STEREOCHEMISTRY OF OLEFIN FORMATION IN THE PYROLYSIS OF 3-CARBOMETHOXY PYRAZOLINES

BY

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We accept this Thesis as conforming to the required standard.

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September, 1966
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Date October 21, 1966
ABSTRACT

The thermal decomposition of cis- and trans-3-methyl-4-ethyl-3-carbomethoxy-Δ¹-pyrazoline (cis- implies that the methyl and ethyl groups are cis) and trans-3-methyl-4-ethyl-3-carbomethoxy-Δ¹-pyrazoline gave a mixture which contained cyclopropane products, cis- and trans-1-methyl-2-ethyl-1-carbomethoxycyclopropane; α,β-unsaturated ester products, methyl cis- and trans-2,3-dimethyl-2-pentenoate (cis and trans refer the two methyl groups); and the β,γ-unsaturated ester, methyl 2-methyl-3-ethyl-3-butenoate.

The α,β-unsaturated esters are formed stereospecifically since cis-3-methyl-4-ethyl-3-carbomethoxy-Δ¹-pyrazoline gave only methyl trans-2,3-dimethyl-2-pentenoate (56% in the liquid phase and 28% in the vapor phase). Similarly in the pyrolysis of trans-3-methyl-4-ethyl-3-carbomethoxy-Δ¹-pyrazoline methyl cis-2,3-dimethyl-2-pentenoate (13% in the liquid phase and 6% in the vapor phase) was obtained while only a trace of methyl trans-2,3-dimethyl-2-pentenoate was found in both the liquid and vapor phase pyrolysis.

The cyclopropane products formed from pyrolysis of cis- and trans-3-methyl-4-ethyl-3-carbomethoxy-Δ¹-pyrazoline have shown some degree of stereospecificity with a predominance of the isomer having the same stereochemistry as the starting pyrazoline being obtained.

The results of the above experiments suggest that the mechanism of thermal pyrolysis of pyrazolines requires that the nitrogen leaves from the same side as the ethyl group, i.e. trans to the hydrogen which is migrating.

The photolysis of cis- and trans-3-methyl-4-ethyl-3-carbomethoxy-Δ¹-pyrazoline has been found to be stereospecific in cyclopropane formation with the absence of isomeric olefin products. A small amount of the olefin corresponding to loss of CH₂N₂ was also found having the same stereochemistry as
the pyrazoline.

Since the products from photolysis are different from that of pyrolysis, a modified mechanism is required. Insufficient evidence is available to clearly define that mechanism.
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INTRODUCTION

A route that has been known for some time for the preparation of cyclopropane derivatives is based on the synthesis of $\Delta^1$-pyrazolines by the addition of a diazoalkane to an $\alpha,\beta$-unsaturated ester (1-3) followed by pyrolysis of the pyrazoline at temperatures from 100-200°C (4-6). For example, 1-methyl-1-carbomethoxycyclopropane (III) can be made (7) as shown in the Figure I.

\[
\begin{align*}
\text{CH}_3 \\
\text{CH}_2\text{N}_2 + \text{CH}_2\text{=C-CO}_2\text{CH}_3 & \rightarrow \text{C}_3\text{N} \text{CH}_3 \rightarrow \Delta \\
\text{I} & \quad \text{II} \\
\text{CH}_3 \text{CO}_2\text{CH}_3 & + \text{CH}_3 \text{CO}_2\text{CH}_3 \\
\text{III} & \quad \text{IV} \quad \text{V} \\
& 65\% \quad 15\% \quad 15\% \\
\end{align*}
\]

Figure I. Preparation of 1-Methyl-1-carbomethoxycyclopropane.

In addition to cyclopropane products there are usually also formed $\alpha,\beta$- and $\beta,\gamma$-unsaturated ester products. It is the purpose of this thesis to examine this reaction in some detail in the hope that a better understanding of the mechanism of this pyrolysis reaction will result.

Preparation of Pyrazolines

The addition reaction of a diazoalkane to the $\alpha,\beta$-unsaturated carbonyl compound to form a $\Delta^1$-pyrazoline has recently been suggested to be a one-step
multiple centre reaction (8,9) rather than a two-step mechanism (10) suggested earlier. The basis of this suggestion has been due to the absence of the isomeric $\Delta^1$-pyrazoline in a synthesis where two isomers should be possible by the two-step mechanism. The two proposed mechanisms are shown in Figure II and an example illustrating the cis addition/diazomethane with formation of a single pyrazoline product is shown for the addition to methyl tiglate (IV) and methyl angelate (V) to give cis- and trans-3,4-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazolines (XI and XII) (11) respectively as shown in Figure III.

This feature of the pyrazoline synthesis provides a means to obtaining isomeric pyrazolines differing only in their geometrical configurations like IX and X.

Figure III. Synthesis of cis- and trans-3,4-Dimethyl-3-carbomethoxy-$\Delta^1$-pyrazolines.
Other pairs of geometrical isomers have been obtained by separation of the pyrazoline pair prepared as a mixture by distillation, vapor chromatography and crystallization. The cis- and trans-3,5-dimethyl-3-carbomethoxy-\(\Delta^1\)-pyrazolines (XI and XII) were separated by distillation (12), cis- and trans-3,5-dimethyl-\(\Delta^1\)-pyrazoline (XIII and XIV) were separated by vapor chromatography (13) and cis- and trans-3,5-di-(p-anisyl)-\(\Delta^1\)-pyrazoline (XV and XVI) were separated by crystallization (14).

\[ \text{Pyrolysis of Pyrazolines} \]

Early suggestions concerning the mechanism for the pyrolysis of pyrazolines have involved intermediates resulting from bond breaking of one or both of the C-N bonds as shown in Figure IV.

Figure IV. C-N Bond Breaking During Pyrolysis of Pyrazolines.
Thus ionic or free radical species (10,15,16,17) have been considered which by hydrogen migration can give olefin products and by ring closure can give cyclopropane products.

Some recent experimental results leading to mechanistic suggestions are given below.

Van Auken and Rinehart (11) - Thermal pyrolysis of cis-3,4-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline (IX) gave as decomposition products cis-1,2-dimethyl-1-carbomethoxy-cyclopropane (XVII), trans-1,2-dimethyl-1-carbomethoxy-cyclopropane (XVIII), methyl 2,3-dimethyl-2-butenoate (XIX) and methyl 2,3-dimethyl-3-butenoate (XX) in the ratio of 17.6 %, 12.3 %, 65.8 %, 4.3 % whereas in the pyrolysis of trans-3,4-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline (X), the ratio of these products were 28.4 %, 34.6 %, 32.9 %, 4.1 % respectively as shown in Figure V.

That these two pyrazolines (IX and X) gave almost a 50:50 mixture of cis- and trans-cyclopropanes (XVII and XVIII) respectively suggested to the authors that the intermediate (XXI) has free rotation around the C-3-C-4 bond as shown in Figure VI.

![Figure V. Thermal Pyrolysis of cis- and trans-3,4-Dimethyl-3-carbomethoxy-$\Delta^1$-pyrazolines](image-url)
Overberger (18) - Thermal pyrolysis of trans-3,5-diphenyl-Δ1-pyrazoline (XXII, n = 1) gave only trans-1,2-diphenylcyclopropane. On the other hand, larger ring derivatives gave cis and trans products. Assuming a free radical intermediate (XXIV), Overberger et al suggest that the intermediate has much less time to become free to rotate in the formation of cyclopropane than in the case of formation of the cyclopentane or the cyclohexane products as shown in Figure VII.

Figure VI. Free Rotation in the Intermediate of the C-3-C-4 Bond.

![Chemical structures and reaction diagram]

Figure VII: Pyrolysis of trans-3,5-Diphenyl-Δ1-pyrazoline.
In a later paper (14), however, they have observed results that do suggest free rotation in the intermediate. (cis-3,5-Di-(p-anisyl)-Δ^1-pyrazoline (XV) on pyrolysis gives a product containing 43.0% of the cis cyclopropane and 57% of the trans).

McGreer and coworkers (12) - Thermal pyrolysis of cis- and trans-3,5-dimethyl-3-carbomethoxy-Δ^1-pyrazolines (XI and XII) gave the products cis-1,2-dimethyl-1-carbomethoxy cyclopropane (XVII), trans-1,2-dimethyl-1-carbomethoxy cyclopropane (XVIII), methyl cis-2-methyl-2-pentenoate (XXV), methyl trans-2-methyl-2-pentenoate (XXVI) and methyl 2-methyl-3-pentenoate (XXVII) in the ratio of 18%, 48%, 32%, 0%, 2% and 60%, 15%, 0%, 22%, 3% respectively as shown in Figure VIII.

![Figure VIII. Liquid Phase Pyrolysis of cis- and trans-3,5-Dimethyl-3-carbomethoxy-Δ^1-pyrazolines.](image)

The major cyclopropanes (XVII and XVIII) obtained have the stereochemistry opposite to pyrazoline from which they were formed respectively, (XI and XII), and the olefins are formed by a stereospecific process. This therefore suggests a concerted hydrogen migration with loss of nitrogen in
the olefin forming step as illustrated by the intermediate shown in Figure IX.

![Figure IX. Intermediate Showing Concerted Hydrogen Migration.](image)

Crawford and Mishra (13) - Kinetic studies for pyrolysis of 4-methyl-Δ¹-pyrazoline (XXIX) and its C-4 deuterated substituent (XXX) gave a cyclopropane and an olefin product in a nearly 50:50 ratio. The kinetic deuterium effect was 1.07 while the effect of deuterium on the product forming step indicated a kinetic isotope effect for step III of 1.80 (see Figure X). This suggests that the hydrogen migration takes place after the rate determining transition state and suggests an intermediate common to both cyclopropane and olefin formation.

The structure of the intermediate has been suggested to be a planar symmetric molecule with a π-bond between two of the carbons in the cyclopropane ring. This so called "π-cyclopropane" is shown in Figure XI.

Pyrolysis of cis-3,5-dimethyl-Δ¹-pyrazoline (XI) gave cis-1,2-dimethylcyclopropane (XVII), trans-1,2-dimethylcyclopropane (XVIII) and trans-2-pentenoate (XXXIV) in the ratio of 33.24 %, 66.08 %, 0.68 % whereas the pyrolysis of trans-3,5-dimethyl-Δ¹-pyrazoline (XIV) gave the cis-2-pentenoate (XXXV) in addition to the above three products in the ratio of 72.61 %, 25.42 % 1.08 % and 0.91 % by the order of compounds XXXII, XXXIII, XXXIV, and XXXV as shown in the Figure XII.
XXIX H at C-4
XXX D at C-4

\[
\left( \frac{k_H}{k_D} \right)_{\text{I}} = \left( \frac{k_H}{k_D} \right)_{\text{kinetic}} = 1.07
\]

\[
\left( \frac{k_H}{k_D} \right)_{\text{III}} \neq \left( \frac{k_H}{k_D} \right)_{\text{products}} = 1.80
\]

Figure X. Kinetic Studies for Pyrolysis of 4-Methyl-Δ⁴-pyrazoline and its C-4 Deuterated Substituent.

Figure XI. π-Cyclopropane Intermediate.

Figure XII. Pyrolysis of cis- and trans-3,5-Dimethyl-Δ⁴-pyrazoline.
Loss of nitrogen from XIII would be expected to give intermediate XXXVI which by hydrogen migration from C-4 to C-3 or C-5 can only give trans-2-pentene (XXXIV). However, in the intermediate XXXVII expected from XIV hydrogen migration from C-4 to C-3 would give trans-2-pentene (XXXVI) and from C-4 to C-5 would give cis-2-pentene (XXXV) as shown in Figure XIII.

\[ \text{CH}_3 \text{N=N} \text{CH}_3 \quad \rightarrow \quad \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{H} \]

\[ \text{XXXVI} \]

\[ \text{CH}_3 \text{N=N} \text{CH}_3 \quad \rightarrow \quad \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{H} \text{CH}_3 \]

\[ \text{XXXVII} \]

Figure XIII. Intermediates from cis- and trans-3,5-Dimethyl-\( \Delta^1 \)-pyrazolines.

These two p-orbitals at C-4 and C-3 of intermediates XXXVI and XXXVII form a weak \( \pi \)-bond. Conversion of this \( \pi \)-bond to a \( \sigma \)-bond is possible by two forms of internal rotation. These are defined as conrotation and disrotation as shown in Figure XIV.

\[ \text{Conrotation} \quad \text{Disrotation} \quad \text{Represents a p-orbital} \]

Figure XIV. Conrotation and Disrotation.
Quantum mechanical evaluation of the symmetry changes in going from the $\pi$ type bond to a $\sigma$-bond suggests that conrotation would be more favored than disrotation (19). The experimental results of Crawford (13) and McGreer (12) when evaluated in terms of this mechanism show a preference to conrotation. On the other hand, Overberger's (18) results do not.

### Photolysis of Pyrazolines

Irradiation of $\Delta^1$-pyrazolines at the wave length of their absorption (about 320 nm with $\epsilon_{\text{mol.}}$ of 500) results in loss of nitrogen and products similar to the products from pyrolysis. Major differences in the stereochemical results for the cyclopropane formation, however, suggest that here a new or modified mechanism is involved. Results of significance are the following; however, no attempt has been made to identify the species which is fragmenting (i.e. whether it is an excited state or a high energy ground state molecule etc.).

Van Auken and Rinehart (11) have observed the photolysis of cis- and trans-3,4-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline (IX and X) to give as main products cis- and trans-1,2-dimethyl cyclopropane derivatives (XVII and XVIII) with the same geometrical configuration as the pyrazoline from which they were obtained. Additional compounds in the products were identified as the $\alpha,\beta$-unsaturated esters, methyl tiglate (IV) and methyl angelate (V) respectively resulting from loss of $\text{CH}_2\text{N}_2$ from the pyrazoline. The other products found in the pyrolysis reaction were present in only trace amounts as shown in Figure XV and therefore suggested a concerted molecular reaction.

The transition states in photolysis have been suggested to be either XXXVIII or XXXIX in the Figure XVI.
McGreer et al (12) have observed the photolysis of cис- and трансп-3,4-Dimethyl-3-carbomethoxy-Δ1-pyrazolines (XI and XII) to give the products with the proportional distributions as shown in the Figure XVII.

The cyclopropane products in contrast to the pyrolysis results are predominantly of the same stereochemistry as the starting pyrazoline. It was
therefore suggested that the fragmenting molecule is a "hot ground state molecule" which due to its high energy is reacting from a different average conformation than in the thermal reaction.

\[
\begin{align*}
\text{XVII} & \quad \text{CH}_3 & \quad \text{CO}_2\text{CH}_3 \\
\text{XVIII} & \quad \text{H} & \quad \text{CH}_3 & \quad \text{CO}_2\text{CH}_3 \\
\text{XXV} & \quad \text{H} & \quad \text{C}_2\text{H}_5 & \quad \text{CO}_2\text{CH}_3
\end{align*}
\]

|     | ether | 35° | 61% | 23% | 6%  \\
|-----|-------|-----|-----|-----|-----|
| XI  | ether  | 35° | 22% | 65% | 0%  \\
| XII | ether  | 35° | 2%  | 2%  | 6%  \\
|     | ether  | 35° | 5%  | 2%  | 6%  \\

Figure XVII. Photolysis of cis- and trans-3,5-Dimethyl-3-carbomethoxy-\(\Delta^1\)-pyrazolines.

Because of the stereospecificity observed by McGreer et al. in the formation of the \(\alpha,\beta\)-unsaturated products for the pyrolysis of cis- and trans-3,5-dimethyl-3-carbomethoxy-\(\Delta^1\)-pyrazolines (XI and XII) (12) it was proposed that this phase of the reaction could be studied further by examining a pyrazoline pair related to those studied by Van Auken and Rinehart (11). The olefins obtained by Van Auken and Rinehart are symmetrical and thus provide little information for the olefin-forming reaction. By working with an ethyl group at C-4 rather than a methyl both cis and trans-\(\alpha,\beta\)-unsaturated products are possible as shown in Figure XVIII.
Figure XVIII. Possible Pyrolysis Reactions of cis- and trans-3-Methyl-4-ethyl-3-carbomethoxy-$\Delta^1$-pyrazolines.
II RESULTS

Synthesis of cis- and trans-3-Methyl-4-ethyl-3-carbomethoxy-$\Delta^1$-pyrazolines (XL and XLI).

The cis- and trans-3-methyl-4-ethyl-3-carbomethoxy-$\Delta^1$-pyrazolines (XL and XLI) were synthesized by adding diazomethane to methyl trans- and cis-2-methyl-2-pentenoate (XXVI and XXV) respectively as shown in the Figure XIX.

\[
\begin{align*}
\text{C}_2\text{H}_5 & \quad \text{CH}_3 \\
\text{H} & \quad \text{CO}_2\text{CH}_3 \\
\text{XXVI} & \\
+ & \\
\text{CH}_2\text{N}_2 & \\
\rightarrow & \\
\text{C}_2\text{H}_5 & \quad \text{CH}_3 \\
\text{H} & \quad \text{CO}_2\text{CH}_3 \\
\text{XL} & \\
\text{C}_2\text{H}_5 & \quad \text{CH}_3 \\
\text{H} & \quad \text{CO}_2\text{CH}_3 \\
\text{XXV} & \\
+ & \\
\text{CH}_2\text{N}_2 & \\
\rightarrow & \\
\text{C}_2\text{H}_5 & \quad \text{CH}_3 \\
\text{H} & \quad \text{CO}_2\text{CH}_3 \\
\text{XLI} & \\
\end{align*}
\]

Figure XIX. Preparation of cis- and trans-3-Methyl-4-ethyl-3-carbomethoxy-$\Delta^1$-pyrazolines.

The cis- and trans-2-methyl-2-pentenoate (XXV and XXVI) used were isolated from the pyrolysis in the liquid phase of a mixture of cis- and trans-3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazolines (XLIII) which were synthesized from methyl methacrylate (I) and diazoethane (XLII) (20) as shown in the Figure XX. The n.m.r. spectra showed the mixture to contain two isomeric pyrazolines; trans-3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline (XII) 64% and cis-3,5-dimethyl-3-carbomethoxy-$\Delta^1$-pyrazoline (XI) 36 %.

Thermal pyrolysis of the pyrazoline mixture XLIII in the liquid phase without solvent at a temperature about 90° to 120°C gave five products which
have been identified earlier (20 and 12) and are illustrated together with the percentage distributions in Figure XXI.

![Chemical structures and percentages]

**Figure XX.** Synthesis of cis- and trans-3,5-Dimethyl-3-carbomethoxy-$\Delta^1$-pyrazolines.

![Chemical structures with percentages]

**Figure XXI.** Liquid Phase Pyrolysis of Mixture of cis- and trans-3,5-Dimethyl-3-carbomethoxy-$\Delta^1$-pyrazolines.

**Separation of Methyl cis- and trans-2-Methyl-2-pentenoate**

The product from pyrolysis of mixture XLIII was distilled using an annular Teflon spinning-band distillation column with an automatic reflux ratio controller under atmosphere pressure. The residue contained 90.2% methyl trans-2-methyl-2-pentenoate (XXVI) and 9.8% cis-1,2-dimethyl-1-carbomethoxycyclopropane (XVII) and redistillation of this residue, gives pure...
XXVI in a yield of 11.4% based on pyrazoline used.

It was impossible to completely purify the methyl cis-2-methyl-2-pentenoate (XXV) by the distillation method. It was obtained pure by gas chromatographic separation of the enriched fractions with a final percentage yield of 4%.

The methyl cis- and trans-2-methyl-2-pentenoate (XXV and XXVI) were reacted with excess diazomethane respectively and in a few days gave trans- and cis-3-methyl-4-ethyl-3-carbomethoxy-$\Delta^1$-pyrazolines (XLI and XL) respectively.

**Pyrolysis of cis- and trans-3-Methyl-4-ethyl-3-carbomethoxy-$\Delta^1$-pyrazolines**

The products isolated from the pyrolysis of these pyrazolines (XL and XLI) and their distributions as measured by chromatography are given in the Figure XXII. Some features of interest in the results are the following.

Pyrolysis of cis-3-methyl-4-ethyl-3-carbomethoxy-$\Delta^1$-pyrazoline (XL) without solvent around 115° to 145°C gave as the major product methyl trans-2,3-dimethyl-2-pentenoate (XLIV) (56%). None of the isomeric unsaturated olefin cis-2,3-dimethyl-2-pentenoate (XLV) was formed. Both cyclopropane products cis-1-methyl-2-ethyl-1-carbomethoxycyclopropane (XLVI) (31%) and trans-1-methyl-2-ethyl-1-carbomethoxycyclopropane (XLVII) (9%) were formed with the major isomer having the same stereochemistry as the starting pyrazoline. Methyl 2-methyl-3-ethyl-3-butenoate (XLVIII) (4%) was found as a minor product.

On the other hand, liquid phase pyrolysis of a neat sample of trans-3-methyl-4-ethyl-3-carbomethoxy-$\Delta^1$-pyrazoline (XLI) at around 105° to 140°C gave cis-2,3-dimethyl-2-pentenoate (XLV) (13%) as the $\alpha,\beta$-unsaturated olefin product. The percentage of the cyclopropane derivatives (XLVI and XLVII) and the $\beta,\gamma$-unsaturated olefin (XLVIII) were 11%, 72% and 4% respectively with
again a tendency for retention of stereochemistry in the cyclopropane product. Similar results were obtained for the vapor phase pyrolysis and are also shown in the Figure XXII.

**Photolysis of cis- and trans-3-Methyl-4-ethyl-3-carbomethoxy-\(\Delta^1\)-pyrazolines**

Ultraviolet irradiation of cis- and trans-3-methyl-4-ethyl-3-carbomethoxy-\(\Delta^1\)-pyrazolines (XL and XLI) gave as the main products cis- and trans-1-methyl-2-ethyl-1-carbomethoxycyclopropanes (XLVI and XLVII) respectively and each of the two isomeric pyrazolines gave a small amount of the \(\alpha,\beta\)-unsaturated olefin corresponding to stereospecific loss of \(\text{CH}_2\text{N}_2\) as shown in Figure XXIII.

\[
\begin{array}{cccc}
\text{C}_2\text{H}_5 & \text{CH}_3 & \text{CH}_3 & \text{C}_2\text{H}_5 \\
\text{CH}_3 & \text{CO}_2\text{CH}_5 & \text{C}_2\text{H}_5 & \text{CO}_2\text{CH}_3 \\
\text{XLIV} & \text{XLV} & \text{XLVI} \\
\text{XL} & \text{L.P.} & 56\% & - \\
 & \text{V.P.} & 28\% & 31\% \\
\text{XLI} & \text{L.P.} & \text{trace} & 13\% \\
 & \text{V.P.} & \text{trace} & 6\% \\
\end{array}
\]

\[
\begin{array}{cccc}
\text{C}_2\text{H}_5 & \text{CH}_3 & \text{CO}_2\text{CH}_3 \\
\text{XLVII} & \\
\text{XLVIII} & \text{C}_2\text{H}_5 & \text{CH}_3 & \text{CO}_2\text{CH}_3 \\
\text{XL} & \text{L.P.} & 9\% & 4\% \\
 & \text{V.P.} & 19\% & 6\% \\
\text{XLI} & \text{L.P.} & 72\% & 4\% \\
 & \text{V.P.} & 74\% & 2\% \\
\end{array}
\]

Figure XXII. Pyrolysis of cis- and trans-3-Methyl-4-ethyl-3-carbomethoxy-\(\Delta^1\)-pyrazolines.
Compound Identification

Most sample identifications were based on the physical data obtained from infrared, n.m.r. elemental microanalysis and gas chromatography.

a. Infrared Spectra

The cis-3-methyl-4-ethyl-3-carbomethoxy-$\Delta^1$-pyrazoline (XL) showed a carbonyl band at 1748 cm$^{-1}$ and the $-\text{N}=\text{N}-$ band was at 1538 cm$^{-1}$, whereas the trans-3-methyl-4-ethyl-3-carbomethoxy-$\Delta^1$-pyrazoline (XLI) showed the carbonyl group band at 1742 cm$^{-1}$ and the $-\text{N}=\text{N}-$ at 1529 cm$^{-1}$.

Infrared spectra of methyl cis- and trans-2,3-dimethyl-2-pentenoate showed the carbonyl bands at 1718 cm$^{-1}$, 1712 cm$^{-1}$, consistent with the $\alpha,\beta$-unsaturated ester structure assigned and the carbon-carbon double bond at 1647 cm$^{-1}$, 1631 cm$^{-1}$ respectively.

The two cyclopropane derivatives, cis- and trans-1-methyl-2-ethyl-1-carbomethoxycyclopropanes (XLVI and XLVII) showed no carbon-carbon double bond adsorption bands and the carbonyl group appeared at 1721 cm$^{-1}$ and 1730 cm$^{-1}$ respectively.
b. N.M.R. Spectra

All the n.m.r. spectra are shown in the Appendix. The n.m.r. spectral data of pyrazolines XL and XLI are summarized in the Table I.

The spectra of the pyrazolines XL and XLI closely resemble the published spectra of Van Auken and Rinehart (11) for cis- and trans-3,4-dimethyl-3-carbomethoxy-\(\Delta^1\)-pyrazolines (IX and X).

The assignment made to the isomeric cis- and trans-3-methyl-4-ethyl-3-carbomethoxy-\(\Delta^1\)-pyrazolines (XL and XLI) were based on a consideration of the chemical shift of the \(H_{C-4}\). When \(H_{C-4}\) is cis to the ester group, its peak should be at lower field. The assignment of configuration to these pyrazolines could also be obtained from the photolysis results for which the products are the cyclopropane derivatives with retention of the geometry of the starting material. These will be described in detail later.

Geometric configuration assignment of two isomeric \(\alpha,\beta\)-unsaturated olefins (XXIV and XXV) by n.m.r. was based on the position of the \(\beta\)-methyl group peak. The group cis to the ester group is expected to be less shielded than that of the group trans (21). Data are summarized as in the Table II.

The n.m.r. spectral data of two cyclopropanes (XLVI and XLVII) are summarized as in the Table III.

Comparison of the n.m.r. spectra with those of cis- and trans-1,2-dimethyl-1-carbomethoxy cyclopropane (XVII and XVIII (11) show sufficient similarities for structural assignments. Particularly a peak at 9.65\(\tau\) in XLVI corresponds to a peak at 9.8\(\tau\) in the cis-isomer (XVII). In addition Chiu (22 (a) and (b)) has worked on the pyrolysis at 258\(^\circ\)C of both compounds XLVI and XLVII and found that trans- cyclopropane XLVII underwent ring opening to yield methyl cis- and trans-2-methyl-4-butenoate (LII and LI) while the cis-cyclopropane (XLVI) did not react. Since the ethyl group must be on the
### TABLE I

The n.m.r. Data of cis- and trans-3-Methyl-4-ethyl-3-carbomethoxy-Δ¹-pyrazolines

<table>
<thead>
<tr>
<th>Compound</th>
<th>CH₃ of CO₂CH₃ at C-3</th>
<th>CH₃ of C₂H₅</th>
<th>CH₂ of C₂H₅</th>
<th>He⁺ Value</th>
<th>Ha⁺ Value</th>
<th>Hc⁺ Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>s</td>
<td>s</td>
<td>d.t.</td>
<td>m</td>
<td>m</td>
<td></td>
</tr>
</tbody>
</table>

- $J_{HeHa} = 17$
- $J_{HeHC-4} = 8.2$
- $J_{HaHC-4} = 7.9$
- $J_{vic} = 8$
- $\Delta_{HeHa} = 48$
- $J_{HeHC-4} = J_{HaHC-4} = 8.0$
- $\Delta_{HeHa} = 52$

- $s = \text{singlet}$
- $d.t. = \text{distorted triplet}$
- $q = \text{quartet}$
- $m = \text{multiplet}$

*H₃ and CH₂ of the ethyl group were not resolved. Lie in the region 8.0 - 9.0 τ

† See Figure XXVIII page 27.
### TABLE II

The n.m.r. Data of Methyl cis- and trans-2,3-Dimethyl-2-pentenoate

<table>
<thead>
<tr>
<th>Compound</th>
<th>CH$_3$ of CO$_2$CH$_3$</th>
<th>CH$_3$ at C-2</th>
<th>CH$_3$ at C-3</th>
<th>CH$_2$ of C$_2$H$_5$</th>
<th>CH$_3$ of C$_2$H$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Value</td>
<td>Multiplicity</td>
<td>Coupling Constants in c.p.s. Unit</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.34</td>
<td>s</td>
<td>unresolved</td>
<td>$\nu$ = 7.5</td>
<td>$\nu$ = 7.5</td>
</tr>
<tr>
<td></td>
<td>8.21</td>
<td>q</td>
<td></td>
<td>$\Delta \approx 81$ c.p.s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(overlap)</td>
<td>t</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_5$</td>
<td>CH$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$</td>
<td>s</td>
<td>q</td>
<td>long distance coupling</td>
<td>$\nu$ = 7.5</td>
<td>$\nu$ = 7.5</td>
</tr>
<tr>
<td>C$_2$H$_5$</td>
<td>CH$_3$</td>
<td></td>
<td></td>
<td>$\Delta \approx 66$ c.p.s</td>
<td></td>
</tr>
<tr>
<td>CH$_3$</td>
<td>s</td>
<td>q</td>
<td>7.87</td>
<td>8.98</td>
<td></td>
</tr>
<tr>
<td>CO$_2$CH$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$s$ = singlet  
$q$ = quartet  
$t$ = triplet
TABLE III
The n.m.r. Data of cis- and trans-1-Methyl-2-ethyl-1-carbomethoxycyclopropanes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\text{CH}_3$ of $\text{CO}_2\text{CH}_3$ at C-1</th>
<th>$\text{CH}_3$ of $\text{C}_2\text{H}_5$</th>
<th>$\text{CH}_2$ of $\text{C}_2\text{H}_5$</th>
<th>ring hydrogens</th>
<th>$\tau$ Values</th>
<th>Multiplicity</th>
<th>Coupling Constant in c.p.s. Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_2\text{H}_5$ (\text{CH}_3) (\beta\text{CO}_2\text{CH}_3)</td>
<td>6.40 s</td>
<td>8.76 s</td>
<td>8.98 d.t.</td>
<td>o m</td>
<td>J$\text{vic}$ = 5</td>
<td>J$\text{vic}$ = 5</td>
<td>$\Delta$ = 19 c.p.s.</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5$ (\text{CH}_3) (\beta\text{CO}_2\text{CH}_3)</td>
<td>6.40 s</td>
<td>8.74 s</td>
<td>9.11 t</td>
<td>q m</td>
<td>J$\text{vic}$ = 7</td>
<td>J$\text{vic}$ = 7</td>
<td>$\Delta$ = 27 c.p.s.</td>
</tr>
</tbody>
</table>

s = Singlet  t = triplet  o = overlap
m = multiplet  q = quartet
same side as the ester group for reaction to occur by the six-membered intermediate XLIX as shown in the Figure XXIV the geometry is defined by this reaction.

![Chemical Structures](attachment:image.png)

Figure XXIV. Ring Opening of trans-1-Methyl-2-ethyl-carbomethoxy-cyclopropane.

When the vicinal ester and alkyl groups are trans to each other the compounds are inert under the reaction conditions.

The n.m.r. of the $\beta,\gamma$-unsaturated olefin, methyl 2-methyl-3-ethyl-3-butenoate (XLVIII) shows for the CH$_3$ of ester group a singlet at 6.40$\tau$ and for the CH$_3$ at the C-2 position a doublet at 8.76$\tau$ with a coupling constant of $J_{\text{vic}} = 7.0$ c.p.s. The hydrogen at C-2 is a quartet at 6.89$\tau$ with a coupling constant of 7 c.p.s. The CH$_2$ is at 5.11$\tau$ with 1 c.p.s. splitting by long range coupling. The hydrogens on C-5 appears a triplet at 8.96$\tau$ with a coupling constant of 7.4 c.p.s. This spectrum is in complete accord with the structure assigned.
III. DISCUSSION

The preferred conformation of the starting pyrazoline has in a previous case (12) been found important for the discussion of the reaction. Evaluation of the conformation of the two pyrazolines cis- and trans-3-methyl-4-ethyl-3-carbomethoxy-Δ1-pyrazolines (XL and XLI) is therefore given below in some detail.

Steric Conformation of Pyrazoline Rings

It is suggested by a comparison to the structure of cyclopentene that the five member ring is not a planar and has conformation minima in the envelope form (23,24) as shown in the Figure XXV.

Figure XXV. Conformation of Pyrazoline Ring.

By considering the coupling between two C-4 hydrogens and one C-5 hydrogen and with reference to the Karplus equation (12,25) the angle between the plane of C-3, C-4, C-5 and C-3, N-2, N-1, C-5 can be estimated. For a number of pyrazolines which are expected to be predominantly folded in one direction. The angle was found to be 25° for the average conformation.

The Karplus equation (25) is given as 

\[ J_{H,H'} = 8.5 \cos^2 \phi - 0.28 \text{ (c.p.s.)} \] 

(0° ≤ φ ≤ 90°) or 

\[ J_{H,H'} = 9.5 \cos^2 \phi - 0.28 \text{ (c.p.s.)} \] 

(90° ≤ φ ≤ 180°). The term \( J_{H,H'} \) is the coupling constant of two vicinal hydrogens. The angle \( \phi \) is
the dihedral angle between these two hydrogens and all the numerals are constants.

The conformational assignment to cis- and trans-3-methyl-4-ethyl-3-carbomethoxy-$\Delta^1$-pyrazolines (XL and XLI) has been derived below with the assumption that all projected geminal angles are 120°.

The two hydrogens at the C-5 position of pyrazoline XL (and also for XLI) appear in the n.m.r. at the $\tau$ values of 5.25 and 6.04. These differences are not expected to be due to the influence of the ester group at the C-3 position, since the two hydrogens at the C-5 position of 3-methyl-3-carbomethoxy-$\Delta^1$-pyrazoline have the same $\tau$ value of 5.43 (26). Inversion of the ring in this case results in an averaging of the chemical shift for the pseudo axial and pseudo equatorial shifts of these hydrogens.

Since in pyrazoline XL (and XLI) the hydrogen at the C-5 position are not equivalent, one folded conformation appears more favored than the other.

Presumably the two hydrogens at the C-5 position are shielded differently by the azo group due to their different relative positions with that group. We can consider the two positions to be axial and equatorial ($H_a$ and $H_e$). The hydrogen $H_a$ is expected to receive more shielding than $H_e$ as shown in Figure XXVI.

This is supported by the fact that the axial hydrogen in the cis-3, 5-di-(p-anisyl)-$\Delta^1$-pyrazoline(14) appears at 4.80$\tau$ due to a greater shielding by the azo group than in trans-3,5-di(p-anisyl)-$\Delta^1$-pyrazoline where the corresponding hydrogen appears at 4.25$\tau$ as a result of averaging between the conformations in this molecule in which it would alternate between axial and equatorial positions.
Figure XXVI. Axial and Equatorial Hydrogens at the C-5 Position of the Pyrazoline Ring.

The coupling constants found for pyrazoline XL are $J_{HeH_C-4} = 8.2$ c.p.s. and $J_{HaH_C-4} = 7.9$ c.p.s. are given in the Table I (for pyrazoline XLI the corresponding constants are $J_{HeH_C-4} = J_{HaH_C-4} = 8.0$ c.p.s.). The calculated coupling constants for angles of 26° and 146° using the Karplus equation (25) are 6.59 and 6.25 c.p.s. and for angles 27° and 147° are 6.47 and 6.40 c.p.s. The observed values are about 1.6 c.p.s. larger but of the same relative magnitude. This suggests that the dihedral angles of $He-H_C-4 = 26°$ and $Ha-H_C-4 = 146°$ for pyrazoline XL and $He-H_C-4 = 27°$ and $Ha-H_C-4 = 147°$ for pyrazoline XLI showing a preference to the conformation as shown in the Figure XXVII.

Figure XXVII. Dihedral Angles of $He-H_C-4$ and $Ha-H_C-4$ of the Pyrazoline.
The relative position of the ethyl group to the groups on C-3 are assumed to be the same as that the olefin used to prepare the pyrazolines as discussed earlier giving the preferred conformations of the two pyrazolines XL and XLI to be as in the Figure XXVIII.

![Figure XXVIII. Preferred Conformation of cis- and trans-3-Methyl-4-ethyl-3-carbomethoxy-Δ^1-pyrazolines.](image)

Similar evaluation of the degree of folding by applying the Karplus equation to three other pyrazolines IX, X and XV reported in the literature give the following results.

![Formulas for IX, X, and XV](image)

For pyrazoline IX (11) the dihedral angles are calculated to be \( \theta_{He-H-C-4} = 16^\circ \) and \( \theta_{Ha-H-C-4} = 136^\circ \) based on the Karplus values of 7.6 c.p.s. and 4.6 c.p.s. (Karplus value for 16° = 7.6 c.p.s. and for 136° = 4.6 c.p.s.). The observed values are about 1.4 c.p.s. larger but of the same
magnitude again. For the pyrazoline X (11), the dihedral angles are calculated to be $\text{He-H}_C-4 = 24^\circ$ and $\text{H_a-H}_C-4 = 144^\circ$ based on the coupling constants of $J_{\text{HeH}_C-4} = 8.1$ c.p.s. and $J_{\text{H_aH}_C-4} = 7.3$ c.p.s. (Karplus values for $24^\circ = 6.8$ c.p.s. and for $144^\circ = 5.9$ c.p.s.). The observed values are again about 1.4 c.p.s. larger. For pyrazoline XV (14), the dihedral angles are calculated to be $\text{H}_D-\text{H}_E-4 = 40^\circ$ and $\text{H}_C-\text{H}_E = 160^\circ$ based on the $J_{\text{H}_D-\text{H}_E} = 8.0$ c.p.s. and $J_{\text{H}_A-\text{H}_E} = 11.5$ c.p.s. (Karplus values for $40^\circ = 4.7$ c.p.s. and for $160^\circ = 8.1$ c.p.s.). This indicates that the bulky p-anisyl groups in this cis-3,5-relationship gives the largest degree of folding yet observed.

Considerations of Possible Mechanism for the Pyrolysis Reaction

The stereochemistry for the formation of $\alpha,\beta$-unsaturated esters from pyrazolines XL and XLI suggests that the pyrolysis is taking place on the conformation with the C-4 hydrogen in the equatorial position. Since this is not the preferred conformation and since it has the C-4 hydrogen in a position trans to the nitrogen to be lost it suggests that a requirement of this reaction is that the nitrogen is lost on the side trans to the hydrogen which is migrating as shown in the Figure XXIX.

![Figure XXIX. Transition States of $\alpha,\beta$-Unsaturated Esters Formation.](image)

Consideration of this requirement may however explain the variation in olefin
yield for pyrazoline IX, X, XL and XLI. The pyrazoline IX which has the greatest tendency to folding to the conformation with the C-4 hydrogen equatorial (favorable for olefin reaction) gives the highest olefin yield (70 %) while the pyrazoline XLI with the lowest tendency to fold into the conformation with an equatorial C-4 hydrogen gives the lowest olefin yield (17 %).

Application of this mechanism to the pyrolysis of a pyrazoline mixture reported earlier by McGreer (12) correctly predicts the structure of the olefin formed. A mixture of 90 % cis,trans-3,4,5-trimethyl-3-carbomethoxy-\( \Delta^1 \)-pyrazoline (LV) and 10 % cis,cis-3,4,5-trimethyl-3-carbomethoxy-\( \Delta^1 \)-pyrazoline (LVI) gave 6 % methyl 2,3-dimethyl-2-pentenoate (XLV) as the only \( \alpha,\beta \)-unsaturated olefin product as shown in the Figure XXX.

![Diagram of pyrazolines and products](image)

Figure XXX. Pyrolysis of cis,trans- and cis-cis-3,4,5-Trimethyl-3-carbomethoxy-\( \Delta^1 \)-pyrazolines.

This olefin, which is only now positively identified through the isolation of its isomer in this work, would result from each of the pyrazolines by loss of nitrogen trans to the hydrogen at C-4.

Crawford and Mishra (13) proposed a mechanism for the pyrolysis of some alkyl-\( \Delta^1 \)-pyrazolines. The kinetic evidence showed that the formation of olefin and cyclopropane products occurred through the same intermediate which they have proposed to be a planar symmetric molecule (LIX) through
overlap of a pair of \( \sigma \)-orbitals between the two carbons C-1 and C-3 as shown in Figure XXXI.

![Overlap of p-orbitals](image)

**Figure XXXI. Intermediate with a Pair of \( \sigma \)-Orbitals.**

This intermediate (LIX) can easily yield cyclopropane and olefin products by \( \sigma \)-bond formation or by hydrogen migration respectively and it is predicted to yield cyclopropane through a conrotatory process (19).

If we apply this mechanism to the pyrazolines XL and XLI presented in this thesis, the intermediate (LX) would result by loss of nitrogen from XL on the side \textit{trans} to the hydrogen at the C-4 position and from XLI on the side \textit{cis} to the hydrogen at the C-4 position (similar but opposite loss of nitrogen from XL and XLI will give intermediate LXI) as shown in the Figure XXXII.

Paths 1 and 3 are not favorable in comparison with the paths 2 and 4 due to the additional energy for conformational inversion. For the migration of hydrogen and olefin formation intermediate LX would be expected to give the \textit{trans}-olefin (XXVI) and intermediate LXI would give the \textit{cis}-olefin (XXV).

The experimental results show that pyrazolines XL and XLI give olefins XXVI and XXV respectively. That pyrazoline XL should give only the intermediate via the less favored conformation is unexpected. This observation therefore makes application of Crawfords's mechanism to this system unlikely.
In discussion of pyrolysis of pyrazolines, both of ionic (10,11) and diradical (15,16,18) mechanisms have been suggested. The ionic mechanism proposed (12) that the bond between N-1 and C-3 of pyrazoline ring opened to give the diazonium betaine intermediate (LXII) and that bond C-3 and C-4 would be restricted in its rotation to some degree because of the gauche interaction by the bulky groups as shown in the Figure XXXIII.
Rotation in this way could explain the fact that the cyclopropane formation was not stereospecific for the present study.

The possibility that an intermediate like LXII is involved in the ring closure is not supported by the fact that the partial pyrolysis of cis-3,5-dimethyl-3-carbomethoxy-Δ¹-pyrazoline (XI) (12) gave none of the isomeric pyrazoline in the recovered unreacted pyrazoline and it has been concluded that the loss of nitrogen from such a species must be faster than bond rotation.

The ionic intermediate suggests a more polar transition state than starting material. The variation of rate for the pyrolysis of cis- and trans-3,5-dimethyl-3-carbomethoxy-Δ¹-pyrazolines (12) in a number of solvents indicated that in this case the intermediate is not more ionic than the starting material. The intermediate for pyrolysis of pyrazoline XI and XII is not expected to be ionic since a study of the rates of pyrolysis of a similar series earlier in this laboratory by N. W. K. Chiu (12) showed little variation with dielectric constant of the solvents.

Mechanism of the Photolysis Reaction

Photolysis of cis- and trans-3-methyl-4-ethyl-3-carbomethoxy-Δ¹-
pyrazolines (XL and XLI) gave as main products the cyclopropane derivative with retention of the geometry of the pyrazoline and as minor products the olefins corresponding to loss of CH₂N₂, methyl trans- and cis-2-methyl-2-pentenoate pentenoate (XXVI and XXV). The mechanism of photolysis is therefore considerably different from that of pyrolysis. Two possible transition states (LXIV and LXV) have been suggested for giving these products by a molecular mechanism by Van Auken and Rinehart as shown in the Figure XXXIV.

Figure XXXIV. Transition States of Photolysis.

Conversion to a cyclopropane with the same stereochemistry as the original pyrazoline by photolysis is not always 100 % stereospecific although there is always a greater tendency than in the thermal reaction (pyrazoline XII gives about 70:30 ratio by photolysis with retention predominating while pyrolysis give 20:80 ratio for 3,5-dimethyl-3-carbomethoxy-Δ¹-pyrazolines]. Although a molecular mechanism is still therefore suggested further factors must be evaluated.
IV. EXPERIMENTAL

Experimental Instruments and Procedures

a. Nuclear Magnetic Resonance (n.m.r.) spectra were recorded on a Varian Associates Model A-60 spectrophotometer by Mrs. A. Brewster. Samples were dissolved in carbon tetrachloride (usually 20 % by volume and tetramethylsilane was used as an internal standard).
b. Infrared Spectra were run on a Perkin-Elmer Model 137 spectrophotometer with sodium chloride optics.
c. Vapor phase chromatography was carried out using an Aerograph Model A-90-P.
d. Elemental microanalysis were performed by A. Bernhardt (W. Germany) and P. Borda of the Chemistry Department, University of British Columbia.
e. Boiling points given were determined on 10 μl samples by the inverted capillary method.

Sample Preparation

a. Preparation of N-Nitroso-N-methylurea.

N-Nitroso-N-methylurea was prepared by the procedure given in Organic Synthesis (27). A yield of 106 g (67 %) was obtained.
b. Preparation of N-Nitroso-N-ethylurea.

N-Nitroso-N-ethylurea was prepared by the procedure worked out by N. Chiu (28). The method was adapted with some modification. A sample of 300 g (5 moles) of urea was dissolved in a solution of 123 g (1.5 moles) of ethylamine hydrochloride, mixed well with 300 ml of water and a few drops of concentrated hydrochloric acid. The mixture was boiled gently under reflux for four hours. After cooling to room temperature, 110 g (1.5 moles) of 98 % 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 H₂SO₄ in 110 g. of ice with stirring at such a rate that the temperature remained below 5°C. The N-nitroso-N-ethylurea, 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. The yield was 87 g. (0.75 mole) or 50 % of the theoretical yield.

c. Preparation of Diazomethane.

Diazomethane was prepared also by the procedure given in Organic Synthesis (29). It was used in the ether solution without distillation.

d. Preparation of Diazoethane (30).

A sample of 50 g. (0.285 mole) N-nitroso-N-ethylurea was added to a stirred ice-cold solution of 300 ml. of anhydrous ether and 125 ml. of 40 % KOH at such a rate that the reaction was under control and the reaction temperature was kept below 5°C. The orange colored diazoethane-ether 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 %.

e. Preparation of cis- and trans-3,5-Dimethyl-3-carbomethoxy-Δ¹-pyrazolines (XI and XII) (12).

Methyl methacrylate (I) was added slowly to the diazoethane in the absolute ether until the solution was discolored. The ether was removed using a rotary evaporator. The crude product was distilled under a reduced pressure of 0.3 mm., b.p. 52°C. The n.m.r. spectrum showed that the cis and trans forms of XI and XII were presented in the proportions of 36 % and 64 % respectively (20).
TABLE IV

Distillation Fractions in the Separation to Yield Methyl cis- and trans-2-Methyl-2-pentenoate (XXV and XXVI)

<table>
<thead>
<tr>
<th>Fraction No.</th>
<th>Boiling Point °C</th>
<th>Wt. Yield g.</th>
<th>Wt. % of Compd. XXV</th>
<th>Wt. % of Compd. XXVI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>132-135</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>135-139</td>
<td>8.01</td>
<td>trace</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>139-142</td>
<td>0.35</td>
<td>9</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>142-143.5</td>
<td>2.67</td>
<td>19</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>143.5-145</td>
<td>2.86</td>
<td>24</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>145-147</td>
<td>6.09</td>
<td>23</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>147-148</td>
<td>5.47</td>
<td>16</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>148-153</td>
<td>3.79</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>Residue</td>
<td></td>
<td>6.02</td>
<td>-</td>
<td>98</td>
</tr>
<tr>
<td>Total Wt.</td>
<td></td>
<td>35.66</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fraction No.</th>
<th>Boiling Point °C</th>
<th>Wt. Yield g.</th>
<th>Wt. % of Compd. XXV</th>
<th>Wt. % of Compd. XXVI</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>134-136</td>
<td>1.12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>136-139</td>
<td>3.02</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>139-143</td>
<td>2.69</td>
<td>11</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>143-144</td>
<td>2.38</td>
<td>21</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>144-148</td>
<td>10.10</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>148-153</td>
<td>5.02</td>
<td>7</td>
<td>-</td>
</tr>
<tr>
<td>Residue</td>
<td></td>
<td>5.82</td>
<td>-</td>
<td>90</td>
</tr>
<tr>
<td>Total Wt.</td>
<td></td>
<td>30.15</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Liquid Phase Pyrolysis of 3,5-Dimethyl-3-carbomethoxy-Δ1-pyrazoline (XXV) (20)

Liquid phase pyrolysis under reflux at normal pressure started from 90°C and became vigorous at 120°C. Pyrolysis was continued until bubbles of nitrogen were no longer evolved. Five products have been identified previously as cis-1,2-dimethyl-1-carbomethoxycyclopropane (VI, b.p. 145°C, 45%), trans-1,2-dimethyl-1-carbomethoxycyclopropane (VII, b.p. 136°C, 27%), methyl cis-2-methyl-2-pentenoate (XIII, b.p. 143°C, 10%), methyl trans-2-methyl-2-pentenoate (XIV, b.p. 156°C, 15%) and methyl 1-methyl-2-pentenoate (XV, b.p. 139°C, 3%).

Separation of Methyl cis- and trans-2-Methyl-2-pentenoate

A 73.42 g. sample from pyrolysis of cis- and trans-3,5-dimethyl-3-carbomethoxy-Δ1-pyrazoline (XLIII) was divided into two parts (38.8 g. and 34.6 g.) and distilled by means of a 24-inch annular Teflon spinning-band distillation column with an automatic reflux-ratio controller at a reflux ratio 5:1.

The results of the two distillations are given in the Table IV.

a. Separation of Methyl trans-2-methyl-2-pentenoate (XXVI).

The residues from the two fractional distillations (11.8 g.) were combined and redistilled to give the separation shown in the Table V.

TABLE V

Purification of trans-2-Methyl-2-pentenoate by Distillation

<table>
<thead>
<tr>
<th>Fraction No.</th>
<th>Boiling Point °C</th>
<th>Wt. Yield g.</th>
<th>Wt. % of Compound XXVI</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>147-156</td>
<td>1.73</td>
<td>63</td>
</tr>
<tr>
<td>16</td>
<td>157-158</td>
<td>8.38</td>
<td>&gt;99</td>
</tr>
<tr>
<td>residue</td>
<td></td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>Total Wt.</td>
<td></td>
<td>11.13</td>
<td></td>
</tr>
</tbody>
</table>
b. Separation of Methyl cis-2-methyl-2-pentenoate (XXV).

Fractions 4-7 and 12-14 were combined and were redistilled to give the results listed in the Table VI.

### Table VI

Attempted Purification of cis-2-Methyl-2-pentenoate by Distillation

<table>
<thead>
<tr>
<th>Fraction No.</th>
<th>Boiling Point °C</th>
<th>Wt. Yield g.</th>
<th>Wt. % of Compound XXV</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>134-140</td>
<td>1.46</td>
<td>12</td>
</tr>
<tr>
<td>18</td>
<td>140-143</td>
<td>3.55</td>
<td>22</td>
</tr>
<tr>
<td>19</td>
<td>143-145</td>
<td>2.47</td>
<td>31</td>
</tr>
<tr>
<td>20</td>
<td>145-146</td>
<td>1.97</td>
<td>34</td>
</tr>
<tr>
<td>21</td>
<td>146-146.5</td>
<td>3.63</td>
<td>28</td>
</tr>
<tr>
<td>22</td>
<td>146.5</td>
<td>5.37</td>
<td>27</td>
</tr>
<tr>
<td>residue</td>
<td></td>
<td>1.23</td>
<td></td>
</tr>
<tr>
<td>Total Wt.</td>
<td></td>
<td>19.68</td>
<td></td>
</tr>
</tbody>
</table>

In order to obtain the cis-ester XXV pure, fractions 18-21 were separated further by vapor chromatography using a 10-ft. dinonyl phthalate column until the purity was greater than 99%. In this way 1.29 g. of pure methyl cis-2-methyl-2-pentenoate (XXV) was obtained.

Preparation of cis- and trans-3-Methyl-4-ethyl-3-carbomethoxy-Δ1-pyrazolines (XL and XLI).

a. Preparation of cis-3-Methyl-4-ethyl-3-carbomethoxy-Δ1-pyrazoline (XL).

Methyl trans-2-methyl-2-pentenoate (8.36 g.) was reacted with excess diazomethane solution over several days with fresh diazomethane solution being added every second day. The ether was removed on the rotary evaporator to give the crude pyrazoline (10.8 g.) corresponding to a crude yield of 97%.
Attempts to distill this product in the normal way were unsuccessful due to decomposition. The pyrazoline XXI was distilled by use of a bulb to bulb distillation apparatus (as shown in the Figure XXXV) at a reduced pressure of 0.22 mm. and with the oil bath temperature maintained between 70-75°C. The pure cis-3-methyl-4-ethyl-3-carbomethoxy-Δ¹-pyrazoline (XXI) was obtained. Calc. for C₉H₁₄N₂O₂; C, 56.45; H, 8.29; N, 16.46. Found: C, 56.31; H, 8.17; N, 16.75. nD²₁ : 1.4565.

b. Preparation of trans-3-Methyl-4-ethyl-3-carbomethoxy-Δ¹-pyrazoline (XLI).

By a procedure similar to that used in the preparation of the cis-isomer (XL) there was obtained 1.70 g. of crude trans-3-methyl-4-ethyl-3-carbomethoxy-Δ¹-pyrazoline (XLI) corresponding to a crude yield of 99%. The pyrazoline was distilled by means of the bulb to bulb distillation apparatus under a reduced pressure of 0.1 mm. and with the oil bath maintained at 75°C to give pure trans-3-methyl-4-ethyl-3-carbomethoxy-Δ¹-pyrazoline (XLI). Calc. for C₉H₁₄N₂O₂: C, 56.45; H, 8.29; N, 16.46. Found: C, 56.38; H, 8.32; N, 16.41. nD²₁ : 1.4535. The characterization of these pyrazolines is based on the n.m.r. and is given in the results section and the n.m.r. spectra are presented in the Appendix.

Figure XXXV. Bulb to Bulb Distillation Apparatus.
Pyrolysis and Photolysis of cis- and trans-3-Methyl-4-ethyl-3-carbomethoxy-$\Delta^1$-pyrazolines (XL and XLI).

All pyrolysis mixtures were analyzed by vapor chromatography using a 0.25-inch by 10-ft. dinonyl phthalate column at 143°C with a head pressure of 50 p.s.i. The chromatograms are given as obtained with each experiment and the retention times reported have been normalized to the above conditions. The components were separated where possible using a 10-ft. dinonyl phthalate column. When separation was not possible identification was based on the coinjection of the unknown mixture with a known sample of the anticipated compounds.

a. Liquid Phase Pyrolysis of cis-3-Methyl-4-ethyl-3-carbomethoxy-$\Delta^1$-pyrazoline (XL).

Pyrolysis of 100 µl of the pyrazoline in the liquid phase was carried out by heating the sample in a tube in an oil bath. Pyrolysis started at 105°C and became vigorous at 140°C. Heating was continued until there were no nitrogen bubbles evolved. The product distribution as determined by chromatogram is shown in Figure XXXVI.

Peaks III and V were separated and identified.

Peak V: Methyl trans-2,3-dimethyl-2-pentenoate (XLIV) showed a retention time of 30.3 minutes, b.p. 170°C and $n_D^{25}$: 1.4490. Calc. C$_8$H$_{14}$O$_2$: C, 67.57; H, 9.92. Found: C, 67.39; H, 9.90. Since the 8-methyl was found at lower field (8.03T) than in the cis-ester (8.21T, see below) it is assumed to be cis to the ester group. See appendix for the n.m.r. spectrum.

Peak III: cis-1-Methyl-2-ethyl-1-carbomethoxycyclopropane (XLVI) showed a retention time of 24.2 minutes, b.p. 165°C and $n_D^{25}$: 1.4318. Calc. for C$_8$H$_{14}$O$_2$: C, 67.57; H, 9.924. Found: C, 67.40; H, 10.02. The n.m.r. of the ...
cyclopropane ring hydrogens gave peaks in the region 8.6-9.72\(\tau\) (see the result part and appendix). A peak at 9.64\(\tau\) corresponds to one found in the cis-1,3-dimethyl-1-carbomethoxycyclopropane at 9.76\(\tau\) \cite{11}.

Peak I was identified as by injection of a known sample obtained by photolysis of trans-3-methyl-4-ethyl-3-carbomethoxy-\(\Delta^1\)-pyrazoline (XLI) to be described later.

Peak II: It is assigned by n.m.r. as methyl 2-methyl-3-ethyl-3-butenolate (XLVIII) b.p. 160°C See the n.m.r. data and spectrum in results part and appendix.

Figure XXXVI. Vapor Chromatogram of the product from the Liquid Pyrolysis of cis-3-Methyl-4-ethyl-3-carbomethoxy-\(\Delta^1\)-pyrazoline.

b. Vapor Phase Pyrolysis of cis-3-Methyl-4-ethyl-3-carbomethoxy-\(\Delta^1\)-pyrazoline (XL).

A sample of the pyrazoline was injected in the v.p.c. with a 10-ft. D.N.P. column at 160°C and with the temperature of injector at 290°C. The product distribution is shown in the Figure XXXVII.
c. Photolysis of cis-3-Methyl-4-ethyl-3-carbomethoxy-Δ^1-pyrazoline (XL).

A sample of 0.5 g. of pyrazoline in 25 ml. absolute ether was irradiated with a 450 W Hanovia lamp for 6 hours under reflux. The ether was removed using a rotary evaporator and the crude product analyzed by v.p.c. to give the chromatogram shown in Figure XXXVIII.

Figure XXXVIII. Vapor Chromatogram of the product from the photolysis of cis-3-Methyl-4-ethyl-3-carbomethoxy-Δ^1-pyrazoline.
Peak III was isolated and shown by n.m.r. to be identical cis-1-methyl-2-ethyl-1-carbomethoxycyclopropane (XLV) isolated from the liquid phase pyrolysis.

The small peak (retention time 21.2 minutes) which was 15.6 % was shown by n.m.r to be methyl trans-2-methyl-2-pentenoate (XXVI). This is the ester that was used to prepare the pyrazoline.

d. Liquid Phase Pyrolysis of trans-3-Methyl-4-ethyl-3-carbomethoxy-$\Delta^1$-pyrazline (XLI).

Liquid phase pyrolysis started at 105°C and became vigorous at 140°C. The product distribution as determined by v.p.c. was as given in Figure XXXIX.

![Graph of product distribution](image)

Figure XXXIX. Liquid Phase Pyrolysis of trans-3-Methyl-4-ethyl-3-carbomethoxy-$\Delta^1$-pyrazline.

By reducing the attenuation a trace of methyl trans-2,3-dimethyl-2-pentenoate became apparent as shown in the Figure XL.
Figure XL. The Product Distribution of Thermal Pyrolysis of trans-3-Methyl-4-ethyl-3-carbomethoxy-Δ¹-pyrazoline with Reduced Attenuation (see Figure XL).

Peak IV: Methyl cis-2,3-dimethyl-2-pentenoate (XXVII) showed a retention time of 27.0 minutes. The n.m.r. data proved it to be identical with an earlier prepared sample (b.p. 163°C) (12). The n.m.r. position of 8.21τ for the β-CH₃ compared with 8.03τ in the trans-isomer confirms this structure assignment.

e. Vapor Phase Pyrolysis of trans-3-Methyl-4-ethyl-3-carbomethoxy-Δ¹-pyrazoline (XLI).

A sample of pyrazoline was injected in the v.p.c. with a 10-ft. D.N.P. column at 150°C and the injection was 330°C. The products distribution as shown in the Figure XLI.
Figure XLI. Products Distribution of the Product from the Vapor Phase Pyrolysis of trans-3-Methyl-4-ethyl-3-carbomethoxy-Δ1-pyrazoline.

f. Photolysis of trans-3-Methyl-4-ethyl-3-carbomethoxy-Δ1-pyrazoline (XLI).

The same procedure used for photolysis of cis-3-methyl-4-ethyl-3-carbomethoxy-Δ1-pyrazoline (XL). The products distribution are shown in the Figure XLII.

Figure XLII. Product Distribution of the Product from the Photolysis of trans-3-Methyl-4-ethyl-3-carbomethoxy-Δ1-pyrazoline.
Peak 1: \textit{trans}-1-Methyl-2-ethyl-1-carbomethoxycyclopropane (XLVII) showed a retention time of 17.0 minutes, b.p. 147-8°C and \( n_D^{25} \): 1.4328. Calc. C\(_8\)H\(_{14}\)O\(_2\): C, 67.57; H, 9.924. Found: C, 67.72; H, 9.84. The n.m.r showed the peaks of cyclopropane ring hydrogens distributed over the region 8.9-9.28\( \tau \) (see the result part and appendix) with no peak near 9.7\( \tau \) as found in the other isomer.

The small peak (retention time 21.2 minutes, 15.6\%) was shown by n.m.r. to be methyl \textit{cis}-2-methyl-2-pentenoate (XXV). This is the ester that was used to prepare the pyrazoline.
BIBLIOGRAPHY


   b) N. W. K. Chiu and D. E. McGreer, private communication.


26. I. Masters, private communication.


The n.m.r. spectrum of cis-3-Methyl-4-ethyl-3-carbomethoxy-$\Delta^1$-pyrazolines.
The n.m.r. spectrum of trans-3-Methyl-4-ethyl-3-carbomethoxy-Δ¹-pyrazolines.
The n.m.r. spectrum of cis-2,3-Dimethyl-2-pentenoate.
The n.m.r. spectrum of trans-2,3-Dimethyl-2-pentenoate.
The n.m.r. spectrum of cis-1-Methyl-2-ethyl-carbomethoxy-cyclopropane.
The n.m.r. spectrum of trans-1-Methyl-2-ethyl-1-carbomethoxy-cyclopropane.
The n.m.r. spectrum of Methyl 2-methyl-3-ethyl-3-butenoate.