 7: Ground and Excited State Resonance forms of Azides.
at C4 than at C5 which induces the partial dipolar character in the N1-C5 bond. (Figure 8).

The electronic effects of the alkene substituents on the orientation of azide addition, in all cases reported to date, have been quite pronounced. In order to gain an insight into the effect of more remote substituents we have determined the orientation of addition to bicyclic homoconjugated dienes, 36, 37, and 38 (Figure 9). All of these dienes have one alkene bond which is highly strained and therefore should react rapidly with azide10,21. In each case only exo approach to the π cloud of the reactive
5-METHYLENE-2-NORBORNE

ENDO-DICYCLOPENTADIENE

Figure 9: Bicyclic Dienes.
alkene bond is sterically feasible \textsuperscript{21}. Furthermore, there are no steric interactions which would favour either of the two possible orientations for addition of an azide to the \textit{exo} side of the reactive double bonds of these dienes. Any preference for one orientation of \textit{exo} addition of azide would therefore be a measure of the extent to which the distant unreactive double bond of each diene provided stabilization to the dipolar transition state.

**Part 2: Thermal Decomposition of 1,2,3-\(\Delta^2\)-triazolines**

The mechanism of the thermal decomposition of triazolines is not as clearly understood as are the cycloaddition reactions leading to their synthesis. The usual products of triazoline thermal decomposition are aziridines and imines. These products are sometimes isolated directly from reactions of azides and alkenes. This usually occurs when 1,2,3-\(\Delta^2\)-triazolines possess a strong electron-withdrawing group at \(N_1\). (Figure 10). In these cases the thermal decomposition of triazolines is rapid compared with 1,3-dipolar cycloaddition leading to
Figure 10: Two Path Scheme of Triazoline Thermal Decomposition.
their formation $^{18,44-50}$. The thermal decomposition of triazolines is considered to proceed via initial heterolytic cleavage of the $N_1-N_2$ bond to produce diazonium-betaine intermediates, such as $^{42}$ (Figure 10). Several decomposition paths from $^{42}$ are then possible depending on the substituents at $C_4$, $C_5$ and $N_1$. Two principle modes of decomposition of $^{42}$ appear to be cleavage of the $N_3-C_4$ bond (Path 1) and cleavage of the $C_4-C_5$ bond (Path 2). Decomposition by Path 1 has been reported in the thermal decomposition of triazolines produced from the reaction of organic azides with norbornene, $^{13,18,26,43-54}$, monocyclic alkenes $^{18,20,56-58}$, acyclic alkenes $^{2,4,5,11,43}$, $^{59}$, enol ethers $^{30}$, and enamines $^{29,31,32,60}$. Decomposition by Path 2 has been reported for the triazolines formed by reaction of azides with styrene $^7$, enamines $^{60}$, $\alpha,\beta$-unsaturated alkenes $^{61}$, and has been suggested for norbornene, $^{13}$, adducts $^{26,27,55,62}$.

A discussion of triazoline thermal decomposition falls logically into three categories based on the starting alkenes, namely the: 1) Norbornyl triazolines, such as $^{43}$; 2) Bicyclic triazolines, such as $^{44}$; and 3) Monocyclic
Figure 11: Examples of 1,2,3-Δ²-triazolines.
triazolines, such as 45 (Figure 11).

Many studies of the thermal decomposition of norbornyl triazolines have been carried out 24, 46, 48-9, 52, 57. Generally, it has been found that, when R in 43 is strongly electron-withdrawing, e.g. benzenesulphonyl 27, nitrile 48, and 2,4,6-trinitrophenyl 57, thermal decomposition leads mainly to aziridine products, 48 (Figure 12). Where R is aryl 49, 53 or carbomethoxy 24 the aziridine yield decreases and significant amounts of imine, 49, are formed along with some Wagner-Meerwein rearrangement products 51-53. When R is PO(OEt)2 or PO2 50, 51 imine 49 is formed almost exclusively.

Interpretation of the course of triazoline decomposition in terms of initial formation of the diazonium-betaine, 46, followed by a loss of nitrogen to give the betaine, 47, leads to a consideration of product formation in terms of the following:

1) Ring closure (N3-N6) to give aziridines such as 48 46;
2) 2,6-endo-hydride shift to form imines such as 49 51;
3) Hydrogen transfer from C2 to N3 to give enamines such as 50 24, 51-2;

Another interpretation would be the concerted loss of
Figure 12: Mechanism of Product Formation from Betaine 46.
nitrogen from 46 with product formation analogous to the processes 1-4.

We wish to present evidence that the thermal decomposition of triazolines such as 43 may proceed via both Path 1 and Path 2 as in Figure 10. The possibility of C₂-C₆ bond cleavage in triazolines like 43 was suggested by the observation that 55 (Figure 13) is produced by the decomposition of 54 in the presence of phenylisocyanate 62 and that benzenesulphonyl azide reacts with the anhydrides 56 and 57 (Figure 13), to give predominantly the endo aziridines 58 and 59 respectively 27 (Figure 13). We also wish to propose a mechanism which can account for the product distributions found in the norbornyl type triazoline systems.

Thermal decomposition of bicyclic triazolines such as 44 (Figure 11) leads to aziridine and imine products. Several studies 14,20,34,49,56-58 have indicated that the ratio of aziridine to imine product is dependent on the nature of the azide substituents as well as on the ring size of the alkene. Electron-withdrawing groups on N₁ of the triazoline favour the
Figure 13: Schemes suggesting C-C bond cleavage in Norbornyl Triazolines.
formation of imines \(^{56,57}\) whereas electron-releasing
groups favour the formation of aziridines \(^{14,20}\). (Table 2).
The effect of increasing the size of the alkene ring favours
the formation of aziridine \(^{20,34}\). (Figure 14).

The difference in product distribution found
for the adduct of phenyl azide and cis-cyclooctene (Table 2)
may be explainable since the methods of decomposition
were not the same.

The thermal decomposition of triazolines, formed
by reaction of cyclopentene and cyclohexene with a series
of para-substituted phenyl azides, was carried out in
this laboratory \(^{59}\) in order to gain some insight into
the effect of ring size and the effect of azide
substituents on the aziridine-imine ratio. A discussion
of the results will be given later.

Thermal decomposition of monocyclic triazolines
such as \(^{45}\) leads to aziridines such as \(^{60}\) \(^2,12,34,43,63,65\)
(Figure 15) and imines such as \(^{61}\) \(^5,34,43,60,63,64\). The
imines formed may, however, result from R group migration
as in \(^{62}\) rather than from hydride shift as in \(^{61}\) depending
on the substituents. In addition to these expected
<table>
<thead>
<tr>
<th>Alkene</th>
<th>$2,4,6$-trinitrophenyl 56</th>
<th>para-Br phenyl 55</th>
<th>phenyl 20</th>
<th>phenyl 14</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>IM 21% AZ 79% IM 75% IM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>IM 79% AZ 21% IM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>IM 54% AZ 46% IM 80% IM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis 8</td>
<td>IM 55% AZ 45% IM 87% IM 22% IM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans 8</td>
<td>-- 85% AZ 63% IM</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

AZ = AZIRIDINE  IM = IMINE
Figure 14: Thermal Decomposition of Bicyclic Triazolines.
Figure 15: Thermal Decomposition of Monocyclic Triazolines
products, the intermediates such as 63 (Figure 15) may undergo C₂→C₅ bond cleavage to give the corresponding imine products, 64, and diazoalkanes, 65. In the presence of base the triazoline may be in equilibrium with a diazoalkane-amine like 66 which may undergo thermal decomposition 12,65.

One would expect the product distribution and decomposition rates to be dependent on the substituents at N₁, C₄ and C₅. However, the thermal decomposition has not been studied in detail.

Huisgen and coworkers 65 have examined the rates of decomposition of triazolines such as 67 where R₄=CO₂CH₃ and R₅=H with para-substituted phenyl substituents on N₁. A Hammett plot of the first order rate constants given in Table 3 does not give a linear relationship. (Figure 16). The reported values of enthalpy and entropy of activation for the decomposition of 67 with X=H are 28.2 kcal/mole and 4.7 e.u. respectively. These values seem reasonable for a unimolecular loss of N₂. However, the non-linear
### Table 3. Rates of Thermal Decomposition for Triazolines, \(^{67}\ 65\).

<table>
<thead>
<tr>
<th>(X)</th>
<th>(10^4 k_1/\text{sec})</th>
<th>(%N_2)</th>
<th>(k_1\text{ (rel.)})</th>
<th>(\sigma_p) (Hammett)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_3)</td>
<td>22.4</td>
<td>99.5</td>
<td>4.48</td>
<td>-0.268</td>
</tr>
<tr>
<td>(\text{CH}_3)</td>
<td>7.94</td>
<td>100</td>
<td>1.59</td>
<td>-0.170</td>
</tr>
<tr>
<td>(\text{H})</td>
<td>5.00</td>
<td>99.5</td>
<td>1.00</td>
<td>0.0</td>
</tr>
<tr>
<td>(\text{Cl})</td>
<td>9.14</td>
<td>100</td>
<td>1.82</td>
<td>0.227</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_5\text{CO})</td>
<td>4.86</td>
<td>96</td>
<td>0.98</td>
<td>0.459</td>
</tr>
<tr>
<td>(\text{NO}_2)</td>
<td>5.83</td>
<td>99.5</td>
<td>1.16</td>
<td>0.778</td>
</tr>
</tbody>
</table>

**Figure 16.** Hammett Plot of Triazolines, \(^{67}\).
Hammett correlation suggests that a more complex mechanism may be operating.

Electron-withdrawing groups on $N_1$ favour the formation of imine products $60, 63-4$.

Electron-withdrawing groups on $C_4$ favour the formation of aziridine products $12, 63, 65$.

Electron-releasing groups on $C_5$ favour the formation of aziridines and also $C_4-C_5$ bond cleavage $7, 55, 60$.

However, none of these trends are firmly established in terms of a general mechanism. We have studied the thermal decomposition of a series of triazolines.
with para-substituted phenyl substituents at C₅ in an effort to elaborate the mechanism for the acyclic cases.

**Part 3: Photodecomposition of 1,2,3-Δ²-triazolines**

The photodecomposition of 1,2,3-Δ²-triazolines normally produces aziridines and minor amounts of imines 13-4, 34, 49, 53-4, 66.

Norbornyl triazolines such as 43 give aziridines almost exclusively (> 90%) regardless of the N₁ substituent 34, 49, 53-4. (Table 4).

**TABLE 4. AZIRIDINE YIELD IN THE PHOTODECOMPOSITION OF NORBORNYL TRIAZOLINES, 43**

<table>
<thead>
<tr>
<th>Substituent (R)</th>
<th>Aziridine (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅CH₂⁻</td>
<td>53</td>
</tr>
<tr>
<td>C₆H₅⁻</td>
<td>53</td>
</tr>
<tr>
<td>(4)CH₃C₆H₄⁻</td>
<td>53</td>
</tr>
<tr>
<td>(3)ClC₆H₄⁻</td>
<td>53</td>
</tr>
<tr>
<td>(4)BrC₆H₄⁻</td>
<td>34</td>
</tr>
<tr>
<td>PO(OEt)₂⁻</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>90⁺</td>
</tr>
</tbody>
</table>
Bicyclic triazolines such as \([44]\) photodecompose to form aziridines but slightly increased yields of imines are observed \([34]\). Scheiner \([34]\) suggests that increasing flexibility about the \(C_4-C_5\) bonds in a series of triazolines such as \([44]\) accounts for the increased yield of imine. (Table 5).

Aratani and coworkers \([14]\) have elegantly demonstrated the effect of ring stereochemistry on product distribution (Table 6) in the photodecomposition of the optically active trans \((12)\) and the cis \((62)\) 1-phenyl-4,5-hexamethylene-1,2,3-\(\Delta^2\)-triazolines (Figure 17). Their observations indicate a high degree of configurational retention at \(C_4\) and \(C_5\) in both the photodecomposition and thermal decomposition.

<table>
<thead>
<tr>
<th>Ring Size</th>
<th>Imine (%)</th>
<th>Aziridine (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n = 5)</td>
<td>6</td>
<td>94</td>
</tr>
<tr>
<td>(n = 7)</td>
<td>11</td>
<td>89</td>
</tr>
<tr>
<td>(n = 8) (cis)</td>
<td>12</td>
<td>88</td>
</tr>
</tbody>
</table>
Figure 17. Scheme of Products formed in the decomposition of 1-phenyl-4,5-hexamethylene-1,2,3-Δ²-triazolines.
<table>
<thead>
<tr>
<th>Conditions</th>
<th>Triazoline</th>
<th>% of Total</th>
<th>Products (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>70 (trans)</td>
</tr>
<tr>
<td>Thermolysis (Inject of V.P.C. at 310°C.)</td>
<td>12 (trans)</td>
<td>86</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>69 (cis)</td>
<td>100</td>
<td>11</td>
</tr>
<tr>
<td>Direct Photolysis (Benzene Solution Pyrex Filtered Hg Arc)</td>
<td>12 (trans)</td>
<td>75</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>69 (cis)</td>
<td>99</td>
<td>2</td>
</tr>
<tr>
<td>Sensitized Photolysis (Benzene Solution sensitized with Triphenylamine 366 nm. source).</td>
<td>12 (trans)</td>
<td>85</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>69 (cis)</td>
<td>91</td>
<td>10</td>
</tr>
</tbody>
</table>
Monocyclic triazolines such as form aziridines with up to 20% imine. The photodecomposition of para-bromophenyl azide - simple alkene \(^3^4\), cis (2), and trans (10)-\(\beta\)-methylstyrene \(^1^3,6^6\) adducts have suggested a mechanism which involves the formation of diradical intermediates such as \(^7^3\) and \(^7^4\) as the initial step. The intermediates \(^7^3\) and \(^7^4\) may then undergo \(\text{C}_4-\text{C}_5\) bond rotation with subsequent ring closure or hydride shift to give products \(^7^5-7^7\) (Figure 18). The observed product distributions for the styrene (9 and 10), 1-hexene (78), 3-hexene (79), and 2-methyl-2-butene (80) triazolines tend to support such a mechanism (Table 7).

We have studied the photodecomposition of adducts formed from phenyl azide and \(\text{para}\)-substituted styrenes. We wished to compare the photodecomposition and thermal decomposition with the idea that the similar products observed for both types of decomposition may be caused by some mechanistic principle governing both forms of activation. On the basis of our observations we wish to propose a general mechanistic scheme which accounts for our observations and those of others.
Figure 18. Mechanism of Photodecomposition of cis and trans-1,5-Diphenyl-4-methyl-1,2,3-$\Delta^2$-triazoline.
TABLE 7. PRODUCT DISTRIBUTION FOR PHOTODECOMPOSITION OF MONOCYCLIC TRIAZOLINES FORMED FROM THE β-METHYLYSTYRENES (2,10), 1-HEXENE (78), 3-HEXENE (79) AND 2-METHYL-2-BUTENE (80).

<table>
<thead>
<tr>
<th>Alkene</th>
<th>Aziridine</th>
<th>Imine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cis</td>
<td>trans</td>
</tr>
<tr>
<td>9</td>
<td>65% (76)</td>
<td>17% (72)</td>
</tr>
<tr>
<td>10</td>
<td>22% (76)</td>
<td>66% (72)</td>
</tr>
<tr>
<td>78</td>
<td>88%</td>
<td></td>
</tr>
<tr>
<td>79</td>
<td>84%</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>83%</td>
<td></td>
</tr>
</tbody>
</table>
Results

Addition of Azides to Homoconjugated Dienes

The reaction of $6$ with $36$ in inert solvent leads to the formation of a monoaddition product, $81$. The nuclear magnetic resonance spectrum of $81$ (Figure 19) shows absorptions in the region $8$ of 3.6-5.1 which are attributed to the hydrogens attached to the carbons of the triazole ring. The two AB patterns in this region definitely indicate the presence of two isomeric triazolines. Two interpretations of this result are possible. First, $81$ could be a mixture of isomeric triazolines resulting from addition of azide to both the $\Delta^6$ ($81a$ and $81b$) and $\Delta^2$ ($81c$ and $81d$) double bonds of $36$. Second, addition could have occurred only to the more strained $\Delta^6$ double bond, but in two orientations to give $81a$ and $81b$. Under the conditions of this reaction $6$ does not add to bicyclo (3.2.1) oct-2-ene $67$ but addition to $13$ is facile. Therefore addition of azide to the $\Delta^6$ and not the $\Delta^2$ bond is the correct interpretation. The mixture of isomers is therefore $81a$ and $81b$. (Figure 20).
Figure 19. Nuclear magnetic resonance spectrum of product 81 from reaction of phenyl azide and bicyclo(3.2.1)octa-2,6-diene.

Figure 20. Isomeric Triazoline Adducts of Phenyl azide and Bicyclo(3.2.1)octa-2,6-diene, 36.
Assignment of N.M.R. signals to H₂ and H₆ in 81a and 81b was made by comparison of the position of these signals with those due to similar hydrogens in 82 ⁵³, and other triazolines ¹⁵. Huisgen et al ⁵³, report that

\[
\begin{align*}
\text{ signals due to } H_2 \text{ and } H_6 \text{ in } 82 \text{ and its aryl-substituted derivatives are doublets (9.2-9.5 Hz) appearing at } \\
\delta & \ 3.64-3.68 \text{ and } \delta \ 4.51-4.58 \text{ respectively. Scheiner reports } ¹⁵ \text{ hydrogens attached to C}_5 \text{ of monocyclic triazolines give N.M.R. signals between } \delta \ 3.6 \text{ and } 4.0 \text{ whereas } C_4 \text{ hydrogens resonate between } \delta \ 4.1 \text{ and } 4.7. \text{ The two pairs of doublets (9.2 Hz) centered at } \delta \ 3.91 \text{ and}
\end{align*}
\]
4.17 in the N.M.R. spectrum of 81 were assigned to H$_2$ of the isomers. Since H$_2$ of 81a is sterically situated in the shielding portion of the π cloud of the Δ9 double bond, the N.M.R. signal due to this hydrogen would be expected at higher field than H$_2$ of 81b. The doublet centered at δ 3.91 is assigned to H$_2$ in 81a and the doublet at δ 4.17 is assigned to H$_2$ in 81b. In a similar manner the doublets centered at δ 4.74 and δ 4.98 were assigned to H$_6$ of 81b and 81a respectively. This assignment is substantiated by the intensity build-up of the inner peaks of the AB pattern at δ 4.17 and δ 4.74 of 81b when compared with the peaks of the corresponding doublets at δ 3.91 and δ 4.98 for 81a. This is characteristic of AB systems. Integration also shows the pairs of doublets assigned to 81a and 81b to be correctly assigned and gives the ratio 81a:81b as 1.3:1.

The addition of para-nitrophenyl azide to 36 gave a mixture of para-nitrophenyl substituted isomers 81'a and 81'b. By analogy with the treatment used to obtain the isomer ratio of 81a and 81b, the isomer ratio
$81^{a}:81^{b}$ was found to be 1.5:1.

Benzene, as an N.M.R. solvent, caused all of the hydrogens to resonate at higher field. That the effect is not uniform is evident from Table 8. The shielding experienced by $H_2$ of both $81^{a}$ and $81^{b}$ is greater (0.30-0.40 p.p.m.) than that experienced by $H_6$ (0.18-0.23 p.p.m.) in these isomers. We consider this to be caused by unsymmetrical complexation of the benzene with $81^{a}$ and with $81^{b}$.

Ledaal has summarized the chemical shifts induced in the N.M.R. spectra of solutes placed in aromatic solvents. The model he proposes which allows the most reliable predictions of ASIS is based upon the assumption of near neighbour orientation (complexation) induced in the solvent by polar bonds in the solute. For solutes with a dipole the solvent shift of different hydrogens of the solute increased as their proximity to the positive end of the dipole increased (i.e., the hydrogen lying in the diamagnetic shielding cone of the benzene nucleus was solvent-shifted the greatest amount).
<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>Isomer a</th>
<th>Isomer b</th>
</tr>
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<td>CC14</td>
<td></td>
<td>H1 2.63</td>
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<td></td>
<td></td>
<td>H7 2.76</td>
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</tr>
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<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td>H6 4.53</td>
<td>H6</td>
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<tr>
<td></td>
<td></td>
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<td>J2,6(=)</td>
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<td>0.40 0.18</td>
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<td>- - 4.17</td>
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<td>4.74 9.2</td>
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<td></td>
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<td>3.12 4.17</td>
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<tr>
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<td>0.40 0.26</td>
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<tr>
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<td></td>
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<td>81</td>
<td>C6H6</td>
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<tr>
<td></td>
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<td>2.36 3.01</td>
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<td>3.29 4.41</td>
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<tr>
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<tr>
<td></td>
<td></td>
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<td>- - 0.05</td>
</tr>
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<td>0.01 0.08</td>
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<td></td>
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<td>0.05 0.05</td>
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<td></td>
<td>4.37 9.0</td>
<td>4.37 9.0</td>
</tr>
<tr>
<td></td>
<td>C6H6</td>
<td>- - 3.27</td>
<td>- - 3.27</td>
</tr>
<tr>
<td>δCC1 δC6F6</td>
<td></td>
<td>- - 0.10</td>
<td>- - 0.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.10 0.29</td>
<td>0.10 0.29</td>
</tr>
<tr>
<td>C6F6</td>
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</tr>
<tr>
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<td></td>
<td>3.59 4.46</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>0.05 0.05</td>
<td>0.05 0.05</td>
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<tr>
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<td>- - 0.09</td>
<td>- - 0.09</td>
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<tr>
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<td></td>
<td>0.11 0.11</td>
<td>0.11 0.11</td>
</tr>
<tr>
<td>δCCl3</td>
<td></td>
<td>- - 3.65</td>
<td>- - 3.65</td>
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<tr>
<td></td>
<td></td>
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<td>4.48 9.5</td>
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<tr>
<td>δCCl3</td>
<td>δCCl3</td>
<td>- - 0.09</td>
<td>- - 0.09</td>
</tr>
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<td></td>
<td></td>
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<td>- - 0.11</td>
</tr>
<tr>
<td>δCCl3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE 8. CHEMICAL SHIFTS OF H1, H7, H2, AND H6 OF TRIAZOLINE ADDUCTS
The larger the dipole moment, the larger the solvent shift for solutes of similar type.

Using the above model and the observed changes in chemical shift in $81a$ and $81b$ it is possible to designate the form of the $81a$-benzene and $81b$-benzene collision complexes. In both cases the benzene nucleus appears to lie below the solute molecule and to the side near the phenyl substituted nitrogen. The possibility that the benzene nucleus is situated at the end of the phenyl substituent of $81$ as well as its location above the bicyclic ring system may be discounted because of the shifts observed.

The addition of phenyl azide to $27$ gave a mixture of triazolines $83a$ and $83b$. That addition occurred to only the highly strained $\Delta^2$ double bond was evident from the appearance of signals due to the $C_{11}$ methylene hydrogens at $\delta 4.75$ and $5.05$. The hydrogens at $C_2$ and $C_6$ of $83a$ and $83b$ have an orientation with respect to the methylene bond similar to that of $H_2$ and $H_6$ in $81a$ and $81b$ with respect to the nuclear double bond in those triazolines. Thus, although in $CCl_4$, $H_2$ and $H_6$ in $83a$ and $83b$ were
exhibited as a single AB quartet for both isomers, in benzene the two sets of AB quartets were sufficiently resolved to allow the assignment specified in Table 8. The ratio was calculated in this case from integration of $H_1$ and $H_7$ signals in the benzene spectrum of these isomers to be 1.3:1. The bridgehead signal occurring at highest field in the benzene spectrum of the isomer mixture was assigned to $H_1$ of 83b because of its similarity in chemical shift to $H_1$ of 82. Likewise, the signal at $\delta$ 2.79 was assigned to $H_7$ of 83a. Since the lowest field bridgehead hydrogen ( $\delta$ 3.10) should be $H_7$ of 83b, the signal at $\delta$ 2.98 is deduced to be due to $H_1$ of 83a.
Addition of phenyl azide to endo-dicyclopentadiene has been reported several times \textsuperscript{71,72} but no evidence as to the homogeneity of the product has been available. Indeed the rather sharp melting range of the product could be construed as evidence for formation of a single triazoline adduct \textsuperscript{73}.

The N.M.R. spectrum of the addition product, \textsuperscript{84}, revealed the presence of two olefinic hydrogens. Since phenyl azide addition proceeds readily with \textit{exo}-1,2-dihydro-\textsuperscript{38} \textsuperscript{72,74} but not with \textit{exo}-5,6-dihydro-\textsuperscript{38} \textsuperscript{74} addition, in the present case, must have occurred to the \( \Delta^5 \)-double bond of \textsuperscript{38}. The \( 3.5-4.5 \) region of the N.M.R. spectrum of \textsuperscript{84} revealed the presence of two isomeric triazolines.

4B quartet patterns of \( H_2 \) and \( H_6 \) in \textsuperscript{84} were assigned as shown in Table 8. Integration of the to \( H_2 \) and \( H_6 \) gave a \( \textsuperscript{84a}:\textsuperscript{84b} \) ratio of 1.3:1.
Thermal Decomposition of Norbornyl Triazolines

We have studied the thermal decomposition of 82 under various conditions and have found 85-89 (Figure 21) to be the products of decomposition. The amount of each product was determined by gas chromatography and the results are recorded in Table 9.

The exo-aziridine, 85, was isolated from the pyrolysate of 82 in decalin by preparative gas chromatography. It was identical with a sample of 85 prepared by photolysis of 82 49,53. 85 was previously
Figure 21. Products of Thermal Decomposition of 82.
### TABLE 9. PRODUCTS OF DECOMPOSITION OF TRIAZOLINE 82 a.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Product % Yield (g.l.p.c.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>Conc.</td>
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<tr>
<td>Decalin</td>
<td>0.1</td>
</tr>
<tr>
<td>Decalin</td>
<td>0.025</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>0.1</td>
</tr>
<tr>
<td>3,5-Lutidine</td>
<td>0.1</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td>0.1</td>
</tr>
<tr>
<td>Dimethylsulphoxide</td>
<td>0.1</td>
</tr>
<tr>
<td>Photolysis</td>
<td></td>
</tr>
<tr>
<td>Acetone, HCl excess</td>
<td></td>
</tr>
</tbody>
</table>

a determined after 95% reaction, the relative yields did not change observably on prolonged heating.

b see experimental

c ~ 5% 7-syn-N-phenylamine-2-exo-bicyclo (2.2.1) heptanol
reported as a product in the pyrolysis and photolysis of \( \text{82} \). The structure of \( \text{85} \) was confirmed by its characteristic N.M.R. spectrum which exhibited a high field doublet \( (J=9.5 \text{ Hz.}) \) at \( \delta 0.72 \) attributable to the anti-C\( _8 \) hydrogen, a doublet of triplets \( (J=9.5 \text{ Hz.}, \text{ and } J=1.8 \text{ Hz.}) \) at \( \delta 1.62 \) attributable to the syn-C\( _8 \) hydrogen and a sharp singlet at \( \delta 2.10 \) which was assigned to the hydrogens at C\( _2 \) and C\( _4 \). These signals are particularly characteristic of 3-azatricyclo \( (3.2.1.0 ^{2,4-\text{exo}}) \) octanes.

The imine, \( \text{86} \), was identified by its hydrolysis to bicyclo \( (2.2.1) \) heptanone and aniline and by comparison with a sample prepared by condensation of these latter two reagents by azeotropic distillation. Hüsgen et al. have previously reported \( \text{86} \) as a product of the pyrolysis of \( \text{82} \).

The structure of \( \text{87} \) was determined by a combination of spectroscopic analysis and chemical degradation. Significantly the infrared spectrum of the compound in question contained no N-H absorption. The
N.M.R. spectrum of this compound exhibited four distinct signals in the ratio of 5:2:2:6 in the direction of stronger field. Specifically the signals appeared as a multiplet centered at δ 6.90, a triplet (J=2.0 Hz.) centered at δ 2.69, a multiplet centered at δ 2.37 and a complex signal in the region between δ 1.1 and δ 1.7. The δ 2.69 signal may be assigned to hydrogens attached to carbon bearing nitrogen and the δ 2.37 signal to bridgehead hydrogens. Three structures may be proposed which are consistent with the spectral data and which are reasonable on mechanistic grounds. These are 87, 90 and 91. The formation of 90 from 82 would be analogous to the formation of 2-exo-7-syn-dibromobicyclo (2.2.1) heptane during the bromination of 13. Azetidines of this type have been considered previously as possible products of triazoline decomposition 23,44. The azetidine 91 could arise as shown in Figure 22.

The equivalence of the bridgehead hydrogens in the N.M.R. spectrum of the compound in question and the appearance of a triplet for the hydrogens attached to
Figure 22. Azetidine Formation
carbon bearing nitrogen 76 led us to favour structure 87 for this compound. To confirm the structure the compound was treated with hot potassium thiophenate in alcohol, conditions which should lead to S\textsubscript{n2} opening of 87, 90 and 91 and give no skeletal rearrangement 77. Such cleavage would be expected to yield a trans-2,3-disubstituted bicyclo (2.2.1) heptane derivative only in the case of structure 87. The product of this reaction exhibited an N.M.R. spectrum clearly indicating the trans-2,3-disubstituted bicyclo (2.2.1) heptane, 95. A quartet \( (J_{2,2}=4.0 \text{ Hz}; J_{3,7a}=2.5 \text{ Hz}) \) centered at \( \delta 2.58 \) was observed for the 3-endo hydrogen and a triplet \( (J_{2,3}=J_{2,4}=4.0 \text{ Hz}) \) centered at \( \delta 3.50 \) was observed for the 2-exo-hydrogen. The assigned couplings are consistent with those observed in similar systems 70.

Treatment of 95 with Raney nickel in isopropanol gave an aminobicyclo (2.2.1) heptane. This amine was identical in all respects with that formed upon the LAH reduction of 86. Since this latter reduction should proceed from the exo side of the carbon-nitrogen double
bond of 86, the product must be 2-endo-N-phenylamino-
bicyclo (2.2.1) heptane, 96.

The structure of 88 was determined by an analysis of its infrared and N.M.R. spectra. The infrared spectrum significantly exhibited absorptions at 3450 and 3070 and 1701 cm⁻¹ which were assigned to the N-H and olefinic groups respectively. The N.M.R. spectrum of 88 contained signals in the ratio of 5:2:1:1:2:1:4 in the direction of stronger field. Two olefinic hydrogens appeared as a symmetrical triplet (J=2.0 Hz.) centered at δ 5.97. A broad signal at δ 2.90 was assigned to the two bridgehead hydrogens. A one hydrogen singlet at δ 3.74 which was easily exchanged with deuterium oxide was assigned to the hydrogen attached to nitrogen. This treatment did not significantly alter the appearance of the singlet at δ 3.42 which was assigned to the hydrogen attached to the carbon bearing the nitrogen function. Since this latter hydrogen was not significantly coupled to vicinal hydrogens the nitrogen function must be attached to C7 70. Mechanistic considerations lead to the assignment of the
syn-7-stereochemistry to this nitrogen function. The formation of 88 during the pyrolysis of 82 is analogous to the formation of syn-2-norbornene-7-methyl carbamate during the pyrolysis of the corresponding triazoline 24.

A sample of 88 was also prepared by treatment of 82 with acid. Under similar conditions 97 is reported to give 98 72.

The structure of 89 was also deduced by analysis of its infrared and N.M.R. spectra. The infrared spectrum of 89 contained N-H absorption at 3475 cm.\(^{-1}\) and absorption at 840 cm.\(^{-1}\) which is attributed to the presence of the nortricyclene system 78.
The N.M.R. spectrum of 89 exhibited signals in the ratio 5:1:1:1:7 in the direction of stronger field. A high field signal (δ 1.02) which appeared as a relatively sharp signal was assigned to the three hydrogens attached to the cyclopropane ring. A four hydrogen signal which was observed as a complex multiplet between δ 0.9 and δ 1.7 was assigned to the C₅ and C₇ hydrogens. A broad singlet (1H) at δ 2.01 was assigned to the C₄ bridgehead hydrogen. This hydrogen absorbs at 0.39 p.p.m. higher field than the C₁ hydrogen of 26. This difference is readily attributable to diamagnetic shielding of C₄ by the cyclopropane ring in 89.79. Two further one hydrogen singlets were observed in the N.M.R. spectrum of 89. One occurred at δ 3.31 and was assigned to the hydrogen at C₃. The other (δ 3.47) disappeared upon the addition of deuterium oxide and was thus due to the hydrogen attached to the nitrogen. A sample of 89 was prepared by the treatment of 82 with acid (Table 9).

To determine if there were substituent effects in the thermal decomposition of norbornyl triazolines such
as the four para-substituted phenyl triazolines (Table 10) were decomposed in pyridine-d$_5$ at 112°C. in N.M.R. sample tubes. The N.M.R. spectra were recorded at intervals to assay the extent of reaction and to determine if any product rearrangement was occurring.

As was found with 82 there was no detectable change in product distribution with time even with prolonged heating after the reaction was complete.

In view of Huisgen's work with 67.12, 53, 65, the possibility of triazoline isomerization in the presence of base (pyridine) to a diazoalkane-amine such as 66 was considered. To remove any doubt as to the isomerization possibility the N.M.R. spectra of 100 were measured in CDCl$_3$, C$_6$D$_6$ and in C$_5$D$_5$N. The only observable differences could be attributed to solvent effects and solvent impurities. Finally, a sample of 100 in C$_5$D$_5$N was kept at 99°C. for 177 minutes while repeated scans of the N.M.R. spectrum were recorded. There was no observable change in the appearance of the N.M.R. spectrum. The infrared spectrum recorded before and after heating showed only a solvent peak at 2263 cm.$^{-1}$
<table>
<thead>
<tr>
<th>Compound</th>
<th>Substituent</th>
<th>Rxn. Time</th>
<th>% Rxn.</th>
<th>Product % Yield</th>
<th>Aziridine</th>
<th>Imine</th>
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<td></td>
<td></td>
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<td>hr</td>
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<td>endo</td>
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<tr>
<td>29</td>
<td>pNO₂Ø</td>
<td>7</td>
<td>&gt;95</td>
<td>48</td>
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<tr>
<td>100</td>
<td>pBrØ</td>
<td>8</td>
<td>&gt;96</td>
<td>47</td>
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<td>101</td>
<td>pCH₃Ø</td>
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<tr>
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<td>pCH₃OØ</td>
<td>12</td>
<td>&gt;92</td>
<td>53</td>
<td>27</td>
<td>12</td>
</tr>
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</table>
in the 2000-2400 cm⁻¹ region.

It does not appear that isomerization to
diazoalkane-amine in the presence of pyridine is a route
for decomposition of norbornyl triazolines.

The presence of endo aziridine products 26,27,55,62
in the thermal decomposition of triazolines, such as 43,
and the observation 26,51 that nitrogen does not appear to
be evolved in a simple first order manner suggested that
C₂-C₆ bond cleavage was occurring to give an intermediate
such as 92. We attempted to detect the appearance of
such an intermediate.

\[ \text{82} \]

\[ \text{92} \]
by carrying out the thermal decomposition of 82 in an I.R. Hot Cell at 165°C. A band at 2175 cm.⁻¹ was observed which increased in intensity to a maximum after 30 minutes and subsequently decreased and disappeared as the reaction progressed. With our preliminary observation suggesting an intermediate such as 93 which would explain the formation of endo-aziridine, 87, we chose the system 103 as a model.

![Chemical structure diagram](image-url)
This system might be expected to give a larger amount of an intermediate such as because of a larger yield of endo-aziridine observed in the thermal decomposition of 103. In collaboration with Dr. L. H. Zalkow we repeated the I.R. experiments on 103 and were able to detect a band at 2150 cm.\(^{-1}\) which increased in intensity and subsequently decreased as the reaction progressed.

On the basis of the apparent non-first order kinetics, the infrared bands detected by decomposing 82 26 and 103 82 and the endo-aziridine products we consider that intermediates such as 93 are involved in the thermal decomposition of norbornyl triazolines.
Thermal Decomposition of 1-Phenyl-5-para-Xphenyl-1,2,3-\(\Delta^2\)-triazolines, 105.

The thermal decomposition of monocyclic triazolines such as 105 produces aziridines, 106, imines, 107, and nitrogen. (Table 11).

We have carried out the neat pyrolysis of 105a-105f at 171°C. and analyzed the resulting products by N.M.R. At this temperature decomposition was complete after two hours. Analysis of the pyrolysate after partial reaction indicated product distributions did not change observably during the course of reaction. A sample N.M.R. spectrum is given in Figure 23 for the pyrolysate of 105c indicating the region of \(A_3\) absorption for the imine product and the \(ABX\) absorptions for the aziridine 83.
TABLE 11. PRODUCT DISTRIBUTION FOR THE THERMAL DECOMPOSITION OF TRIAZOLINES, 105 a.

<table>
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<tr>
<th>Compound</th>
<th>X</th>
<th>m.p. °C.</th>
<th>% Products</th>
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<th>107</th>
<th>( \sigma_p )</th>
</tr>
</thead>
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<tr>
<td>105a</td>
<td>Cl</td>
<td>126.5-127.0</td>
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<td>75</td>
<td>0.23</td>
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</tr>
<tr>
<td>105b</td>
<td>Br</td>
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<tr>
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<td>H</td>
<td>126.0-126.5</td>
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<td>42</td>
<td>0</td>
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<tr>
<td>105d</td>
<td>H</td>
<td>126.0-126.6</td>
<td>63</td>
<td>36</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>105e</td>
<td>CH₃</td>
<td>110.5-111.5</td>
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<td>45</td>
<td>-0.17</td>
<td></td>
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<tr>
<td>105f</td>
<td>CH₂O</td>
<td>107.0-107.5</td>
<td>49</td>
<td>51</td>
<td>-0.27</td>
<td></td>
</tr>
</tbody>
</table>

a The % yield determinations are accurate to ± 5% of the value given.
Figure 23: N.M.R. Spectrum of Pyrolysate of 105c.
We have prepared 1-phenyl-5-d-5-phenyl-1,2,3-\(\Delta^2\)-triazoline, \textit{105d}, and compared the product distribution with that of \textit{105c}. The apparent reduction in the amount of imine formed by \textit{105d} remains to be explained.

**Thermal Decomposition of cis (9) and trans (10)-1,5-Diphenyl-4-methyl-1,2,3-\(\Delta^2\)-triazolines.**

The thermal decomposition of \textit{9} and \textit{10} in pyridine-d\textit{5} at 112\textdegree C. lead to the expected products 75, 76 and 77 as well as a product imine, \textit{108}, in which the phenyl group had migrated from \textit{C}\textsubscript{5} to \textit{C}\textsubscript{4} of the original triazoline. The yields of products are given in Table 12 and were obtained by N.M.R. analysis of the pyrolysates. The ratios of aziridines were substantiated by g.l.p.c. analysis on Column \textit{F}. The imine-enamine
### TABLE 12. PRODUCTS OF THERMAL DECOMPOSITION OF TRIAZOLINES 2 AND 10.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Compound</th>
<th>Aziridines</th>
<th></th>
<th></th>
<th>Imines</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cis</td>
<td>trans</td>
<td>H-shift</td>
<td>Ø-shift</td>
<td></td>
</tr>
<tr>
<td>cis (2)</td>
<td>76%</td>
<td>7%</td>
<td>74%</td>
<td>7%</td>
<td>75%</td>
</tr>
<tr>
<td>trans (10)</td>
<td>5%</td>
<td>74%</td>
<td>-</td>
<td>-</td>
<td>108c</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The % yields are accurate to ± 10% of the value given.
products were apparently isomerizing on the column and the relative amounts could not be ascertained by g.l.p.c.

The aziridines 76 and 77 were isolated from the pyrolysates of 2 and 10 by preparative g.l.p.c. on Column F at 230°C. The spectral data obtained (see Experimental) for 76 and 77 fully characterized the compounds in agreement with Scheiner's data 66. The imine 75 was isolated by g.l.p.c. and compared with an authentic sample prepared from acetophenone and aniline 66. (See Experimental).

The remaining detectable product, 108, was characterized by comparing it with the products derived by condensation of aniline with 2-phenylpropionaldehyde. (See Experimental). The N.M.R. spectrum of 108 showed the presence of three products in the ratio of 1:2.5:4.2. On the basis of the N.M.R. and I.R. data these were assigned structures 108a, 108b and 108c. The product imine, 108a, was easily distinguished from the other components because of the J coupling characteristic of the methyl groups on carbon bearing a
hydrogen ($\sim 7$ Hz.) $^{84}$. This assignment is substantiated by the C=N absorption in the I.R. The two enamines $^{108b}$ and $^{108c}$ were assigned on the basis that the thermodynamically more stable species would be present in greater amount since the synthesis is performed under equilibrating conditions. Hence $^{108c}$ was assigned the N.M.R. (CH$_3$) absorption at higher field. The presence of the enamines is substantiated by the I.R. absorptions due to (C$_6$H$_5$-NH- ) and ($\Phi$-C=C) $^{80,81}$. (Figure 24).
Figure 24. Isomeric Imine and Enamine Products of 2-Phenylpropionaldehyde.
Photodecomposition of 1-Phenyl-5-para-Xphenyl-1,2,3-$\Delta^2$-triazolines, 105.

Photodecomposition of triazolines, 105, was found to produce mainly aziridine, 106, with some imine, 107, products. (See Table 14). The yields of products were determined by analysis of the N.M.R. spectra. No other products were observed. The triazolines 105c and 105d had U.V. maxima which had the same order of extinction coefficients and similar wavelengths as those of 2 and 10 66 (Table 15).
### Table 13. Products of Photodecomposition of Triazolines, 105$^a$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>X-Substituent</th>
<th>Solvent</th>
<th>N.M.R. Tube</th>
<th>Aziridine</th>
<th>Imine</th>
</tr>
</thead>
<tbody>
<tr>
<td>105b</td>
<td>Br</td>
<td>CD$_3$CN</td>
<td>Quartz</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>105c</td>
<td>H</td>
<td>CD$_3$CN</td>
<td>Quartz</td>
<td>95$^+$</td>
<td>-</td>
</tr>
<tr>
<td>105c</td>
<td>H</td>
<td>CDCl$_3$</td>
<td>Pyrex</td>
<td>90$^+$</td>
<td>-</td>
</tr>
<tr>
<td>105d</td>
<td>H</td>
<td>CDCl$_3$</td>
<td>Pyrex</td>
<td>84</td>
<td>16</td>
</tr>
<tr>
<td>105f</td>
<td>CH$_3$O</td>
<td>CD$_3$CN</td>
<td>Quartz</td>
<td>83</td>
<td>17</td>
</tr>
<tr>
<td>105f</td>
<td>CH$_3$O</td>
<td>CDCl$_3$</td>
<td>Pyrex</td>
<td>81</td>
<td>18</td>
</tr>
</tbody>
</table>

$^a$ The % yield values are accurate to $\pm$ 10% of the value given.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$\lambda_1$ (nm.)</th>
<th>$\epsilon_1$</th>
<th>$\lambda_2$ (nm.)</th>
<th>$\epsilon_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>EtOH 66</td>
<td>307</td>
<td>8320</td>
<td>287</td>
<td>7430</td>
</tr>
<tr>
<td>10</td>
<td>EtOH 66</td>
<td>303</td>
<td>8120</td>
<td>286</td>
<td>7840</td>
</tr>
<tr>
<td>105c</td>
<td>CH$_3$CN</td>
<td>305</td>
<td>6.9x10$^3$</td>
<td>286</td>
<td>7.4x10$^3$</td>
</tr>
<tr>
<td>105d</td>
<td>CH$_3$CN</td>
<td>303.5</td>
<td>7.6x10$^3$</td>
<td>286</td>
<td>8.2x10$^3$</td>
</tr>
</tbody>
</table>
Conformational Analysis of Triazolines 2, 10 and 105.

The preferred conformations of 2, 10 and 105 are based on N.M.R. chemical shifts, coupling constants, and conformational energy considerations.

McGreer 85 has found that methyl groups in the pseudo-equatorial position, of pyrazolines like 109, absorb at 18-26 Hz. toward lower field than methyl groups in the pseudo-axial positions.

The chemical shift difference between the methyl groups in 2 and 10 is 18 Hz. 66 with the cis (2) isomer being at higher field. This observation implies, by analogy, that the methyl group in 2 is pseudo-axial. Of the four possible envelope conformations for 2 only two
(9a and 9b) have a methyl group pseudo-axial. These two conformers may interconvert by nitrogen inversion. However, 9a should be more stable because 9b has energetically unfavourable 1,3-diaxial (C₆H₅-CH₃) and 1,2-axial-equatorial (C₆H₅-C₆H₅) interactions. 

The large coupling constant (12 Hz.) that was observed for 2 further implies the conformational preference for 9a by analogy with McGreer's observations. If the hydrogens of 2 were undergoing exchange between axial and equatorial sites with a significant population of conformations with equatorial hydrogens then one would expect much
smaller coupling constants (∼ 7 Hz.) \(^85\). On the basis of
the above arguments the conformation 2a is preferred for the
\textit{cis} triazoline, 2.

The \textit{trans} triazoline, 10, is considered to have a
preferred conformation 10a based on conformational energy
considerations similar to those of 2.

The observation that the H\textsubscript{4} - H\textsubscript{5} coupling constant (8.8 Hz.) \(^66\) in 10 is similar to that found in 109 (8.4 Hz.) \(^85\) is an
indication of the conformational preference for 10. The
upfield shift of H\textsubscript{4}, and H\textsubscript{5} of 10 relative to H\textsubscript{4} and H\textsubscript{5} in
2 is a strong indication of the diaxial preference of the
hydrogens in 10 again by analogy with McGreer's observa-
tions \(^85\) for 109.
The preferred conformation of a triazoline ring like $105$ was determined from the calculated dihedral angles of the ring hydrogens. The dihedral angles were calculated from coupling constants obtained by analysis of the N.M.R. spectrum of the triazoline. The coupling constants were determined by using the LAOCOON III computer program $86b$. The resulting data is tabulated in Table 16. For the purposes of discussion the hydrogens of the ring which are exhibited as an ABC system have been labelled as in $110$. From the calculated coupling constants obtained (Table 16) it was then possible to apply the DAERM technique $86c$ ("Dihedral Angle Estimation by the Ratio Method") to calculate appropriate Karplus constants and dihedral angles for the ABC hydrogens of $105$. The results are tabulated in Table 17. On the basis of this calculation method and by making the assumption that the ring geometry of $105c$ is similar to $2$, $10$ and cyclopentene, we have predicted the preferred conformation of the triazoline ring for $105c$ (Figure 25). Two possible conformations, $111a$ and $111b$, which are a consequence of using the DAERM technique are given in Figure 25. The first conformation, $111a$, was
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Chemical Shift (δ)</th>
<th>Coupling Constants (Hz.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>105e</td>
<td>C$_5$D$_5$N</td>
<td>4.97</td>
<td>4.75</td>
</tr>
<tr>
<td>105e</td>
<td>C$_5$D$_5$N</td>
<td>4.89</td>
<td>4.70</td>
</tr>
<tr>
<td>105f</td>
<td>CD$_3$CN</td>
<td>5.04</td>
<td>4.75</td>
</tr>
<tr>
<td>Compound</td>
<td>$J_{\text{cis}(4-5)}$</td>
<td>$J_{\text{trans}(4'-5)}$</td>
<td>$\text{cis}$</td>
</tr>
<tr>
<td>----------</td>
<td>----------------</td>
<td>----------------</td>
<td>-------------</td>
</tr>
<tr>
<td>H</td>
<td>7.4 Hz</td>
<td>12.3 Hz</td>
<td>400°</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>12.3</td>
<td>7.5</td>
<td>150°</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>12.4</td>
<td>7.3</td>
<td>160°</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>12.4</td>
<td>7.3</td>
<td>150°</td>
</tr>
</tbody>
</table>
Figure 25. Styrene Adduct with Phenyl Azide
t$1,5$-Diphenyl-$1,2,3$-$\Delta^2$-Triazoline 105e.

Most probable

**Calculated Dihedral Angles**

- $\text{cis (H}_4\text{-H}_5 \text{)} \sim 40^\circ$
- $\text{trans (H}_4\text{-H}_5 \text{)} \sim 160^\circ$
- $\text{cis (H}_4\text{-H}_5 \text{)} \sim 15^\circ$
- $\text{trans (H}_4\text{-H}_5 \text{)} \sim 135^\circ$

111a 111b
ruled out on the basis of N.M.R. chemical shifts and coupling constants.

Crawford \(^8^7\) has found that in the methylene containing pyrazoline \(^1^1^2\), cis vicinal couplings are larger than trans vicinal couplings.
As previously mentioned, the *cis* vicinal coupling (12.0 Hz.) in 2 is larger than the *trans* vicinal coupling (8.8 Hz.) in 10. A methyl group is not expected to have a large effect on the coupling constants between vicinal hydrogens (c.f. 2 and 10 with 105c) when compared with hydrogen. In 112 the *trans* vicinal coupling constants $J(H_4-H_3)$ and $J(H_4-H_5)$ are 7.5 and 8.0 Hz., respectively, a difference of only 0.5 Hz. in going from methyl to hydrogen substituents.

On the basis of *cis* vicinal couplings being larger than *trans* vicinal couplings, by analogy to 2, 10, and 109, the conformer 111b is preferred for the triazoline 105c. The triazolines 105e and 105f are found to have essentially the same conformational preference (see Tables 16 and 17). An additional piece of evidence which supports the argument for *cis* couplings being greater than *trans* couplings in 110 is the deuterium-hydrogen couplings of 105d. If $H_4$, is at higher field than $H_4$, as expected, and the low field doublet of the $H_4$, $H_4$, AB quartet is coupled more strongly to deuterium than is the high field doublet, as observed, then $H_4$ is coupled more strongly to $D_5$ and the
cis coupling must be greater than the trans coupling in 105d.

Two further observations arising from this treatment are: 1) that the geminal coupling constants in 105 appear to be negative for this type of methylene unit, by analogy to 112, and 2) that the preferred conformation of the triazolines 105 has the least amount of steric repulsion between the phenyl groups.
Discussion

In any discussion of reaction mechanisms it is essential that one keep in mind that no mechanistic scheme is proven. Mechanisms are simply logical constructs providing a convenient way of describing what we think is happening in a reaction. As our data about a reaction improves and accumulates we must be prepared to modify our view of a mechanism rather than try to force data to fit a rigid mechanistic scheme. To prove a mechanism one must be in a position to observe a molecule undergoing reaction from start to finish; a procedure which is beyond our present technology and may, in fact, be impossible because of the Heisenberg Uncertainty Principle.

In the introduction to this thesis the author has attempted to review the reported data concerning the synthesis and decomposition of triazolines. In the results the author has attempted to describe experiments which further our understanding of the mechanisms involved.
**Homoconjugative Addition of Azides to Bicyclic Dienes.**

The mechanism of addition of azides to alkenes is postulated to be a concerted 1,3-dipolar cycloaddition (see Introduction) which may involve a dipolar transition state depending on the substituents of the azide and alkene.

In the present study the observation that there is a higher proportion of "a" isomer than "b" isomer in 81, 83 and 84 has been interpreted in terms of stabilization of a positive charge generated at C2 in the transition state leading to the "a" isomers. In each case (81, 83 and 84) studied, the π-cloud of the unreacting double bond is favourably situated for such homoconjugative stabilization. Supporting evidence for the homoconjugative stabilization effect is found in McLean's work 28 in which phenyl azide, 6, was added to a mono-triazolone adduct of norbornadiene, 15, and formed diadducts of norbornadiene (Figure 5). Thus when 6 reacted with 17 the diadducts 20 and 21 were formed in the ratio 1 to 1.5. This result is exactly analogous to the result we obtained
with 38 to give the $^{84b}:^{84a}$ ratio of 1:1.3. In addition, McLean 28 found that $^{18}$ and $^{19}$ were produced in the ratio of $5:13$. Both $^{19}$ and $^{21}$ are the species expected to be formed from a homoconjugatively stabilized transition state.

The observation that the $^{81'a}:^{81'b}$ ratio of 1.5:1 is greater than the $^{81'a}:^{81'b}$ ratio of 1.3:1 may be explained by the observation that the transition state for cycloaddition is stabilized by electron-withdrawing substituents on $N_3$ of $^{81}$ vide supra. This has the effect of enhancing the preferred orientation of the homoconjugatively stabilized cycloaddition reaction. These observations are completely consistent with a dipolar intermediate like 35. It is noteworthy that the addition of formic acid to 26 gives over 90% of 112, the result of homoconjugative participation by the $\Delta^2$ double bond 88. Likewise 37 is reported to give a high proportion of 114 with formic acid 89. The orientation effect of the unreacting double bond in the dienes studied is significantly less in the azide reaction than in the formic acid
addition. The origin of this difference presumably lies in the amount of electron deficiency generated at C₂ in each type of reaction. The greater the electron deficiency, the greater the orientation effect.

![Chemical Structures](image)

The possibility of an ionic path would be supported by a rate enhancement for the addition of azides to homoconjugated alkenes. Bailey \(^{18}\) has observed that the reaction of picryl or phenyl azide with \(^{15}\) and \(^{28}\) (homoconjugated alkenes) is slower than the reaction of these azides with \(^{13}\) which, in the author's view tends to refute the possibility of an ionic path.

Thus, even though dipolar stabilization seems to occur for homoconjugated alkenes the concerted
cycloaddition is still the correct mechanism and the rate reduction observed due to homoconjugation is a case of reduction in reactivity of the alkene (see Introduction).

Thermal Decomposition of Norbornyl Triazolines.

Our first consideration of a mechanism for the thermal decomposition of 82 is given below.

The formation of 85, 86, 88 and 89 during the pyrolysis of 82 was visualized as proceeding via the diazonium betaine intermediate, 92. The formation of 87, however, was noteworthy for it required a molecular rearrangement involving the cleavage of the C2-C6 bond of the bicyclo (2.2.1) heptyl system or several hydride shifts. We visualized the pyrolysis of 82 as proceeding via the initial heterolytic cleavage of the N3-N4 bond (82 → 92) followed by carbon-carbon bond cleavage to give 93. The diazoimine, 93, then underwent internal 1,3-dipolar cycloaddition to give 82 and/or 119 which decomposed in the usual fashion to give products. (Figure 26).
TABLE 17. RELATIVE RATES OF DECOMPOSITION OF TRIAZOLINE 82 IN DIFFERENT SOLVENTS AT 160°.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$t_{1/2}$ (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decalin</td>
<td>74</td>
</tr>
<tr>
<td>Dimethyl Sulfoxide</td>
<td>66</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>36</td>
</tr>
</tbody>
</table>

The first fundamental process in this mechanism is the heterolytic cleavage of the $N_3-N_4$ bond of 82 to give 92. This proposal was based upon the observation by others 24, 51, 58 and ourselves (Table 18) that the thermal
Figure 26. Ionic Path for Norbornyl Triazoline Thermal Decomposition.
decomposition of triazolines is accelerated in more polar solvents. The direction of heterolysis has been determined by substitution of electron-withdrawing groups at N₃ of the triazoline ring 51, 58, 60, 77, 90. Thus the reaction under investigation was found to be accelerated by such substitution (Table 19).

**TABLE 18. RELATIVE RATES OF DECOMPOSITION OF ARYL SUBSTITUTED DERIVATIVES OF 82 IN NITROBENZENE AT 141.6 ± 0.1°C**

<table>
<thead>
<tr>
<th>para Substituent</th>
<th>t₁/₂ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>39.3</td>
</tr>
<tr>
<td>Br</td>
<td>66.4</td>
</tr>
<tr>
<td>H</td>
<td>279.0</td>
</tr>
<tr>
<td>CH₃</td>
<td>473</td>
</tr>
<tr>
<td>CH₃O</td>
<td>521</td>
</tr>
</tbody>
</table>

The second fundamental process in the proposed mechanism was the cleavage of the C₂-C₆ bond of 92 to give the diazoimine intermediate, 93. In agreement with the postulation of a multistep mechanism is the observation
that nitrogen evolution during the pyrolysis of 82 did not appear to follow first order kinetics (Figure 27).

If one postulated a mechanism which involves first order appearance of nitrogen then a plot of $\log_e \left( \frac{V_\infty(N_2)}{(V_\infty(N_2)-V_t(N_2))} \right)$ against time should produce a straight line with the slope representing the first order rate constant. The fact that we were unable to produce such a result may be explained in two ways: 1) our techniques were unsuitable; or 2) the reaction really does not evolve nitrogen in a first order manner. Our studies seem to indicate that the rate of nitrogen loss is less than expected during the early stages of the reaction and more than expected in the latter stages. This type of deviation may be explained by the kinetic scheme diagrammed below (Figure 28).

Berlin et al have reported an analogous deviation from first order kinetics in the rate of nitrogen evolution during the pyrolysis of the phosphorylated triazoline, 115. Their detailed analysis of the kinetic data favoured a reaction scheme involving two consecutive first order reactions with accumulation of a diazo intermediate in the early stages of reaction 51. In the present case the deviation noted could
Figure 27. Triazoline 82 Pyrolysis in Decalin at 140.1 °C. (Graph to 43% reaction).
Figure 28. Proposed variation of concentration of triazoline 82 (---) intermediates (-Δ-) and nitrogen (-----) with time during pyrolysis of 82.
arise from accumulation of the diazonium betaine, 92 or the diazoimine, 93, during the early stages of reaction. When the pyrolysis of triazoline, 82, was carried out neat in a variable temperature infrared cell at 165° an adsorption centered at 2175 cm.⁻¹ appeared and grew to a maximum intensity at thirty minutes. This absorption then decreased in intensity throughout the remaining portion of the pyrolysis. The absorption is not due to phenyl azide which absorbs at 2130 cm.⁻¹. We feel this absorption is due to the presence of 92 or 93. Although it is difficult to make a definite assignment of the observed absorption, 93 would be expected to have a finite existence as diazoalkanes and imines combine in 1,3-dipolar addition reactions only at moderate rates 6.

![Diagram](attachment:image.png)

Carbon-carbon bond cleavage during the pyrolysis of triazoline 82 has been elegantly employed by Baldwin and coworkers to account for the formation of 55 from 82 in
phenyl isocyanate 62. We have found that decomposition of triazoline 82 in phenyl isocyanate is very rapid and that the formation of both the imine, 86, and endo-aziridine, 87, are suppressed relative to the exo-aziridine, 85 26. Since the aziridine products are stable to phenyl isocyanate under the conditions of the decomposition, this result may represent a trapping of 93 before it is converted to endo-aziridine. It is interesting that Baldwin was able to obtain a 60% yield of 55 from decomposition of 82 in phenyl isocyanate but that only 5-20% of endo-aziridine is formed from the triazoline, 82, in its absence. This may indicate that at least part of the diazoimine, 93 is converted to exo products (e.g. 85, 86 and 87). The 92→93 reaction would thus appear to be reversible.

There is a noticeable decrease in the amount of endo-aziridine formed when the decomposition is performed in more polar solvents (Table 9). This was readily interpretable in terms of the proposed mechanism which allows decomposition of the diazonium betaine, 92, to nitrogen and a norbornyl cation or the diazoimine 93.
Since the former of these modes of decomposition involves a greater charge separation, it would be expected to increase in importance in solvents of higher dielectric constant. Accordingly the amount of endo-aziridine, 87, which is formed via the less polar mode of decomposition of 92 to the diazoimine, decreases in more polar solvents.

The mechanistic postulate outlined above to account for the formation of the endo-aziridine, 87, upon pyrolysis of 82 has been used by Zalkow et al to explain the reaction of benzenesulfonyl azide with the bicyclic anhydrides 56 and 57. The reaction of benzenesulfonyl azide with 56 yields 60% of the endo-aziridine, 58, and 19% of the corresponding exo-aziridine, while reaction with 57 gives 74% of the endo-aziridine, 59, and 22% of the corresponding exo-aziridine. These reactions are considered to proceed via an unstable 1-benzenesulfonyl triazoline 76 which would be expected to decompose in a manner similar to 82. It is interesting that in these latter cases the endo-aziridines 58 and 59 account for a major portion of the reaction
products whereas in the present case only a minor amount of the endo-aziridine \( \text{87} \) was formed. These results and the isolation of \( \text{55} \) in 60% yield \( \text{62} \) from the reaction of phenyl isocyanate with \( \text{54} \) indicate a similar amount of \( \text{C}_2\text{-C}_6 \) bond breakage occurs in both reactions. Evidently the inductive and field effects of the anhydride groups in \( \text{56} \) and \( \text{57} \) may not facilitate the development of negative charge on \( \text{C}_3 \) of the bicyclo (2.2.1) heptyl system which occurs during the formation of a diazocimine (e.g. \( \text{92} \)) from a diazonium betaine (e.g. \( \text{92} \)) \( \text{91} \).

One further aspect of the reaction which requires comment is the amount of imine \( \text{82} \) formed. Several investigators \( \text{51} \) have suggested that imine products are formed in norbornyl triazoline decompositions from diazonium betaines (e.g. \( \text{92} \)) via 2,3-endo hydride shifts. This type of rearrangement is very slow in the norbornyl system. Indeed, even production of imine from endo-diazonium betaine analogs of \( \text{92} \) via 2,3-exo hydride shifts should be slow with respect to Wagner-Meerwein rearrangement \( \text{92,93} \) in this system. If either 2,3-endo or 2,3-exo
hydride shifts were occurring in the present case one would expect to find much more Wagner-Meerwein rearrangement products such as 88 and 89 than imine (this was not observed).

An attractive alternative which has been suggested recently $^{24}$ is proton transfer from C$_2$ to nitrogen in diazonium betaines analogous to 92 to give the enamine form of 82. In the present case all products including 85 and 86 were stable under the pyrolysis conditions.

Imine is formed more readily at the expense of both exo and endo aziridine where the phenyl substituent is an electron-withdrawing group in the case of triazolines 99-102. This result is difficult to explain. In the case where the electron-withdrawing azide substituent is C$_6$H$_5$SO$_2$ $^{23,45}$ aziridine is formed exclusively at low temperatures whereas some imine is formed at higher temperatures. In the case where the electron-withdrawing azide substituent is PO(OEt)$_2$, 115 $^{52}$, almost exclusive imine formation is observed. Cram $^{94,95}$ has pointed out that where a carbanion substituent is -PO(OR)$_2$ then the
carbanion tends to be symmetrical, and where a carbanion substituent is $\text{ArSO}_2^-$ then the carbanion tends to be unsymmetrical. One may then postulate that aryl carbanions are intermediate cases and, by analogy, the nitrogen anions would be the same.

An ionic mechanism which can explain the product distributions would be one in which the unsymmetrical nitrogen anion is better able to undergo ring closure to the developing carbonium ion at C$_6$ in 22 (Figure 27) when nitrogen is leaving because of the greater electron density produced between N$_3$ and C$_6$. Where the nitrogen anion is more symmetrical then a higher energy 2,3-endo-hydride shift could compete successfully with the ring closure reaction and in the completely symmetric case (PO(0Et)$_2$) dominate the reaction. A similar argument could be applied for imine production via an enamine. That the imine forming reaction is normally a higher energy process is demonstrated by the increase in imine production upon reaction at higher temperatures 23,77.
Thermal Decomposition of Triazolines 116 and 117. 59.

The thermal decomposition of the series of bicyclic triazolines 116 is found to be quite analogous to the norbornyl triazolines in that electron-withdrawing aryl substituents favour formation of imine over aziridine.

The reaction of a series of azides with cyclohexene is found to produce aziridines and imines. The triazolines 117 that are assumed to form initially in this reaction appear to yield larger amounts of aziridine than was the case with the respective triazolines 116. (Table 20).

The effect of substituents can be explained with an ionic mechanism as for the norbornyl triazolines but the effect of increasing the ring size is not quite as straightforward. In this case an increase in aziridine yield with increasing ring size may be explained on the basis of a more favourable conformation of the intermediate for ring closure.
TABLE 19. THERMAL DECOMPOSITION OF TRIAZOLINES FORMED FROM CYCLOPENTENE AND CYCLOHEXENE 59.

<table>
<thead>
<tr>
<th>Alkene</th>
<th>Azide Substituent X</th>
<th>% Aziridine</th>
<th>% Imine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclopentene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>116a NO₂</td>
<td>b CO₂CH₃</td>
<td>8</td>
<td>89</td>
</tr>
<tr>
<td>c Cl</td>
<td>d Br</td>
<td>22</td>
<td>75</td>
</tr>
<tr>
<td>e H</td>
<td>f CH₃</td>
<td>23</td>
<td>74</td>
</tr>
<tr>
<td>g CH₃O</td>
<td>h SO₂N₃</td>
<td>28</td>
<td>71</td>
</tr>
<tr>
<td>117a NO₂</td>
<td>b Cl</td>
<td>32</td>
<td>55</td>
</tr>
<tr>
<td>c Br</td>
<td>d H</td>
<td>38</td>
<td>55</td>
</tr>
<tr>
<td>e CH₃</td>
<td>f CH₃O</td>
<td>94.5</td>
<td></td>
</tr>
</tbody>
</table>

104
Thermal Decomposition of Styryl Triazolines $105a-f$.

The thermal decomposition of the styryl triazolines $105a-f$ if considered to proceed by an ionic mechanism should, on the basis of the above arguments, produce relatively greater amounts of aziridine than imine. This has, in fact, been observed for monocyclic systems by other authors $20,34$.

The reason for determining the conformations of some of the styryl triazolines, $105$, was to see if changes in the para-substituent affected the conformation of the triazoline ring significantly. A sample N.M.R. spectrum and a LAOCOON III spectrum are given in Appendix 1 for $105c$. In all of the styryl cases, $105a-c, e-f$, the observed spectra have the same general appearance. Tables 16 and 17 show essentially the same conformations for $105c, e, f$. The spectra obtained for $105a, b$ were not of a high quality sufficient to allow a good refinement by the LAOCOON-DAERM $86c$ method. However, preliminary results indicated the same conformations for $105a, b$ as for the
others. It is safe to say that within the limits of accuracy of the DAERM technique the conformations of the triazolines \( 105a-c, e-f \) are the same. Therefore any changes in product distribution for the thermal decomposition of \( 105 \) should be attributable to electronic rather than conformational or steric effects.

Table 11 indicates that the yield of aziridine product decreases relative to imine for the para-substituted triazolines, \( 105 \). This seems to imply that a para-substituent either decreases the energy barrier to imine formation or else increases the energy barrier to aziridine formation. Since imine formation involves the hydrogen situated on \( C_5 \) which has the substituted phenyl group it appears reasonable that the imine forming process is being enhanced. The aziridine forming process does not appear to require the intermediacy of the \( C_5 \) carbon. An additional point is that in the case of \( 105d \) in which deuterium is substituted for hydrogen on \( C_5 \) the yield of imine is smallest. This may be rationalized on
the basis that the C-D bond has a lower zero-point energy than the C-H bond and reactions involving breakage of this bond would be slowed down because of the increased energy barrier to bond breakage. It is not possible to speculate on the exact nature (i.e. resonance or inductive effect) of the substituent effect, with the limited data available, beyond saying that it probably has the greatest effect on the imine forming reaction. If the mechanism involved purely ionic processes one would expect a linear relationship between the rate of imine formation and $\sigma_p$. The product distributions observed suggested that this was probably not the case.

Thermal Decomposition of cis (2) and trans (10) Triazolines.

Thermal decomposition of 2 and 10 gives aziridines 76 and 77 with some imine 75 in similar quantities to that found in the case of 105c and 105d. The major aziridine component is of a similar configuration to the triazoline from which it was derived. This was not expected on the basis of an ionic mechanism.
Mechanism for Thermal Decomposition of Triazolines.

The high degree of stereoselectivity found in the thermal decomposition of 2 and 10 suggests that the transition state for reaction retains the stereochemical factors present in the triazoline. Such a condition would be the case for concerted breaking of the two C-N bonds with developing overlap of the new bonds being formed at the transition state $^{85, 119}$. The thermal decomposition could be thought of as a $2 + 2$ cycloreversion (Figure 29). This however requires a highly strained transition state in which bond cleavage must be a $\sigma^2_s + \sigma^2_a$ process to be allowed. Since the geometry of the starting triazoline is maintained in the product aziridines, viewing the process as a concerted process requires inversion of $N_1$ to be energetically more favourable than inversion at $C_4$.

An alternative, but equivalent explanation, involves the loss of $N_2$ to form a three atom intermediate $^{119a}$ which is analogous to the trimethylene unit found by
Figure 29. Cycloreversion Mechanism.
Crawford in the gas phase thermal decomposition of pyrazolines. The intermediate then behaves as a trimethylene unit and forms products in a stereoselective manner based on the symmetry calculations of Hoffman. 

McGreer proposes that, like trimethylene, interaction of the orbitals on C4 with the C-N bonds of a pyrazoline before loss of nitrogen can cause the three carbon fragment to act as a symmetric or antisymmetric component depending on steric and electronic factors. This would allow a variety of stereochemical results to be in competition with each other. This may in fact be analogous to a 2+2+2 pericyclic reaction.

Pursuing the idea that thermal decompositions of triazolines are concerted processes then one may describe the formation of products as involving: 1) concerted loss of N2 with ring closure (or formation of a C-C-N unit) to form aziridines stereoselectively (Figure 29, Activation Process 1) or; 2) the formation of diazoalkanes by concerted N1-N2 and C4-C5 bond cleavage
(Figure 29, Activation Process 2) or; 3) imine formation via concerted loss of $N_2$ with hydride shift in a $2 + 2 + 2$ pericyclic reaction (Figure 29, Activation Process 3).

To explain the anomalous cases, where charge seems to be involved, as in the case of Wagner-Meerwein shifts in the norbornyl systems, one must realize that polarization of bonds involved in these pericyclic reactions does not alter the orbital symmetry requirements to which the reaction is subject. In other words, cycloreversions as cycloadditions may proceed via dipolar transition state intermediates and thus be subject to small solvent and substituent effects.

Photodecomposition of Triazolines.

Exactly the same types of symmetry arguments may be applied to the photodecomposition of triazolines except that the symmetry rules now require a $\sigma^2_s + \sigma^2_s$ cycloreversion $^{99}$. This implies an even greater stereo-selectivity as was observed by Scheiner $^{66}$ and Aratani $^{14}$. 
The author now takes the view that the synthesis and decomposition (both thermal and photolytic) reactions are two manifestations (Cycloaddition and Cycloreverslon) of a single type of process. A simple view of this proposition is suggested in Figures 29 and 30.

**Alternative Mechanism for 1,3-Dipolarcycloaddition of Azides to Alkenes.**

Huisgen \(^{10b}\) favours a mechanism for 1,3-dipolar-cycloadditions which involves bending of the azide simultaneously with orientation of the alkene. This implies that the kinetics of cycloaddition must be second order overall, i.e. Azide and Alkene \(\text{k}_2 \rightarrow\) Triazoline.

Huisgen \(^{53}\) finds that the kinetics of cycloaddition of 6 or 25 in the presence of a two-fold excess of alkene, 121, is second order.

\[
\begin{align*}
\text{C}_2\text{H}_5\text{O}_2\text{C} & \quad + \\
\text{N} & \quad \text{N} \\
\text{C}_2\text{H}_5\text{O}_2 & \\
\end{align*}
\]

6 or 25 + 121
Figure 30. Cycloaddition Mechanism.
In addition he observed a small inverse solvent effect which suggested that the transition state was less polar than the starting materials.

Scheiner\textsuperscript{16} found that the kinetics of cycloaddition of \textit{6} to \textit{123} is pseudo-first order in both azide and alkene when alkene is in an hundred-fold excess. By the method of initial rates this indicated a mechanism which was second order overall\textsuperscript{100}. He also found no general solvent effect.

The apparent lack of a significant solvent effect found by both Huisgen\textsuperscript{53} and Scheiner\textsuperscript{16} indicates that the mechanism does not involve a zwitterion intermediate, \textit{122}, like that proposed by Awad\textsuperscript{63} for the reaction of \textit{6} with \textit{123}.

\begin{center}
\begin{tikzpicture}
\node (c1) at (0,0) {\(6\)};
\node (c2) at (2,0) {\(\left\lbrack \begin{array}{c}
\text{H-C} \\
\text{C} \\
\text{N} \\
\text{Ar} \\
\end{array} \right\rbrack\)};
\node (c3) at (4,0) {\(\left\lbrack \begin{array}{c}
\text{H-C} \\
\text{C} \\
\text{N} \\
\text{C}_6\text{H}_5-\text{N} \\
\end{array} \right\rbrack\)};
\node (c4) at (6,0) {\(\left\lbrack \begin{array}{c}
\Theta \\
\text{CH-C} \\
\text{O} \\
\end{array} \right\rbrack\)};
\node (c5) at (2,1.5) {\(\text{O}\)};
\node (c6) at (4,1.5) {\(\Theta \)};
\node (c7) at (6,1.5) {\(\Theta \)};
\node (c8) at (2,3) {\(\text{O}\)};
\node (c9) at (4,3) {\(\text{N}\)};
\node (c10) at (6,3) {\(\text{N}\)};
\draw (c1) -- (c2);
\draw (c2) -- (c3);
\draw (c3) -- (c4);
\end{tikzpicture}
\end{center}

\textit{123} \hspace{1cm} \textit{122}
A potential energy, entropy, and activation energy scheme for the simultaneous mechanism proposed by Huisgen \(^{10b}\) should resemble Figure 31 (Process 1).

An alternative description for the mechanism of cycloaddition is one which is described by Figures 30 and 32 (Process 2). In this process the azide is first activated to a bent configuration with a corresponding increase in the potential energy of the reactants. Later in the sequence the bent azide is oriented with respect to the alkene with a corresponding decrease in the entropy of the system. The metastable intermediate which is formed may then proceed to products as indicated in Figure 32'.

As Huisgen \(^{101}\) has pointed out it is not always possible to distinguish between reactive intermediates on the basis of kinetics since the rate determining step is the only one about which information is provided by the determination of overall kinetics and activation parameters. The available kinetic data does not allow one to make a clear distinction between Process 1 and Process 2 as the
Figure 31. Energy Schemes for a Concerted Cycloaddition. (Process 1)
Figure 32. Energy Schemes for a Stepwise Cycloaddition.
(Process 2)
results mentioned above always involved excess alkene which could mask a process like 2 in which the azide is equilibrating with activated azide. (Figure 30).

Process 2 allows an alternative explanation for the reversing sign of the $\rho$ values found in Table 1. For example, if the bending of the azide is the rate determining step then one expects to see the azide with the lowest activation energy reacting most rapidly with a given alkene. This implies a positive $\rho$ value. If, however, the rate determining step is the orientation of alkene with bent azide and transition to products then one would expect the most electron-rich azide to orient with the most electron-deficient alkene with the lowest activation energy. This implies a negative $\rho$ value.

The kinetic arguments presented by Scheiner favor a stabilization of negative charge on $N_1$ in the transition state and also the more rapid formation of the bond between $N_3$ and $C_4$ than between $N_1$ and $C_5$ - resulting in a dipolar transition state like $35$ (see Introduction). An equivalent result may be found in process 2, i.e. an
electron-withdrawing group on $N_1$ would stabilize a negative charge on $N_1$ but it also favours the formation of the bent configuration $3^4d$ (Figure 7) which has a positive terminal nitrogen and hence reacts faster with the alkene double bond.
To obtain more information about the decomposition of triazolines under conditions involving electron impact we studied the mass spectra of the norbornyl triazolines 99-102 and the styryl triazolines 105a-f (Tables 21 and 22). Figures 33 and 34 give general cracking patterns for the two systems of triazolines. A detailed cracking pattern for 105c is given in Figure 22.

The most general observations of the cracking patterns of both systems are that the parent radical ion is normally not observed, the P-28 radical ion is always present corresponding to loss of N₂ from the parent, the P-28 radical ion loses a hydrogen radical to give a P-29 ion, and the P-28 to P-29 process usually exhibits a metastable ion at P-30. Beyond this the cracking patterns become specific to the system being examined.

In the norbornyl systems the P-28 radical ion loses the elements of ethylene to form a P-56 radical ion which in turn loses a hydrogen radical to form a P-57 ion with the accompanying metastable ion at P-58. This type
TABLE 20. RELATIVE INTENSITIES OF MASS SPECTRAL IONS IN THE NORBORNYL TRIAZOLINE SYSTEMS a.

<table>
<thead>
<tr>
<th>Compound:</th>
<th>99</th>
<th>100</th>
<th>101</th>
<th>102</th>
</tr>
</thead>
<tbody>
<tr>
<td>para-Substituent X:</td>
<td>NO₂</td>
<td>Br</td>
<td>CH₃</td>
<td>CH₃O</td>
</tr>
<tr>
<td>Ion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-28</td>
<td>19</td>
<td>16</td>
<td>28</td>
<td>31</td>
</tr>
<tr>
<td>P-29</td>
<td>5</td>
<td>5</td>
<td>13</td>
<td>7</td>
</tr>
<tr>
<td>P-43</td>
<td>1</td>
<td>1</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>P-56</td>
<td>28</td>
<td>28</td>
<td>38</td>
<td>39</td>
</tr>
<tr>
<td>P-57</td>
<td>68</td>
<td>67</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>m*(P-56→P-57)</td>
<td>~1</td>
<td>~1</td>
<td>~10</td>
<td>~20</td>
</tr>
<tr>
<td>P-69</td>
<td>1</td>
<td>2</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>P-83</td>
<td>2</td>
<td>4</td>
<td>11</td>
<td>4</td>
</tr>
<tr>
<td>P-94</td>
<td>18</td>
<td>13</td>
<td>27</td>
<td>25</td>
</tr>
<tr>
<td>P-109</td>
<td>12</td>
<td>14</td>
<td>36</td>
<td>32</td>
</tr>
<tr>
<td>P-136</td>
<td>5</td>
<td>24</td>
<td>70</td>
<td>10</td>
</tr>
<tr>
<td>m/e 93</td>
<td>100</td>
<td>100</td>
<td>41</td>
<td>28</td>
</tr>
</tbody>
</table>

a Direct Probe Injection
Ambient Temp. 80°C.
Ionization Voltage 80V.
Figure 33. Generalized Mass Spectral Cracking Pattern for Norbornyl Triazolines.

**Initial Fragmentation**

\[
\text{Initial Fragmentation} \quad \begin{align*}
\text{P}^+ & \quad \xrightarrow{-e^+} \quad \text{N}^+ & \quad \xrightarrow{-N_2} & \quad \text{N}^+ \\
pXC_6H_4 & \quad & & \quad pXC_6H_4
\end{align*}
\]

**Breakdown**

\[
\begin{align*}
(P-28)^+ & \quad \xrightarrow{-H} & \quad (P-29)^+ \quad (X=\text{CH}_3, m^* = 197) \\
(P-28)^+ & \quad \xrightarrow{-C_2H_4} & \quad (P-56)^+ \quad \xrightarrow{-H/m^*} & \quad (P-57)^+ \\
(P-28)^+ & \quad \xrightarrow{-N_3} & \quad (P-136)^+ \\
(P-28)^+ & \quad \xrightarrow{-Y} & \quad m/e (93)^+ & \quad \text{(strongly favoured by } X - e^- \text{ donating group)}
\end{align*}
\]

- favoured by \( X - e^- \) donating group

- favoured by \( X - e^- \) donating group

- strongly favoured by \( X - e^- \) donating group

- strongly favoured by \( X - e^- \) withdrawing group
### TABLE 21. RELATIVE INTENSITIES OF MASS SPECTRAL IONS IN THE STYRYL TRIAZOLINE SERIES, 105.

<table>
<thead>
<tr>
<th>Compound</th>
<th>105a</th>
<th>105b</th>
<th>105c</th>
<th>105d</th>
<th>105e</th>
<th>105f</th>
</tr>
</thead>
<tbody>
<tr>
<td>para-X</td>
<td>Cl</td>
<td>Br</td>
<td>H</td>
<td>H</td>
<td>Me</td>
<td>MeO</td>
</tr>
<tr>
<td>Ion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(P-28)</td>
<td>9</td>
<td>5</td>
<td>28</td>
<td>18</td>
<td>23</td>
<td>18</td>
</tr>
<tr>
<td>(P-29)</td>
<td>5</td>
<td>2</td>
<td>16</td>
<td>16</td>
<td>14</td>
<td>12</td>
</tr>
<tr>
<td>m*(P-28-P-29)-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(P-42)</td>
<td>6</td>
<td>3</td>
<td>13</td>
<td>18</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>(P-43)</td>
<td>38</td>
<td>24</td>
<td>75</td>
<td>(11)</td>
<td>92</td>
<td>15</td>
</tr>
<tr>
<td>(P-44)</td>
<td></td>
<td></td>
<td></td>
<td>(60)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>m/e(122)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>81</td>
</tr>
<tr>
<td>m/e(106)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>45</td>
<td>-</td>
</tr>
<tr>
<td>m/e(105)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(84)</td>
<td></td>
</tr>
<tr>
<td>m/e(104)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>(16)</td>
<td>100</td>
<td>69</td>
</tr>
<tr>
<td>m/e(91)</td>
<td>8</td>
<td>6</td>
<td>15</td>
<td>11</td>
<td>25</td>
<td>12</td>
</tr>
<tr>
<td>m/e(77)</td>
<td>97</td>
<td>84</td>
<td>93</td>
<td>100</td>
<td>93</td>
<td>100</td>
</tr>
</tbody>
</table>

\[ a \] Direct Probe Injection

Ambient Temp. 80°C.

Ionization Voltage 80V.
Figure 34. Generalized Mass Spectral Cracking Pattern for Styryl Triazolines.

Initial Fragmentation

Breakdown

\[ \begin{align*}
(P-28)^+ & \rightarrow H \rightarrow (P-29)^+ \quad (m^*, P-28 \rightarrow P-29) \\
(P-28)^+ & \rightarrow CH_3^+ \rightarrow (P-43)^+ \\
(P-29)^+ & \rightarrow OCH \rightarrow m/e (104)^+ \quad (C_6H_5 - N=C-H)^+ \\
(P-29)^+ & \rightarrow ONC \rightarrow m/e (91)^+ \quad (C_6H_5CH_2)^+ \\
m/e (104)^+ & \rightarrow NCH \rightarrow m/e (77)^+ \quad (C_6H_5)^+ 
\end{align*} \]
of process is important for all the norbornyl systems but is more important, forming the base ion, where the aryl substituent is electron-donating. The loss of the elements of norbornene (P-94) from the parent radical ion seems to be occurring significantly and is favoured when the aryl substituents are electron-donating groups. The resulting (P-94) ion is simply an azide radical ion. One other process favoured by electron-withdrawing aryl substituents is the P-28 to P-109 transformation which may be loss of a bicyclo (2.1.1) hexane radical. The only process which seems favoured by electron withdrawing aryl substituents is the formation of the norbornyl cation (m/e 93)$^+$. 

In the styryl system the processes are more straightforward because of the presence of many metastable peaks in the spectrum of 105c. There are four processes of importance in the styryl series. The first is the loss of a CH$_3$ radical from the P-28 radical ion to give a P-43 ion. The second is loss of a substituted phenyl carbene to give an ion (m/e 104) corresponding to
C\textsubscript{6}H\textsubscript{5}-N\textsubscript{=}\textsubscript{C}-H. This ion can in turn lose HCN to give an ion (m/e 77)	extsuperscript{+} corresponding to C\textsubscript{6}H\textsubscript{5}. Finally the P-29 ion can lose C\textsubscript{6}H\textsubscript{5}NC to give an ion (m/e 91)	extsuperscript{+} corresponding to the tropylium ion. This last being common in systems with aromatic rings \textsuperscript{102}. 
Figure 35. Mass Spectral Scheme for 1,5-Diphenyl-1,2,3-Δ²-triazoline.
Summary

The results of our studies on the addition of azides to homoconjugated dienes essentially support the commonly accepted theory that azides add to olefins in a concerted 1,3-dipolar cycloaddition.

The results of our studies on the thermal decomposition of triazolines, however, cause us to propose a multi-path mechanism involving as major paths concerted cycloreversions and as minor paths the currently accepted stepwise ionic modes of decomposition.

The predominance of steric retention during aziridine formation from 2 and 10 is most easily explained in terms of either 1) the concerted elimination of nitrogen to form products, or 2) formation of symmetric and antisymmetric CCN intermediates which form products in a stereoselective fashion. Both of these possible routes have been advanced to explain the stereoselectivity observed in pyrazoline decomposition. It is not possible to distinguish which of these routes is correct in the triazoline system with the data available.
Either of these routes is consistent with the high degree of stereoselectivity reported in the photodecomposition of 2 and 10.

On the basis of the products formed in the thermal decomposition of 82, 99-102 (present study) and the results of other studies 27, 55, 62, it seems reasonable that one route of norbornyl triazolone decomposition involves cleavage of the C-C bond of the triazolone ring. Triazolone C-C bond cleavage has been demonstrated in other systems 7, 60, 61. Whether the C-C bond cleavage is concerted with N-N bond cleavage of the triazolone ring (i.e., a cycloreversion) or whether these two bonds cleave independently can not be determined in the norbornyl system with the present data. However, it seems likely that a concerted process operates in those systems where diazoalkanes have been detected by product and spectroscopic analysis 7, 60, 61.

If stepwise cleavage of the N-N and C-C bonds were to occur the diazonium ion thus produced would be expected to lose N₂ very rapidly under the thermolysis conditions. In decalin solution, the products of 82 arising from Wagner-
Meerwein rearrangement (expected of the cation produced upon loss of $N_2$ from the diazonium ion), account for $\sim 1\%$ of the reaction mixture. The relative increase in 88 and 89 for thermal decomposition in more polar solvents may in fact indicate that an ionic mechanism is competing with the concerted ones but that it is a relatively high energy process in non-polar solvents.

By adding cycloreversions to the mechanisms thus far advanced for triazoline thermal decomposition and photodecomposition it is now possible to explain the results of all the triazoline systems studied. The cycloreversions considered to be an integral part of the triazoline decomposition routes contrast well with the symmetry allowed synthetic routes which produce triazolines. The possibility of the synthesis and decomposition being two aspects of a single type of process is especially appealing.
To properly clarify these proposals additional work is required, particularly in the area of kinetics of the thermal decomposition. Much more definitive data is needed and some suggestions have been made in the following section.
Suggestions for Further Study

The mechanism for 1,3-dipolar cycloaddition of azides to alkenes is fairly clearly established as a

\[ \pi_1^s + \pi_2^s \] concerted cycloaddition \(^{10,99}\).

The mechanism for thermal decomposition of triazolines has been proposed as a stepwise ionic process by many authors. This author has proposed a concerted mechanism which operates in a manner dictated by orbital symmetry considerations.

There are some observations that are open to debate in choosing a mechanism for the decomposition of triazolines. 1) The non-linear Hammett correlation found by Huisgen \(^65\) (see Table 3 and Figure 16) does not seem to be consistent with an ionic mechanism. Schreck \(^103\) has pointed out that non-linear concave upward Hammett plots (Figure 16) indicate a change in the mechanism or transition state of the reaction, as one proceeds from electron-donating to electron-withdrawing groups. If the mechanism of triazoline decomposition is constant and ionic
then one expects a linear relationship with a fairly large change in rates over a reasonable change in \( \sigma \). In going from \( \sigma_p - 0.268 \) (pCH\(_3\)O) to 0.778 (pNO\(_2\)) a rate change of less than a factor of 5 was observed for 67. This behaviour is more characteristic of reactions involving isopolar transition states 96. In the norbornyl system (present work) 26 (82, 99-102) over the same range of \( \sigma_p \) the rate of decomposition changed by a factor of only 16, but in the opposite direction. To sort out some of the apparent difficulties it is necessary to examine the kinetics of decomposition for a much larger group of substituents on \( N_1 \) and \( C_4 \) of some simple triazoline systems which do not appear to involve complicating side reactions. A good series may be the parent triazolines such as 124 which appear to give mainly aziridine product.
A study of the kinetics of nitrogen evolution should be attempted initially but a word of caution is in order. In the norbornyl systems such as 82 and 115 the kinetics appear to obey a complex rate law which is tentatively consecutive first order 51. Similarly the kinetics for the styryl cases 105 do not appear to obey a simple rate law. Huisgen 65, however, claims first order kinetics for the cases of 67. Once the order of the reaction is clearly established for 124 then the effect of nitrogen substituents should be clear and the ionic or isopolar character of the mechanism may be considered. A second series of triazolines with varying substituents on C4, such as 125, should be analyzed kinetically to further
establish the order of nitrogen evolution and hence gain an insight into the mechanism of thermal decomposition and determine whether or not the mechanism changes. The triazolines of the 125 series could probably be synthesized by the addition of substituted phenyl diazoalkanes to imines. The conformations of all of these triazolines should be determined to be sure that conformational effects are relatively constant.

2) The observation of a deuterium isotope effect (Table 11) in the case of 105d cannot be explained by a simple ionic hydride shift mechanism concerted with loss of nitrogen. It can be accommodated by a pericyclic reaction. The difference in bond energy between C-H and C-D bonds may cause the \( \sigma^2_s + \sigma^2_s + \sigma^2_s \) pericyclic reaction to be less favoured than the \( \sigma^2_s + \sigma^2_a \) pericyclic reaction. An idea already supported by the reduced amount of imine in 105d thermal decomposition. In the photodecomposition of 105d the reverse product distribution is noted, i.e. the relative amount of imine increases. If the mechanism involves the formation
of symmetric and antisymmetric C-C-N units (by analogy to the trimethylenes proposed by Crawford 97). Then the reversal in relative product distribution because of the method of activation may be explained on the basis of reversal of symmetry requirements and as is expected if orbital symmetry is conserved (i.e., photoactivation has the opposite symmetry requirement to thermal activation in cycloreversion reactions). The kinetic evidence for this is certainly not well established. It would be instructive to study the kinetics and product distributions for some simple triazolines with deuterium on C5.

3) The retention of nitrogen by an intermediate in the thermal decomposition of 115 51 was explained on the basis of a complex ionic cyclic intermediate like 92 or a non-polar intermediate like 93 was postulated. A third alternative which might explain the deviation from first order kinetics may be an equilibrium process between the triazoline and the azide-olefin pair. This cycloreversion could cause a retention of nitrogen in the form of an azide and therefore a deviation from first order kinetics.
To test for this possibility one could observe the infrared spectrum of a triazoline as a function of temperature and see if an azide band is present. The equilibrium should shift as the temperature is changed which may be observable provided allowance is made for decomposition. If such a process was observed it would be an example of the third type of cycloreversion reaction that is allowed for this type of system.

4) To verify the mechanisms of decomposition a quantitative N.M.R. study should be performed to establish the rate law governing the disappearance of triazoline. Since we were able to detect an intermediate by infrared methods it should be possible to quantitatively analyze the reaction by this method. In addition to monitoring the triazoline disappearance it is possible to monitor the rate of appearance of products by N.M.R. and establish the rate laws for their appearance.
Having accumulated data for the processes described above it should be possible to clearly show if there are intermediates involved in the mechanism. The data reduction would probably require the use of a computer to perform iterative procedures but if all of the above suggested evidence was available the data reduction should not be difficult for a competent programmer.
Experimental

General

C, H and N analyses were performed by Mr. Alfred Bernhardt, Microanalytical Laboratory, Mulheim, West Germany.

Infrared spectra were recorded on a Unicam SP 200, Perkin-Elmer 457, or Beckman IR 12 spectrophotometers.

Nuclear Magnetic Resonance spectra were recorded on a Varian A-56/60 spectrometer with line positions being reported in $\delta$ units using TMS as an internal standard ($\delta$ 0).

Melting Points were obtained on a Fisher-Johns melting point apparatus and are uncorrected.

Ultraviolet spectra were recorded on a Unicam SP 800 or a Cary 14 spectrophotometer.

Gas-Liquid partition chromatography was performed on Varian Aerograph Autoprep A-705 and Hi-Fy gas chromatography units. Planimeters or disc integrators were used to obtain peak areas. Calibration of peak areas was obtained by injecting known amounts of a sample in question or of a related isomer. The following columns were used: column A, 1.5 ft. x 0.25 in., containing 20%
SE Silicon oil stationary phase on 60-80 mesh Chromosorb W support; column B, 6 ft. x 0.25 in., containing 20% XF-1150 Cyano Silicon oil stationary phase on 60-80 mesh Chromosorb W support; column C, 5 ft. x 0.50 in., containing packing identical to column B; column D, 5 ft. x 0.125 in., containing packing material identical to column B; column E, 20 ft. x 0.375 in., containing 30% SE Silicon oil stationary phase on 40-60 mesh Chromosorb W support; column F, 5 ft. x 0.25 in., containing Carbowax 20M on 60-68 mesh Chromosorb W support.

Mass Spectra were recorded on an Hitachi Perkin-Elmer RU-6 mass spectrometer.

Preparation of 3-phenyl-3,4,5-triazotricyclo (5.2.1.0^2,6) dec-4-ene. 82.

The phenyl azide adduct of bicyclo (2.2.1) hept-2-ene was prepared in the usual manner 16 and had m.p. 99-100°; recorded 16 m.p. 101-102°. The N.M.R. spectra confirmed the structure and purity of the adduct 53.
Preparation of 3-phenyl-3,4,5-triazotricyclo (5.3.1.0²,6) undec-4,8(9)-dienes, 81.

A solution of 0.5 g. of phenyl azide and 0.5 g. of bicyclo (3.2.1) octa-2,6-diene in 25 ml. of petroleum ether (b.p. 60-110°) was allowed to stand for several days. The excess phenyl azide was removed under vacuum and the crystalline sample was analyzed by N.M.R. Recrystallization from CHCl₃-petroleum ether (b.p. 30-60°) gave a white solid in 85% yield, m.p. 67.5-69°. The N.M.R. analysis of the recrystallized product (Figure 19) revealed no detectable change in 8₁ₐ; 8₁₈ had occurred during the recrystallization.

Anal. Calcd. for C₁₄H₁₅N₃: (M)⁺ 225. Found (mass spectrometry): (M)⁺ 225; (M-28)⁺ 197.

The p-nitrophényl analogue of 8₁ had m.p. 168-90°; N.M.R. (pyridine) δ 1-2 (m, 4H), 2-3 (m, 8H), 4.0-5.2 (m, 2H Table 8 ) and 5.35-6.3 (m, 2H).

Preparation of 3-phenyl-8(9)-methylenec-3,4,5-triazotricyclo (5.2.1.0²,6) dec-4-enes, 83.

The phenyl azide adduct of 5-methylene-2-norbornene
(K and K Laboratories, Inc.) was prepared in the usual manner by reaction at room temperature for several days. The crude product showed the same \(83a:83b\) as that (70%) recrystallized from CHCl\(_3\)-petroleum ether (b.p. 30-60\(^\circ\)) m.p. 60.5-62\(^\circ\).

Anal. Calcd. for C\(_{14}\)H\(_{15}\)N\(_3\): (M\(^+\)) 225. Found (mass spectrometry): (M\(^+\)) 225; (M-28\(^+\)) 197.

The p-nitrophenyl analogue of \(83\) had m.p. 159-160\(^\circ\) (decomposition) N.M.R. (pyridine) \(\delta\ 1.14\) (AB, J=11 Hz., 2H\(_{10}\)), 1.83-2.35 (b, 2H\(_8\)(g)), 2.42-2.92 (m, 2H\(_{BH}\)), 3.12 (m, 1H\(_2\)), 3.82 (d, J=9 Hz., 1H\(_6\)), 4.80 and 5.08 (H\(_2\)C=C\_\). The AB quartets due to H\(_2\) and H\(_6\) of isomers a and b were also uncompletely resolved in benzene, chloroform.

**Preparation of 84**

The phenyl azide adduct of *endo*-dicyclopentadiene (Aldrich Chemical Co.) was prepared by reaction at room temperature for several days. Recrystallization of the crude product gave 75% \(84\), m.p. 117-118\(^\circ\) (lit. 72 127-128\(^\circ\).
(MeOH); for N.M.R. see Table 8.

Anal. Calcd. for C$_{13}$H$_{17}$N$_3$: (M)$^+$ 251. Found (mass spectrometry): (M)$^+$ 251; (M-28)$^+$ 223.

The p-nitrophenyl analogue of 84 had m.p. 183-184$^\circ$ (decomposition); N.M.R. (CHCl$_3$) δ 1.28 (AB, J= 11 Hz., 2H$_3^1$), 2.2-2.8 (m, 4H), 2.8-3.5 (m, 2H$_{BH}$), 3.72 (d, J=9.2 Hz., 1H$_2^1$), 4.62 (d, J=9.2 Hz., H$_{6b}$), 4.67 (d, J=9.2 Hz., H$_{6a}$), and 5.72 (s, 2H).

Isolation of products of pyrolysis of 82 in decalin.

A soln. of 16 g. of 82 in 600 ml. decalin was heated for 5 hr. at 160$^\circ$ after which time N$_2$ evolution ceased. The solvent was removed at 40$^\circ$ under vacuum (2 mm.). Gas chromatographic analysis of the pyrolysate on column B (injector 180$^\circ$, column 160$^\circ$) gave the product distribution recorded in Table 9. The five components were separated by preparative gas chromatography on column E (injector 180$^\circ$, column 160$^\circ$). The first component of the pyrolysate to be eluted was 87 which was isolated as an oil, b.p. 80$^\circ$ (0.10 mm.). (Found:
C, 84.00; H, 7.99. Calc. for C_{13}H_{15}N: C, 84.24; H, 8.16%.

The second component to be eluted from the column was 85. This component was isolated as an oil, b.p. 80° (0.10 mm.). (Found: C, 83.89; H, 8.08. Calc. for C_{13}H_{15}N: C, 84.28; H, 8.16%). This component was identical in all respects with the product of photolysis of 82 which is described below. The anil, 86, was eluted third and was identical with an authentic sample prepared as described below. The component eluted fourth was 88. This component was distilled at 100° (0.1 mm.) and melted at room temperature (27°). (Found: C, 84.11; H, 8.22; N, 7.54. Calc. for C_{13}H_{15}N: C, 84.28; H, 8.16; N, 7.56%). The last component to be eluted was 89. This nortricyclene derivative was isolated as an oil, b.p. 97° (0.13 mm.). (Found: C, 83.78; H, 8.11; Calc. for C_{13}H_{15}N: C, 84.28; H, 8.16%). These latter two components (88 and 89) were prepared in larger quantity by the treatment of the triazoline, 82, with acid as described below. The isolated components were tested for purity by thin layer chromatography in several solvent systems.

Each component isolated was reinjected and found to be stable under the gas chromatographic conditions. In addition
each component was tested under the reaction conditions and found to be unchanged.

**Preparation of 3-phenyl-3-azatricyclo (3.2.1.0²,⁴ exo) octane (85) by photolysis of 82.**

A soln. of 10.0 g. of 82 in 250 ml. ether was irradiated in a quartz vessel with a 200 watt Hanovia lamp for 1 hr. The ether was evaporated and the product was vacuum distilled, b.p. 84.5-85.0° (0.11 mm.) (reported b.p. 90° at 0.06 mm.).

The exo-aziridine, 85, was isolated in 75% yield. Analysis of both the crude photolysate and the distilled product by T.L.C. and by gas chromatography on column A (injector 180°, column 163°) and column B (injector 180°, column 163°) indicated a single component.

**Preparation of N-phenyl-bicyclo (2.2.1) hept-2-imine, 86.**

A soln. of 2.6 g. bicyclo (2.2.1) heptane-2-one and 2.1 g. aniline in 10 ml. benzene containing a catalytic amount (30 mg.) of p-toluensulfonic acid was refluxed for 6 hr. The benzene was removed and the product, 86, was
distilled under reduced pressure, b.p. 83.0-85.5° (0.10 mm.) (reported b.p. 85.93° at 0.03 mm.). Analysis of the distillate by gas chromatography of column B (injector 180°, column 160°) revealed a single component which was identical in all respects to the imine, 86, isolated from the pyrolysis of 82.

**N.M.R.** 6 7.4-6.6 (5H), 2.85 (1H), 2.47 (1H), 2.22 (1H) and 2.0-1.2 (7H).

**Preparation of 2-exo-thiophenoxy-2-endo-N-phenylaminobicyclo (2.2.1) heptane, 95.**

To 4.3 ml. of a 0.127 N potassium thiophenate in t-BuOH was added 0.2022 g. of 87. The reaction was refluxed for 50 hr. then passed onto 20 ml. water and the resulting mixture neutralized by the addition of dry ice. The suspension was extracted with ether which was dried over MgSO₄, filtered and evaporated. The crude ether extract (0.6 g.) was chromatographed on 3 g. of Silica Gel. Elution with petroleum ether (b.p. 30-60°) gave 100 mg. pure 95 as an oil, b.p. 180° (1.0 mm.). (Found: C, 77.32; H, 7.00. Calc. for C₁₉H₁₉NS: C, 77.26; H, 7.17%.)
Raney nickel reduction of 95.

A soln. of 0.050 g. of 95 in 2 ml. 2-propanol containing 1 g. W-2 Raney Ni was stirred at room temperature over night. The solution was filtered and the catalyst washed with 2-propanol. The alcohol was evaporated and the residue was analyzed by T.L.C. and gas chromatography on columns A and B (injector 200°, column 185°). Analysis by these techniques revealed a single component which behaved in a fashion identical to 96, prepared from 86 as described below. Samples of 96 prepared from 87 and 86 exhibited identical N.M.R. and I.R. spectra.

Preparation of 2-endo-N-phenylaminobicyclo (2.2.1) heptane, 96, from 86.

An etheral soln. of 2.0 g. of 86 was treated with excess LAH. The soln. was stirred for 1 hr. after which the reaction was poured onto water. The ether phase of the reaction mixture was separated, dried over MgSO₄, filtered and evaporated. The ether extract (2.34 g.) showed one major component by T.L.C. This crude extract
was chromatographed on 60 g. of Silica Gel using petroleum ether (b.p. 30-60°) and benzene as eluent. The product, 96, was isolated as an oil, b.p. 85° (1.0 mm.). (Found: C, 83.53; H, 9.31. Calc. for C\textsubscript{13}H\textsubscript{17}N: C, 83.37; H, 9.15%).

Preparation of 7-syn-N-phenylaminobicyclo (2.2.1) hept-2-ene, 88, and 3-N-phenylaminonortricyclene, 89.

A soln. of 3 g. of 82 in 60 ml. acetone was treated in a dropwise manner with 5 ml. 2N HCl at room temperature. The reaction was neutralized with saturated aqueous Na\textsubscript{2}CO\textsubscript{3}, concentrated in vacuo and extracted with ether. The ether extract was dried over MgSO\textsubscript{4}, filtered and the ether evaporated. The resulting product mixture was chromatographed on 200 g. of neutral alumina. Elution with petroleum ether:ether (9:1) gave, in the initial fractions, pure 88. Continued elution with this eluent gave a mixture of 88 and 89 which was separated into the pure components by preparative gas chromatography on column E (injector 230°, column 215°). Elution of the alumina column with petroleum ether:methanol (8:2) gave syn-7-N-phenylamino-2-exo-bicyclo
(2.2.1) heptanol. This substance was identical with an authentic sample prepared from the exo aziridine, 85, by the method of Huisgen 53. The amount of each product was determined by gas chromatography of the crude ether extract (Table 9).

**Preparation of 3-p-nitrophenyl-3,4,5-triazatricyclo (5.2.1.0) dec-4-ene, 99.**

The p-nitrophenyl azide adduct of bicyclo (2.2.1) hept-2-ene was prepared in the usual manner 16 and had m.p. 164.5-165.5°; recorded 16 m.p. 164-165°.

Anal. Calcd. for $C_{13}H_{14}N_4O_2$: (M)$^+$ 258. Found (mass spectrometry): (M-28)$^+$ 230.

**Preparation of 3-p-bromophenyl-3,4,5-triazabicyclo (5.2.1.0) dec-4-ene, 100.**

The p-bromophenyl azide adduct bicyclo (2.2.1) hept-2-ene was prepared in the usual manner 16 and had m.p. 121.6-122.6°; recorded 16 m.p. 123-124°.
Anal. Calcd. for $\text{C}_{13}\text{H}_{14}\text{N}_3\text{Br}$: $(\text{M})^+ \ 291, 293$.

Found (mass spectrometry): $(\text{M}-28)^+ \ 263, 265$.

Preparation of 3-p-tolyl-3,4,5-triazatricyclo (5.2.1.0) $\text{dec-4-ene, 101}$.

The p-tolyl azide adduct of bicyclo (2.2.1) hept-2-ene was prepared in the usual manner $^{16}$ and had a m.p. of $79-80.5^\circ$; recorded $^{16}$ m.p. $79-80^\circ$.


Preparation of 3-p-anisyl-3,4,5-triazatricyclo (5.2.1.0) $\text{dec-4-ene, 102}$.

The p-anisyl azide adduct of bicyclo (2.2.1) hept-2-ene was prepared in the usual manner $^{16}$ and had a m.p. of $89.3-90.3^\circ$; recorded $^{16}$ m.p. $90-91^\circ$.

Kinetic determinations of the pyrolysis of triazolines.

The extent and rates of pyrolysis of some of the triazolines studied were determined by measurement of \( \text{N}_2 \) gas evolution by two methods. (See Appendix 2).

**Method 1**

For solutions, the temperature of the reaction was regulated by immersion of the reaction vessel in a five gallon oil bath maintained at constant temperature \( (\pm 0.2^\circ) \). The measurements of gas evolution were made with the aid of a thermostated \( (\pm 0.05^\circ \text{C.}) \) 100 ml. gas burette attached by a 2 mm. glass capillary to the reaction vessel. A typical kinetic determination was as follows: The solvent (30 ml.) was placed in the reaction vessel and the solution was allowed to equilibrate with stirring for 10-20 minutes. During this time the system was flushed continuously with dry \( \text{N}_2 \). The triazoline (0.002 mole to 0.003 mole) was then injected into the stirred solution as a solid plug or as a concentrated solution and the system was sealed. The zero reading on the gas measuring burette was taken and the volume and pressure of \( \text{N}_2 \) collected was
recorded at intervals until >80% reaction. Plots of \( \log_e (V_\infty/V_\infty-V_t) \) versus \( t \) gave smooth lines which exhibited divergence from linearity in the initial and latter stages of reaction. The \( t_1/2 \) values from various determinations are recorded in Tables 18 and 19 (see Figure 27).

**Method 2**

For neat samples, the temperature of the reaction vessel was regulated by placing it in an aluminum block maintained at constant temperature (± 0.5°C). The only other difference from method 1 is the very small reaction vessel which is not stirred.

To test that the system was not introducing error by either method, blank determinations were carried out. The blanks were mechanically identical to the normal runs, only the triazoline was excluded.

**Estimation of error in the kinetics of nitrogen evolution.**

In the plot of \( Y = \log_e (V_\infty/V_\infty-V_t) \) against time the expected error is represented by \( \Delta Y/Y \).

\[
\frac{\Delta Y}{Y} = \frac{\Delta V_\infty}{V_\infty} + \frac{\Delta V_\infty}{V_\infty - V_t}.
\]
Where the error in $V_\alpha$ or $\Delta V_\alpha = \pm 0.1$ ml. and the error in $V_t$ or $\Delta V_t = \pm 0.2$ ml. is based on gravimetric and volumetric measurements respectively. If one considers a typical run in which 50 ml. of nitrogen are evolved then an estimate of the errors in the $\log e$ plot are:

at 0% rxn $\Delta Y/Y = 0.008$

20% $= 0.009$

50% $= 0.014$

98% $= 0.3$

The average error for this type of plot in the range 0-50% reaction is $\sim 0.01$ which is approximately indicated in Figure 27 by the length of the vertical bar of the + markers.

A sharp break in the graph (Figure 27) was noticed about 10-15 minutes after the reaction had started ($\leq 5\%$ reaction). It was assumed that the system had achieved equilibrium by this time. From this point onward a fairly smooth curve was apparent that was concave upward, an indication that the nitrogen was being evolved more rapidly with increasing time. In the range of 5% to 43% reaction (a period of about 425 minutes) a linear graph could not be fitted to the data points within the limits of error.
calculated above. In other kinetic runs the divergence from linearity was even more pronounced than that represented by Figure 27, however, the nature of the divergence was the same.

The data used to plot Figure 27 was reduced by a simple linear regression analysis program which plotted the results on a Calcomp Plotter. The program was designed to correct for pressure and temperature variations of the $N_2$ volume recorded at each point. A hand calculation of one set of data indicated that the program was functioning correctly. The results for Figure 27 are given below in Table 22.
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<th>Time (min)</th>
<th>Volume (ml.)</th>
<th>log \left( \frac{\text{V}_{0}-\text{V}<em>t}{\text{V}</em>{0}} \right)</th>
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<tr>
<td>5.33</td>
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<tr>
<td>103.00</td>
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<td>139.00</td>
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<td>0.2508</td>
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<td>43.17</td>
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Pyrolysis of $^{82}$ and $^{103}$ in an I.R. hot cell.

In this study a variable temperature I.R. cell (VLT-2) manufactured by the Research and Industrial Instruments Co., London, England) was used. The cell was equipped with potassium bromide windows spaced 0.020 in. apart. The temperature of the cell was controlled by the rheostat setting (± 5°C.) of the PS-1 power supply.

In a typical experiment the sample cell was filled with 0.5-1.0 gm. of the appropriate triazoline and sealed. The cell holder was placed in the sample beam of a Beckman IR 12 spectrophotometer and heated to the required temperature. Once the cell holder had equilibrated the cell was inserted as quickly as possible and the IR 12 was set to repetitively scan the 2020-2450 cm. $^{-1}$ region of the spectrum. The reaction was assumed to start once the sample had melted. This could be observed visually and by the very sudden change in the optical density of the I.R. cell. The scanning was continued for at least five hours. In both cases an absorption peak appeared in the I.R. a short time after the reaction started, grew to maximum intensity at approximately
30 minutes and then slowly disappeared as the reaction progressed. It was not possible to calibrate the intensity of the instrument readings absolutely, however, in both cases the signal to noise ratio was at least $10^1$ for the maximum absorptions recorded.

In the case of 82 the cell was heated to $165^\circ$C. ($\pm 5^\circ$) and an absorption at 2175 cm.$^{-1}$ was observed which rose to a maximum at 30 minutes after the reaction commenced. This absorption was reproduced in three separate experiments.

In the case of 103 the cell was maintained between 200 and $235^\circ$ C. during which time an absorption at 2150 cm.$^{-1}$ appeared, rose to a maximum at approximately 31 minutes and disappeared slowly for a period in excess of one hour. This absorption was reproduced in a separate experiment.

To check for cell contamination the same experiments were performed on the empty cell and with the cell containing decalin. No absorptions were recorded in either case.
General Procedure for Synthesizing Styryl Triazolines, 105^4.66

A solution of 5 g. of the appropriate p-substituted styrene (Borden Chemicals) was reacted with excess phenyl azide by refluxing in 10 ml. of spectrograde ethyl acetate (Fisher or Matheson Coleman Bell) for four hours. On cooling the solution a precipitate usually formed which was then filtered off and washed with Na-dried 30-60 petroleum ether. The precipitate was dried by placing it under vacuum. A second crop of crystals could be obtained by pumping off the solvent and starting materials under high vacuum. These were washed with petroleum ether and dried as before. The first crop of crystals were invariably white and had very sharp melting points (Table 11). They were used without further treatment. The N.M.R. spectra in pyridine-d5 showed the absence of any impurities and gave typical ABC spectra (Table 16). The yields of product ranged from 15-50% and tended to be lower for the halogen substituted styrenes probably due to more facile decomposition of the
product triazolines. The mass spectra indicated the correct molecular weight for the adducts formed (Table 22).

Preparation of 1-phenylethanol-1-d

1.9 g. (0.045 moles) of LiAlD₄ (I.C.N.) was added to 40 ml. Et₂O (freshly distilled from LiAlH₄) and kept under a dry nitrogen atmosphere while stirring for one hour. To this white slurry was added 16.4 g. (0.137 moles) of acetophenone (Matheson Coleman Bell - freshly distilled and fractionated at 203.0-203.5°C.). The solution was stirred overnight under a dry nitrogen atmosphere. The work-up involved the cautious addition of distilled H₂O in sufficient quantity to make an amorphous mass of the Li salts. The Et₂O solution was removed from the sludge and the Et₂O distilled off at 33°/725.5 mm. The product was recovered in 69% yield (11.6 g.) by distillation at 61°/~1 mm. (lit. 51-4° at 0.5 mm.). G.l.p.c. analysis at 230°C. on column F showed a single component. I.R. (film) 3410 cm⁻¹ (OH).
2150 cm\(^{-1}\) (C-D) \(^{80,81}\) N.M.R. (CDCl\(_3\)) \delta 1.34 (bs, 3H),
\delta 3.16 (bs, 1H), \delta 7.17 (s, 5H). The addition of D\(_2\)O
caused the hydrogen signal at \delta 3.16 to disappear and a
DOH to appear.

Anal. Calcd. for C\(_8\)H\(_9\)DO: (M\(^+\)) 123. Found (mass
spectrometry): (M\(^+\)) 123.

Preparation of \(\sigma\)-Deuteriostyrene \(^{105,106}\)

To 11.6 g. (0.095 moles) of 1-phenylethanol-1-d
was added 9.8 mg. of p-benzoquinone (Matheson, Coleman
& Bell, Practical Grade) and 12 mg. of I\(_2\) (ACS grade
Allied Chemical). The solution was slowly heated to
270°C. and the distillate was collected over 4 mg. of
sym-trinitrobenzene (Eastman). Distillation was steady
from about 125°C. when it slowed additional I\(_2\) was
added. 1.5 ml. H\(_2\)O and 8.5 ml. of an organic phase
was collected. The distillate was taken up in Et\(_2\)O,
washed with 10% Na\(_2\)S\(_2\)O\(_4\) solution, washed with distilled
H\(_2\)O, and dried over MgSO\(_4\). The Et\(_2\)O was removed on a
rotary evaporator to yield 6.7 g. of product. G.I.p.c.
analysis at 230°C on column F indicated a mixture of 10% starting alcohol and 90% of a product with the same retention time as styrene. I.R. (film) 3030 cm⁻¹ (aromatic C-H), 3060 and 3080 cm⁻¹ (vinyl C-H), 2235 cm⁻¹ (vinyl C-D) ① N.M.R. (CDCl₃) δ 5.15 (m, 1H), δ 5.64 (complex t, J_DH(trans) = 2.5 Hz, 1H), δ 7.23 (m, 5H).


Preparation of 1,5-Diphenyl-5-d-1,2,3-三角₃-triazoline, 105d.

4.0 g. (0.034 moles) of 90% pure o-deuteriostyrene was added to 6.5 g. (0.055 moles) of phenyl azide in 10 ml. of ethyl acetate. The solution was refluxed for 4 hr. and 15 min. then cooled to room temperature and the white fluffy crystals were filtered off to yield 0.45 g. of triazoline. A second crop of 0.65 g. was recovered by removing some of the solvent. The two crops were washed with 30-60 petroleum ether and dried under vacuum. The total yield of pure 105d was 14% (1.1 g.) based on
starting alkene. M.p. 126-126.6°C; N.M.R. (pyridine-d5)
δ 4.28 (AB, J=-17.0 Hz., J_DH = 0.7 Hz., 1H), δ 4.86 (AB, J=-17.0 Hz., J_DH = 1.5 Hz., 1H).

Anal. Calcd. for C_{14}H_{12}N_3: (M)^+ 224. Found (mass spectrometry): (M-28)^+ 196.

Preparation of 1-Phenylacetylideneaniline, 107c

A solution of 13.5 g. (0.112 moles) of acetophenone (Matheson, Coleman & Bell), 10.4 g. (0.113 moles) of aniline (Fisher reagent), and a few grains of para-toluenesulphonic acid in 300 ml. of toluene was refluxed under a Dean-Stark trap until no further H_2O was being azeotroped out of solution. The toluene was distilled off leaving 25.2 g. of a yellow crystalline material. This residue was fractionated and 10.5 g. (b.p. 143-155°C.) was used for G.L.I.p.c. analysis. The gas chromatogram (using Column P at 230°C.) showed a single component. I.R.(film) 1635 cm.{-1} (C=N) 80; N.M.R. (CDCl_3) δ 2.14 (s, 3H).
Preparation of cis-1,5-Diphenyl-4-methyl-1,2,3-$\Delta^2$-triazoline, 9 \textsuperscript{4,66}.

9 was synthesized from cis-$\beta$-methylstyrene, 2, (K and K Laboratories) in 20% yield by the same procedure used to synthesize 10. \textsuperscript{5} N.M.R. \textsuperscript{66} (pyridine-d$_5$) $\delta$ 1.03 (d, $J=6.7$ Hz., 3H), $\delta$ 4.85, $\delta$ 5.12 (complex, $J=6.7$ Hz., $J=12$ Hz., 2H).

Anal. Calcd. for C$_{15}$H$_{15}$N$_3$ (M)$^+$ 237. Found (mass spectrometry): (M)$^+$ 237, (M-28)$^+$ 209, (M-29)$^+$ 208, (m*; 209$\rightarrow$208) 207.

Preparation of trans-1,5-Diphenyl-4-methyl-1,2,3-$\Delta^2$-triazoline, 10 \textsuperscript{4,66}.

10 was synthesized from trans-$\beta$-methylstyrene, 8, (K and K Laboratories) in 15% yield by the same procedure used to synthesize 10. \textsuperscript{5} N.M.R. \textsuperscript{66} (pyridine-d$_5$) $\delta$ 1.37 (d, $J=6.8$ Hz., 3H), $\delta$ 4.25, $\delta$ 4.45 (complex, $J=6.8$ Hz., $J=8.5$ Hz., 2H).
Isolation of Thermal Decomposition Products of 2 and 10.

The cis-aziridine, 76, was isolated from the crude pyrolysates of 2 by preparative G.L.P.C. on column F at 230°C. Reinjection of a collected sample showed a single component. N.M.R. (CDCl₃) δ 1.10 (d, J=5.6 Hz., 3H), δ 2.47 (quintet (unresolved d of quartets), J=5.6 Hz., J=6.5 Hz., 1H), δ 3.22 (d, J=6.5 Hz., 1H); N.M.R. (pyridine-d₅) δ 1.10 (d, J=5.6 Hz., 3H), δ 2.49 (quintet (unresolved d of quartets), J=5.6 Hz., J=6.6 Hz., 1H), δ 3.30 (d, J=6.6 Hz., 1H). (Lit. 66 N.M.R. (CDCl₃) δ 3.20 (d, J=6.2 Hz., 1H)).


The trans-aziridine, 77, was isolated from the crude pyrolysate of 10 in the same manner as 76. Reinjection of a sample showed a component 95+% with a trace of a component with the same retention time as 76. The N.M.R. indicated that 77 was contaminated with 76 (≤ 5%). N.M.R. (CDCl₃) δ 1.11 (d, J=5.7 Hz., 3H).
δ 2.50 (d of quartets, J=5.7 Hz., J=3.0 Hz., 1H),
δ 2.88 (d, J=3.0 Hz., 1H); N.M.R. (pyridine-d5) δ 1.04
(d, J=5.7 Hz., 3H), δ 2.48 (d of quartets, J=5.7 Hz.,
J=2.8 Hz., 1H), δ 2.92 (d, J=2.8 Hz., 1H).

Anal. Calcd. for C₁₅H₁₅N: (M)+ 209. Found
(mass spectrometry): (M)+ 209, (M-1)+ 208, (m+; 209→208)
207.

Preparation of 1-Phenylpropylideneaniline, 75.

Propiophenone was synthesized in good yield (70%) by Friedel-Crafts acylation of benzene with propionyl chloride (freshly prepared in 69% yield, b.p. 78.5-82.0°C.
at 733 mm. Hg, by treatment of propionic acid with SOCl₂).
I.R. (film) 1685 cm⁻¹ (ϕ - ς = 0) 80; N.M.R. (CDCl₃)
δ 1.18 (t, J=7.3 Hz., 3H), δ 2.91 (q, J=7.3 Hz., 2H),
b.p. 218°C.

A solution 66 of 8 g. (0.06 moles) of propiophenone, 5.6 g. (0.061 moles) of aniline (Fisher reagent), and a trace of para-toluenesulphonic acid in 300 ml. toluene was refluxed for 36 hr. under a
Dean-Stark trap until no further \( \text{H}_2\text{O} \) was being azeotroped out of solution. The toluene was distilled off at atmospheric pressure leaving 12.2 g. of crude orange crystalline product. 6 g. of the crude product was fractionated under vacuum and the center fraction (3 g., b.p. 120-125°C./1 mm.) was used for G.l.p.c. analysis. The gas chromatogram (using Column F at 230°C.) showed a single component, 75. I.R. (film) 1620 cm." (C=N) \( \nu \); N.M.R. (CDCl\(_3\)) \( \delta \) 1.05 (t, \( J=7.5 \) Hz., 3H), \( \delta \) 2.64 (q, \( J=7.5 \) Hz., 2H).

Anal. Calcd. for \( \text{C}_{15}\text{H}_{15}\text{N} \): (M)\(^+\) 209. Found (mass spectrometry): (M)\(^+\) 209, (M-1)\(^+\) 208, (m\(^*\); 209,208) 207, (M-29) 180.

Preparation of Imine of 2-Phenylpropionaldehyde, 108

A solution of 13.5 g. (0.1 moles) of 2-phenylpropionaldehyde (Aldrich, 90% ; I.R. (film) 1720 cm." (C=O) \( \nu \); 2720, 2820 (H-C=O) \( \nu \); N.M.R. (CDCl\(_3\)) \( \delta \) 1.41 (d, \( J=7.0 \) Hz., 3H), \( \delta \) 3.60 (d of quartets unresolved, \( J=7.0 \) Hz., 1H), \( \delta \) 7.23 (m, 5H), \( \delta \) 9.58
(d, J=1.7 Hz., 1H).) and 10.0 g. (0.11 moles) of aniline in 300 ml. toluene was refluxed under a Dean-Stark trap until no more H₂O was azeotroping out. The toluene was distilled off and 20.7 g. of a yellow oil was recovered. The gas chromatogram (run on Column P at 230°C.) showed the presence of starting aldehyde, aniline and a very broad peak accounting for >95% of the mixture.

I.R. (film) 80 3430 cm⁻¹ (N-H), 1650 (C=N), 1600 (conj. C=C), 1500, 1510 (conj arom.), 1320, 1265 (C-N-Ø). The N.M.R. spectrum indicated three sets of peaks in the ratio of 1:4.2:1.5 (in the direction of decreasing field) which are due to methyl groups and which indicate three discrete compounds. N.M.R. (CDCl₃) 1) δ 1.50 (d, J=7.0 Hz.), δ 3.74 (d of quartets, J=7.0 Hz., J=2.1 Hz.), 2) δ 1.94 (d, J=1.3 Hz.), 3) δ 2.01 (d, J=1.0 Hz.).
The photodecomposition of several of the 105 triazolines was carried out in quartz and in pyrex N.M.R. tubes. The solvent used for irradiation in quartz was CD$_3$CN and for irradiation in pyrex, CDCl$_3$. The irradiation source was a 250 W. Hanovia Medium Pressure Hg Arc lamp. The lamp was placed in a quartz cooling jacket and the N.M.R. tube was placed about 1 inch from the lamp outside the cooling jacket. The lamp was left on and samples were placed in front of it. The total irradiation time was 90 minutes for any given sample. To check for possible intermediates the samples were removed from the source at intervals and checked by N.M.R. before the irradiation was complete. No observable changes in product distribution were found as a function of time of irradiation.
Appendix 1
Figure 36. Actual N.M.R. spectrum for 105c.
Appendix 2
Capillary Manometer tests for pressure equivalence between rxn. vessel and room (filled with glycol).

Three way Stopcock

Ball Joint

Ball Joint

2 mm. Capillary

Calibrated Burettes

Hg Reservoir

Hg

To reaction vessel (See Figures 39 and 40).

Thermostated H₂O jacket

Figure 38. Nitrogen Evolution Measuring Apparatus.
Figure 39. Reaction Vessel for N₂ Kinetics Measurements of Solutions.
Figure 40. Reaction vessel for $N_2$ Kinetics Measurements of Solids.
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