PYROLYSIS AND PHOTOLYSIS OF

\textit{cis} AND \textit{trans}-3,5-DIMETHYL-3-ACETYL-\(\Delta^1\)-PYRAZOLINE AND
\textit{cis} AND \textit{trans}-3,5-DIMETHYL-3-CARBOMETHOXY-\(\Delta^1\)-PYRAZOLINE

by

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We accept this thesis as conforming

to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

July, 1964
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Department of CHEMISTRY

The University of British Columbia, Vancouver 8, Canada

Date August 6, 1967
ABSTRACT

The thermal and photolytic decomposition of cis and trans-3,5-dimethyl-3-acetyl-$\Delta^1$-pyrazoline have been found to give six products. They have been separated and identified as 2,3,5-trimethyl-$\Delta^2$-dihydrofuran, cis and trans-1,2-dimethyl-1-acetylcyclopropane, cis and trans-3-methyl-3-hexen-2-one and 3-methyl-4-hexen-2-one. The formation of cyclopropanes by photolysis showed some degree of stereospecificity. Both pyrolysis and photolysis yielded olefins with high degree of stereospecificity. 2,3,5-Trimethyl-$\Delta^2$-dihydrofuran was a major product from the decomposition of cis-3,5-dimethyl-3-acetyl-$\Delta^1$-pyrazoline only. Pyrolysis gave a higher ratio of olefins to cyclopropanes than photolysis. These decomposition reactions gave results analogous to those of cis and trans-3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline.

The product compositions from both the pyrolysis and photolysis of cis and trans-3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline have been found to show a small and regular influence of the solvent and this has been related to the dielectric constant of the solvent. Pyrolysis and photolysis gave an olefin to cyclopropane ratio of 57:43 and 21:79, respectively, in formamide, and 7:93 and 5:95, respectively, in cyclohexane.

A small kinetic solvent effect has been observed for the pyrolysis of 3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline. The rate of pyrolysis as followed by the rate of nitrogen evo-
lution has been found to decrease for the following series of solvents: di-n-butyl ether, tetralin, nitrobenzene and formamide. These rates were all within a factor of three. The absence of rate enhancement in a solvent of high dielectric constant has been used as an argument against an ionic intermediate in these reactions.

Liquid phase photolysis of trans-3,5-dimethyl-3-carbomethoxy-Δ¹-pyrazoline at various temperatures ranging from -55° to 58° did not show appreciable change in the product compositions attributable to the influence of temperature. The solvent temperature therefore does not effect the amount of quenching of any "hot" intermediate.

Photolysis and pyrolysis of cis and trans-3,5-dimethyl-3-carbomethoxy-Δ¹-pyrazoline under identical conditions did not give the same product composition. This suggested the two reactions do not have a common intermediate.

No isomerization between the cis and trans-3,5-dimethyl-3-carbomethoxy-Δ¹-pyrazolines has been observed as shown by the partial pyrolysis and photolysis of the trans-pyrazoline.

These results are discussed in view of current mechanistic proposals for the pyrolysis and photolysis of Δ¹-pyrazolines.
ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation to Dr. D. E. McGreer who suggested this research project and under whose guidance and encouragement this research was performed.

The author is indebted to Mrs. E. Brion and Mr. P. Horn for the nuclear magnetic resonance spectra, to Dr. A. Bernhardt, Mrs. A. Aldridge and Mrs. C. Jenkins for the microanalyses.

Financial assistance from the National Research Council of Canada for this research project is deeply appreciated.
TABLE OF CONTENTS

I. Introduction .......................................................... 1

II. Synthesis and Identification of 3,3,5-Trisubstituted \(\Delta^1\)-Pyrazolines
   1. cis and trans-3,5-dimethyl-3-carbomethoxy-\(\Delta^1\)-pyrazoline .................................................. 7
   2. cis and trans-3,5-dimethyl-3-acetyl-\(\Delta^1\)-pyrazoline .................................................. 9

III. Separation and Identification of Products from the Decomposition of 3,5-Dimethyl-3-acetyl-\(\Delta^1\)-pyrazolines 13

IV. Decomposition of 3,3,5-Trisubstituted \(\Delta^1\)-Pyrazolines 21

V. Discussion .................................................................. 30

VI. Experimental
   1. General statement ................................................. 41
   2. N-Nitroso-N-ethyl urea ......................................... 41
   3. Diazoethane .......................................................... 42
   4. Methyl isopropenyl ketone ...................................... 43
   5. 3,5-Dimethyl-3-acetyl-\(\Delta^1\)-pyrazoline .................. 43
   6. Separation of cis and trans-3,5-dimethyl-3-acetyl-\(\Delta^1\)-pyrazoline ........................................... 44
   7. Separation of cis and trans-3,5-dimethyl-3-carbomethoxy-\(\Delta^1\)-pyrazoline ........................................... 44
   8. trans-3,5-Dimethyl-3-carbomethoxy-\(\Delta^1\)-pyrazoline hydrobromide ........................................... 45
   9. Thermal pyrolysis of 3,5-dimethyl-3-acetyl-\(\Delta^1\)-pyrazoline .................................................. 46
   9a. 2,4-Dinitrophenyl hydrazones ................................ 59
10. Thermal pyrolysis of cis and trans-3,5-dimethyl-3-acetyl-Δ¹-pyrazoline .................. 50
11. Vapor phase pyrolysis of cis and trans-3,5-dimethyl-3-acetyl-Δ¹-pyrazoline .................. 50
12. Liquid phase pyrolysis of 3,5-dimethyl-3-acetyl-Δ¹-pyrazoline .......................... 51
13. Liquid phase pyrolysis of cis and trans-3,5-dimethyl-3-acetyl-Δ¹-pyrazoline .................. 52
14. Photolysis of 3,5-dimethyl-3-acetyl-Δ¹-pyrazoline .......................... 52
15. Photolysis of cis and trans-3,5-dimethyl-3-acetyl-Δ¹-pyrazoline .......................... 53
16. Vapor phase pyrolysis of cis and trans-3,5-dimethyl-3-carbomethoxy-Δ¹-pyrazoline .......... 53
17. Liquid phase pyrolysis of cis and trans-3,5-dimethyl-3-carbomethoxy-Δ¹-pyrazoline in various solvents .......................................................... 53
18. Photolysis of trans-3,5-dimethyl-3-carbomethoxy-Δ¹-pyrazoline at various temperatures ........ 54
19. Photolysis of cis and trans-3,5-dimethyl-3-carbomethoxy-Δ¹-pyrazoline in Formamide at 23° .......... 56
20. Partial pyrolysis of trans-3,5-dimethyl-3-carbomethoxy-Δ¹-pyrazoline .......................... 56
21. Partial liquid phase pyrolysis of trans-3,5-dimethyl-3-carbomethoxy-Δ¹-pyrazoline ............. 57
22. Kinetic studies of the pyrolysis of 3,5-dimethyl-3-carbomethoxy-Δ¹-pyrazoline in various solvents ...... 57

BIBLIOGRAPHY ................................................................. 60
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>Mechanism of $\Delta^1$-pyrazoline formation</td>
<td>1</td>
</tr>
<tr>
<td>II.</td>
<td>Ionic mechanism for the pyrolysis of 3,4-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazolines</td>
<td>3</td>
</tr>
<tr>
<td>III.</td>
<td>Products from the photolysis of 3,4-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazolines</td>
<td>5</td>
</tr>
<tr>
<td>IV.</td>
<td>N.m.r. absorption showing the separation of 3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline into its cis and trans isomers</td>
<td>8</td>
</tr>
<tr>
<td>V.</td>
<td>N.m.r. spectra of $\text{trans}-3,5$-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline showing splittings of $C_4$-hydrogens</td>
<td>12</td>
</tr>
<tr>
<td>VI.</td>
<td>Products from the decomposition of 3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazolines</td>
<td>13</td>
</tr>
<tr>
<td>VIIA.</td>
<td>Preparative vapor chromatogram showing the separation of products from the decomposition of 3,5-dimethyl-$\Delta^1$-pyrazolines</td>
<td>14</td>
</tr>
<tr>
<td>VIIIB.</td>
<td>Analytical vapor phase chromatogram showing the separation of 3-methyl-4-hexen-2-one and $\text{trans}$-1,2-dimethyl-1-acetylcyclopropane</td>
<td>14</td>
</tr>
<tr>
<td>VIII.</td>
<td>Products from the decomposition of 3,5-dimethyl-3-acetyl-$\Delta^1$-pyrazolines</td>
<td>15</td>
</tr>
<tr>
<td>IX.</td>
<td>N.m.r. spectrum of 2,3,5-trimethyl-$\Delta^2$-dihydrofuran</td>
<td>17</td>
</tr>
<tr>
<td>X.</td>
<td>Stereochemistry of the formation of olefins from $\Delta^1$-pyrazoline</td>
<td>38</td>
</tr>
<tr>
<td>XI.</td>
<td>Apparatus for photolysis at low temperature</td>
<td>55</td>
</tr>
<tr>
<td>XII.</td>
<td>First order plot of $\log \frac{V_0}{(V_0-V_t)}$ verses time for the pyrolysis of 3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline in various solvents</td>
<td>58</td>
</tr>
</tbody>
</table>
### LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. N.m.r. data of cis and trans-3,5-dimethyl-3-acetyl-$\Delta^1$-pyrazoline and cis and trans-3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline</td>
<td>11</td>
</tr>
<tr>
<td>II. Product compositions for the decomposition of 3,5-dimethyl-3-acetyl-$\Delta^1$-pyrazolines</td>
<td>22</td>
</tr>
<tr>
<td>III. Product compositions for the decomposition of 3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazolines</td>
<td>23</td>
</tr>
<tr>
<td>IV. Product compositions for the sealed-tube pyrolysis of cis and trans-3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline in various solvents at 125°C</td>
<td>26</td>
</tr>
<tr>
<td>V. Product compositions of photolysis of cis and trans-3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline</td>
<td>27</td>
</tr>
</tbody>
</table>
I. INTRODUCTION

The addition of diazoalkanes to $\alpha,\beta$-unsaturated carbonyl compounds to form $\Delta^1$-pyrazolines (1-5) and the pyrolysis of these $\Delta^1$-pyrazolines to form cyclopropanes (6,7) have been known for many years. Both the addition and pyrolysis mechanisms have been the subject of discussion. In particular, the mechanism for the pyrolysis of $\Delta^1$-pyrazolines is still not settled at present.

The addition mechanism has been proven recently, by Huisgen and coworkers (8-10) to be a one-step multiple-center addition, similar to the 1,3-dipolar addition reaction, rather than the two-step ionic mechanism (6,11) previously proposed. These routes to pyrazolines are shown in Figure I. It has also been shown (6,7) that the carbon $\alpha$ to the nitrogen in the diazoalkane adds to the double bond at the carbon $\beta$ to the carbonyl

\[
\begin{align*}
\text{FIGURE I - Mechanisms of } \Delta^1\text{-pyrazoline formation,}
\end{align*}
\]
group in the olefin. Cis-addition (6,7) is indicated by the reaction of diazomethane with methyl tiglate (IV) and methyl angelate (V) to give cis and trans-3,4-dimethyl-3-carbomethoxy-Δ1-pyrazoline (VI and VII) respectively (12).

The thermal decomposition of Δ1-pyrazolines has been reported to yield a product mixture consisting of cyclopropane and olefins (6,7,13-19) in some instances, while in others the mixture also contained the corresponding Δ2-pyrazoline (20) or no olefins (3,21) at all. Few studies have been made to determine the mechanism of the pyrolysis reactions. From limited information both ionic (6,11,12) and diradical (20,22-24) mechanisms for the thermal decomposition of Δ1-pyrazolines have been proposed to explain these products. These proposals were made on the assumption that cyclopropanes are formed with retention of the geometry present in the original pyrazolines. Recent observations of partial and complete loss of the above mentioned geometry have been reported (12,21,25). For example, van Auken and Rinehart reported (12) that the pyrolysis of trans-3,4-dimethyl-3-carbomethoxy-Δ1-pyrazoline (VII) gives cis-1,2-dimethyl-1-carbomethoxycyclopropane (X), trans-1,2-dimethyl-1-carbomethoxycyclopropane (XI), methyl 2,3-dimethyl-2-butenoate (XII) and methyl 2,3-dimethyl-3-butenoate (XIII) in the ratio 1.00:1.22:1.16:0.15; and similarly, cis-3,4-dimethyl-3-carbomethoxy-Δ1-pyrazoline (VI) gives X, XI, XII and XIII in the ratio 1.00:0.70:3.73:0.24. These authors have suggested the following modified ionic mechanism (Figure II), which postu-
VI (methyls cis) or VII (methyls trans)

FIGURE II - Ionic mechanism for the pyrolysis of 3,4-dimethyl-3-carbomethoxy-3-pyrazolines.

lates that rotation occurs in the diazonium betaine intermediate (VIII), and thus racemization at the anion center can take place. The slight degree of stereoselectivity, that is, 1.22:1.00 in favor of the trans-cyclopropane XI from the trans-pyrazoline VII and 1.00:0.70 in favor of the cis-cyclopropane X from the cis-pyrazoline VI, was explained by the suggestion that the loss of nitrogen in going from VIII to IX is slightly faster than the rotation in VIII due to the fact that the latter involves consecutive eclipsed interaction of methyl-carbo-
methoxy and methylenediazonium-methyl which provides some barrier to rotation. Inspite of the proposed common intermediate for the pyrolysis of pyrazolines VI and VII, the ratio of cyclopropanes to olefins are different, that is, 1.70:3.97 for the cis-pyrazoline VI and 2.22:1.31 for the trans-pyrazoline VII. Although this mechanism would predict the conversion of the intermediate VIII to pyrazolines VI or VII faster than nitrogen loss from VIII, it was shown that the partial pyrolysis of cis-3,4-dimethyl-3-carbomethoxy-\( ^1 \)-pyrazoline (VI) gives no rearrangement in the recovered pyrazoline sample (12). Therefore the validity of this ionic mechanism for the thermal decomposition of \( ^1 \)-pyrazolines needs further examination.

Photolysis of cis and trans-3,4-dimethyl-3-carbomethoxy-\( ^1 \)-pyrazoline (VI and VII) has been reported (12) to give stereospecifically cis and trans-1,2-dimethyl-1-carbomethoxy,cyclopropane (X and XI) respectively, and methyl tiglate (IV) and methyl angelate (V) respectively (Figure III). Rinehart and van Auken (12) have proposed a molecular mechanism to explain these observations of photolysis of \( ^1 \)-pyrazolines. The transition state involved would be XIV in which the breakage of bonds N\(_1\)-C\(_5\) and N\(_2\)-C\(_3\) and the formation of bonds C\(_3\)-C\(_5\) and N\(_1\)-N\(_2\) are simultaneous, hence the cyclopropanes formed retain the geometry which is present in the pyrazolines. Similarly, the stereospecific regeneration of methyl tiglate (IV) and methyl angelate (V) could then be explained through a similar transition state XV. Therefore on the basis of these photolysis
results, the photolysis of $\Delta^1$-pyrazolines has been assumed to be stereospecific in general.

![Figure III](image)

**FIGURE III** - Products from the photolysis of 3,4-di-methyl-3-carbomethoxy-$\Delta^1$-pyrazolines.

In this laboratory however, a preliminary investigation (26) has shown that the photolysis reactions of cis and trans-3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline (XVI and XVII) give mixtures of cyclopropanes, with some loss of stereospecificity, and olefin products.
With the finding that cis and trans-3,5-dialkyl-Δ^1-pyrazolines could be separated by fractional distillation, a new system for studying the stereochemistry has become available. Thus, the purpose of the present investigation is to examine the thermal and photolytic decompositions of cis and trans-3,5-dimethyl-3-carbomethoxy-Δ^1-pyrazoline (XVI and XVII) and their analogs, cis and trans-3,5-dimethyl-3-acetyl-Δ^1-pyrazoline (XVIII and XIX) in an attempt to find out more information about these reactions.
II. SYNTHESIS AND IDENTIFICATION OF 3,3,5-
TRISUBSTITUTED $\Delta^1$-PYRAZOLINES

II-l. cis and trans-3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline 
(XVI and XVII)

3,5-Dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline (XX) prepared 
by the addition of methyl methacrylate (XXI) to diazoethane in 
ether (17) has been shown by n.m.r. analysis to be a 40:60 
mixture of the two possible geometric isomers. Separation of 

\[
\begin{align*}
\text{XXI} & \quad \text{ether} \\
\text{XX} & 
\end{align*}
\]

this mixture (Figure IV) by fractional distillation using a 
Nester and Faust 18-inch by 6-mm. spinning band still gave a 
lower boiling fraction up to 93% pure and a higher boiling 
fraction of 99.4% purity. N.m.r. analyses of these two fractions 
and the original mixture pyrazoline showed that the lower 
boiling isomer was the 40% component and the higher boiling 
isomer was the 60% component.

Photolysis reactions have been carried out on both the 
lower and the higher boiling fractions, and it was found 
(complete results will be discussed later) that the former 
gives mainly cis-1,2-dimethyl-1-carbomethoxycyclopropane (X) 
and the latter gives mainly trans-1,2-dimethyl-1-carbomethoxy-
FIGURE IV - N.m.r. absorptions showing the separation of 3,5-dimethyl-3-carbomethoxy-Δ^2-pyrazoline (XX) into its cis (XVI) and trans (XVII) isomers.
cyclopropane (XI). On the basis of the fact that the photolysis of $\Delta^1$-pyrazolins gives cyclopropane stereospecifically (12), the lower boiling isomer was assigned the structure cis-3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline (XVI) and the higher boiling isomer was assigned the structure trans-3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline (XVII). Further proof of structural assignments is based on the higher yield of the trans-pyrazoline XVII than the cis-pyrazoline XVI on preparation. Steric hindrance due to the $C_3$ and $C_5$ methyl groups cis to each other in XVI would slow down its formation when compared to XVII. In order to obtain more evidence, the hydrobromide salt (XXII) of trans-3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline (XVII) has been prepared and is presently being analyzed by the single crystal X-ray method. XXII is white crystalline solid with melting point at 152-153°.

II-2. cis and trans-3,5-dimethyl-3-acetyl-$\Delta^1$-pyrazoline (XVIII and XIX)

3,5-Dimethyl-3-acetyl-$\Delta^1$-pyrazoline (XXIII) was prepared by the addition of methyl isopropenyl ketone to an ether-methanol solution of diazoethane. It is a colorless liquid

\[
\text{CH}_3\text{C}=\text{C}-\text{COCH}_3 + \text{CH}_3\text{CHN}_2 \xrightarrow{\text{ether-methanol}} \text{XXIII}
\]

which boils at 56-57°/1.2 mm. and turns yellowish on prolonged
exposure to atmosphere. The n.m.r. spectrum of XXIII showed it to be a 40:60 mixture of the two possible geometric isomers and there was no absorption of proton attached to a nitrogen atom. Fractional distillation of XXIII by spinning band still at reduced pressure gave a lower and a higher boiling fraction of 81% and 97% purity respectively, and they were found to be the 40% and 60% components of XXIII respectively.

The results of the photolysis reactions of the lower boiling and the higher boiling isomers showed that the former gives mainly cis-1,2-dimethyl-3-acetylcyclopropane (XXIV) and the latter gives mainly trans-1,2-dimethyl-3-acetylcyclopropane (XXV). Therefore on the basis of steric hindrance during the formation of 3,5-dimethyl-3-acetyl-Δ₁-pyrazoline (XXIII) and the results of the photolysis reactions, the lower boiling isomer was assigned to be cis-3,5-dimethyl-3-acetyl-Δ₁-pyrazoline (XVIII) and the higher boiling isomer was assigned to be trans-3,5-dimethyl-3-acetyl-Δ₁-pyrazoline (XIX). This is analogous to the assignment to the cis and trans-3,5-dimethyl-3-carbomethoxy-Δ₁-pyrazoline (XVI and XVII).

The n.m.r. data of cis and trans-3,5-dimethyl-3-carbomethoxy-Δ₁-pyrazoline (XVI and XVII) and cis and trans-3,5-dimethyl-3-acetyl-Δ₁-pyrazoline (XVIII and XIX) are tabulated in Table I.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Acetyl methyl hydrogens</th>
<th>Ester methyl hydrogen</th>
<th>C₃-methyl hydrogen</th>
<th>C₅-methyl hydrogens</th>
<th>C₅-hydrogens</th>
<th>C₄-hydrogens</th>
</tr>
</thead>
<tbody>
<tr>
<td>XVI</td>
<td>6.33 singlet</td>
<td>8.38 singlet</td>
<td>8.51 doublet J=7.0</td>
<td>5.42 sextet J=7.5</td>
<td>7.68 2 doubles Jgem≈12.9</td>
<td>9.14 2 doubles Jgem≈12.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Jvic≈8.5</td>
<td></td>
</tr>
<tr>
<td>XVII</td>
<td>6.27 singlet</td>
<td>8.63 singlet</td>
<td>8.55 doublet J=7.0</td>
<td>5.43 sextet J=7.5</td>
<td>8.28 2 doubles Jgem≈12.8</td>
<td>8.56 2 doubles Jgem≈12.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Jvic≈8.0</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>8.43 doublet J=8.0</td>
<td>8.45 doublet J=8.0</td>
</tr>
<tr>
<td>XVIII</td>
<td>7.78 singlet</td>
<td>8.40 singlet</td>
<td>8.52 doublet J=7.0</td>
<td>5.66 sextet J=7.4</td>
<td>7.57 2 doubles Jgem≈13.0</td>
<td>9.30 2 doubles Jgem≈12.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Jvic≈8.7</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>8.53 multiplet</td>
<td></td>
</tr>
<tr>
<td>XIX</td>
<td>7.65 singlet</td>
<td>8.63 singlet</td>
<td>8.48 doublet J=6.0</td>
<td>5.67 sextet J=7.4</td>
<td>7.67 multiplet</td>
<td></td>
</tr>
</tbody>
</table>

Note: 1) XVIII and XIX were done on 20% solution in CCl₄, XVI and XVII were done on 30% solution in CCl₄, and the values in parentheses were observed in 10% solution.
2) Chemical shift in δ unit and coupling constant in c.p.s.
#) Due to the small chemical shift separation the outer doublets of the AB system were not observed (see Figure V).
FIGURE V - N.m.r. spectra of trans-3,5-dimethyl-3-carboxymethoxy-$\Delta^1$-pyrazoline (XVII) showing splittings of C4-hydrogens.
III. SEPARATION AND IDENTIFICATION OF PRODUCTS FROM THE DECOMPOSITION OF 3,5-DIMETHYL-3-ACETYL-Δ¹-PYRAZOLINES

Preliminary studies (17,26) on the decomposition of 3,5-dimethyl-3-carbomethoxy-Δ¹-pyrazoline (XX), its cis (XVI) and trans (XVII) isomers have shown five products to be formed as shown in Figure VI (for photolysis, an additional product XXI was obtained).

\[
\begin{align*}
\text{XX} & : \begin{array}{c}
\text{COOCH}_3 \\
\text{H}_3\text{C} \\
\text{N} \\
\text{CH}_3
\end{array} \\
\text{XVI} & : \begin{array}{c}
\text{COOCH}_3 \\
\text{H}_3\text{C} \\
\text{N} \\
\text{CH}_3
\end{array} \\
\text{XVII} & : \begin{array}{c}
\text{COOCH}_3 \\
\text{H}_3\text{C} \\
\text{N} \\
\text{CH}_3
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{X} & : \begin{array}{c}
\text{COOCH}_3 \\
\text{H}_3\text{C} \\
\text{CH}_3
\end{array} \\
\text{XI} & : \begin{array}{c}
\text{COOCH}_3 \\
\text{H}_3\text{C} \\
\text{CH}_3
\end{array} \\
\text{XXVI} & : \begin{array}{c}
\text{CH}_3\text{CH}_2 \text{C} = \text{C} \text{COOCH}_3 \\
\text{CH}_3\text{CH}_2 \text{C} = \text{C} \text{COOCH}_3
\end{array} \\
\text{XXVII} & : \begin{array}{c}
\text{H}_2\text{C} = \text{C} \text{COOCH}_3 \\
\text{H}_2\text{C} = \text{C} \text{COOCH}_3
\end{array}
\end{align*}
\]

**FIGURE VI** - Products from the decomposition of 3,5-dimethyl-3-carbomethoxy-Δ¹-pyrazolines.

In the present study, the decomposition of 3,5-dimethyl-3-acetyl-Δ¹-pyrazoline (XXIII), its cis (XVIII) and trans (XIX)
FIGURE VII

A. Preparative vapor chromatogram showing the separation of products from the decomposition of 3,5-dimethyl-1-acetyl-Δ-pyrazolines.

B. Analytical vapor phase chromatogram showing the separation of 3-methyl-4-hexen-2-one (XXXII) and trans-1,2-dimethyl-1-acetylcyclopropane (XXV)
isomers afforded a mixture of six products as shown by analytical vapor phase chromatography (Figure VII) with boiling points ranging from 119° to 152°. These products are shown in Figure VIII and have been identified as described below. Pre-

![Chemical structures](image)

**FIGURE VIII** - Products from the decomposition of 3,5-dimethyl-3-acetyl-\(\Delta^1\)-pyrazolines.

parative vapor phase chromatographic separation gave five fractions in which the second fraction was found to be a mixture (Figure VII) of 1-acetyl-\(\text{trans}\)-1,2-dimethylcyclopropane (XXV) and 3-methyl-4-hexen-2-one (XXXII) in the ratio of approximately 85:15 depending on the condition of decomposition. The separation of this mixture of XXV and XXXII will be discussed later. The pyrolysis products have been charac-
2,3,5-Trimethyl-$\Delta^2$-dihydrofuran (XXIX) has been reported (27) to boil at 118.5° at 746 mm, which agreed with the value, 120°, of this work. Its infrared spectrum indicated the presence of carbon-carbon double-bond absorption at 5.87 μ and vinyl ether absorption at 8.21 μ and 9.63 μ (28). There was no indication of absorption in the infrared or n.m.r. (Figure IX) spectra attributable to the acetyl methyl protons. N.m.r. absorption of an unresolvable multiplet centered at 8.43 τ was attributable to the methyl groups attached to C₂ and C₃. There were three groups of multiplet centered at 7.98 τ, 7.40 τ and 5.59 τ which can be assigned to the hydrogens on C₄ (two hydrogens) and C₅ (one hydrogen). These three protons constituted a typical ABX system (29) with $J_{AB} \approx 14.5$ c.p.s., $J_{AX} \approx 8.0$ c.p.s., $J_{BX} \approx 9.5$ c.p.s., $\Delta_{AB} \approx 35.5$ c.p.s., $\Delta_{AX} \approx 144.5$ c.p.s. and $\Delta_{BX} \approx 109$ c.p.s. In order to establish the cyclic structure of this 2,3,5-trimethyl-$\Delta^2$-dihydrofuran (XXIX), the n.m.r. spectrum of a similar cyclic compound, the 2-methyl-$\Delta^2$-dihydrofuran (XXX-III) (30) was obtained for comparison. The n.m.r. spectrum of XXXIII showed absorption at 8.30 τ (multiplet), 5.55 τ (multiplet), 7.47 τ (multiplet) and 5.78 τ (triplet with $J \approx 9.3$ c.p.s.) attributable to C₂ methyl hydrogens, C₃ vinyl hydrogen, C₄ and C₅ hydrogens respectively. A comparison of the n.m.r. spectra of XXIX and XXXIII showed good correlation between similarly situated protons, conforming the structural assign-
FIGURE IX - N.m.r. spectrum of 2,3,5-trimethyl-\( \alpha^2 \)-dihydrofuran (XXIX)
ment of 2,3,5-trimethyl-\(\Delta^2\)-dihydrofuran (XXIX).

\textit{cis}-3-Methyl-3-hexen-2-one (XXX) and \textit{trans}-3-methyl-3-hexen-2-one (XXXI) have been found to have boiling points at 145-145.5\(^\circ\) and 156.5-158\(^\circ\) respectively. Rohrmann and Shoule (31) reported the synthesis of 3-methyl-3-hexen-2-one and gave its boiling point value, 151\(^\circ\). It is possible that their \(\alpha,\beta\)-unsaturated ketone was a mixture of the two possible geometric isomers XXX and XXXI. The presence of carbon-carbon double-bond and \(\alpha,\beta\)-unsaturated carbonyl function were indicated by infrared bands at 6.18 \(\mu\) and 5.91 \(\mu\) respectively, for the \textit{cis}-3-methyl-3-hexen-2-one (XXX) and at 6.07 \(\mu\) and 5.96 \(\mu\) respectively, for the \textit{trans}-3-methyl-3-hexen-2-one (XXXI). The n.m.r. spectra of XXX and XXXI showed absorption at 7.86 \(\tau\) (singlet) and 7.81 \(\tau\) (singlet) due to acetyl methyl hydrogens, at 8.12 \(\tau\) (multiplet) and 8.39 \(\tau\) (multiplet) due to vinyl methyl hydrogens and at 4.44 \(\tau\) (multiplet) and 3.52 \(\tau\) (multiplet) due to vinyl hydrogens, respectively. The assignment of geometry to \textit{cis} and \textit{trans}-3-methyl-3-hexen-2-one (XXX and XXXI) were based on the lower field vinyl proton absorption of the latter at 3.52 \(\tau\) than the former at 4.44 \(\tau\). In XXXI the vinyl hydrogen is \textit{cis} to the acetyl group, whereas in XXX, the vinyl hydrogen is \textit{trans} to the acetyl group. In other words, the vinyl hydrogen in XXXI is closer to the acetyl group than in XXX, therefore the diamagnetic anisotropy of the carbon-oxygen double-bond in acetyl group would deshield the vinyl proton in XXXI to a greater extent to give a lower field absorption
19. This shift in the vinyl hydrogen region has been observed in many other cis and trans pairs of olefins (38).

1-Acetyl-cis-1,2-dimethylcyclopropane (XXIV) and 1-acetyl-trans-1,2-dimethylcyclopropane (XXV) showed no infrared absorption bands attributable to carbon-carbon double-bond but carbonyl conjugated to the cyclopropane ring (33) at 5.90 μ for XXIV and 5.96 μ for XXV; and in addition, there was a band at 9.76 μ for XXV due to absorption of cyclopropane ring (34). Their n.m.r. spectra showed no signal due to proton attached to the carbon-carbon double-bond but high field absorption characteristic of cyclopropane ring protons. These ring proton absorptions appeared as two groups of signals centered at 8.68 τ (two hydrogens) and 9.74 τ (one hydrogen) in the case of 1-acetyl-cis-1,2-dimethylcyclopropane (XXIV) and in the region of 8.75 τ to 9.06 τ in the case of 1-acetyl-trans-1,2-dimethylcyclopropane (XXV). These multiplets were partly obscured by absorption of methyl groups. The stereochemistry of XXIV and XXV were made by comparison of their n.m.r. spectra to those of the analogous carbomethoxy-cyclopropanes, namely 1-carbomethoxy-cis-1,2-dimethylcyclopropane (X) and 1-carbomethoxy-trans-1,2-dimethylcyclopropane (XI) whose stereochemistry has already been determined by van Auken and Rinehart (12) on the basis of competitive saponifications in which the less hindered carbomethoxy group of X was consumed more rapidly than that of XI.
3-Methyl-4-hexen-2-one (XXXII) was eluted at the same time as 1-acetyl-trans-1,2-dimethylcyclopropane (XXV) from the preparative vapor phase chromatography column. Attempts to separate this \( \beta, \gamma \)-unsaturated ketone XXXII by using columns packed with various substances were not successful. Bromination of the mixture consisting 3-methyl-4-hexen-2-one (XXXII) and 1-acetyl-trans-1,2-dimethylcyclopropane (XXV) in carbon tetrachloride gave XXV and trans-3-methyl-3-hexen-2-one (XXXI) instead of the dibromide of XXXII as indicated in the preparative vapor phase chromatogram. Since 3-methyl-4-hexen-2-one (XXXII) was stable at the temperature of the column, the conversion of XXXII or its dibromide to XXXI must have occurred before it was injected into the column. Although 3-methyl-4-hexen-2-one (XXXII) was not isolated pure, its presence was indicated in the n.m.r. spectrum of the mixture with 1-acetyl-trans-1,2-dimethylcyclopropane (XXV). Those absorptions attributable to XXXII are shown below. It was not possible to distinguish whether the vinyl hydrogens in the molecule are cis or trans to each other. Elemental microanalysis of the mixture containing 3-methyl-4-hexen-2-one (XXXII) and 1-acetyl-trans-1,2-dimethylcyclopropane (XXV) was in good agreement to the empirical formula \( C_{7}H_{12}O \), which is common to both XXV and XXXII.
IV. DECOMPOSITION OF 3,3,5-TRISUBSTITUTED \( \Delta^1 \)-PYRAZOLINES

Preliminary investigations have been shown that the pyrolysis of cis and trans-3,5-dimethyl-3-carbomethoxy-\( \Delta^1 \)-pyrazoline (XVI and XVII) affords five products (Figure VI, p. 13); namely, cis and trans-1,2-dimethyl-1-carbomethoxy-cyclopropane (X and XI), methyl cis and trans-2-methyl-2-pentenoate (XXVI and XXVII) and methyl 2-methyl-3-pentenoate (XXVIII); on photolysis, an additional peak, methyl methacrylate (XXI), was found. Similar pyrolysis reactions, as reported in this work, were carried out on 3,5-dimethyl-3-acetyl-\( \Delta^1 \)-pyrazoline (XXIII), its cis (XVIII) and trans (XIX) isomers and found to give six products (Figure VIII, p. 15): 1-acetyl-cis and trans-1,2-dimethylcyclopropane (XXIV and XXV), 2,3,5-trimethyl-\( \Delta^2 \)-dihydrofuran (XXIX), cis and trans-3-methyl-3-hexen-2-one (XXX and XXXI) and 3-methyl-4-hexen-2-one (XXXII). Photolysis of these acetyl-pyrazolines (XXIII, XVIII and XIX) gave no additional product. These results are tabulated in Tables II and III.

It can be seen that the decomposition reactions of 3,5-dimethyl-3-acetyl-\( \Delta^1 \)-pyrazoline (XXIII), its cis (XVIII) and trans (XIX) isomers give results that resemble those of 3,5-dimethyl-3-carbomethoxy-\( \Delta^1 \)-pyrazoline (XX), its cis (XVI) and trans (XVII) isomers respectively. Pyrolysis gave higher ratio of olefins to cyclopropanes than did photolysis. In the
TABLE II

Product compositions for the decomposition of 3,5-dimethyl-3-acetyl-Δ1-pyrazolines

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction conditions</th>
<th>Cyclopropane cis</th>
<th>Cyclopropane trans</th>
<th>Unsaturated ketone cis-Δβ</th>
<th>Unsaturated ketone trans-Δβ</th>
<th>Dihydrofuran</th>
</tr>
</thead>
<tbody>
<tr>
<td>XVIII (cis)</td>
<td>Vapor phase pyrolysis at 125°</td>
<td>27</td>
<td>48</td>
<td>7</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>XIX (trans)</td>
<td>Vapor phase pyrolysis at 125°</td>
<td>67</td>
<td>19</td>
<td>2</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>XXIII (mixt.)</td>
<td>Liquid phase pyrolysis, 100°</td>
<td>36</td>
<td>18</td>
<td>15</td>
<td>18</td>
<td>4</td>
</tr>
<tr>
<td>XVIII (cis)</td>
<td>Liquid phase pyrolysis, 100°</td>
<td>22</td>
<td>25</td>
<td>27</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>XIX (trans)</td>
<td>Liquid phase pyrolysis, 100°</td>
<td>62</td>
<td>17</td>
<td>1</td>
<td>17</td>
<td>3</td>
</tr>
<tr>
<td>XXIII (mixt.)</td>
<td>Thermal pyrolysis at 250°</td>
<td>48</td>
<td>32</td>
<td>5</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>XVIII (cis)</td>
<td>Thermal pyrolysis at 250°</td>
<td>28</td>
<td>41</td>
<td>12</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>XIX (trans)</td>
<td>Thermal pyrolysis at 250°</td>
<td>60</td>
<td>27</td>
<td>1</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>XXIII (mixt.)</td>
<td>Photolysis in ether at 35°</td>
<td>39</td>
<td>42</td>
<td>4</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>XVIII (cis)</td>
<td>Photolysis in ether at 35°</td>
<td>59</td>
<td>28</td>
<td>1</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>XIX (trans)</td>
<td>Photolysis in ether at 35°</td>
<td>21</td>
<td>70</td>
<td>2</td>
<td>1</td>
<td>4</td>
</tr>
</tbody>
</table>
### TABLE III

Product compositions for the decomposition of 3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazolines

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction conditions</th>
<th>Cyclopropane</th>
<th>Unsaturated ester</th>
<th>Methyl methacrylate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>cis trans</td>
<td>cis-trans-trans-$\beta$</td>
<td></td>
</tr>
<tr>
<td>XX (mixt.)</td>
<td>Vapor phase pyrolysis (17)</td>
<td>X</td>
<td>XI</td>
<td>XXVI</td>
</tr>
<tr>
<td></td>
<td></td>
<td>53</td>
<td>42</td>
<td>3</td>
</tr>
<tr>
<td>XVI (cis)</td>
<td>Vapor phase pyrolysis (17)</td>
<td></td>
<td></td>
<td>XXVIII</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>XVII (trans)</td>
<td>Vapor phase pyrolysis (17)</td>
<td></td>
<td></td>
<td>XXVIII</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>XX (mixt.)</td>
<td>Liquid phase pyrolysis (17)</td>
<td></td>
<td></td>
<td>XXI</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>XVI (cis)</td>
<td>Liquid phase pyrolysis (17)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XVII (trans)</td>
<td>Liquid phase pyrolysis (17)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XVI (cis)</td>
<td>Photolysis in ether at 35°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XVII (trans)</td>
<td>Photolysis in ether at 35°</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
olefin fraction of the products, cis-3,5-dimethyl-Δ⁻¹-pyrazolines gave predominantly the α,β-cis-olefins and trans-3,5-dimethyl-Δ⁻¹-pyrazolines gave predominantly the α,β-trans-olefins. In the cyclopropane fraction of the products, cis and trans-3,5-dimethyl-Δ⁻¹-pyrazolines gave more trans and cis-1,2-dimethyl-cyclopropane respectively, whereas on photolysis, they were in reversed abundance.

The only significant difference between the keto and ester pyrazolines was the dihydrofuran product XXIX which was formed from the decomposition reactions of the keto pyrazolines. It is noteworthy that this product was formed from only one of the keto pyrazolines, cis-3,5-dimethyl-3-acetyl-Δ⁺⁻¹-pyrazoline (XVIII), in significant amount.

On the basis of the postulated polar intermediate in the pyrolysis reaction it is anticipated that the polarity of the solvent might influence the product ratio and the rate of reaction, hence pyrolysis in a number of solvents with dielectric constants varying from 2D for cyclohexane to 109D for formamide have been carried out on the cis and trans-3,5-dimethyl-3-carbomethoxy-Δ⁻¹-pyrazoline (XVI and XVII). Samples of 0.2 ml. of the ester pyrazoline in 20 ml. of solvent in a sealed tube were heated for 90 minutes at 125°. For low boiling solvents, the solvent was removed by distillation through a spinning band column under reflux condition, and the concentrated solution was analysed by analytical vapor phase chromatography. For
formamide, the products were recovered from the solvent on a vacuum line by pumping for two hours. These results (Table IV) showed a small and regular influence of the dielectric constant of the solvent on the product composition. In formamide, up to 57% of the product was olefins, whereas in cyclohexane, only 7% of the product was olefins.

Photolysis of cis and trans-3,5-dimethyl-3-carbomethoxy-\( \Delta^1 \)-pyrazoline (XVI and XVII) in solvents of varying dielectric constants showed a similar solvent effect on the product composition as in the pyrolysis reactions but in lesser degree; for example, in formamide, up to 21% of the product was olefins whereas in cyclohexane, it was 5%.

The kinetic solvent effect has been examined for the pyrolysis of 3,5-dimethyl-3-carbomethoxy-\( \Delta^1 \)-pyrazoline (XX) in various solvents and it was found that the rate of pyrolysis decreased in the order of di-n-butyl ether, tetralin, nitrobenzene and formamide. The rates in these solvents were all within a factor of three (Figures XII and XIII).

Liquid phase photolysis of trans-3,5-dimethyl-3-carbomethoxy-\( \Delta^1 \)-pyrazoline (XVII) has been carried out in solvents such as 2,3-dimethylbutane and diethyl ether at various temperatures ranging from -55° to 58° in an attempt to determine the temperature effect on photolysis of \( \Delta^1 \)-pyrazolines. Product analysis by analytical vapor phase chromatography showed no appreciable change attributable to the influence of tem-
### TABLE IV

Product compositions for the sealed-tube pyrolysis of cis and trans-3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline in various solvents at 125°

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>$D_{20}$ (44)</th>
<th>Cyclopropane</th>
<th>Unsaturated ester</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>cis trans</td>
<td>cis-$\alpha\beta$</td>
</tr>
<tr>
<td>XVI (cis)</td>
<td>Cyclohexane#</td>
<td>2.07 D</td>
<td>25 62</td>
<td>12 0</td>
</tr>
<tr>
<td>XVI (cis)</td>
<td>Cyclohexane</td>
<td>2.07 D</td>
<td>30 55</td>
<td>11 3</td>
</tr>
<tr>
<td>XVI (cis)</td>
<td>Ethyl ether</td>
<td>4.34 D</td>
<td>25 56</td>
<td>16 2</td>
</tr>
<tr>
<td>XVI (cis)</td>
<td>Methanol</td>
<td>33.6 D</td>
<td>21 39</td>
<td>34 4</td>
</tr>
<tr>
<td>XVI (cis)</td>
<td>Acetonitrile</td>
<td>37.5 D</td>
<td>21 42</td>
<td>31 4</td>
</tr>
<tr>
<td>XVI (cis)</td>
<td>Formamide</td>
<td>109 D</td>
<td>19 33</td>
<td>44 2</td>
</tr>
<tr>
<td>XVII (trans)</td>
<td>Cyclohexane#</td>
<td>2.07 D</td>
<td>70 23</td>
<td>1 5</td>
</tr>
<tr>
<td>XVII (trans)</td>
<td>Cyclohexane</td>
<td>2.07 D</td>
<td>72 20</td>
<td>0 6</td>
</tr>
<tr>
<td>XVII (trans)</td>
<td>Ethyl ether</td>
<td>4.34 D</td>
<td>66 18</td>
<td>0 13</td>
</tr>
<tr>
<td>XVII (trans)</td>
<td>Methanol</td>
<td>33.6 D</td>
<td>48 6</td>
<td>0 44</td>
</tr>
<tr>
<td>XVII (trans)</td>
<td>Acetonitrile</td>
<td>37.5 D</td>
<td>67 6</td>
<td>0 25</td>
</tr>
<tr>
<td>XVII (trans)</td>
<td>Formamide</td>
<td>109 D</td>
<td>31 12</td>
<td>0 52</td>
</tr>
</tbody>
</table>

# at 81°, not in sealed-tube.
TABLE V
Product compositions of photolysis of cis and trans-3,5-di-
methyl-3-carbomethoxy-A1-pyrazoline

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent and temperature</th>
<th>Cyclopropane cis</th>
<th>Cyclopropane trans</th>
<th>Unsaturated ester cis-&amp;b trans-&amp;b</th>
<th>Methyl methacrylate</th>
</tr>
</thead>
<tbody>
<tr>
<td>XVII (trans)</td>
<td>2,3-Dimethyl butane 58°</td>
<td>28 63</td>
<td></td>
<td>XXVI 4 XXVII 2 XXVIII 2 XI 0</td>
<td></td>
</tr>
<tr>
<td>XVII (trans)</td>
<td>Ethyl ether (26) 35°</td>
<td>22 65</td>
<td></td>
<td>0 5 2 6</td>
<td></td>
</tr>
<tr>
<td>XVII (trans)</td>
<td>Ethyl ether 0°</td>
<td>27 56</td>
<td></td>
<td>1 7 3 6</td>
<td></td>
</tr>
<tr>
<td>XVII (trans)</td>
<td>Ethyl ether -20°</td>
<td>25 55</td>
<td></td>
<td>1 8 3 8</td>
<td></td>
</tr>
<tr>
<td>XVII (trans)</td>
<td>Ethyl ether -55°</td>
<td>25 53</td>
<td></td>
<td>1 10 4 7</td>
<td></td>
</tr>
<tr>
<td>XVI (cis)</td>
<td>Cyclohexane# 81°</td>
<td>43 45</td>
<td></td>
<td>7 0 1 4</td>
<td></td>
</tr>
<tr>
<td>XVII (trans)</td>
<td>Cyclohexane# 81°</td>
<td>46 45</td>
<td></td>
<td>0 4 1 4</td>
<td></td>
</tr>
<tr>
<td>XVI (cis)</td>
<td>Formamide 23°</td>
<td>54 21</td>
<td></td>
<td>9 5 1 10</td>
<td></td>
</tr>
<tr>
<td>XVII (trans)</td>
<td>Formamide 23°</td>
<td>15 58</td>
<td></td>
<td>2 16 3 6</td>
<td></td>
</tr>
</tbody>
</table>

# at 81, pyrolysis also occurred at a rate three times slower than photolysis.
perature. These results are shown in Table V.

Photolysis and pyrolysis gave the same products, therefore they might well involve the same intermediate. In order to determine whether the product composition was dependent on temperature or on the nature of the reaction, photolysis and pyrolysis of cis and trans-3,5-dimethyl-3-carbomethoxy-\(\Delta^1\)-pyrazoline (XVI and XVII) were carried out at the same temperature, 81°, with cyclohexane as solvent. It was found the evolution of nitrogen to be three to four times faster by photolysis than by pyrolysis. The product compositions from these two reactions were not the same despite the fact that they were run under identical conditions. The results under these conditions indicate as in other systems that photolysis yielded cyclopropanes with a high degree of retention of geometry of the starting pyrazoline than those from pyrolysis. It was also found that the ratio of olefins to cyclopropanes from these reactions was lower for the photolysis than the pyrolysis.

A further test of the earlier proposed mechanism was based on the fact that there should be rotation of the \(C_3-C_4\) bond in the diazonium betaine intermediate XXXIV and that it would form 3,5-dimethyl-3-carbomethoxy-\(\Delta^1\)-pyrazoline (XX) by cyclization faster than loss of nitrogen. Liquid phase pyrolysis of trans-3,5-dimethyl-3-carbomethoxy-\(\Delta^1\)-pyrazoline (XVII) at 90° was carried to 50% completion, and the recovered unreacted pyrazoline was analysed by n.m.r. It was found that
not more than 1% isomerization of XVII to cis-3,5-dimethyl-3-carbomethoxy-Δ¹-pyrazoline (XVI) had occurred. A similar result was observed when trans-3,5-dimethyl-3-carbomethoxy-Δ¹-pyrazoline (XVII) in diethyl ether was partially photolyzed at 35°.
V. DISCUSSION

The thermal pyrolysis of cis and trans-3,4-dimethyl-3-carbomethoxy-\(\Delta^1\)-pyrazoline (VI and VII) has been reported by Rinehart and van Auken (12) to proceed with racemization at C\(_3\) to give cyclopropane products in which the methyls are cis and trans with that cyclopropane which retains the geometry present in the pyrazoline being slightly predominant. For example, the cis-pyrazoline VI gives cis-1,2-dimethyl-1-carbomethoxycyclopropane (X) and trans-1,2-dimethyl-1-carbomethoxycyclopropane (XI) in the ratio of 1.00:0.70 whereas the trans-pyrazoline VII gives X and XI in the ratio of 1.00:1.22. Rinehart and van Auken suggested that rotation about the C\(_3\)-C\(_4\) bond in the diazonium betaine intermediate VIII accounts for the loss of geometric integrity and that
the loss of nitrogen is only slightly slower than rotation to give a higher yield of the cyclopropane which retains the geometry present in the pyrazoline.

In the present work, it was found that the thermal pyrolysis of cis and trans-3,5-dimethyl-3-carbomethoxy-Δ¹-pyrazoline (XVI and XVII), cis and trans-3,5-dimethyl-3-acetyl-Δ¹-pyrazoline (XVIII and XIX) also proceeds with racemization at C₃ to give cyclopropane products in which the methyls are cis and trans but the cyclopropane with inversion of the geometry present in the pyrazoline was found predominant. For example, the ratio of cis and trans-1,2-dimethyl-1-acetylcyclopropane (XXIV and XXV) from the thermal pyrolysis of XVIII and XIX were 22:25 and 62:17 respectively.

![Chemical Structures](image)

A second important feature of the present work is that the formation of olefins from the pyrolysis of 3,5-dimethyl-Δ¹-pyrazolines is highly stereospecific. The ratio of cis and trans-3-methyl-3-hexen-2-one (XXX and XXXI) from the pyrolysis
of cis and trans-3,5-dimethyl-3-acetyl-Δ¹-pyrazoline (XVIII and XIX) were 27:2 and 1:17 respectively. This stereospecificity has not been observed previously since an appropriate model has not been available. The formation of olefins has previously been thought to be formed through the intermediate

XXXIV or XXXV in which rotation around the single bonds would give a mixture of cis and trans olefins. For the diazonium salt XXXIV to give such steric control it would require that the anion center must retain its asymmetry. This is not anticipated on the basis of studies by Cram and coworkers (39).

In the pyrolysis and photolysis of 3,5-dimethyl-3-
acetyl-$\Delta^1$-pyrazoline (XXIII), its cis (XVIII) and trans (XIX) isomers, an additional product 2,3,5-trimethyl-$\Delta^2$-dihydrofuran (XXIX) was obtained. This can be formed through the diazonium betaine intermediate (XXXV) which has a resonance form of XXXVI. Again free rotation around $C_3-C_4$ bond predicts that cis and trans-3,5-dimethyl-3-acetyl-$\Delta^1$-pyrazoline (XVIII and XIX) would give the same intermediate XXXVI on pyrolysis, and hence they should give the same amount of dihydrofuran XXIX. Experimental results, however, showed the amount of XXIX obtained from the isomeric pyrazolines were significantly different. For example, thermal pyrolysis of cis and trans-3,5-dimethyl-3-acetyl-$\Delta^1$-pyrazoline (XVIII and XIX) at the injector of the vapor phase chromatography instrument gave 16% and 3%, respectively, of 2,3,5-trimethyl-$\Delta^2$-dihydrofuran (XXIX), and pyrolysis of neat liquid samples gave 14% and 0% respectively. These results seem to indicate that the formation of the dihydrofuran was predetermined by the molecular structure of the pyrazolines. In fact, the steric interaction of $C_3$ and $C_5$ methyl groups in cis-3,5-dimethyl-3-acetyl-$\Delta^1$-pyrazoline (XVIII) might be expected to force the acetyl group into a favorable position for dihydrofuran formation.
It is anticipated that the formation of an ionic diazonium butaine intermediate like II from $\Delta^1$-pyrazolines (III) would cause the kinetics of the reaction to show a higher rate in more polar solvents, since the process involves the formation of ionic charges from a neutral species (37). In other words, the rate of pyrolysis of $\Delta^1$-pyrazolines should be faster in a solvent of high polarity than a solvent of low polarity. The results of the present work showed the rate of pyrolysis of $\Delta^1$-pyrazolines, as indicated by the rate of nitrogen evolution, to be faster in non-polar solvents, such as di-n-butyl ether or tetralin than in polar solvents, such as nitrobenzene or formamide by the small factor of three. This opposite kinetic effect indicates that the intermediate in pyrolysis has less ionic character than the starting material, the $\Delta^1$-pyrazoline. Therefore, it is not likely that the thermal pyrolysis of $\Delta^1$-pyrazolines proceeds through an ionic mechanism with the diazonium butaine II as the transition state. The small difference in rate of pyrolysis in polar and non-polar solvents suggests the mechanism of the pyrolysis of $\Delta^1$-pyrazolines to be either free radical or molecular since these do not involve large ionic character.
One further argument can be made against the proposed ionic mechanisms for thermal pyrolysis. This mechanism would predict that the diazonium butaine intermediate, for example XXXIV, would form pyrazoline by ring closure faster than the loss of nitrogen. Since the product analysis predicts rotation about C₃–C₄ bond, one would anticipate that when trans-3,5-dimethyl-3-carbomethoxy-Δ¹-pyrazoline (XVII) is partially pyrolysed, the recovered sample should show both XVII and its cis isomer XVI. This has not been found to occur in this work or in the work of van Auken and Rinehart (12). Partial photolysis of XVII also gave a similar result.

The possibility of the diazonium butaine II as the intermediate for the pyrolysis of Δ¹-pyrazolines is therefore eliminated.

Recent work in this laboratory (40) has discovered a pyrazoline system which gives kinetics that are sensitive to
solvent polarity as expected for an ionic intermediate. The

\[
\text{XXXVII} \rightarrow \text{XXXVIII} + \text{other minor products.}
\]

\(\Delta^1\)-pyrazoline XXXVII in this case has two electron withdrawing
groups which can stabilized a diazonium betaine intermediate
to a greater degree.

It is apparent that pyrolysis of \(\Delta^1\)-pyrazolines might
fit a spectrum of conditions in which symmetric substitution
around the azo group leads to breaking of both bonds simultane­
ously in the transition state. In highly unsymmetrical
\(\Delta^1\)-pyrazolines like XXXVII one bond breaks before the other.
Such a situation has been shown to be the case for linear azo
compounds (41) where compounds XXXIX, XL and XLI (\(\phi = \text{C}_6\text{H}_5\))

\[
\begin{align*}
\text{XXXIX} & \quad \text{XL} & \quad \text{XLI} \\
\text{H}_3\text{C} & \quad \phi & \quad \text{H}_3\text{C} \\
\text{CH-N=N-CH} & \quad \phi & \quad \text{CH-N=N-CH} \\
\text{CH}_3 & \quad \phi & \quad \text{CH}_3 \\
\end{align*}
\]

show equal breaking of both bonds, unequal breaking of both
bonds and initial breaking of one bond. These results were
obtained by secondary deuterium effects on the kinetics.

It is apparent that in the pyrolysis of cis and trans-
3,5-dimethyl-3-carbomethoxy-\(\Delta^1\)-pyrazoline (XVI and XVII) we
have an intermediate situation where the C-N bonds are break-
ing in the transition state possibly to different degrees and sufficient polarity develops in the molecule after the transition state to make the products sensitive to the solvent used. Such a model correctly predicts the olefin reaction.

Photolysis of cis and trans-3,4-dimethyl-3-carbomethoxy-Δ¹-pyrazoline (VI and VII) have been reported by van Auken and Rinehart (12) to give stereospecifically cis and trans-1,2-dimethyl-1-carbomethoxycyclopropane (X and XI) respectively, the major side products are methyl tiglate (IV) and methyl angelate (V) respectively.

Photolysis of cis and trans-3,5-dimethyl-3-carbomethoxy-Δ¹-pyrazoline (XVI and XVII), cis and trans-3,5-dimethyl-3-acetyl-Δ¹-pyrazoline (XVIII and XIX) resemble very closely to the pyrolysis of the same. The major difference observed is that, the photolysis gave a higher yield of cyclopropane with retention of the geometry present in the pyrazoline, and the pyrolysis gave a lower yield of cyclopropane with retention of...
The preferred conformation of the pyrazoline isomers places the pseudo equatorial hydrogen on C₄ in a better position for migration to C₅ concerted with nitrogen elimination than the pseudo axial hydrogen.

FIGURE X - Stereochemistry of the formation of olefins from Δ¹-pyrazolines.
the geometry present in the pyrazoline. For example, the ratios of cis and trans-1,2-dimethyl-1-acetylcyclopropane (XXIV and XXV) were 59:28 and 21:70 for the photolysis of XVIII and XIX respectively. A similar solvent effect on the product composition as observed in the pyrolysis was also observed in the photolysis. The two reactions therefore are closely related but not identical as shown by photolysis and pyrolysis at same temperature and solvent in which different product compositions resulted.

It is possible the photolysis involves a different conformation of the same intermediate as the pyrolysis with variation either due to a different amount of available energy or due to induced structural features from the prior electronically excited intermediate. The nuclear magnetic resonance spectra (Table I) of the $\Delta^1$-pyrazolines showed large differences in the chemical shift positions of the hydrogens on $C_4$, especially in cis-3,5-dimethyl-3-acetyl-$\Delta^1$-pyrazoline.
(XVIII) and cis-3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline
(XVI). For example, C₄ hydrogens in XVIII absorbed at 7.57 $\delta$
and 9.30 $\delta$, those of XVI absorbed at 7.68 $\delta$ and 9.14 $\delta$
compared to 8.28 $\delta$ and 8.56 $\delta$ for the trans-ester-pyrazoline
(XVII) and 8.53 $\delta$ for the trans-keto-pyrazoline (XIX). These
differences in chemical shifts could well be related to dif­
ferences in conformation in these species. If this is so then
it is obvious that the molecules in some cases are entering
reaction with considerable differences in their geometry.
VI. EXPERIMENTAL

VI-1. General statement

Melting points and boiling points are uncorrected. Melting points were determined by a microscopic melting point apparatus (Reichart, Austria) and most boiling points were determined by the micro inverted capillary method.

Infrared spectra were measured with a Perkin-Elmer Model 137 spectrophotometer fitted with sodium chloride optics.

Nuclear magnetic resonance spectra were recorded on a Varian Associates Model A-60 spectrophotometer by Mrs. E. Brion and Mr. P. Horn. Tetramethylsilane was used as internal standard.

The vapor phase chromatography units used were an Aerograph Model A-90-P (preparative scale) and a Perkin-Elmer Model 226 (analytical scale).

The elemental microanalyses were performed by Dr. A. Bernhardt of Germany and by Mrs. A. Aldridge and Mrs. C. Jenkins.

VI-2. N-Nitroso-N-ethyl urea

The method for the preparation of N-nitroso-N-methyl urea (35) was adapted with some modification. Three hundred grams (5 moles) of urea was dissolved in a solution of 123 g. (1.5 moles) of ethylamine hydrochloride, 300 ml. of water and a few drops of
concentrated hydrochloric acid. The mixture was boiled gently under reflux for three hours and vigorously for a quarter hour. After cooling to room temperature, 110 g. (1.5 moles) of 98 per cent sodium nitrite was added and the mixture was divided into six equal portions. Each portion was chilled with ice and added to an ice-cold solution of 17 g. (0.17 mole) of concentrated sulfuric acid in 110 g. of ice with stirring at such a rate that the temperature remained below 5°. The N-nitroso-N-ethyl urea, which rose to the surface as pale yellow crystals, was collected on a filter and washed with ice-cold water and dried by suction till constant weight (approximately three hours). The yield was 87 g. (0.75 mole) or 50 per cent of the theoretical yield.

VI-3. Diazoethane

Fifty grams (0.285 mole) of N-nitroso-N-ethyl urea was added to vigorously stirred ice-cold solution of 300 ml. of anhydrous ether-methanol (5:1) and 125 ml. of 40% potassium hydroxide at such a rate that the reaction was under control and the reaction temperature remained below 5°. The orange colored diazoethane-ether-methanol solution was decanted from the aqueous layer, washed with 100 ml. of ice-cold water and dried with anhydrous potassium hydroxide pellets for two hours. The yield was approximately 35-40 per cent as estimated by the reactions with methyl isopropenyl ketone and methyl methacrylate.
VI-4. Methyl isopropenyl ketone

A commercial sample (K and K Laboratory, Plainsville, N.Y.) was purified by mixing with an equal volume of anhydrous ethyl ether with stirring. A polymer residue precipitated instantly and was filtered with fluted filter paper. The filtrate was distilled at atmospheric pressure and the fraction with a boiling point of $95\pm2^\circ$ was collected and used immediately.

VI-5. 3,5-Dimethyl-3-acetyl-$\Delta^1$-pyrazoline (XXIII)

To an ice-cold diazoethane-ether-methanol solution was added the freshly distilled methyl isopropenyl ketone slowly with stirring until the orange color disappeared. The solvent mixture was removed by a flash evaporator at water aspirator pressure and the residue distilled to give a colorless liquid, b.p. $56-57^\circ/1.2$ mm. (50 per cent based on the quantity of methyl isopropenyl ketone used).


The n.m.r. spectrum (20% v/v in CCl$_4$) showed it to be a mixture of 40% cis and 60% trans isomers (see below) as estimated by the integrals of the acetyl methyl hydrogens of the two isomers.
VI-6. Separation of *cis* and *trans*-3,5-dimethyl-3-acetyl-$\Delta^1$-pyrazoline (XVIII and XIX)

The 3,5-dimethyl-3-acetyl-$\Delta^1$-pyrazoline (XXIII) was fractionally distilled using a Nester and Faust 18-inch by 6-mm. spinning-band still at 0.2 to 0.3 mm. with the still pot immersed in oil bath maintained between 65-70°. During the entire distillation, the vapor came over at 32-35°/0.2-0.3 mm. The n.m.r. analyses of the lower and higher boiling fractions showed they contained 81% *cis*-pyrazoline XVIII and 87% *trans*-pyrazoline XIX respectively. These analyses were based on the integrals of the acetyl methyl hydrogens absorptions at 7.78 $\delta$ for the *cis* isomer and at 7.65 $\delta$ for the *trans* isomer. The *cis* and *trans* geometric assignments were based on the comparison of n.m.r. spectral data with those of *cis* and *trans*-3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline (XVI and XVII) (Table I) and the stereospecific formation of *cis* and *trans*-1,2-dimethyl-3-acetylcylopropane (XXIV and XXV) from XVIII and XIX respectively by photolysis.

The n.m.r. spectral data of *cis* and *trans*-3,5-dimethyl-3-acetyl-$\Delta^1$-pyrazoline (XVIII and XIX) are tabulated in Table I.

VI-7. Separation of *cis* and *trans*-3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline (XVI and XVII)

3,5-Dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline (XX) prepared (17) from diazoethane and methyl methacrylate was fractionally
distilled as described for the separation of cis and trans-3,5-dimethyl-3-acetyl-\( \Delta^1 \)-pyrazoline (XVIII and XIX) to give cis and trans-3,5-dimethyl-3-carbomethoxy-\( \Delta^1 \)-pyrazoline (XVI and XVII) of 93% and 99+% pure respectively, at temperature between 48-53°/0.1-0.3 mm. XVI and XVII showed different chemical shifts for the ester methyl hydrogens at 6.33 \( \tau \) and 6.27 \( \tau \) respectively, and this is the basis for distinguishing the two isomers. Geometric assignments were based on the photolysis results in which the cis-3,5-dimethyl-3-carbomethoxy-\( \Delta^1 \)-pyrazoline (XVI) gave cis-1,2-dimethyl-1-carbomethoxycyclopropane (X) and the trans-3,5-dimethyl-3-carbomethyl-\( \Delta^1 \)-pyrazoline (XVII) gave trans-1,2-dimethyl-1-carbomethoxycyclopropane (XI) as main product, and the lower yield of the cis-pyrazoline XVI (40%) due to steric hindrance of the methyl groups at C₃ and C₅.

The n.m.r. spectral data of cis and trans-3,5-dimethyl-3-carbomethoxy-\( \Delta^1 \)-pyrazoline (XVI and XVII) are tabulated in Table I.

VI-8. trans-3,5-Dimethyl-3-carbomethoxy-\( \Delta^1 \)-pyrazoline hydrobromide (XXII)

To a mixture of 0.4 ml. of trans-3,5-dimethyl-3-carbomethoxy-\( \Delta^1 \)-pyrazoline (XVII) in 3 ml. of anhydrous ethyl ether was added slowly with constant stirring a solution of anhydrous ethyl ether saturated with anhydrous hydrogen bromide gas. The pale yellow precipitate was recrystallized from ethanol-ether to give 0.75 g. of white crystals, m.p. 152-153°. Larger
crystals were obtained by slow recrystallisation from ethanol.

Anal. Calcd. for C_{7}H_{13}N_{2}O_{2}Br: C, 35.46; H, 5.53; N, 11.82.
Found: C, 35.47; H, 5.32; N, 12.16.

VI-9. Thermal pyrolysis of 3,5-dimethyl-3-acetyl-Δ^{1}-pyrazoline (XXIII)

The injector port of the vapor phase chromatography unit (Aerograph Model A-90-P) was used as the apparatus for thermal pyrolysis. A sample of the pyrazoline XXIII was injected into the injector port by means of a hypodermic syringe, the pyrolysis products were eluted through the column where separation occurred and collected at the collector separately. Five fractions were obtained and it was found that the second fraction was a mixture of two components. All these six components have been identified as indicated below, where boiling point, refractive index, retention time in the vapor phase chromatogram using a 10-ft. didecyl phthalate column of one quarter inch diameter at 140°, injector at 255° with helium flow pressure at 48 p.s.i., product composition in per cent of total products are given (see Figure VII, P. 14).

2,3,5-Trimethyl-Δ^{2}-dihydrofuran (XXIX): b.p. 119-120°, n_{D}^{24} 1.4305 (lit. (27) b.p. 118.3-118.6°/746 mm., n_{D}^{24} 1.4390), 6.2 minutes and 9%. Infrared bands (5% v/v in CCl₄) at 5.87 μ (s) due to carbon-carbon double-bond stretching, 8.21 μ (s) and 9.63 μ (s) due to vinyl ether stretching (28). The n.m.r. spectrum (30% v/v in CCl₄) showed signals of vinyl methyl
hydrogens at 8.43 χ (multiplet), C₅ methyl hydrogens at 8.79 χ (doublet with J=6.1 c.p.s.), C₄ hydrogens at 7.40 χ (two doublets) and 7.98 χ (two doublets) and C₅ hydrogen at 5.59 χ (sextet with further splitting). The hydrogens at C₄ and C₅ constituted a typical ABX system (29) with Δₐₓ ≈ 14.5 c.p.s., Δₐₐ ≈ 35.5 c.p.s., Δₐₓ ≈ 109 c.p.s., Jₐₓ ≈ 14.5 c.p.s., Jₐₓ ≈ 8.0 c.p.s. and Jₓₓ ≈ 9.5 c.p.s. (Figure IX). These chemical shifts are at expected positions as compared to 2-methyl-Δ²-dihydrofuran (XXXIII) (30) whose chemical shifts are at 8.30 χ (multiplet), 5.55 χ (multiplet), 7.47 χ (multiplet) and 5.78 χ (triplet with J ≈ 9.3 c.p.s.) due to C₂ methyl hydrogens, C₃ vinyl hydrogen, C₄ and C₅ hydrogens respectively.

Anal. Calcd. for C₇H₁₂O: C, 74.95; H, 10.78. Found: C, 74.95; H, 10.90.

cis-3-Methyl-3-hexen-2-one (XXX): b.p. 145-145.5°, n_D 1.4370, 12.2 minutes and 6%. Infrared (5% v/v in CCl₄) bands at 5.91 μ (s) and 6.18 μ (w) attributable to the α,β-unsaturated carbonyl and carbon-carbon double-bond stretching respectively. The n.m.r. spectrum (10% v/v in CCl₄) showed peaks of acetyl methyl hydrogens at 7.86 χ (singlet), vinyl methyl hydrogens at 8.12 χ (multiplet), methylene hydrogens at 7.73 χ (multiplet), alkyl methyl hydrogens at 9.02 χ (triplet with J ≈ 7.3 c.p.s.) and vinyl hydrogen at 4.44 χ (multiplet). Geometric assignment is discussed below.

Anal. Calcd. for C₇H₁₂O: C, 74.95; H, 10.78. Found: C, 75.02; H, 10.77.
trans-3-Methyl-3-hexen-2-one (XXXI): b.p. 156.5-158°, n_D 1.4481, 17.7 minutes and 7%. Infrared spectrum (5% v/v in CCl_4) showed absorptions at 5.96 μ (s) and 6.07 μ (w) due to α,β-unsaturated carbonyl and carbon-carbon double-bond stretching respectively. The n.m.r. spectrum (10% v/v in CCl_4) showed peaks of acetyl methyl hydrogens at 7.81 ′ (singlet), alkyl methyl hydrogens at 8.93 ′ (triplet with J ≈ 7.5 c.p.s.), vinyl methyl hydrogens at 8.39 ′ (multiplet), methylene hydrogens at 7.76 ′ (multiplet) and vinyl hydrogen at 3.52 ′ (multiplet).

The geometric assignments for the cis and trans-3-methyl-3-hexen-2-one (XXX and XXXI) were based on the lower chemical shift of the vinyl proton in XXXI. Since in XXXI, the vinyl proton is cis to the carbonyl and hence closer to the diamagnetic anisotropy of the carbon-oxygen double-bond which deshields the vinyl proton to a greater extent to give a low ′-value (32).

Anal. Calcd. for C_{7}H_{12}O: C, 74.95; H, 10.78. Found: C, 75.03; H, 10.81.

cis-1,2-Dimethyl-1-acetylcyclopropane (XXIV): b.p. 151.5-152.5°, n_D 1.4376, 15.7 minutes and 44%. Infrared (5% v/v in CCl_4) spectrum showed bands at 5.96 μ (s) and 9.76 μ (m) due to stretching of carbonyl conjugated to cyclopropane ring and cyclopropane respectively. The n.m.r. spectrum (20% v/v in CCl_4) showed the following peaks, acetyl methyl hydrogens at 8.00 ′ (singlet), C_1 methyl hydrogens at 8.72 ′ (multiplet), C_2 methyl hydrogens at 8.82 ′ (multiplet with main peak at 8.84 ′), other ring hydrogens at 8.68 ′ (two hydrogens, multiplet under C_1.
methyl hydrogens signal) and 9.74 \( \tau \) (one hydrogen, multiplet). Assignment of geometry will be discussed below. Repeated elemental microanalysis gave low value of carbon composition.

Trans-1,2-Dimethyl-1-acetylcyclopropane (XXV) and 3-methyl-4-hexen-2-one (XXXII): these two components eluted together with retention time of 10.5 minutes, they constituted 34% of the total products. Analytical vapor phase chromatographic analysis showed the mixture to consist of 85% of XXV and 15% of XXXII. Bromination of the mixture using 5% bromine in carbon tetrachloride gave trans-1,2-dimethyl-1-acetylcyclopropane (XXV) and trans-3-methyl-3-hexen-2-one (XXXI) as indicated by preparative vapor phase chromatography separation. The n.m.r. spectrum of the original mixture indicated the presence of XXV and XXXII and will be discussed separately below.

Anal. Calcd. for C\(_{17}\)H\(_{12}\)O: C, 74.95; H, 10.78. Found: C, 74.87; H, 10.91.

Trans-1,2-Dimethyl-1-acetylcyclopropane (XXV): b.p. 136.5-137°, \( n^D_{24} \) 1.4275. Infrared (5% v/v in CCl\(_4\)) band at 5.90 \( \mu \) due to carbonyl conjugated to cyclopropane ring. The n.m.r. spectrum (20% v/v in CCl\(_4\)) showed the absorption of acetyl methyl hydrogens at 7.86 \( \tau \) (singlet), \( C_1 \) methyl hydrogens at 8.62 \( \tau \) (singlet), \( C_2 \) methyl hydrogens at 9.03 \( \tau \) (multiplet), \( C_2 \) and \( C_3 \) hydrogens at two sets of multiplet in the region between 8.75 \( \tau \) and 9.60 \( \tau \). The assignment of geometry to cis and trans-1,2-dimethyl-1-acetylcyclopropane (XXIV and XXV) was based on the comparison of their n.m.r. spectra to those of the analogous cyclopropanes, the cis and trans-1,2-dimethyl-1-carbomethoxycyclopro-
pane (X and XI) whose geometry have been determined (12).

3-Methyl-4-hexen-2-one (XXXII): this compound had not been isolated to give sufficient sample for complete identification. The presence of XXXII was indicated by the n.m.r. spectrum of the mixture of XXXII and trans-1,2-dimethyl-1-acetylcyclopropane (XXV). Some signals of XXXII were obscured by those of XXV, the following were readily observed and assigned as follows, acetyl methyl hydrogens at 7.97 $\tau$ (singlet), $\text{C}_3$ methyl hydrogens at 8.92 $\tau$ (doublet with $J \approx 7$ c.p.s.), vinyl hydrogens at 4.57 $\tau$ (multiplet) and vinyl methyl hydrogens at 8.32 $\tau$ (doublet with $J \approx 4.8$ c.p.s.). The n.m.r. spectrum indicated the sample to be a $\beta,\gamma$-unsaturated ketone because of the high acetyl methyl hydrogens absorption at 7.97 $\tau$ and the olefin proton absorption at 4.57 $\tau$.

VI-10. Thermal pyrolysis of cis and trans-3,5-dimethyl-3-acetyl-$\Delta^1$-pyrazoline (XVIII and XIX)

The same procedure as for the thermal pyrolysis of 3,5-dimethyl-3-acetyl-$\Delta^1$-pyrazoline (XXIII) was used for the thermal pyrolysis of cis and trans-3,5-dimethyl-3-acetyl-$\Delta^1$-pyrazoline (XVIII and XIX). These reactions gave the same products as the thermal pyrolysis of XXIII but in different ratio. These results are recorded in Table II.

VI-11. Vapor phase pyrolysis of cis and trans-3,5-dimethyl-3-acetyl-$\Delta^1$-pyrazoline (XVIII and XIX)
The apparatus for the vapor phase pyrolysis was a one-liter round flask equipped with a ground stopcock and a finger (45-mm. x 10-mm.) opposite the stopcock. Three microliter sample of XVIII or XIX in a capillary tube was placed in the finger and cooled with liquid nitrogen, and the flask was then evacuated below 0.3 mm. The reaction flask was heated in an oven preheated to 125° for thirty minutes. It was then connected to a vacuum line and the products were collected in a U-tube cooled with liquid nitrogen. Fifty microliters of anhydrous ether was added, and the mixture was analysed by analytical vapor phase chromatography using a 150-ft. x 0.01-in. Perkin-Elmer column "R" at 100° with nitrogen flow pressure of 12 p.s.i. The analyses showed that the vapor phase pyrolysis reactions of cis and trans-3,5-dimethyl-3-acetyl-α-pyrazoline (XVIII and XIX) gave the same products as the thermal pyrolysis of the same compound but in different ratio. These results are recorded in Table II.

VI-12. Liquid phase pyrolysis of 3,5-dimethyl-3-acetyl-α-pyrazoline (XXIII)

Nine and a half grams of XXIII in a 25 ml. round flask equipped with a water cooled condenser was heated in an oil bath, pyrolysis started at 90° with the evolution of nitrogen gas and became vigorous at 105°. The heating was stopped when nitrogen gas ceased to come off. The yield was 7 g. or 93 per cent of the theoretical amount. The mixture was separated by preparative vapor phase chromatography using a 10-ft. didecyl phthalate
column of one quarter inch diameter at $140^\circ$ with helium flow pressure at 48 p.s.i. to give the same products as the thermal pyrolysis of the same compound but in different ratio. The result is recorded in Table II.

VI-13. Liquid phase pyrolysis of cis and trans-3,5-dimethyl-3-acetyl-$\Delta^1$-pyrazoline (XVIII and XIX)

One quarter milliliter of XVIII or XIX in a 150-mm. x 8-mm. pyrex tube was heated in an oil bath at $100^\circ$ until the evolution of nitrogen gas ceased. Product composition of the products was analysed by analytical vapor phase chromatography as described above. The results are recorded in Table II.

VI-14. Photolysis of 3,5-dimethyl-3-acetyl-$\Delta^1$-pyrazoline (XXIII)

A mixture of 1 ml. of XXIII and 25 ml. of anhydrous ether in a 50 ml. round flask equipped with a water cooled condenser was irradiated with a 450-watt Hanovia mercury lamp for six hours under reflux condition. The completion of photolysis was determined by the absence of nitrogen peak in the chromatogram when a sample was injected into the preparative vapor phase chromatography unit or alternately, by measuring the theoretical amount of nitrogen that evolved (the top of the condenser was connected to a gas measuring buret). Most of the solvent was distilled off at atmospheric pressure and the concentrate was analysed by either preparative or analytical vapor phase chromatography as described above. The same products but at different
compositions than the liquid phase pyrolysis of the same compound resulted. The result is recorded in Table II.

VI-15. Photolysis of cis and trans-3,5-dimethyl-3-acetyl-$\Delta^1$-pyrazoline (XVIII and XIX)

A mixture of 0.5 ml. of XVIII or XIX and 5 ml. of anhydrous ether in a 25 ml. round flask equipped with a water cooled condenser was photolysis as described above. The mixture after photolysis, without concentrating the solvent, was analysed by analytical vapor phase chromatography. The results are recorded in Table II.

VI-16. Vapor phase pyrolysis of cis and trans-3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline (XVI and XVII)

The same procedure as the vapor phase pyrolysis of cis and trans-3,5-dimethyl-3-acetyl-$\Delta^1$-pyrazoline (XVIII and XIX) was used for the vapor phase pyrolysis of XVI and XVII. Analytical vapor phase chromatogram showed the same products as the vapor phase pyrolysis of 3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline (XX) but in different ratio (17) resulted. These results are recorded in Table III.

VI-17. Liquid phase pyrolysis of cis and trans-3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline (XVI and XVII) in various solvents
A mixture of 0.2 ml. of XVI or XVII and 20 ml. of solvent in a sealed tube (30-cm. x 2.5-cm.) which had been previously evacuated to below 0.1 mm. was heated in an oven at 125-130° for one and a half hours. For volatile solvents, the solvent was removed by distillation through a spinning-band column under reflux condition, the concentrated sample was analysed by analytical vapor phase chromatography. For the solvent formamide, the products were removed from the solvent on a vacuum line by pumping for two hours and similarly analysed. Solvents (dielectric constants at 20° are given in parentheses (44)) used in these pyrolyses were cyclohexane (2.07 D), ethyl ether (4.34 D), methanol (33.6 D), acetonitrile (37.5 D) and formamide (109 D). These results are summarized in Table IV.

VI-18. Photolysis of trans-3,5-dimethyl-3-carbomethoxy-$$\Delta^1$$-pyrazoline (XVII) at various temperatures.

The apparatus for these reactions is shown in Figure XI. A mixture of 0.2 ml of XVII and 5 ml. of anhydrous ether was placed in the reaction vessel A, the centrifugal pump F was turned on which pumped the mobile cooling solution ethanol through F, I into B and back to E. A suitable cooling agent was placed in D and the temperature at E was taken as that of the photolysis. As soon as the temperature at E came to constant, the mercury lamp G (Hanovia, 450-watt) was turned on and the temperature at D was lowered a few degrees in order to keep the temperature at E constant. Irradiation was terminated when the theoretical amount of nitrogen gas had evolved. This experiment
A - Reaction vessel, 13-mm. x 150-mm.
B - Cooling jacket
C - Air jacket
E - Dewar flask with ethanol as mobile cooling solution
D - Dewar flask with cooling agent
F - Centrifugal pump
G - 450-watt Hanovia mercury lamp
H - Gas measuring buret
I - Cooling coil

FIGURE XI - Apparatus for photolysis at low temperature.
had been performed at three different temperatures, 0°, -20° and -55° using ice-salt, carbon tetrachloride-Dry Ice and chloroform-Dry Ice respectively, as cooling agents at D. All reaction products, without concentrating the solvent, were analyzed by analytical vapor phase chromatography and their results are summarized in Table V.

VI-19. Photolysis of cis and trans-3,5-dimethyl-3-carbomethoxy-\( ^1 \Delta \)pyrazoline (XVI and XVII) in formamide at 23°

The same procedure as described in the preceding paragraph was used for these photolyses. The cooling agent at D was water at 22-23°. These results are recorded in Table V.

VI-20. Partial photolysis of trans-3,5-dimethyl-3-carbomethoxy-\( ^1 \Delta \)pyrazoline (XVII)

A mixture of 1 g. of XVII (994%) and 10 ml. of anhydrous ether in a 25 ml. round flask equipped with a water cooled condenser whose top end was connected to a gas measuring buret was irradiated with a 450-watt Hanovia mercury lamp. The irradiation was terminated when 75 ml. (50 per cent of the theoretical amount) of nitrogen gas had evolved, and the resulting solution was connected to a vacuum line to removed the solvent and the products from photolysis. The recovered pyrazoline was analysed by n.m.r. which showed that the n.m.r. spectra of the recovered pyrazoline and the starting pyrazoline were practically identical to each other.
VI-21. Partial liquid phase pyrolysis of trans-3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline (XVII)

One gram of XVII (99%) in a 100-mm. x 13-mm. pyrex tube connected to a gas measuring buret was heated to 95° at an oil bath. Heating was stopped when 75 ml. (50 per cent of the theoretical amount) of nitrogen gas had evolved. After removing the pyrolysis products in a vacuum line, the recovered pyrazoline was analysed by n.m.r. which showed that the n.m.r. spectra of the recovered pyrazoline and the starting pyrazoline were practically identical to each other.

VI-22. Kinetic Studies of the pyrolysis of 3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline (XX) at various solvents

The apparatus consisted of a 150-mm. x 13-mm. pyrex tube whose top end was connected to a gas measuring buret. Six milliliters of solvent in the tube was heated in an oil bath to 100-1°, 0.2 ml. of XX was added into the solvent and pyrolysis begun. The volume of nitrogen evolved and the time were recorded at intervals. It has been shown (45) that the pyrolysis of $\Delta^1$-pyrazolines gives good first order kinetics, and that the half-life, $t_{1/2}$, of the pyrazoline is equal to $(\log 2)/m$, where $m$ is the slope of the straight line obtained by the first order plot of the quantity $\log (V_\infty/V_0-V_t)$ verses time, $t$. This pyrolysis reaction of XX had been done in the following series of solvents, di-n-butyl ether, tetraline, nitrobenzene and formamide, and the half-life of XX in these solvents had been found to be 26.2, 29.0, 43.6 and 83.1 minutes, respectively (Figure XII).
FIGURE XII - First order plot of $\log \frac{V_\infty}{V_\infty - V_t}$ vs. time for the pyrolysis of 3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline in various solvents.
VI-9a. 2,4-Dinitrophenyl hydrazones

To a mixture of fifty microliters of ketone and 3 ml. of 2,4-dinitrophenyl hydrazine-diglyme solution (36) was added 2 drops of concentrated hydrochloric acid and the mixture was allowed to stand for at least 24 hours (otherwise oily residue resulted when water was added). Water was then added dropwise with stirring till cloudy, precipitation normally completed after two or three hours. The precipitate was collected and recrystallized from diglyme-water. The melting points of the 2,4-DNPH derivatives of 2,3,5-trimethyl-Δ²-dihydrofuran (XXIX), cis and trans-1,2-dimethyl-1-acetylcyclopropane (XXIV and XXV) and cis-3-methyl-3-hexen-2-one (XXX) were 295-8°, 118.5-119.5°, 307-9° and 156.5-157° respectively. trans-3-methyl-3-hexen-2-one gave two 2,4-DNPH derivatives; one precipitated before water was added, m.p. 158.5-159°, and the other precipitated after water was added, m.p. 156-156.5°. These two 2,4-DNPH derivatives of trans-3-methyl-3-hexen-2-one (XXXI) were not the same as indicated by their mixed melting point, 154-157°, and by the fact that the second derivative precipitated only after water was added. It has been shown (42,43) that δ,β-unsaturated ketones give two 2,4-DNPH derivatives, Δ²-pyrazoline and syn-alkyl 2,4-DNPH. Hence one of the two 2,4-DNPH derivatives of XXXI obtained could be a Δ²-pyrazoline, and the other a syn-alkyl 2,4-DNPH.


34. *ibid.*, p. 20.


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