PYROLYSIS AND PHOTOLYSIS OF

cis AND trans-3,5-DIMETHYL-3-ACETYL-Δ^1-PYRAZOLINE AND

cis AND trans-3,5-DIMETHYL-3-CARBOMETHOXY-Δ^1-PYRAZOLINE

by

NORMAN WING KWAI CHIU

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ABSTRACT

The thermal and photolytic decomposition of cis and trans-3,5-dimethyl-3-acetyl-Δ^1-pyrazoline have been found to give six products. They have been separated and identified as 2,3,5-trimethyl-Δ^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-Δ^2-dihydrofuran was a major product from the decomposition of cis-3,5-dimethyl-3-acetyl-Δ^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-Δ^1-pyrazoline.

The product compositions from both the pyrolysis and photolysis of cis and trans-3,5-dimethyl-3-carbomethoxy-Δ^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-Δ^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 <u>trans</u>-3,5-dimethyl-3-carbomethoxy-Δ^1-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 <u>cis</u> and <u>trans</u>-3,5-dimethyl-3-carbomethoxy-Δ^1-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 <u>cis</u> and <u>trans</u>-3,5-dimethyl-3-carbomethoxy-Δ^1-pyrazolines has been observed as shown by the partial pyrolysis and photolysis of the <u>trans</u>-pyrazoline.

These results are discussed in view of current mechanistic proposals for the pyrolysis and photolysis of Δ^1-pyrazolines.

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I. INTRODUCTION

The addition of diazoalkanes to α,β-unsaturated carbonyl compounds to form Δ^1-pyrazolines (1-5) and the pyrolysis of these Δ^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 Δ^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
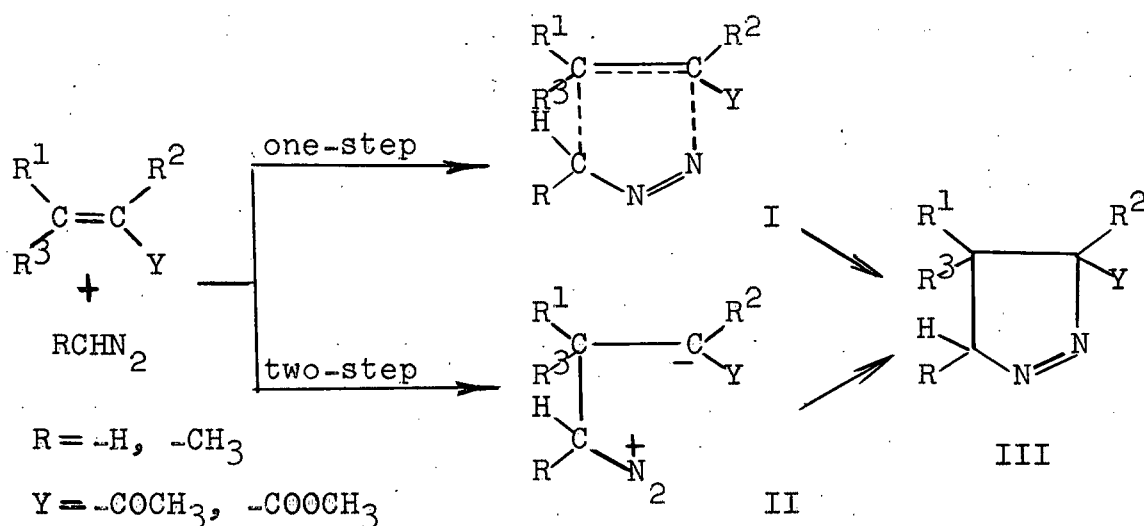
FIGURE I - Mechanisms of Δ^1-pyrazoline formation.

been shown (6,7) that the carbon α to the nitrogen in the diazo-alkane adds to the double bond at the carbon β to the carbonyl

group in the olefin. Cis-addition (6,7) is indicated by the re-
action of diazomethane with methyl tiglate (IV) and methyl
angelate (V) to give cis and trans-3,4-dimethyl-3-carbomethoxy-
Δ^1-pyrazoline (VI and VII) respectively (12).

The thermal decomposition of Δ^1-pyrazolines has been re-
ported 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 Δ^2-pyrazoline (20) or
no olefins (3,21) at all. Few studies have been made to deter-
mine the mechanism of the pyrolysis reactions. From limited in-
formation both ionic (6,11,12) and diradical (20,22-24) mecha-
nisms for the thermal decomposition of Δ^1-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 mention-
ed 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-Δ^1-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-carbo-
methoxy-Δ^1-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-
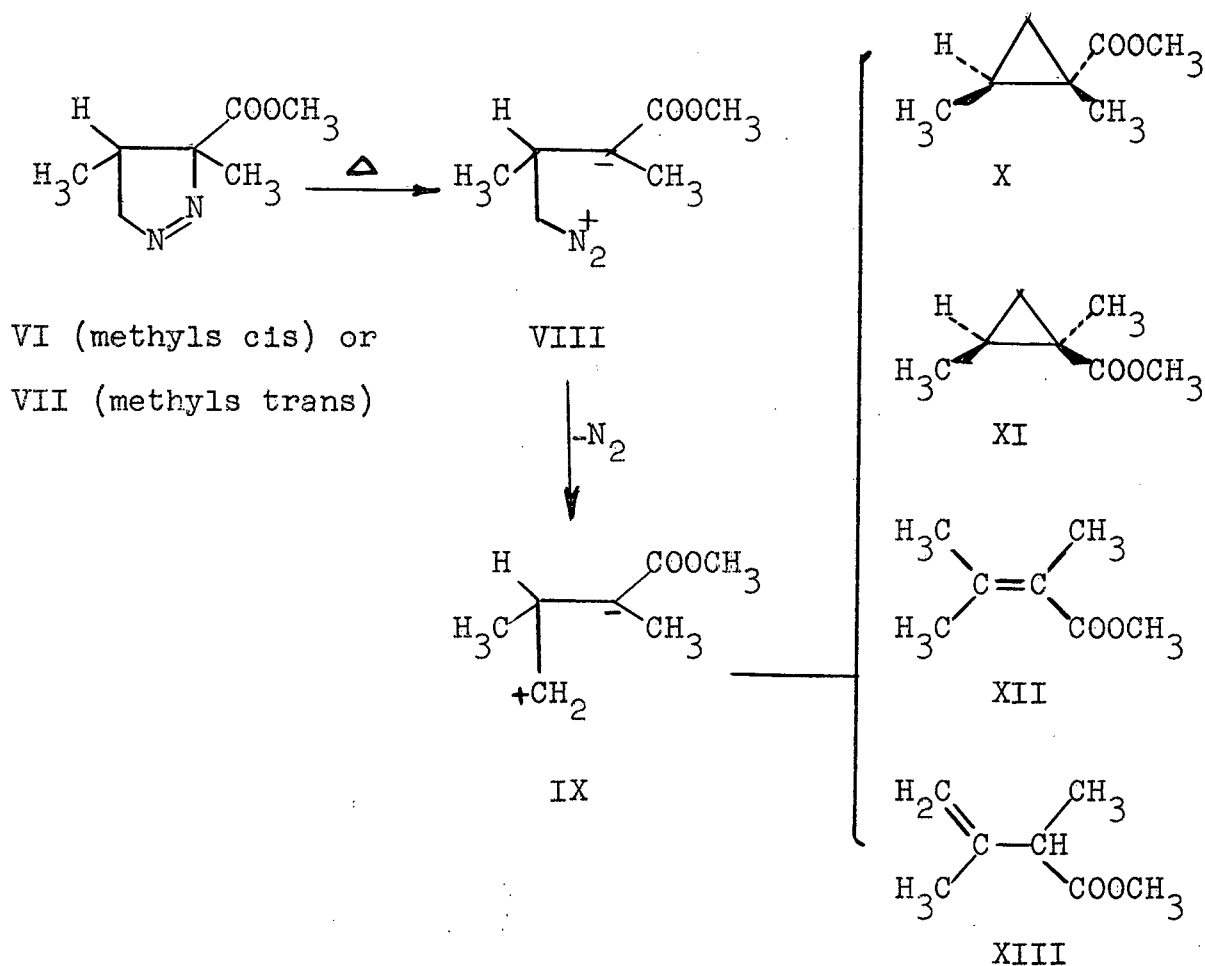
FIGURE II - Ionic mechanism for the pyrolysis of 3,4-
dimethyl-3-carbomethoxy-Δ^1-pyrazolines.

lates that rotation occurs in the diazonium betaine intermedi-
ate (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 lat-
ter 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-Δ^1-pyrazoline (VI) gives no rearrangement in the recovered pyrazoline sample (12). Therefore the validity of this ionic mechanism for the thermal decomposition of Δ^1-pyrazolines needs further examination.

Photolysis of cis and trans-3,4-dimethyl-3-carbomethoxy-Δ^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 Δ^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 Δ^1-pyrazolines has been assumed to be stereospecific in general.
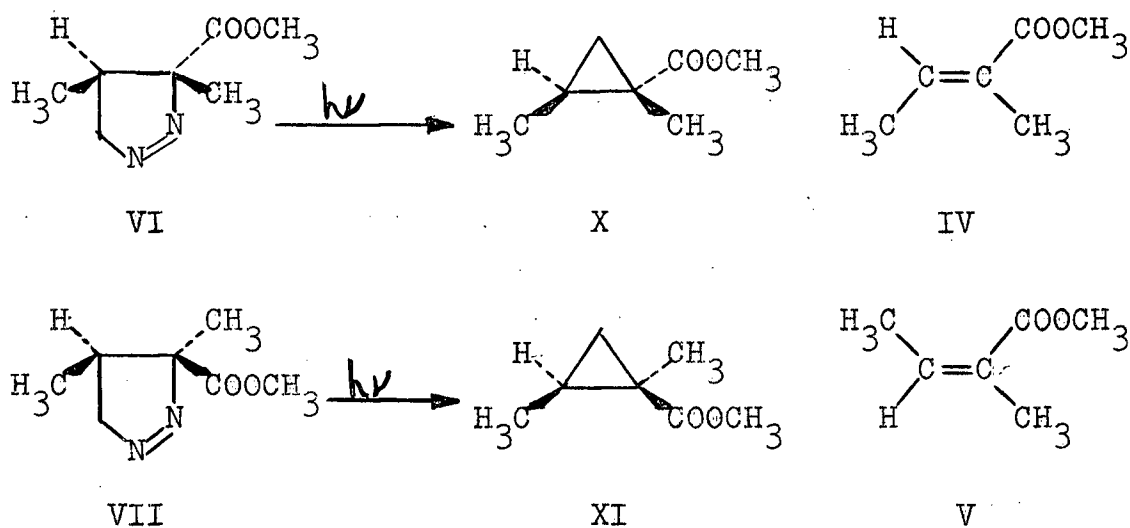
FIGURE III - Products from the photolysis of 3,4-di-methyl-3-carbomethoxy-Δ^1-pyrazolines.

In this laboratory however, a preliminary investigation (26) has shown that the photolysis reactions of cis and trans-3,5-dimethyl-3-carbomethoxy-Δ^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 avail-
able. 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.

XVIII   XIX
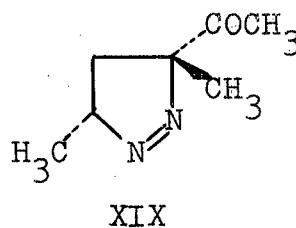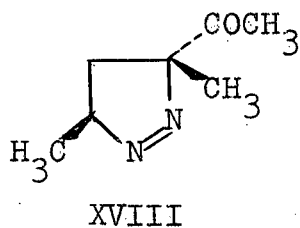
II. SYNTHESIS AND IDENTIFICATION OF 3,3,5-
TRISUBSTITUTED Δ^1-PYRAZOLINES

II-1. cis and trans-3,5-dimethyl-3-carbomethoxy-Δ^1-pyrazoline

(XVI and XVII)

3,5-Dimethyl-3-carbomethoxy-Δ^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

XXI   XX
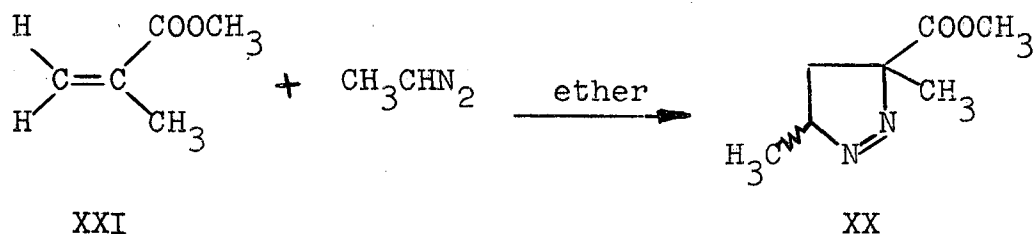
this mixture (Figure IV) by fractional distillation using a
Nester and Faust 18-inch by 6-mm. spinning band still gave a
lower boiling fraction up to 93% pure and a higher boiling
fraction of 99+% purity. N.m.r. analyses of these two fractions
and the original mixture pyrazoline showed that the lower
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-

(A) Lower boiling fraction
(B) Pyrazoline mixture XX
(C) Higher boiling fraction

(B)

(A)

XVII
(60%)

XVI
(93%)

(C)

XVII
(99+%)

XVI
(40%)

XVII
(7%)

XVI

6.3 τ 6.3 τ 6.3 τ
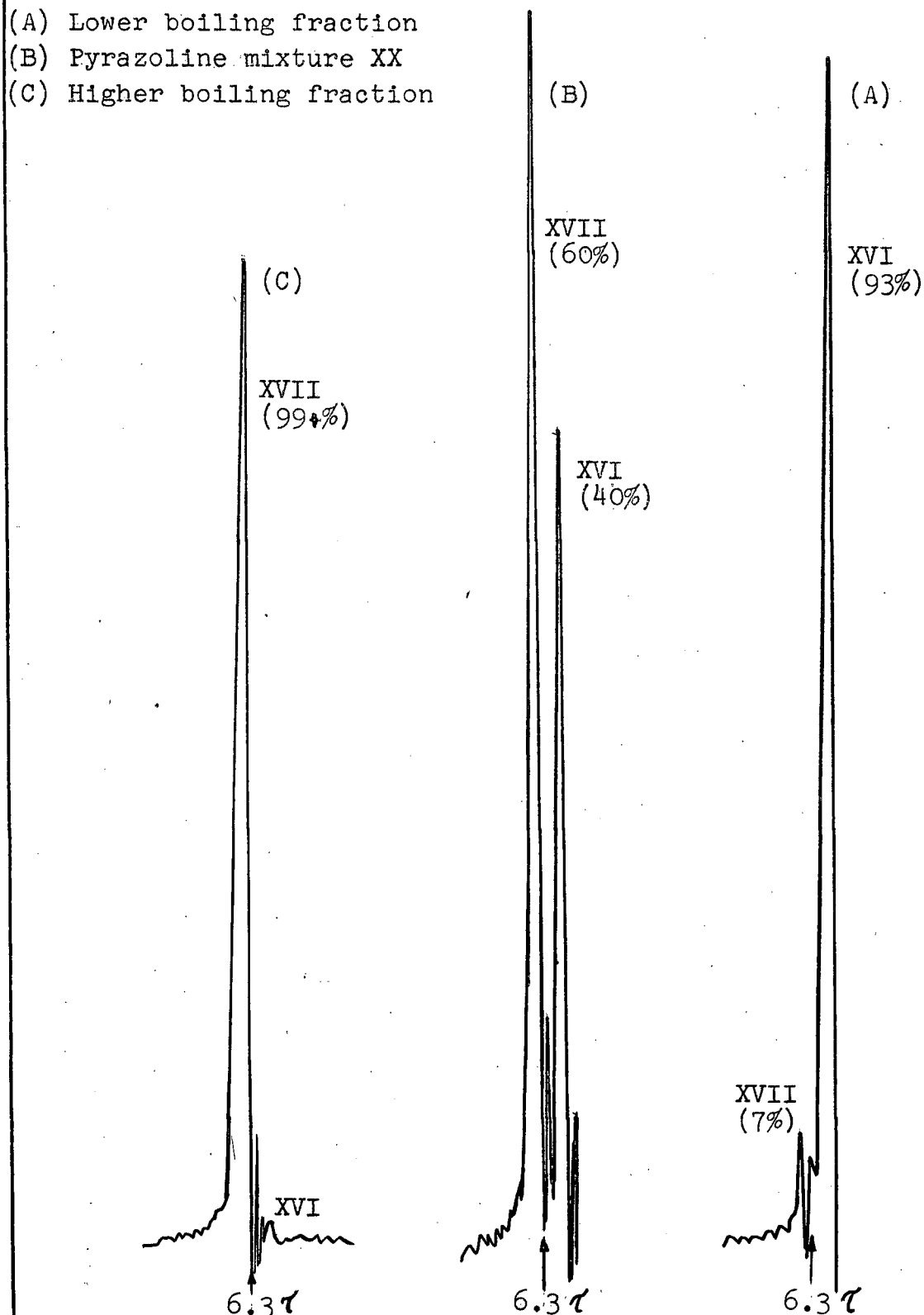
FIGURE IV - N.m.r. absorptions showing the separation of 3,5-
dimethyl-3-carbomethoxy-Δ^1-pyrazoline (XX) into its
cis (XVI) and trans (XVII) isomers.

cyclopropane (XI). On the basis of the fact that the photo-
lysis of Δ^1-pyrazolins gives cyclopropane stereospecifically
(12), the lower boiling isomer was assigned the structure cis-
3,5-dimethyl-3-carbomethoxy-Δ^1-pyrazoline (XVI) and the higher
boiling isomer was assigned the structure trans-3,5-dimethyl-
3-carbomethoxy-Δ^1-pyrazoline (XVII). Further proof of struc-
tural 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-Δ^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-Δ^1-pyrazoline (XVIII
    and XIX)

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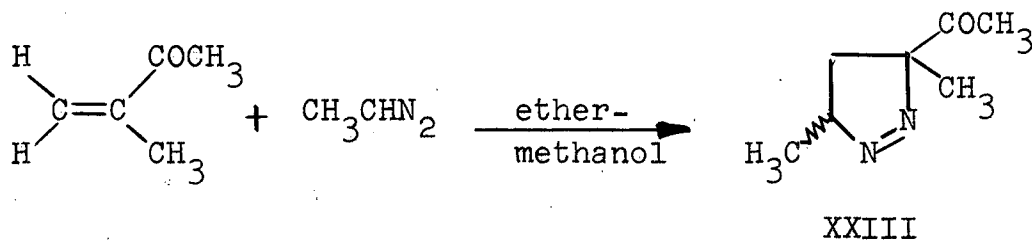
XXIII

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

The n.m.r. data of cis and trans-3,5-dimethyl-3-carbo-methoxy-Δ^1-pyrazoline (XVI and XVII) and cis and trans-3,5-dimethyl-3-acetyl-Δ^1-pyrazoline (XVIII and XIX) are tabulated in Table I.

TABLE I

N.m.r. data of cis and trans-3,5-dimethyl-3-acetyl-Δ^1-pyrazoline (XVIII and XIX) and cis and trans-3,5-dimethyl-3-carbomethoxy-Δ^1-pyrazoline (XVI and XVII)

Sample	Acetyl methyl hydrogens	Ester methyl hydrogen	C_3-methyl hydrogen	C_5-methyl hydrogens	C_5-hydrogens	C_4-hydrogens	
XVI		6.33 singlet	8.38 singlet	8.51 doublet $J \simeq 7.0$	5.42 sextet $J \simeq 7.5$	7.68 2 doublets $J_{gem} \simeq 12.9$ $J_{vic} \simeq 8.5$	9.14 2 doublets $J_{gem} \simeq 12.8$ $J_{vic} \simeq 8.0$
XVII		6.27 singlet	8.63 singlet	8.55 doublet $J \simeq 7.0$	5.43 sextet $J \simeq 7.5$	8.28 2 doublets $J_{gem} \simeq 12.8$ $J_{vic} \simeq 8.0$ [8.43 doublet# $J \simeq 8.0$	8.56 2 doublets $J_{gem} \simeq 12.6$ $J_{vic} \simeq 8.0$ 8.45 doublet# $J \simeq 8.0$]
XVIII	7.78 singlet		8.40 singlet	8.52 doublet $J \simeq 7.0$	5.66 sextet $J \simeq 7.4$	7.57 2 doublets $J_{gem} \simeq 13.0$ $J_{vic} \simeq 8.7$	9.30 2 doublets $J_{gem} \simeq 12.8$ $J_{vic} \simeq 7.7$
XIX	7.65 singlet		8.63 singlet	8.48 doublet $J \simeq 6.0$	5.67 sextet $J \simeq 7.4$	8.53 multiplet	

Note: 1) XVIII and XIX were done on 20% solution in CCl_4, XVI and XVII were done on 30% solution in CCl_4, and the values in parentheses were observed in 10% solution.

2) Chemical shift in τ 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).
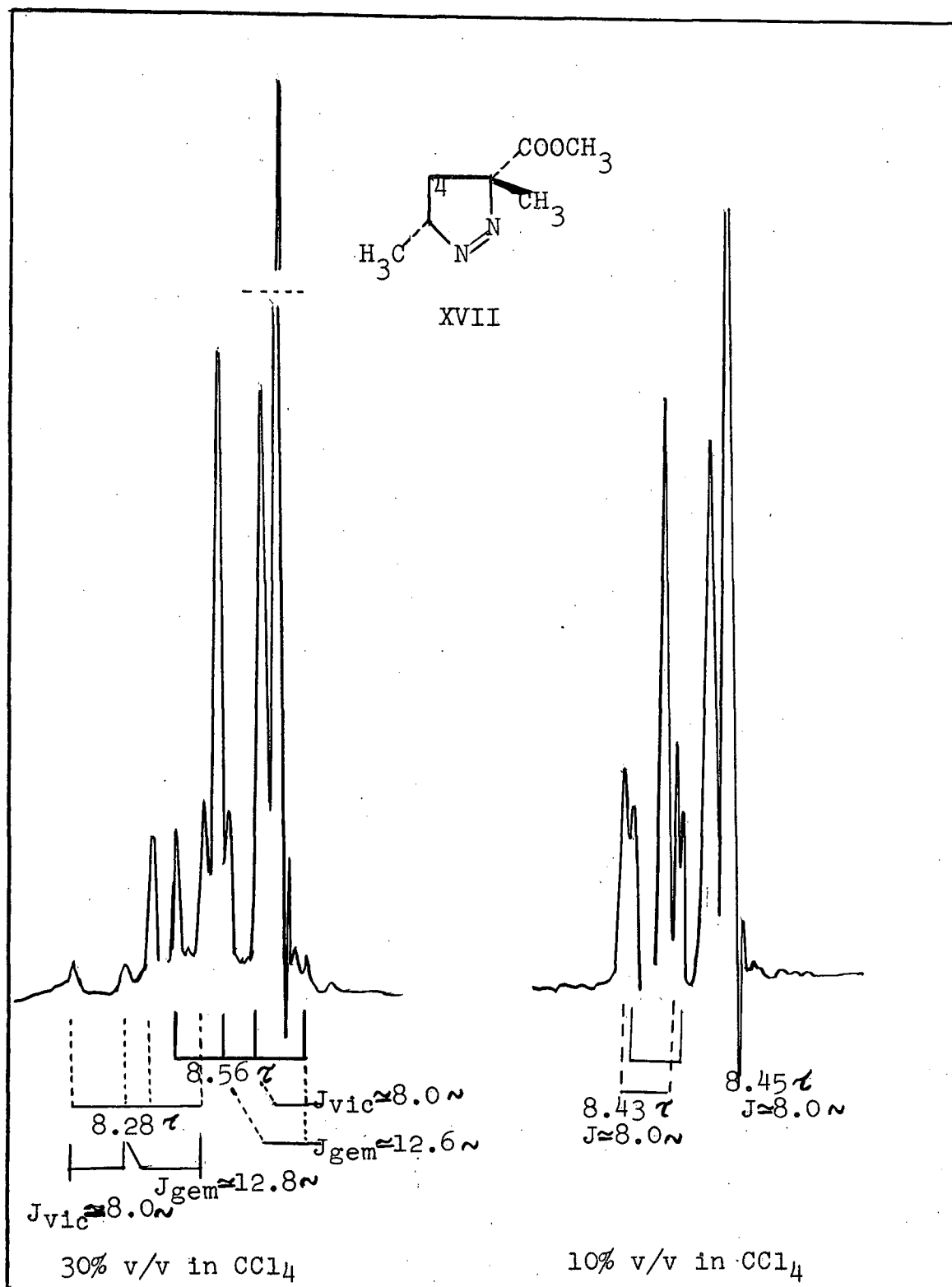
FIGURE V - N.m.r. spectra of trans-3,5-dimethyl-3-carbo-
methoxy-Δ^1-pyrazoline (XVII) showing splittings
of C4-hydrogens.

III. SEPARATION AND IDENTIFICATION OF PRODUCTS FROM THE

DECOMPOSITION OF 3,5-DIMETHYL-3-ACETYL-Δ^1-PYRAZOLINES

Preliminary studies (17,26) on the decomposition of 3,5-dimethyl-3-carbomethoxy-Δ^1-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).
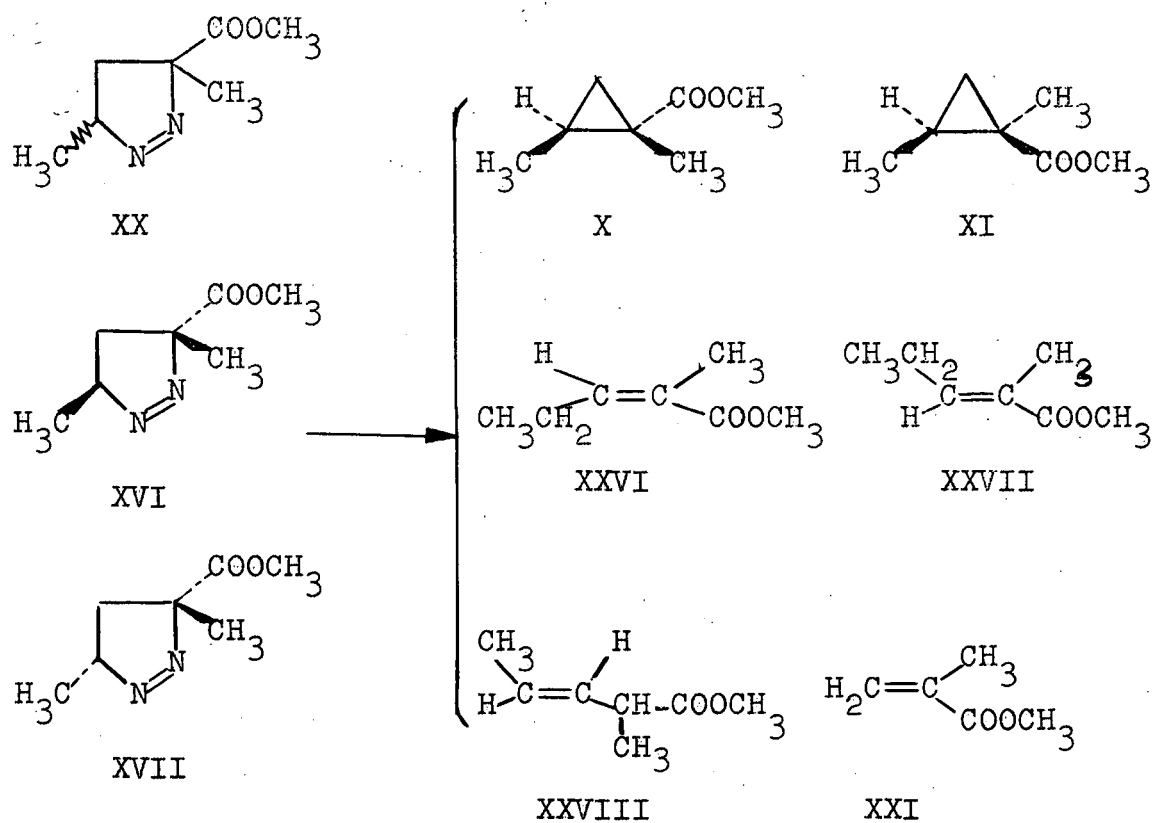
FIGURE VI - Products from the decomposition of 3,5-dimethyl-3-carbomethoxy-Δ^1-pyrazolines.

In the present study, the decomposition of 3,5-dimethyl-3-acetyl-Δ^1-pyrazoline (XXIII), its cis (XVIII) and trans (XIX)
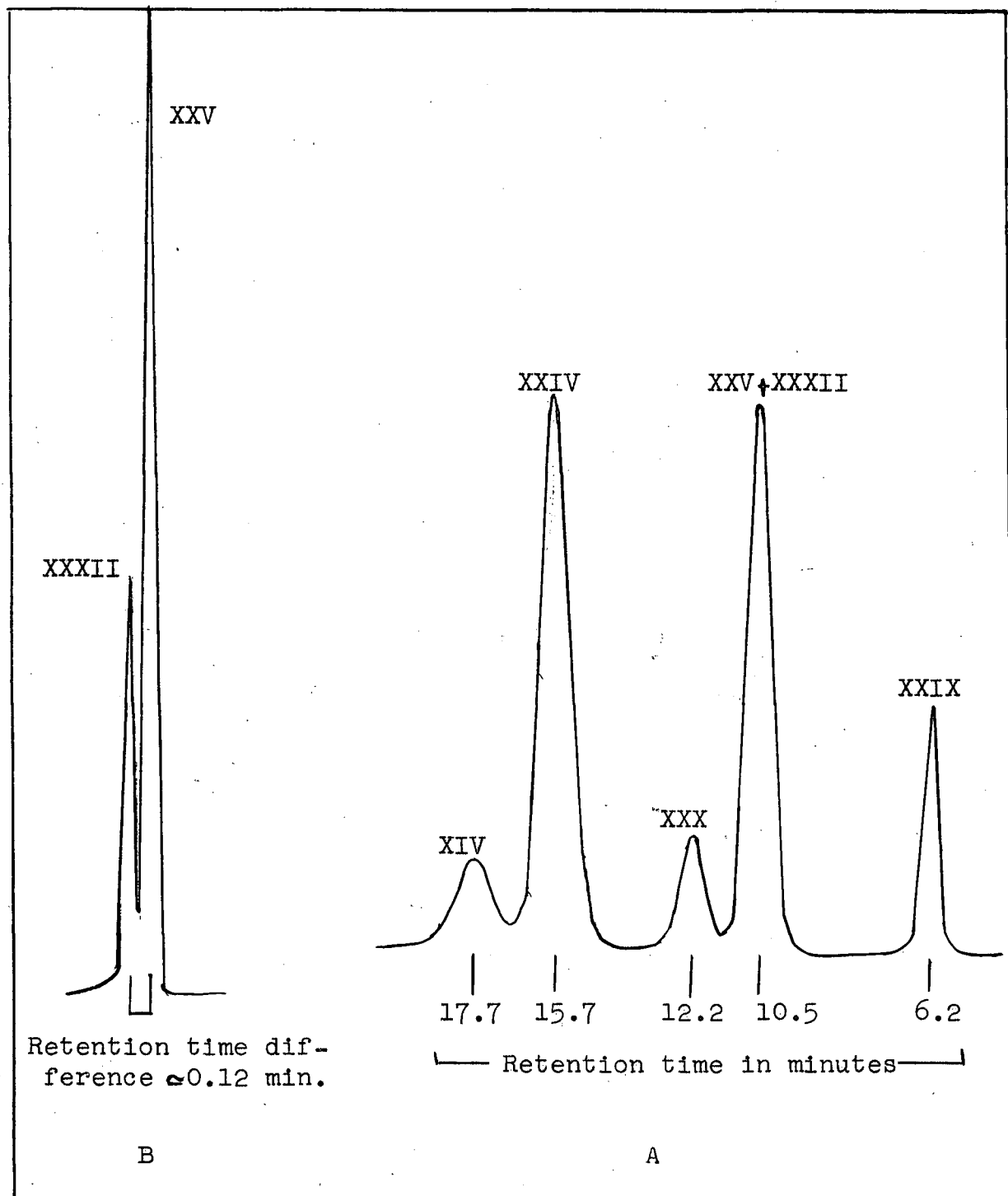
FIGURE VII - A. Preparative vapor chromatogram showing the
separation of products from the decomposition
of 3,5-dimethyl-1-acetyl-Δ^1-pyrazolines.

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 ana-
lytical 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-
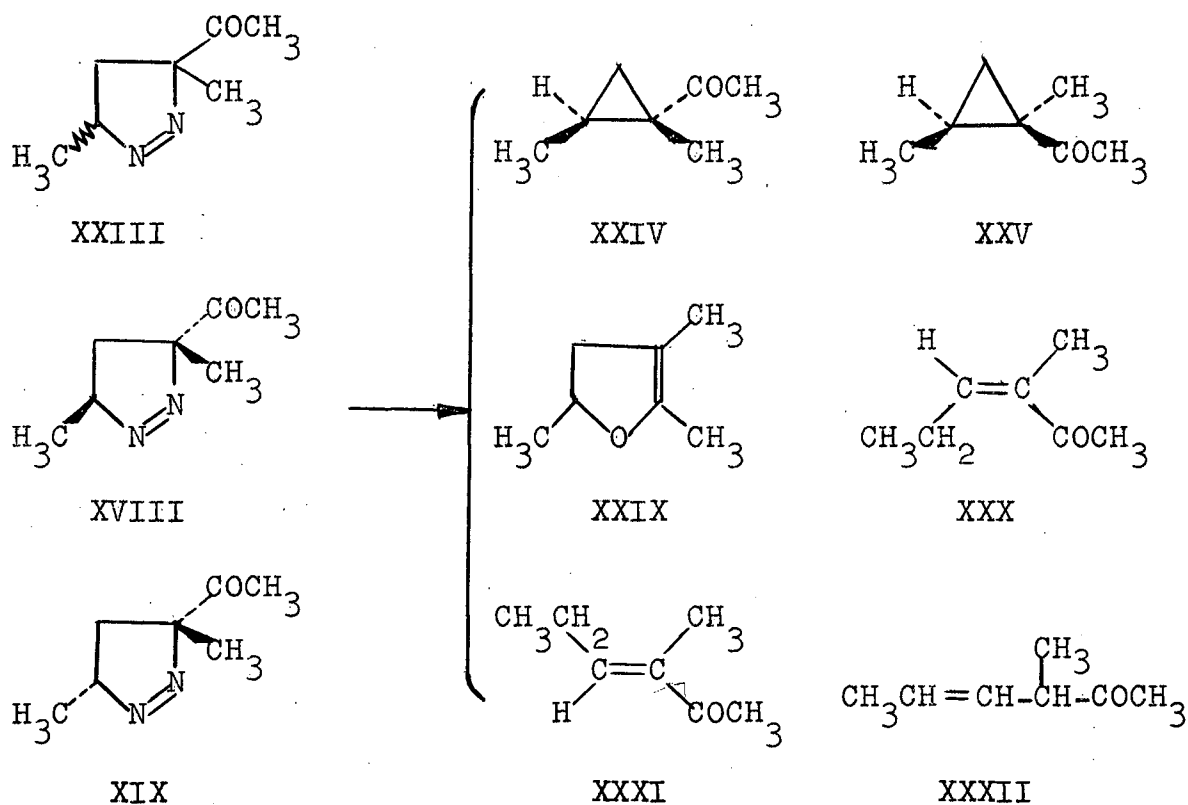
FIGURE VIII - Products from the decomposition of 3,5-
dimethyl-3-acetyl-Δ^1-pyrazolines.

parative vapor phase chromatographic separation gave five
fractions in which the second fraction was found to be a
mixture (Figure VII) of 1-acetyl-trans-1,2-dimethylcyclopro-
pane (XXV) and 3-methyl-4-hexen-2-one (XXXII) in the ratio of
approximately 85:15 depending on the condition of decom-
position. The separation of this mixture of XXV and XXXII will
be discussed later. The pyrolysis products have been charac-

terized on the basis of their n.m.r. and infrared spectral
data and elemental microanalysis and this is described below.

2,3,5-Trimethyl-Δ^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. ab-
sorption of an unresolvable multiplet centered at 8.43 τ was
attributable to the methyl groups attached to C_2 and C_3. 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 C_4 (two hydro-
gens) and C_5 (one hydrogen). These three protons constituted a
typical ABX system (29) with $J_{AB} \cong 14.5$ c.p.s., $J_{AX} \cong 8.0$ c.p.s.,
$J_{BX} \cong 9.5$ c.p.s., $\Delta_{AB} \cong 35.5$ c.p.s., $\Delta_{AX} \cong 144.5$ c.p.s. and $\Delta_{BX} \cong$
109 c.p.s. In order to establish the cyclic structure of this
2,3,5-trimethyl-Δ^2-dihydrofuran (XXIX), the n.m.r. spectrum of
a similar cyclic compound, the 2-methyl-Δ^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 (multi-
plet), 7.47 τ (multiplet) and 5.78 τ (triplet with $J \cong 9.3$ c.p.
s.) attributable to C_2 methyl hydrogens, C_3 vinyl hydrogen, C_4
and C_5 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-
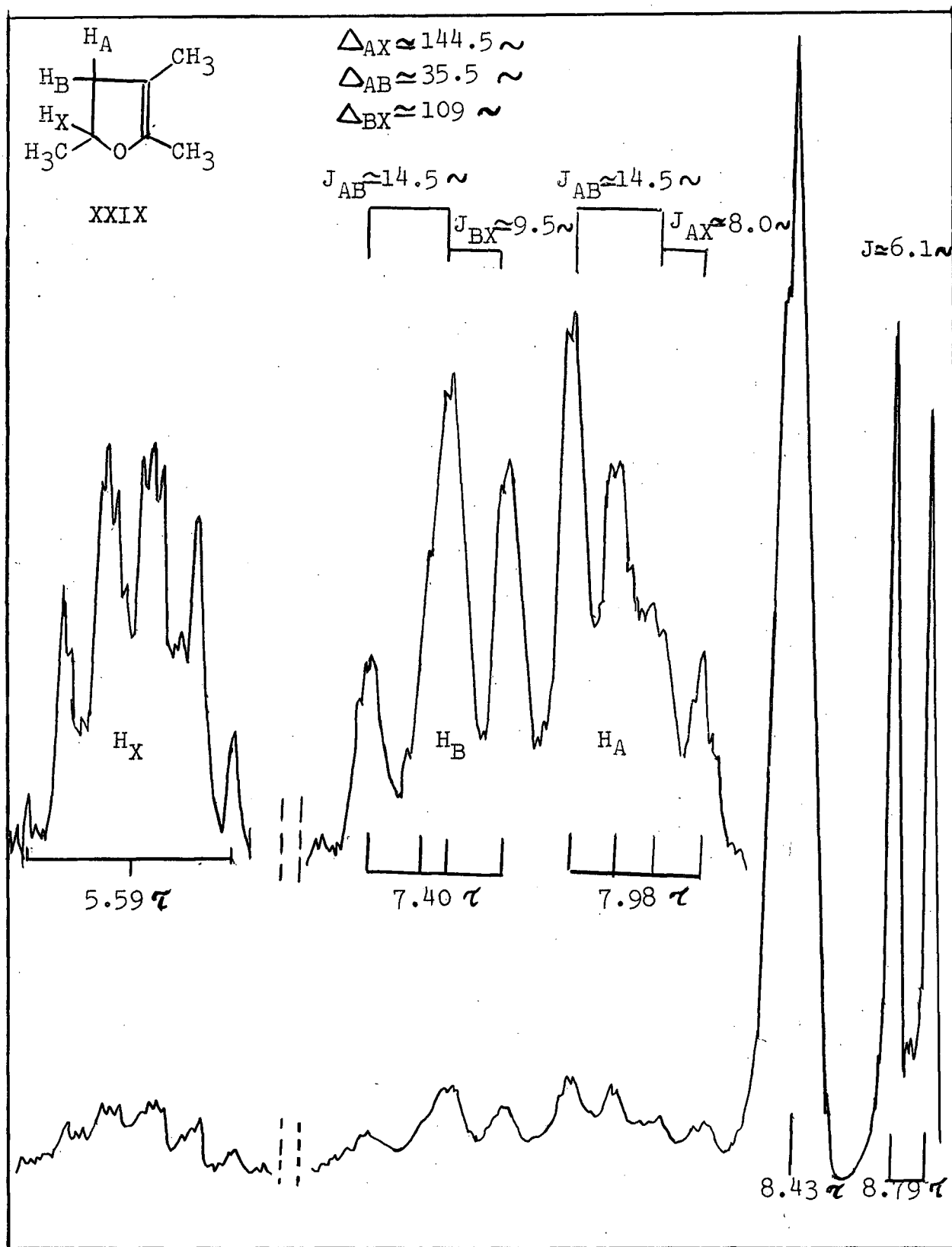
FIGURE IX - N.m.r. spectrum of 2,3,5-trimethyl-Δ^2- dihydro-
furan (XXIX)

ment of 2,3,5-trimethyl-Δ^2-dihydrofuran (XXIX).

cis-3-Methyl-3-hexen-2-one (XXX) and trans-3-methyl-3-hexen-2-one (XXXI) have been found to have boiling points at 145-145.5° and 156.5-158° respectively. Rohrmann and Shoule (31) reported the synthesis of 3-methyl-3-hexen-2-one and gave its boiling point value, 151°. It is possible that their α,β-unsaturated ketone was a mixture of the two possible geometric isomers XXX and XXXI. The presence of carbon-carbon double-bond and α,β-unsaturated carbonyl function were indicated by infrared bands at 6.18 μ and 5.91 μ respectively, for the cis-3-methyl-3-hexen-2-one (XXX) and at 6.07 μ and 5.96 μ respectively, for the trans-3-methyl-3-hexen-2-one (XXXI). The n.m.r. spectra of XXX and XXXI showed absorption at 7.86 τ (singlet) and 7.81 τ (singlet) due to acetyl methyl hydrogens, at 8.12 τ (multiplet) and 8.39 τ (multiplet) due to vinyl methyl hydrogens and at 4.44 τ (multiplet) and 3.52 τ (multiplet) due to vinyl hydrogens, respectively. The assignment of geometry to cis and 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 τ than the former at 4.44 τ. In XXXI the vinyl hydrogen is cis to the acetyl group, whereas in XXX, the vinyl hydrogen is 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

(32). 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 $5.90\,\mu$ for XXIV and $5.96\,\mu$ for XXV; and in addition, there was a band at $9.76\,\mu$ 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 $8.68\,\tau$ (two hydrogens) and $9.74\,\tau$ (one hydrogen) in the case of 1-acetyl-cis-1,2-dimethylcyclopropane (XXIV) and in the region of $8.75\,\tau$ to $9.06\,\tau$ 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 β,γ-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 dis-

4.57 τ (multiplet)   6.94 τ (multiplet)

$$CH_3CH=CH-CH-COCH_3 \longleftarrow 7.97\ \tau \ \text{(singlet)}$$

8.32 τ CH_3 $\longleftarrow$ 8.92 τ (doublet, J$\simeq$7.0 c.p.s.)
(doublet, J$\simeq$4.8 c.p.s.)
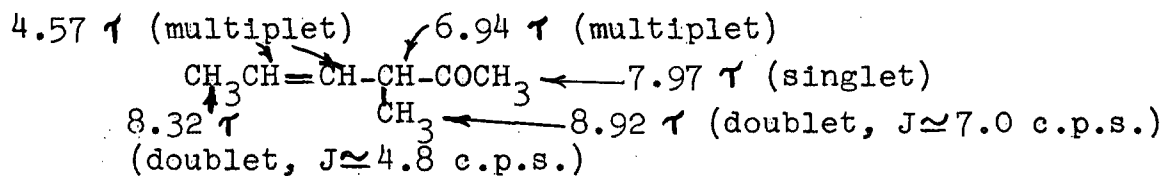
XXXII

tinguish 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 $C_7H_{12}O$, which is common to both XXV and XXXII.

IV. DECOMPOSITION OF 3,3,5-TRISUBSTITUTED Δ^1-PYRAZOLINES

Preliminary investigations have ~~been~~ shown that the pyrolysis of cis and trans-3,5-dimethyl-3-carbomethoxy-Δ^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-Δ^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-Δ^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-Δ^1-pyrazoline (XXIII), its cis (XVIII) and trans (XIX) isomers give results that resemble those of 3,5-dimethyl-3-carbomethoxy-Δ^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-Δ^1-pyrazolines

Sample	Reaction conditions	Cyclopropane		Unsaturated ketone			Dihydro-furan
		cis	trans	cis-α,β	trans-α,β	β,γ	
		XXIV	XXV	XXX	XXXI	XXXII	XXIX
XVIII (cis)	Vapor phase pyrolysis at 125°	27	48	7	3	2	13
XIX (trans)	Vapor phase pyrolysis at 125°	67	19	2	7	2	3
XXIII (mixt.)	Liquid phase pyrolysis, 100°	36	18	15	18	4	9
XVIII (cis)	Liquid phase pyrolysis, 100°	22	25	27	2	10	14
XIX (trans)	Liquid phase pyrolysis, 100°	62	17	1	17	3	0
XXIII (mixt.)	Thermal pyrolysis at 250°	48	32	5	3	3	9
XVIII (cis)	Thermal pyrolysis at 250°	28	41	12	1	2	16
XIX (trans)	Thermal pyrolysis at 250°	60	27	1	6	3	3
XXIII (mixt.)	Photolysis in ether at 35°	39	42	4	6	3	6
XVIII (cis)	Photolysis in ether at 35°	59	28	1	0	6	6
XIX (trans)	Photolysis in ether at 35°	21	70	2	1	4	2

TABLE III

Product compositions for the decomposition of 3,5-dimethyl-3-carbomethoxy-Δ^1-pyrazolines

Sample	Reaction conditions	Cyclopropane		Unsaturated ester			Methyl methacry- late
		cis	trans	cis-$\alpha\beta$	trans-$\alpha\beta$	$\beta\gamma$	
		X	XI	XXVI	XXVII	XXVIII	XXI
XX (mixt.)	Vapor phase pyrolysis (17)	53	42	3	2	1	0
XVI (cis)	Vapor phase pyrolysis (17)	23	65	5	2	5	0
XVII (trans)	Vapor phase pyrolysis (17)	76	15	1	3	5	0
XX (mixt.)	Liquid phase pyrolysis (17)	45	27	10	15	3	0
XVI (cis)	Liquid phase pyrolysis (17)	18	48	32	0	2	0
XVII (trans)	Liquid phase pyrolysis (17)	60	15	0	22	3	0
XVI (cis)	Photolysis in ether at 35°	61	23	6	2	2	6
XVII (trans)	Photolysis in ether at 35°	22	65	0	5	2	6

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-dimethylcyclopropane 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 form-
amide, 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-
Δ^1-pyrazoline (XVI and XVII) in solvents of varying dielectric
constants showed a similar solvent effect on the product com-
position as in the pyrolysis reactions but in lesser degree;
for example, in formamide, up to 21% of the product was ole-
fins whereas in cyclohexane, it was 5%.

The
kinetic solvent effect has been examined for the
pyrolysis of 3,5-dimethyl-3-carbomethoxy-Δ^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, nitro-
benzene and formamide. The rates in these solvents were all
within a factor of three (Figures XIA and XIB).

Liquid phase photolysis of trans-3,5-dimethyl-3-carbo-
methoxy-Δ^1-pyrazoline (XVII) has been carried out in solvents
such as 2,3-dimethylbutane and diethyl ether at various tem-
peratures ranging from -55° to 58° in an attempt to determine
the temperature effect on photolysis of Δ^1-pyrazolines. Pro-
duct 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-Δ^1-pyrazoline in various solvents at 125°

Sample	Solvent	D_{20} (44)	Cyclopropane		Unsaturated ester		
			cis	trans	cis-α,β	trans-α,β	β,γ
			X	XI	XXVI	XXVII	XXVIII
XVI (cis)	Cyclohexane[#]	2.07 D	25	62	12	0	1
XVI (cis)	Cyclohexane	2.07 D	30	55	11	3	1
XVI (cis)	Ethyl ether	4.34 D	25	56	16	2	1
XVI (cis)	Methanol	33.6 D	21	39	34	4	2
XVI (cis)	Acetonitrile	37.5 D	21	42	31	4	2
XVI (cis)	Formamide	109 D	19	33	44	2	2
XVII (trans)	Cyclohexane[#]	2.07 D	70	23	1	5	1
XVII (trans)	Cyclohexane	2.07 D	72	20	0	6	2
XVII (trans)	Ethyl ether	4.34 D	66	18	0	13	3
XVII (trans)	Methanol	33.6 D	48	6	0	44	2
XVII (trans)	Acetonitrile	37.5 D	67	6	0	25	2
XVII (trans)	Formamide	109 D	31	12	0	52	5

at 81°, not in sealed-tube.

TABLE V

Product compositions of photolysis of <u>cis</u> and <u>trans</u>-3,5-di-

methyl-3-carbomethoxy-Δ^1-pyrazoline

Sample	Solvent and temperature	Cyclopropane		Unsaturated ester			Methyl methacry-late
		cis	trans	cis-α,β	trans-α,β	β,γ	
		X	XI	XXVI	XXVII	XXVIII	XXI
XVII (trans)	2,3-Dimethyl butane 58°	28	63	3	4	2	0
XVII (trans)	Ethyl ether (26) 35°	22	65	0	5	2	6
XVII (trans)	Ethyl ether 0°	27	56	1	7	3	6
XVII (trans)	Ethyl ether -20°	25	55	1	8	3	8
XVII (trans)	Ethyl ether -55°	25	53	1	10	4	7
XVI (cis)	Cyclohexane# 81°	43	45	7	0	1	4
XVII (trans)	Cyclohexane# 81°	46	45	0	4	1	4
XVI (cis)	Formamide 23°	54	21	9	5	1	10
XVII (trans)	Formamide 23°	15	58	2	16	3	6

at 81, pyrolysis also occurred at a rate three times slower than ~~pyrolysis~~ 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-Δ^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 ~~high degree of~~ ˌ greater ⁻ 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-Δ^1-pyrazoline (XX) by cyclization faster than loss of nitrogen. Liquid phase pyrolysis of trans-3,5-dimethyl-3-carbomethoxy-Δ^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

XX   XXXIV
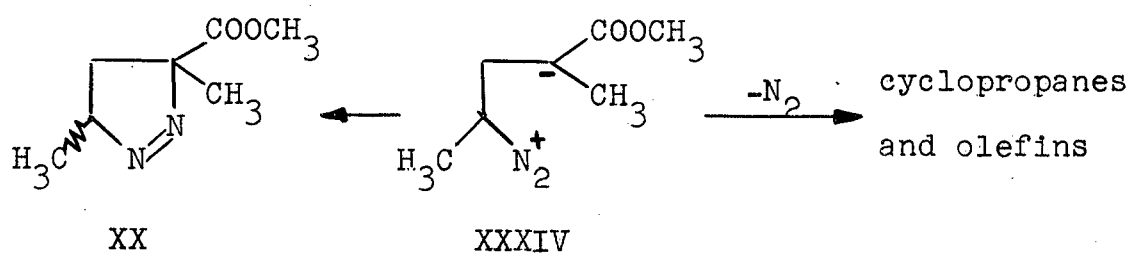
not more than 1% isomerization of XVII to cis-3,5-dimethyl-3-
carbomethoxy-Δ^1-pyrazoline (XVI) had occurred. A similar result
was observed when trans-3,5-dimethyl-3-carbomethoxy-Δ^1-
pyrazoline (XVII) in diethyl ether was partially photolysed at
35°.

V. DISCUSSION

The thermal pyrolysis of cis and trans-3,4-dimethyl-3-carbomethoxy-Δ^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
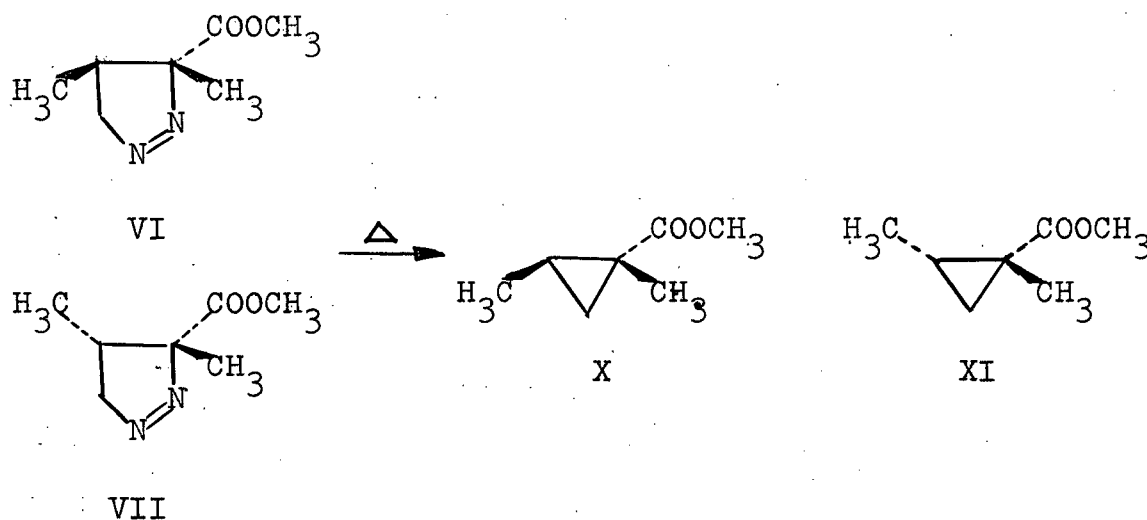
about the C_3-C_4 bond in the diazonium betaine intermediate VIII accounts for the loss of geometric integrity and that
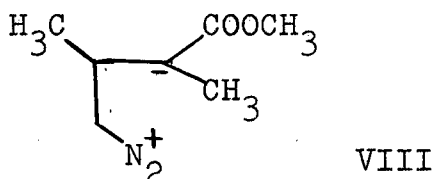
the loss of nitrogen is only slightly slower than rotation to give a higher yield of the cyclopropane which retains the geometry present in the pyrazoline.

In the present work, it was found that the thermal pyrolysis of cis and trans-3,5-dimethyl-3-carbomethoxy-Δ^1-pyrazoline (XVI and XVII), cis and trans-3,5-dimethyl-3-acetyl-Δ^1-pyrazoline (XVIII and XIX) also proceeds with racemization at C_3 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.
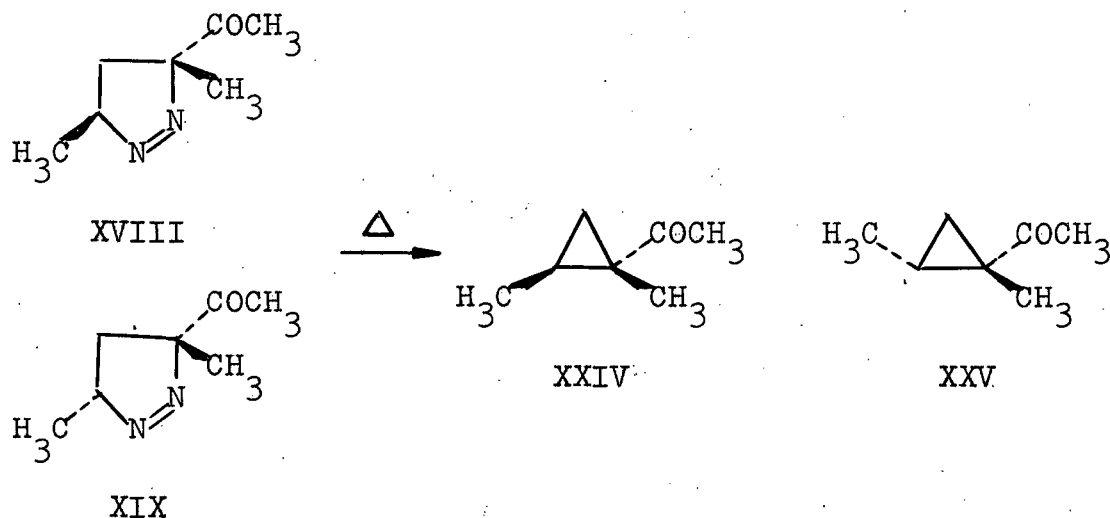
A second important feature of the present work is that the formation of olefins from the pyrolysis of 3,5-dimethyl-Δ^1-pyrazolines is highly stereospecific. The ratio of cis and trans-3-methyl-3-hexen-2-one (XXX and XXXI) from the pyrolysis

of cis and trans-3,5-dimethyl-3-acetyl-Δ^1-pyrazoline (XVIII and XIX) were 27:2 and 1:17 respectively. This stereospecificity has not been observed previously since an appropriate

XVIII   XXX (27%)   XXXI (2%)

XIX   XXXI (17%)   XXX (1%)
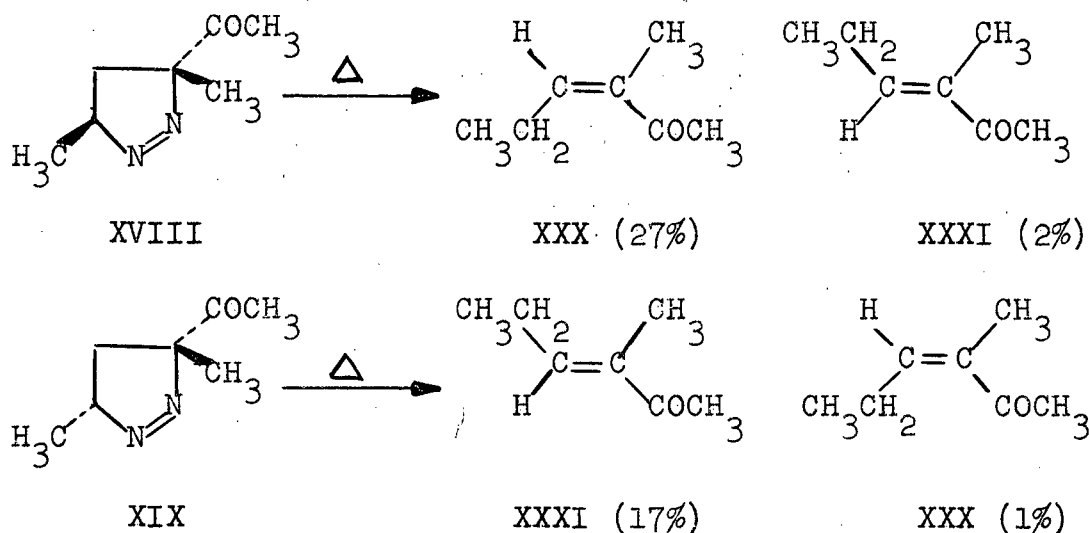
model has not been available. The formation of olefins has previously been thought to be formed through the intermediate

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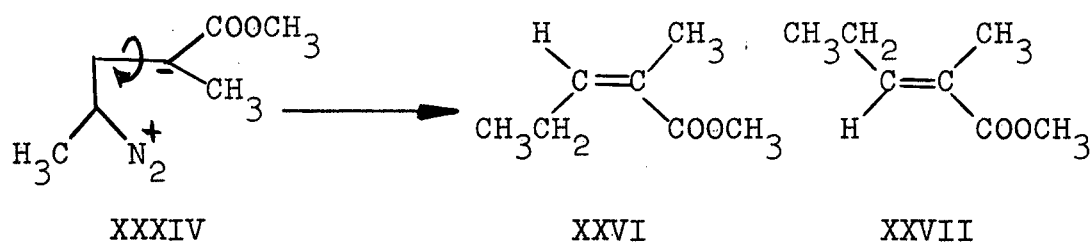
XXXIV or XXXV in which rotation around the single bonds would give a mixture of cis and trans olefins. For the diazonium betaine XXXIV to give such steric control it would require that the anion center must retain its asymmetry. This is not anticipated on the basis of studies by Cram and coworkers (39).

In the pyrolysis and photolysis of 3,5-dimethyl-3-

acetyl-Δ^1-pyrazoline (XXIII), its cis (XVIII) and trans (XIX)
isomers, an additional product 2,3,5-trimethyl-Δ^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

XXXV   XXXVI   XXIX
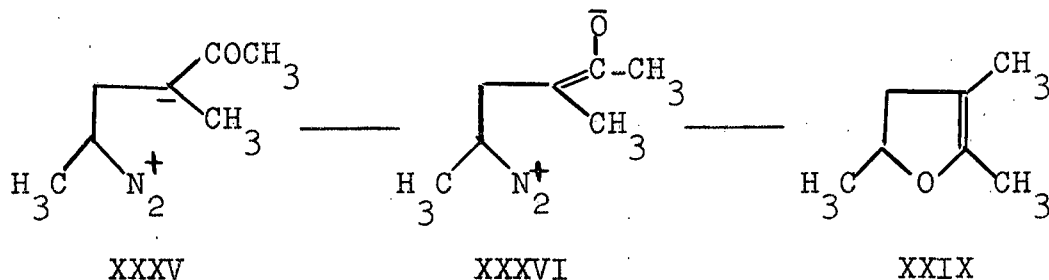
cis and trans-3,5-dimethyl-3-acetyl-Δ^1-pyrazoline (XVIII and
XIX) would give the same intermediate XXXVI on pyrolysis, and
hence they should give the same amount of dihydrofuran XXIX.
Experimental results, however, showed the amount of XXIX ob-
tained from the isomeric pyrazolines were significantly dif-
ferent. For example, thermal pyrolysis of cis and trans-3,5-
dimethyl-3-acetyl-Δ^1-pyrazoline (XVIII and XIX) at the in-
jector of the vapor phase chromatography instrument gave 16%
and 3%, respectively, of 2,3,5-trimethyl-Δ^2-dihydrofuran
(XXIX), and pyrolysis of neat liquid samples gave 14% and 0%
respectively. These results seem to indicate that the forma-
tion 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-Δ^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 Δ^1-pyrazolines (III) would cause the kinetics of the reaction to show a higher rate in more polar solvents, since the process involves the

$$Y = -COCH_3, -COOCH_3$$

III   II
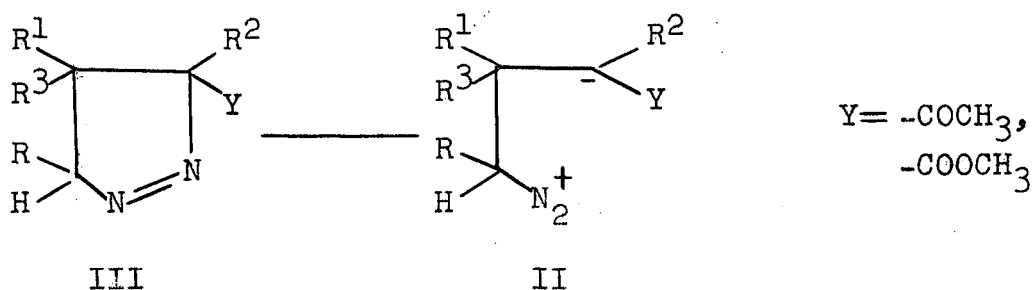
formation of ionic charges from a neutral species (37). In other words, the rate of pyrolysis of Δ^1-pyrazolines should be faster in a solvent of high polarity than a solvent of low polarity. The results of the present work showed the rate of pyrolysis of Δ^1-pyrazolines, as indicated by the rate of 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 Δ^1-pyrazoline. Therefore, it is not likely that the thermal pyrolysis of Δ^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 Δ^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 betaine intermediate, for example
XXXIV, would form pyrazoline by ring closure faster than the
loss of nitrogen. Since the product analysis predicts rotation
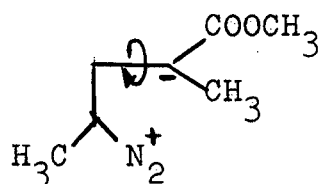
XXXIV

about C_3-C_4 bond, one would anticipate that when trans-3,5-
dimethyl-3-carbomethoxy-Δ^1-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 photo-
lysis of XVII also gave a similar result.

The possibility of the diazonium betaine II as the
intermediate for the pyrolysis of Δ^1-pyrazolines is therefore
eliminated.

II

$Y = -COCH_3,$
$-COOCH_3$
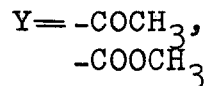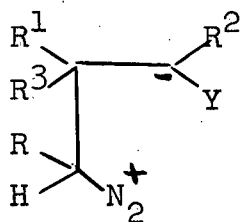
Recent work in this laboratory (40) has discovered a
pyrazoline system which gives kinetics that are sensitive to

solvent polarity as expected for an ionic intermediate. The

XXXVII   XXXVIII   other minor products.
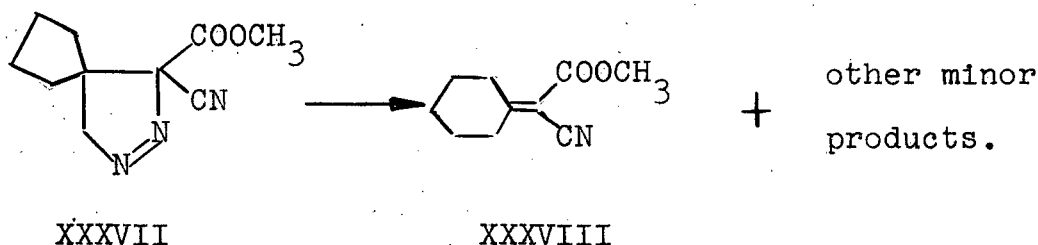
Δ^1-pyrazoline XXXVII in this case has two electron withdrawing groups which can stabilized a diazonium betaine intermediate to a greater degree.

It is apparent that pyrolysis of Δ^1-pyrazolines might fit a spectrum of conditions in which symmetric substitution around the azo group leads to breaking of both bonds simultaneously in the transition state. In highly unsymmetrical Δ^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 ($\emptyset = -C_6H_5$)

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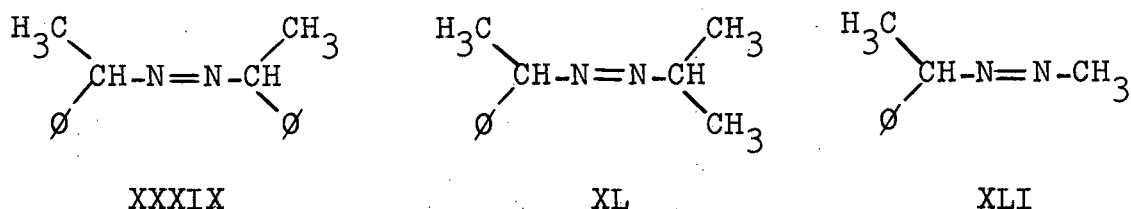
show equal breaking of both bonds, unequal breaking of both bonds and initial breaking of one bond. These results were obtained by secondary deuterium effects on the kinetics.

It is apparent that in the pyrolysis of cis and trans-3,5-dimethyl-3-carbomethoxy-Δ^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 developes in the molecule after the transition state to make the products sensitive to the solvent used. Such a model correctly predicts the olefin reaction. (Figure X)

Photolysis of cis and trans-3,4-dimethyl-3-carbomethoxy-Δ^1-pyrazoline (VI and VII) have been reported by van Auken and Rinehart (12) to give stereospecifically cis and trans-1,2-di-methyl-1-carbomethoxycyclopropane (X and XI) respectively, the major side products are methyl tiglate (IV) and methyl angelate (V) respectively.
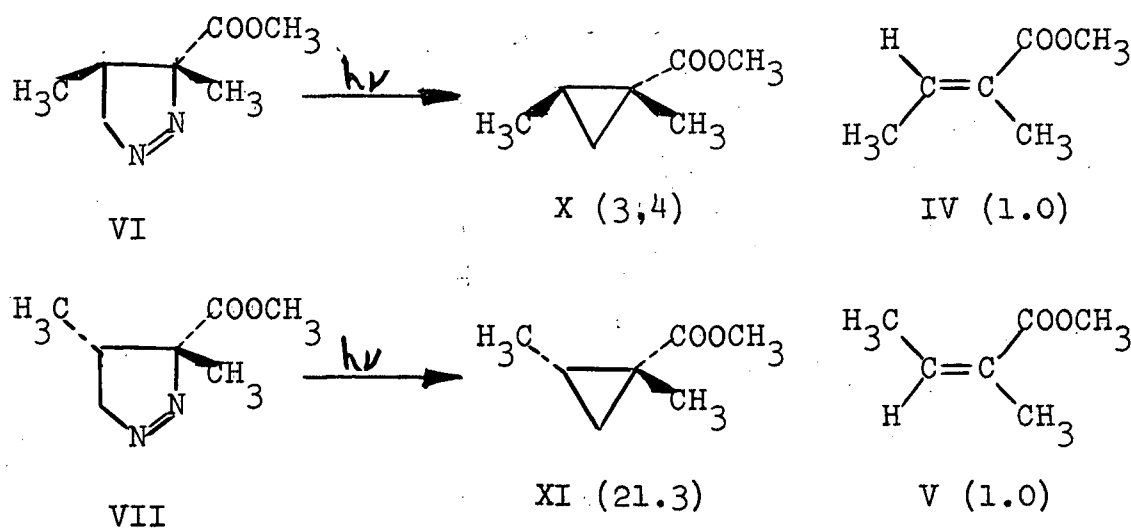
VI   X (3.4)   IV (1.0)

VII   XI (21.3)   V (1.0)

Photolysis of cis and trans-3,5-dimethyl-3-carbomethoxy-Δ^1-pyrazoline (XVI and XVII), cis and trans-3,5-dimethyl-3-acetyl-Δ^1-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

XVI, $Y = COOCH_3$

XVIII, $Y = COCH_3$

cis-olefin product

XVII, $Y = COOCH_3$

XIX, $Y = COCH_3$

trans-olefin product
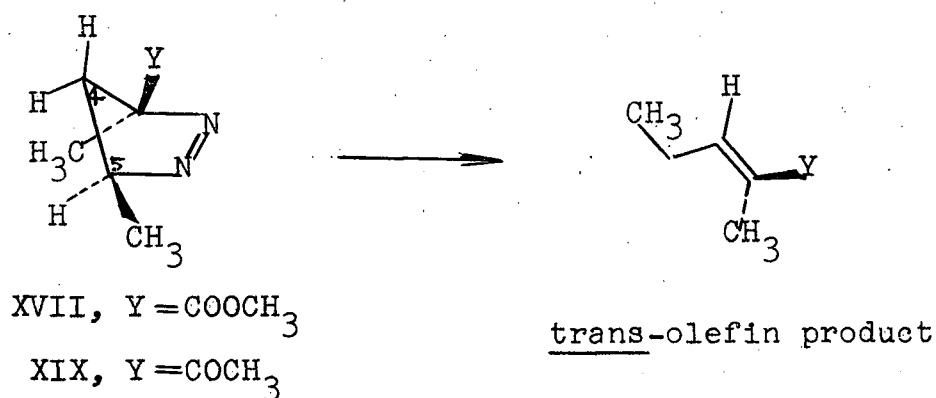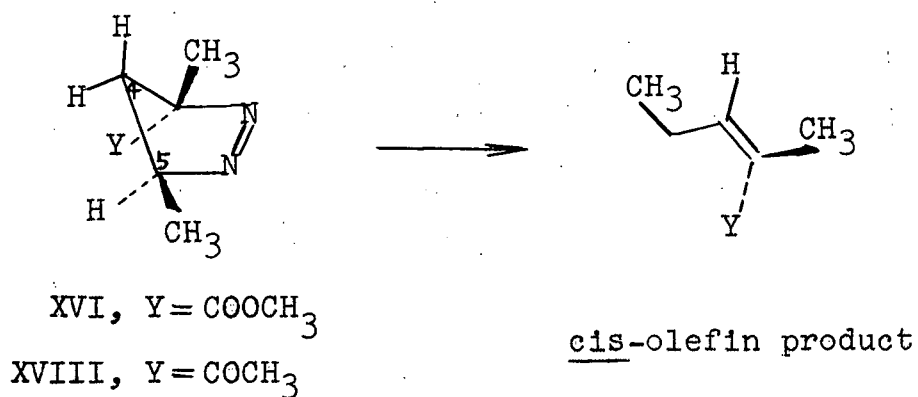
The preferred conformation of the pyrazoline isomers places
the pseudo equatorial hydrogen on C_4 in a better position
for migration to C_5 concerted with nitrogen elimination
than the pseudo axial hydrogen.

FIGURE X - Stereochemistry of the formation of
olefins from Δ^1-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

XVIII   XXIV (59%)   XXV (28%)

XIX   XXV (70)   XXIV (21%)
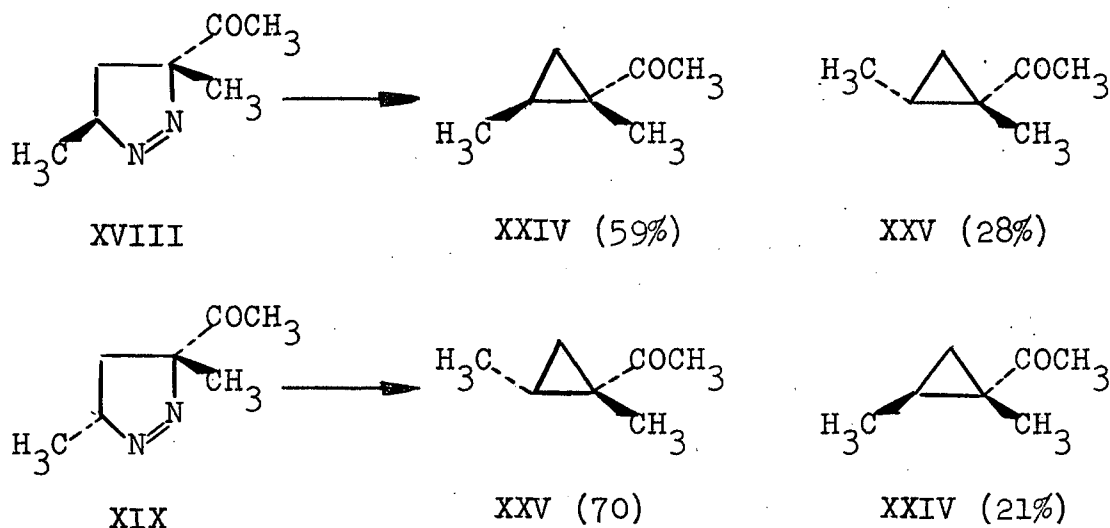
product composition as observed in the pyrolysis was also ob-
served in the photolysis. The two reactions therefore are
closely related but not identical as shown by photolysis and
pyrolysis at same temperature and solvent in which different
product compositions resulted.

It is possible the photolysis involves a different con-
formation 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 elec-
tronically excited intermediate. The nuclear magnetic reso-
nance spectra (Table I) of the Δ^1-pyrazolines showed large
differences in the chemical shift positions of the hydrogens
on C_4, especially in cis-3,5-dimethyl-3-acetyl-Δ^1-pyrazoline

(XVIII) and <u>cis</u>-3,5-dimethyl-3-carbomethoxy-Δ^1-pyrazoline (XVI). For example, C_4 hydrogens in XVIII absorbed at 7.57 τ and 9.30 τ, those of XVI absorbed at 7.68 τ and 9.14 τ compared to 8.28 τ and 8.56 τ for the <u>trans</u>-ester-pyrazoline (XVII) and 8.53 τ for the <u>trans</u>-keto-pyrazoline (XIX). These differences in chemical shifts could well be related to differences 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. Melt-
ing points were determined by a microscopic melting point ap-
paratus (Reichart, Austria) and most boiling points were de-
termined 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 Aero-
graph Model A-90-P (preparative scale) and a Perkin-Elmer
Model 226 (analytical scale).

The elemental microanalyses were performed by Dr. A. Bern-
hardt 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 flutted filter paper. The filtrate was distilled at atmospheric pressure and the fraction with a boiling point of $95 \pm 2^{\circ}$ was collected and used immediately.

VI-5. 3,5-Dimethyl-3-acetyl-Δ^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).

Anal. Calcd. for $C_7H_{12}N_2O$: C, 59.97; H, 8.63; N, 19.99. Found: C, 59.60; H, 8.22; N, 20.27.

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 <u>cis</u> and <u>trans</u>-3,5-dimethyl-3-acetyl-Δ^1-
      pyrazoline (XVIII and XIX)

The 3,5-dimethyl-3-acetyl-Δ^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 en-
tire 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% <u>cis</u>-pyrazoline XVIII and 87% <u>trans</u>-
pyrazoline XIX respectively. These analyses were based on the
integrals of the acetyl methyl hydrogens absorptions at 7.78 τ
for the cis isomer and at 7.65 τ for the trans isomer. The cis
and trans geometric assignments were based on the comparison
of n.m.r. spectral data with those of <u>cis</u> and <u>trans</u>-3,5-di-
methyl-3-carbomethoxy-Δ^1-pyrazoline (XVI and XVII) (Table I)
and the stereospecific formation of <u>cis</u> and <u>trans</u>-1,2-dimethyl-
1-acetylcyclopropane (XXIV and XXV) from XVIII and XIX re-
spectively by photolysis.

The n.m.r. spectral data of <u>cis</u> and <u>trans</u>-3,5-dimethyl-
3-acetyl-Δ^1-pyrazoline (XVIII and XIX) are tabulated in Table I.

VI-7. Separation of <u>cis</u> and <u>trans</u>-3,5-dimethyl-3-carbomethoxy-
      Δ^1-pyrazoline (XVI and XVII)

3,5-Dimethyl-3-carbomethoxy-Δ^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-Δ^1-pyrazoline (XVIII and XIX) to give cis and trans-3,5-dimethyl-3-carbomethoxy-Δ^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 τ and 6.27 τ respectively, and this was the basis for distinguishing the two isomers. Geometric assignments were based on the photolysis results in which the cis-3,5-dimethyl-3-carbo-methoxy-Δ^1-pyrazoline (XVI) gave cis-1,2-dimethyl-1-carbo-methoxycyclopropane (X) and the trans-3,5-dimethyl-3-carbo-methyl-Δ^1-pyrazoline (XVII) gave trans-1,2-dimethyl-1-carbo-methoxycyclopropane (XI) as main product, and the lower yield of the cis-pyrazoline XVI (40%) due to steric hindrance of the methyl groups at C_3 and C_5.

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

VI-8. trans-3,5-Dimethyl-3-carbomethoxy-Δ^1-pyrazoline hydro-bromide (XXII)

To a mixture of 0.4 ml. of trans-3,5-dimethyl-3-carbo-methoxy-Δ^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 $C_7H_{13}N_2O_2Br$: 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 (se 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 CCl_4) 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 CCl_4) showed signals of vinyl methyl

hydrogens at 8.43 τ (multiplet), C_5 methyl hydrogens at 8.79 τ (doublet with $J \simeq 6.1$ c.p.s.), C_4 hydrogens at 7.40 τ (two doublets) and 7.98 τ (two doublets) and C_5 hydrogen at 5.59 τ (sextet with further splitting). The hydrogens at C_4 and C_5 constituted a typical ABX system (29) with $\Delta_{AX} \simeq 144.5$ c.p.s., $\Delta_{AB} \simeq 35.5$ c.p.s., $\Delta_{BX} \simeq 109$ c.p.s., $J_{AB} \simeq 14.5$ c.p.s., $J_{AX} \simeq 8.0$ c.p.s. and $J_{BX} \simeq 9.5$ c.p.s. (Figure IX). These chemical shifts are at expected positions as compared to 2-methyl-Δ^2-dihydro-furan (XXXIII) (30) whose chemical shifts are at 8.30 τ (multiplet), 5.55 τ (multiplet), 7.47 τ (multiplet) and 5.78 τ (triplet with $J \simeq 9.3$ c.p.s.) due to C_2 methyl hydrogens, C_3 vinyl hydrogen, C_4 and C_5 hydrogens respectively.

Anal. Calcd. for $C_7H_{12}O$: 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^{24} 1.4370, 12.2 minutes and 6%. Infrared (5% v/v in CCl_4) 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 CCl_4) showed peaks of acetyl methyl hydrogens at 7.86 τ (singlet), vinyl methyl hydrogens at 8.12 τ (multiplet), methylene hydrogens at 7.73 τ (multiplet), alkyl methyl hydrogens at 9.02 τ (triplet with $J \simeq 7.3$ c.p.s.) and vinyl hydrogen at 4.44 τ (multiplet). Geometric assignment is discussed below.

Anal. Calcd. for $C_7H_{12}O$: 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^{23} 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 τ (singlet), alkyl methyl hydrogens at 8.93 τ (triplet with $J \simeq 7.5$ c.p.s.), vinyl methyl hydrogens at 8.39 τ (multiplet), methylene hydrogens at 7.76 τ (multiplet) and vinyl hydrogen at 3.52 τ (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 τ-value (32).

Anal. Calcd. for $C_7H_{12}O$: 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^{24} 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 follwing peaks, acetyl methyl hydrogens at 8.00 τ (singlet), C_1 methyl hydrogens at 8.72 τ (multiplet), C_2 methyl hydrogens at 8.82 τ (multiplet with main peak at 8.84 τ), other ring hydrogens at 8.68 τ (two hydrogens, multiplet under C_1

methyl hydrogens signal) and 9.74 τ (one hydrogen, multiplet).
Assignment of geometry will be discussed below. Repeated ele-
mental microanalysis gave low value of carbon composition.

trans-1,2-Dimethyl-1-acetylcyclopropane (XXV) and 3-meth-
yl-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 tetra-
chloride 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 $C_7H_{12}O$: 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 μ due
to carbonyl conjugated to cyclopropane ring. The n.m.r. spectrum
(20% v/v in CCl_4) showed the absorption of acetyl methyl hydro-
gens at 7.86 τ (singlet), C_1 methyl hydrogens at 8.62 τ (sin-
glet), C_2 methyl hydrogens at 9.03 τ (multiplet), C_2 and C_3
hydrogens at two sets of multiplet in the region between 8.75 τ
and 9.60 τ. The assignment of geometry to cis and trans-1,2-di-
methyl-1-acetylcyclopropane (XXIV and XXV) was based on the com-
parison of their n.m.r. spectra to those of the analogous cyclo-
propanes, 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 τ (singlet), C_3 methyl hydrogens at 8.92 τ (doublet with J $\simeq$ 7 c.p.s.), vinyl hydrogens at 4.57 τ (multiplet) and vinyl methyl hydrogens at 8.32 τ (doublet with J $\simeq$ 4.8 c.p.s.). The n.m.r. spectrum indicated the sample to be a β,γ-unsaturated ketone because of the high acetyl methyl hydrogens absorption at 7.97 τ and the olefin proton absorption at 4.57 τ.

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

The same procedure as for the thermal pyrolysis of 3,5-dimethyl-3-acetyl-Δ^1-pyrazoline (XXIII) was used for the thermal pyrolysis of cis and trans-3,5-dimethyl-3-acetyl-Δ^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-Δ^1-pyrazoline (XVIII and XIX)

The apparatus for the vapor phase pyrolysis was a one-liter round flask equiped 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 vacumn line and the products were collected in a U-tube cooled with liquid nitrogen. Fifty microliters of anhydrous ether were 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-Δ^1-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-Δ^1-pyrazoline (XXIII)

Nine and a half grams of XXIII in a 25 ml. round flask equiped 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° 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 re-

sult is recorded in Table II.

VI-13. Liquid phase pyrolysis of cis and trans-3,5-dimethyl-3-

acetyl-Δ^{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° until the evo-

lution of nitrogen gas ceased. Product composition of the pro-

ducts 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-Δ^{1}-pyrazoline (XXIII)

A mixture of 1 ml. of XXIII and 25 ml. of anhydrous ether

in a 50 ml. round flask equiped 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 chroma-

tography 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-Δ^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 equiped 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-Δ^1-pyrazoline (XVI and XVII)

The same procedure as the vapor phase pyrolysis of cis and trans-3,5-dimethyl-3-acetyl-Δ^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-Δ^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-Δ^1-pyrazoline (XVI and XVII) in various solvents

A mixture od 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 vacumn 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-Δ^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
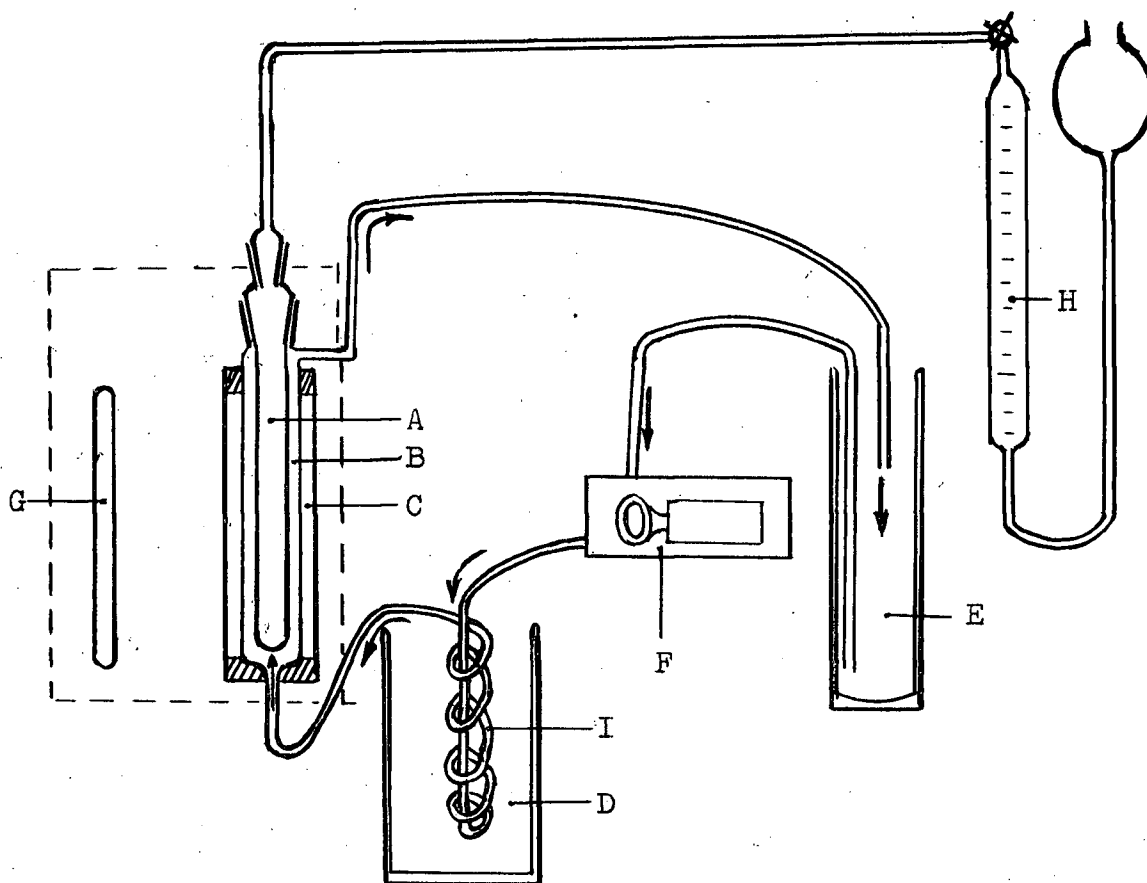
A - Reaction vessel, 13-mm. x 150-mm.

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-Δ^1-pyrazoline (XVI and XVII) in formamide at 23°

The same procedure as described in the preceeding para-graph was used for these photolyses. The cooling agent at D was water at $22\text{-}23^{\circ}$. These results are recorded in Table V.

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

A mixture of 1 g. of XVII (99+%) and 10 ml. of anhydrous ether in a 25 ml. round flask equiped with a water cooled con-denser 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 vacumn line to removed the solvent and the products from photolysis. The recoved 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-Δ^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 theo-
retical amount) of nitrogen gas had evolved. After removing the
pyrolysis products in a vacumn 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 practi-
cally identical to each other.

VI-22. Kinetic Studies of the pyrolysis of 3,5-dimethyl-3-carbo-
methoxy-Δ^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 milli-
liters of solvent in the tube was heated in an oil bath to $1CO-1^{\circ}$,
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 Δ^1-pyrazolines gives
good first order kinetics, and that the half-life, $t_{\frac{1}{2}}$, 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
$\log (V_\infty/V_\infty-V_t)$ 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-live of XX
in these solvents had been found to be 26.2, 29.0, 43.6 and 83.1
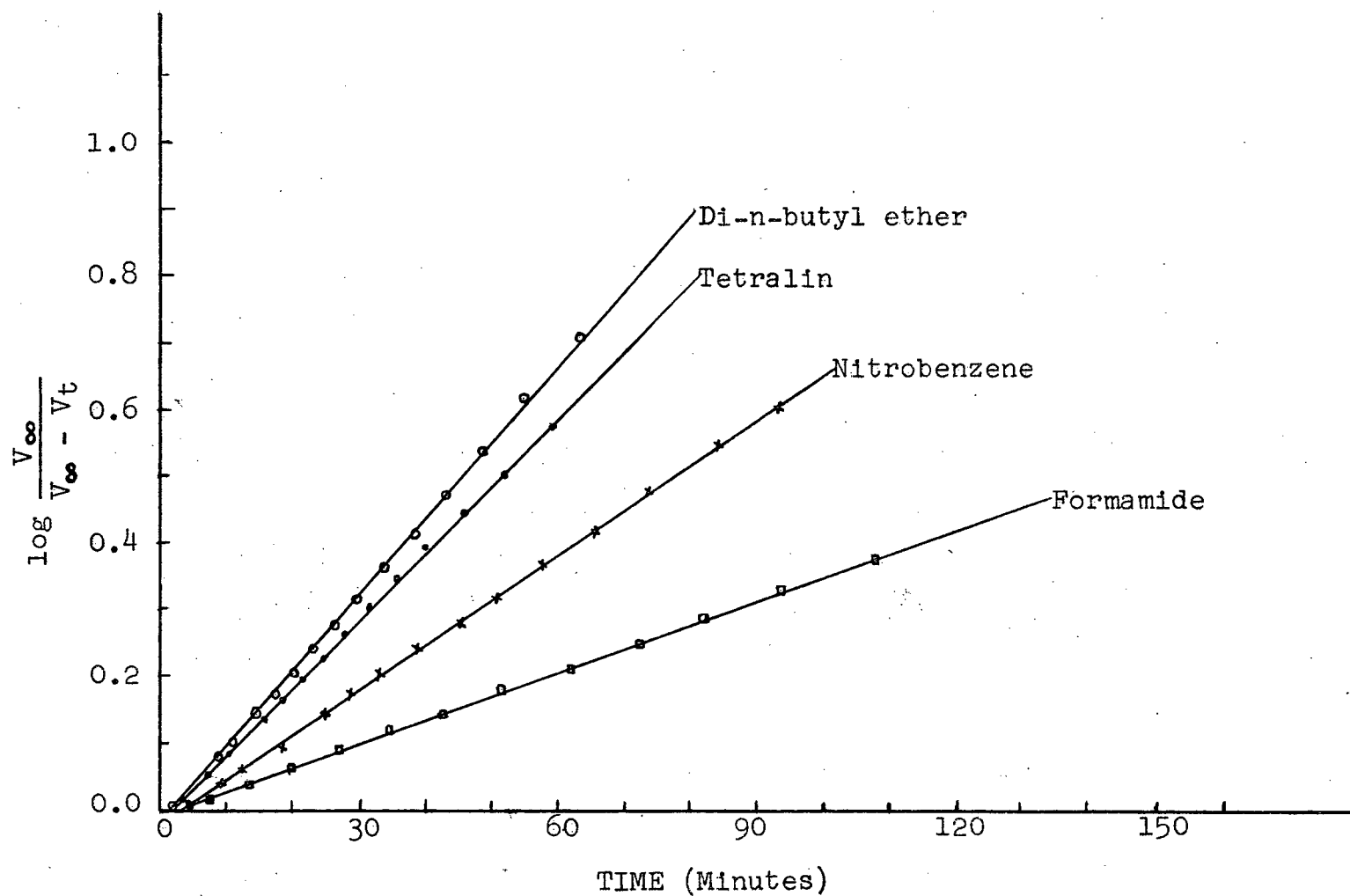minutes, respectively (Figure XII).

FIGURE XII - First order plot of $\log \dfrac{V_\infty}{V_\infty - V_t}$ vs. time for the pyrolysis of 3,5-dimethyl-3-carbomethoxy-Δ^1-pyrazoline in various solvents.

<u>VI-9a</u>. 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-Δ^2-dihydrofuran (XXIX),
<u>cis</u> and <u>trans</u>-1,2-dimethyl-1-acetylcyclopropane (XXIV and XXV)
and <u>cis</u>-3-methyl-3-hexen-2-one (XXX) were 295-8°, 118.5-119.5°,
307-9° and 156.5-157° respectively. <u>trans</u>-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 <u>trans</u>-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 α,β-un-
saturated ketones give two 2,4-DNPH derivatives, Δ^2-pyrazoline
and <u>syn</u>-alkyl 2,4-DNPH. Hence one of the two 2,4-DNPH derivatives
of XXXI obtained could be a Δ^2-pyrazoline, and the other a
<u>syn</u>-alkyl 2,4-DNPH.

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