

THE SYNTHESIS AND PYROLYSIS OF
4,5-DIMETHYL-3-CARBOMETHOXY-2-PYRAZOLINE AND
3,5-DIMETHYL-3-CARBOMETHOXY-1-PYRAZOLINE

by

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September, 1961

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ABSTRACT

The products arising from the liquid-phase pyrolyses of 3,5-dimethyl-3-carbomethoxy-1-pyrazoline and 4,5-dimethyl-3-carbomethoxy-2-pyrazoline have been isolated and identified. The pyrolysis of 3,5-dimethyl-3-carbomethoxy-1-pyrazoline has been found to yield a mixture of 5 isomers consisting of 15% methyl trans-2-methyl-2-pentenoate, 10% methyl cis-2-methyl-2-pentenoate, 3% methyl trans-2-methyl-3-pentenoate, 45% methyl cis-1,2-dimethylcyclopropane-1-carboxylate and 27% methyl trans-1,2-dimethylcyclopropane-1-carboxylate. The pyrolysis of 4,5-dimethyl-3-carbomethoxy-2-pyrazoline yielded a mixture of 7 isomers consisting of 25.5% methyl trans-3-methyl-2-pentenoate, 26% methyl cis-3-methyl-2-pentenoate, 3% methyl trans-3-methyl-3-pentenoate, 2% methyl cis-3-methyl-3-pentenoate, 26% methyl trans-1,2-dimethylcyclopropane-3-carboxylate, 16% methyl cis-1,2-dimethylcyclopropane-3-trans-carboxylate and 0.8% methyl 3-ethyl-3-butenate. Pyrolysis of both pyrazolines has also been obtained in the vapour-phase and under these conditions a higher proportion of cyclopropanecarboxylic esters was formed than that obtained in the liquid-phase pyrolyses: 3,5-dimethyl-3-carbomethoxy-1-pyrazoline yielded a mixture containing 94.5% cyclopropane carboxylic esters and 4,5-dimethyl-3-carbomethoxy-2-pyrazoline yields a mixture containing 67% of cyclopropane carboxylic esters. The vapour-phase pyrolysis of the 1-pyrazoline occurred readily at 200° whereas the vapour-phase pyrolysis of the 2-pyrazoline was found to require a catalyst. This catalyst is believed to facilitate the transformation of the 2-pyrazoline to the readily pyrolysable 1-pyrazoline form. Studies

have been made of the equilibration of the unsaturated esters arising from the pyrolysis of the pyrazolines and have shown that the composition of the olefin portion of the pyrolysis mixture in general is not an equilibrium mixture. A mechanism for the pyrolysis is suggested. The unsaturated esters arising from the pyrolysis of 4,5-dimethyl-3-carbomethoxy-2-pyrazoline have been synthesised and identified and structural assignments have been made.

TABLE OF CONTENTS

| | Page |
|--|------|
| List of Tables | vi |
| List of Figures | vii |
| INTRODUCTION | 1 |
| Section I | |
| THE SYNTHESIS AND PYROLYSIS OF 4,5-DIMETHYL-3-CARBOMETHOXY-2-PYRAZOLINE AND 3,5-DIMETHYL-3-CARBOMETHOXY-1-PYRAZOLINE | 3 |
| Synthesis and identification of the pyrazolines | 3 |
| Liquid-phase pyrolysis of the pyrazolines | 4 |
| Vapour-phase pyrolysis of the pyrazolines | 7 |
| Section II | |
| SYSTEMATIC IDENTIFICATION OF THE PYROLYSIS PRODUCTS | 9 |
| A. 4,5-Dimethyl-3-carbomethoxy-2-pyrazoline | 9 |
| B. 3,5-Dimethyl-3-carbomethoxy-1-pyrazoline | 17 |
| C. Equilibration studies | 22 |
| Section III | |
| DISCUSSION | 25 |
| EXPERIMENTAL | 35 |
| N-Nitroso N-Ethyl Urea | 35 |
| Diazoethane | 36 |
| 4,5-Dimethyl-3-carbomethoxy-2-pyrazoline | 36 |
| 3,5-Dimethyl-3-carbomethoxy-1-pyrazoline | 37 |
| Pyrolysis of 4,5-Dimethyl-3-carbomethoxy-2-pyrazoline | 37 |
| Vapour-Phase Pyrolysis of 4,5-Dimethyl-3-carbomethoxy-2-pyrazoline | 41 |

| | Page |
|---|------|
| Isomerisation Studies on Methyl <u>trans</u> -3-Methyl -2-Pentenoate and Methyl <u>trans</u> -3-Methyl-3-Pentenoate . | 41 |
| Pyrolysis of 3,5-Dimethyl-3-Carbomethoxy-1-Pyrazoline. | 42 |
| Vapour-Phase Pyrolysis of 3,5-Dimethyl-3-carbomethoxy -1-pyrazoline | 44 |
| Isomerisation Studies on Methyl <u>trans</u> -2-Methyl-2- Pentenoate and Methyl <u>trans</u> -2-methyl-3-Pentenoate | 45 |
| Synthesis of Methyl 3-Methyl-2- and -3-Pentenoates ... | 46 |
| (a) Methyl 3-methyl-3-hydroxy valerate | 46 |
| (b) Methyl 3-methyl-2- and -3-pentenoates | 47 |
| The Absolute Configuration of Methyl <u>cis</u> -3-Methyl -3-Pentenoate | 48 |
| (a) 2,3-Dibromo-2-methyl-butyric acid | 48 |
| (b) 2,3-Dibromo-2-methyl-butyryl chloride | 48 |
| (c) Methyl 2,3-dibromo-3-methyl-pentanoate | 49 |
| (d) Methyl <u>cis</u> -3-methyl-3-pentenoate | 50 |
| Synthesis of Methyl 2-Methyl-2- and -3-Pentenoates ... | 51 |
| (a) Methyl 3-keto-3-methyl-pentanoate | 51 |
| (b) Copper Chromite Catalyst | 52 |
| BIBLIOGRAPHY | 53 |

List of Tables

| | Page |
|--|------|
| 1 Product Analysis from Pyrazoline Pyrolyses | 5 |
| 2 The Pyrolysis products from 4,5-dimethyl -3-carbomethoxy-2-pyrazoline | 10 |
| 3 The Pyrolysis products from 3,5-dimethyl -3-carbomethoxy-1-pyrazoline | 18 |
| 4 Equilibrium compositions of the unsaturated esters from the pyrolysis | 23 |

List of Figures

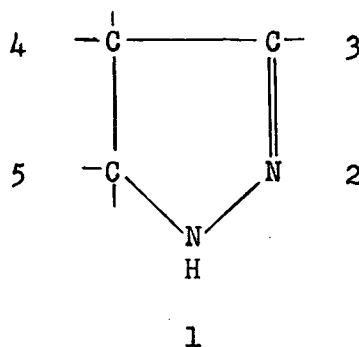
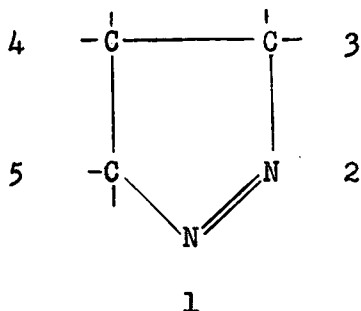
| | Page |
|--|------|
| I Illustration of the products arising from the pyrolyses of 4,5-dimethyl-3-carbomethoxy-2-pyrazoline and 3,5-dimethyl-3-carbomethoxy-1-pyrazoline | 6 |
| II Vapour phase chromatogram of the pyrolysis products from 4,5-dimethyl-3-carbomethoxy-2-pyrazoline | 11 |
| III The absolute configuration of methyl <u>cis</u> -3-methyl-3-pentenoate | 13 |
| IV Vapour phase chromatogram of the pyrolysis products from 3,5-dimethyl-3-carbomethoxy-1-pyrazoline | 19 |
| V Illustration of a possible mechanism for pyrazoline synthesis and pyrolysis | 26 |

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INTRODUCTION

The addition of diazoalkanes to conjugated unsaturated esters is a well known route to pyrazoline-3-carboxylic esters; the addition occurring in such a way that the terminal nitrogen atom of the diazoalkane becomes attached to the activated α -position of the unsaturated ester (1-3, 5, 6). The Δ^1 -pyrazolines that are formed first tautomerize spontaneously to Δ^2 -pyrazolines if this is possible and if the tautomerism results in the formation of a conjugated system (2, 4-7). The structure and numbering of the Δ^1 -pyrazolines and the Δ^2 -pyrazolines is shown below.



It was therefore expected that the addition of diazoethane to methyl crotonate and to methyl methacrylate would yield, respectively, 4,5-dimethyl-3-carbomethoxy-2-pyrazoline (I) and 3,5-dimethyl-3-carbomethoxy-1-pyrazoline (II).

The thermal decomposition of pyrazoline carboxylic esters has been reported to yield cyclopropanecarboxylic esters or unsaturated esters; the distribution of products being dependent upon the degree and position of substituents on the pyrazoline (5, 8-13). The results have often been

interpreted in text-books as offering a general synthetic route to cyclopropane derivatives (30), though, in general, the pyrolysis is of limited value in the preparation of such derivatives. Pyrazolines substituted with ester groups at positions 3 and 4 (5, 8-11) and pyrazolines with an alkyl substituent and a carbalkoxy substituent at position 3 (5, 12, 13) have been reported to give mainly cyclopropane derivatives, but a few exceptions to this rule have been reported (5). 3-carbomethoxy-pyrazolines with alkyl substituents at the 4 or 5 position on the pyrazoline nucleus generally have been found to yield no cyclopropane product on pyrolysis. Von Auwers (5) has reported that 4,5-dimethyl-3-carbomethoxy-2-pyrazoline (I) is pyrolysed to give methyl 3-methyl-3-pentenoate as the sole product, and that 3,5-dimethyl-3-carbomethoxy-1-pyrazoline (II) is pyrolysed to give methyl 1,2-dimethylcyclopropane-1-carboxylate as the sole product.

Contemporaneous evidence has shown that the relative yields of products obtained from the pyrolysis of 3-carbomethoxy-pyrazolines are considerably different from those reported in earlier work (18). For this reason a reinvestigation of the pyrolyses of I and II was felt justified. It was also hoped that further information on the effect of methyl substitution in the pyrazoline nucleus on the product composition would aid in evaluating proposed mechanisms for the pyrolysis step.

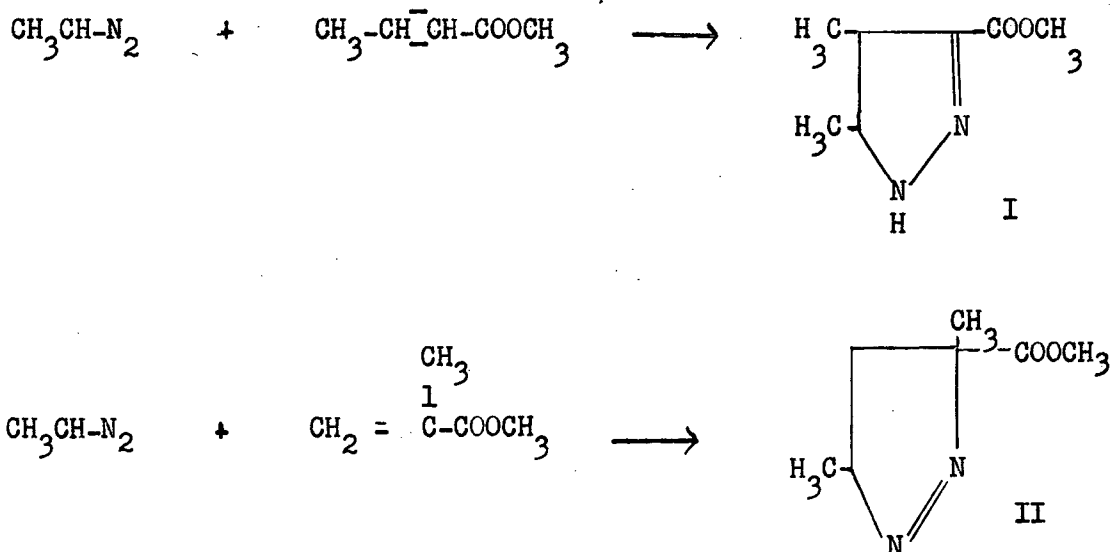
Section I

THE SYNTHESIS AND PYROLYSIS OF 4,5-DIMETHYL-3-CARBOMETHOXY-2-PYRAZOLINE AND 3,5-DIMETHYL-3-CARBOMETHOXY-1-PYRAZOLINE

The two pyrazolines were prepared by the addition of diazoethane to the appropriate unsaturated ester, and were identified on the basis of their physical properties and their infrared spectra. Each has been pyrolysed in the liquid and vapour phase and the relative proportions of the products arising from these pyrolyses determined.

Synthesis and identification of the pyrazolines

4,5-Dimethyl-3-carbomethoxy-2-pyrazoline (I) was prepared by the addition of diazoethane to methyl crotonate, and 3,5-dimethyl-3-carbomethoxy-1-pyrazoline (II) by the addition of diazoethane to methyl methacrylate. The reactions were rapid and were completed at room temper-



ature soon after the addition was finished. The diazoethane, in each case, was prepared from N-nitroso-N-ethyl urea.



4,5-Dimethyl-3-carbomethoxy-2-pyrazoline (I) is a colourless crystalline solid which rapidly darkens in colour in the presence of air and light. On one occasion further oxidation yielded a colourless solid. The nature of these oxidation products has not been ascertained. The pyrazoline isolated from the reaction of diazoethane with methyl crotonate is assigned the Δ^2 -structure, which would result from the conjugation of the double bond with the ester carbonyl group, on the basis of its infrared spectrum which had bands at 3400, 1557 and 1710 cm^{-1} showing N-H stretch, $\text{C}=\text{N}$ stretch and a conjugated ester carbonyl absorption respectively.

3,5-Dimethyl-3-carbomethoxy-1-pyrazoline (II) is a colourless liquid which is stable under conditions which effect the oxidation of I. The infrared spectrum of II shows no absorption in the N-H or $\text{C}=\text{N}$ frequency ranges, and its carbonyl ester absorption at 1735 cm^{-1} indicates that the ester carbonyl group is non-conjugated. Pyrazoline II is accordingly assigned the Δ^1 -structure.

Liquid-phase pyrolysis of the pyrazolines

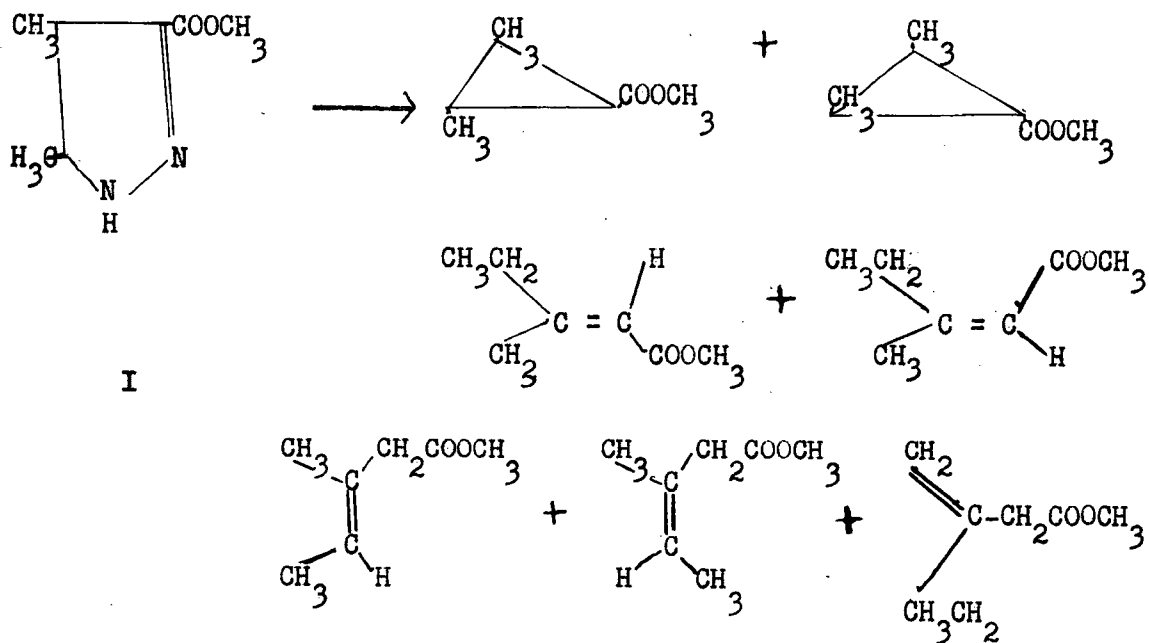
The results of the pyrolysis in the liquid-phase of 4,5-dimethyl-3-carbomethoxy-2-pyrazoline (I) and 3,5-dimethyl-3-carbomethoxy-1-pyrazoline (II) are collected in Table 1 and illustrated in Figure I.

Table 1Product Analysis from Pyrazoline Pyrolyses

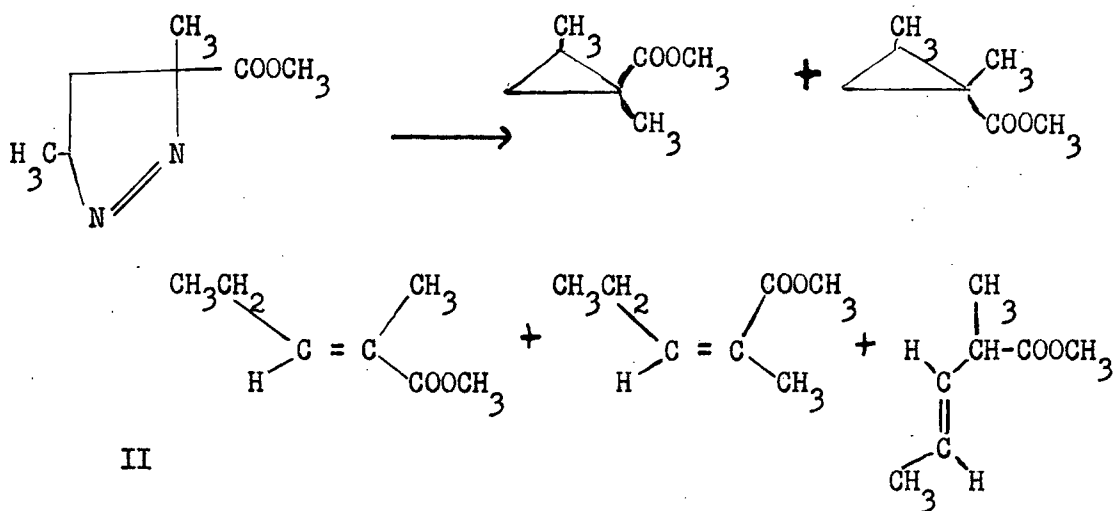
| Substituent in 3-carbomethoxy -pyrazoline | Phase | Percentage of components in the product | | | | | |
|---|--------|---|-------|-----------------|-----------------|--------------------------------------|----------------|
| | | Cyclopropane α,β -Unsaturated ester | | | | β,γ -Unsaturated ester | |
| | | cis | trans | cis | trans | cis | trans |
| 4,5-Dimethyl (I) | Liquid | 16 | 26.5 | 26 | 25.5 | 2 ^a | 3 ^b |
| | Vapour | 24 | 43 | 14 | 15.5 | 2 | 1.5 |
| 3,5-Dimethyl (II) | Liquid | 45 | 27 | 10 ^a | 15 ^a | - | 3 ^a |
| | Vapour | 53 | 41.5 | 2.5 | 2 | - | 1 |

^a These compounds have not previously been reported.

^b Two additional peaks appeared on vapour-phase chromatographic analysis; one of these (0.8% of total product) was tentatively identified as methyl 3-ethyl-3-butenate by comparison of its retention time with an authentic sample.



4,5-Dimethyl-3-carbomethoxy-2-pyrazoline



3,5-Dimethyl-3-carbomethoxy-1-pyrazoline

Figure I

Illustration of the products arising from the pyrolyses of 4,5-dimethyl-3-carbomethoxy-2-pyrazoline and 3,5-dimethyl-3-carbomethoxy-1-pyrazoline

Pyrolysis in the liquid-phase was obtained by heating the appropriate pyrazoline in a distillation apparatus to a temperature at which there was a rapid evolution of nitrogen. For the 2-pyrazoline, I, the pyrolysis temperature of 190° was sufficient to effect distillation of the products as they were formed; the 1-pyrazoline, II, pyrolysed at a temperature of 110° and further heating was required to effect distillation of the products.

The products from the pyrazoline pyrolyses were isolated by vapour phase chromatography. A 10-ft Dinonyl Phthalate column effected separation of all the compounds reported except methyl cis-3-methyl-3-pentenoate and methyl cis-1,2-dimethylcyclopropane-3-trans-carboxylate, which were, in turn, separated on a 10-ft Ucon Polar column using a low flow rate. Structural assignments were made on the basis of physical properties in those cases where data were available in the literature, and these structures were confirmed by the use of N.M.R. and infrared spectral data. Five of the pyrolysis products have not been reported previously and one (methyl trans-3-methyl-3-pentenoate) has a refractive index which is in disagreement with the reported value. The structures of these compounds are assigned from the analysis, N.M.R. and infrared data, from synthetic studies and from equilibrium studies on known isomeric olefins. These assignments are discussed in Section II.

Vapour-phase pyrolysis of the pyrazolines

The results of the vapour-phase pyrolysis of 4,5-dimethyl-3-carbomethoxy-2-pyrazoline (I) and 3,5-dimethyl-3-carbomethoxy-1-pyrazoline (II) are collected in Table 1.

The vapour-phase pyrolyses were effected by dropping the liquid pyrazoline onto pyrex beads or other packing material in a vertical tube heated to 200-250° and connected with a vacuum system which maintained a pressure of 2 to 4 mm in the tube. 3,5-Dimethyl-3-carbomethoxy-1-pyrazoline was readily pyrolysed when a pyrex bead packing was used, but 4,5-dimethyl-3-carbomethoxy-2-pyrazoline failed to pyrolyse under these conditions but did pyrolyse when the tube was charged with freshly-prepared 20-mesh fire brick. It is considered that the fire brick acts as a catalyst and is necessary to promote transformation of the Δ^2 -pyrazoline to the readily pyrolysable Δ^1 -form. This may be taken as evidence that it is the Δ^1 -form which pyrolyses and not the Δ^2 -form. Other authors (2,5, 15-18) have adduced evidence in support of this postulate, as is discussed in detail in Section III.

Vapour-phase pyrolysis of both pyrazolines produces a considerable increase in the proportion of cyclopropane derivative in the product. 3,5-Dimethyl-3-carbomethoxy-1-pyrazoline (II) yields a product which contains 94.5% of Methyl 1,2-dimethylcyclopropane-1-carboxylate: an increase of 22.5% over the liquid-phase reaction. 4,5-Dimethyl-3-carbomethoxy-2-pyrazoline (I) yields a product which contains 67% of methyl 1,2-dimethylcyclopropane-3-carboxylate: an increase of 24.5% over that obtained in the liquid-phase reaction.

Section II

SYSTEMATIC IDENTIFICATION OF THE PYROLYSIS PRODUCTS

A. 4,5-Dimethyl-3-carbomethoxy-2-pyrazoline

Six of the components isolated from the pyrolysis of this pyrazoline have received structural assignments and the seventh has received a tentative assignment. A reproduction of the chromatogram obtained on vapour-phase chromatographic analysis of the pyrolysis products is contained in Figure II, and the results of the investigations on the components separated by vapour-phase chromatography from the mixture of pyrolysis products are collected in Table 2.

The physical properties of components E and G corresponded with those reported in the literature for methyl cis-3-methyl-2-pentenoate and methyl trans-3-methyl-2-pentenoate, respectively. The cis or trans assignments were reported on the basis of the boiling points of the unsaturated esters; the trans ester having a higher boiling point than the cis ester (19). Jackman and Wiley (21, 22), in investigations on the N.M.R. spectra of unsaturated esters, have reported that a substituent β to a carbomethoxy group will give a signal at a lower field strength when oriented cis to the ester group. Signals for the hydrogens of the methyl group attached to the double bond, for G and E respectively, were at 7.70 τ and 8.22 τ ; methylene hydrogen signals were at 7.73 τ and 7.45 τ , thus confirming the cis and trans assignment in the literature. Components G and E are therefore identified as methyl trans-3-methyl-2-

Table 2

| Name of compound | Structure | n_D | b.p. | Other evidence utilised (see text) |
|--|-----------|-------------------|-----------------------|---|
| G - Methyl <u>trans</u> -3-methyl-2-pentenoate | | 1.4424 /25 (a) | 160.0° (a) | N.M.R., infrared synthetic and isomerisation studies |
| E - Methyl <u>cis</u> -3-methyl-2-pentenoate | | 1.4409 /23 (b) | 151.0° (b) | N.M.R., infrared synthetic and isomerisation studies |
| D - Methyl <u>trans</u> -3-methyl-3-pentenoate | | 1.4323 /21 (c) | 150.0° (c) | N.M.R., infrared analysis synthetic and isomerisation studies |
| C - Methyl <u>cis</u> -3-methyl-3-pentenoate | | 1.4321 /20 | 148.0° | N.M.R., infrared analysis synthetic and isomerisation studies |
| F - Methyl <u>cis</u> -1,2-dimethylcyclopropane- <u>trans</u> -3-carboxylate | | 1.4330 /18 (d) | 150.0° /759 (d) | N.M.R., infrared, analysis |
| A - Methyl <u>trans</u> -1,2-dimethyl cyclopropane-3-carboxylate | | 1.4241 /25 (e) | 143.0° (e) | N.M.R., infrared, analysis |
| B - Methyl 3-ethyl-3-butenolate | * | 1.4261 /23 | 146.0° | Infrared, synthetic and isomerisation studies |

* - tentative assignment

(c) - lit. (25) n_D^{20} 1.4306 b.p. 74°/50 mm.(a) - lit. (19) n_D^{20} 1.4446, b.p. 79°/50 mm.(d) - lit. (20) n_D^{20} 1.4306(b) - lit. (19) n_D^{20} 1.4420, b.p. 74°/50 mm.(e) - lit. (20) n_D^{20} 1.4252, b.p. 40-50°/20 mm.

11

INSET

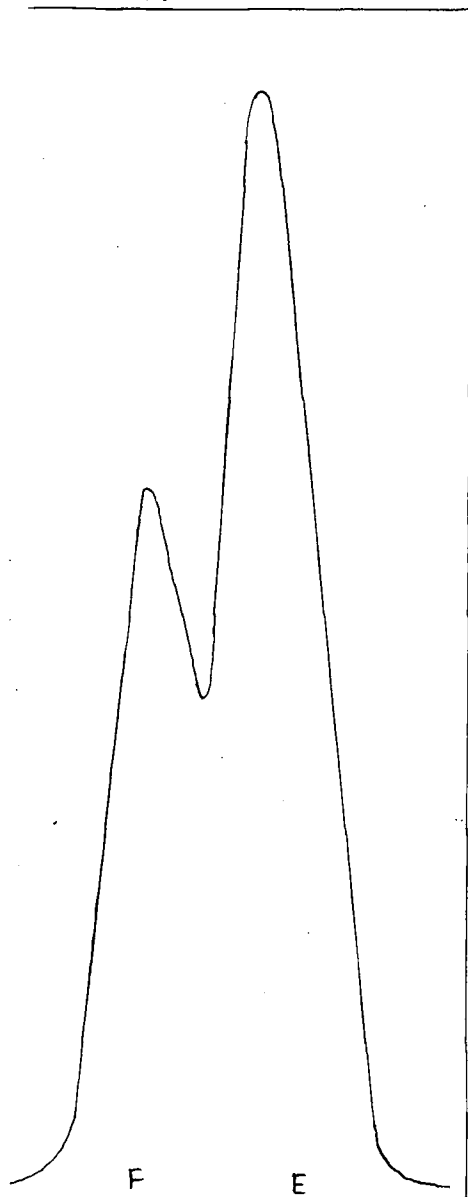
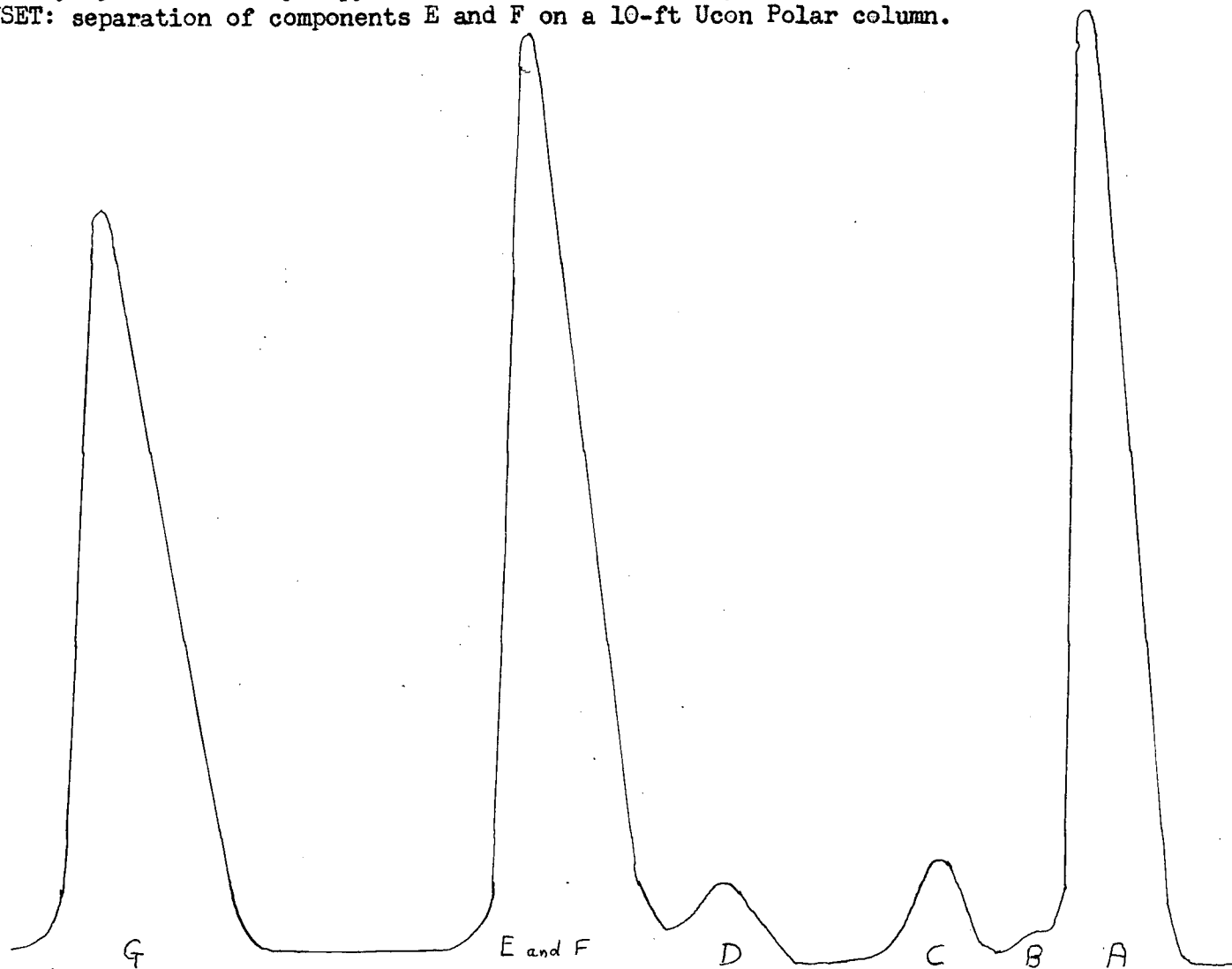


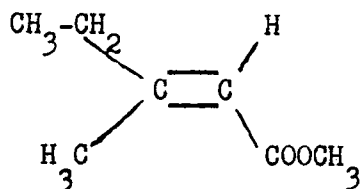
Figure II

Vapour phase chromatographic separation of the pyrolysis products from 4,5-dimethyl-3-carbomethoxy-2-pyrazoline on a 10-ft Dinonyl Phthalate column.

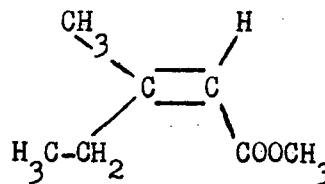
INSET: separation of components E and F on a 10-ft Ucon Polar column.



pentenoate (III) and methyl cis-3-methyl-2-pentenoate (IV), respectively.



III



IV

The analysis of component C provided the empirical formula of $C_7H_{12}O_2$, and its infrared spectrum indicated that it was a non-conjugated unsaturated ester. It was also formed with other methyl 3-methyl-pentenoates by the dehydration of methyl 3-hydroxy-3-methyl-pentanoate, but its physical properties did not correspond with any reported properties for structures that could be assigned from this information. The N.M.R. spectrum of a sample of C was consistent with its assignment as methyl 3-methyl-3-pentenoate, but no distinction could be made between the cis and trans isomers. This distinction was made by a method which is illustrated in Figure III. Tiglic acid having the geometry shown in Figure III was converted by the trans addition of bromine to racemic 2,3-dibromo-2-methyl-butyric acid (23). After conversion of the acid to the acid chloride an Arndt-Eistert Synthesis was performed to effect the introduction of a methylene group. The product was isolated as the methyl ester. The methyl 2,3-dibromo-3-methyl-pentanoate so obtained was debrominated with zinc in water. The elimination of bromine under these conditions has been shown to be trans-stereospecific (24), and, therefore, should lead to a product in which the methyl groups at either end of the double bond are oriented cis to each other. Vapour phase chromatography showed the product to be 97% C, with refractive index and

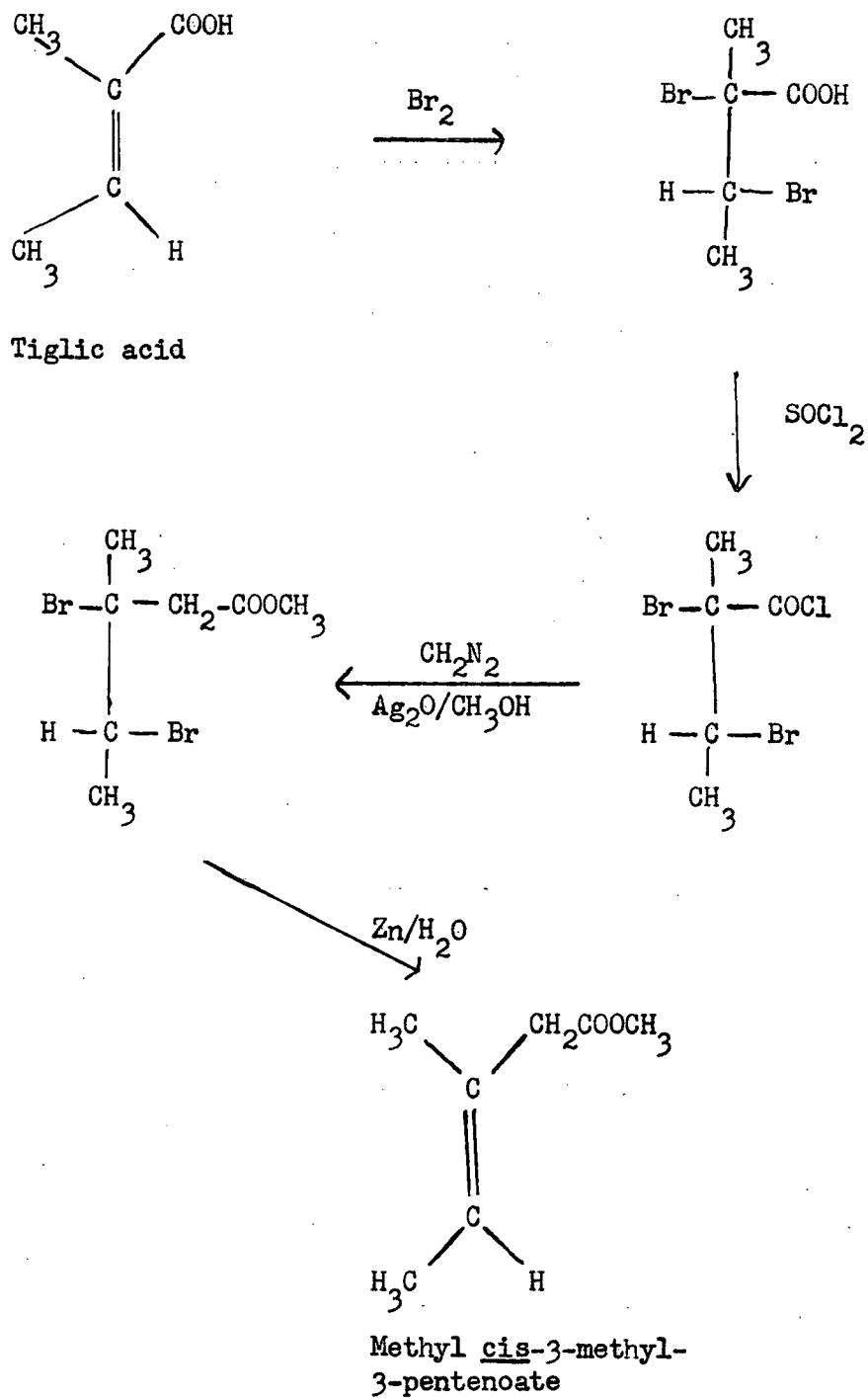
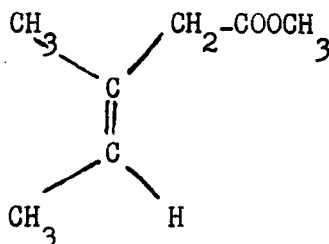


Figure III

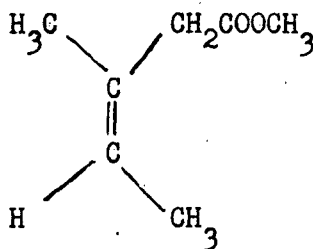
The absolute configuration of methyl cis-3-methyl-3-pentenoate

infrared spectrum equivalent to those of the product isolated from the pyrolysis mixture. The pyrolysis product, C, is, therefore, identified as methyl cis-3-methyl-3-pentenoate, (V).



V

The analysis of component D provided the empirical formula of $C_7H_{12}O_2$, and the infrared spectrum of a sample indicated that it was a non-conjugated unsaturated ester. The N.R.M. spectrum of a sample of D was consistent with its assignment as a methyl 3-methyl-3-pentenoate, and, on this evidence and on the identification of C as methyl cis-3-methyl-3-pentenoate, component D is identified as methyl trans-3-methyl-3-pentenoate, (VI).

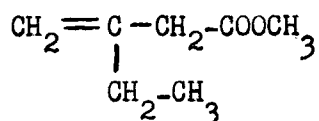


VI

Methyl trans-3-methyl-3-pentenoate has been reported previously (25) but the refractive index of a sample of D (n_D^{21} 1.4323) isolated from the pyrolysis mixture disagreed with the literature value (n_D^{20} 1.4306); the refractive index of a sample of VI isolated from the isomeric mixture

resulting from the dehydration of methyl 3-methyl-3-hydroxy-pentanoate was in agreement with the value determined for D. No reason can be found for the discrepancy between the literature value for the refractive index and that determined for D.

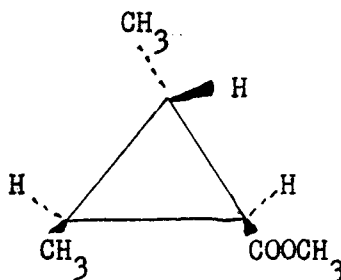
Component B was present in the mixture of pyrolysis products to a maximum extent of 0.8%, and, for this reason, could not be isolated from the mixture. One of the components in the isomeric mixture resulting from the dehydration of methyl 3-methyl-3-hydroxy-pentanoate had the same retention time as component B. The equivalence of the retention times of the two components is not necessarily a proof of the equivalence of the structures, since it is possible that different isomers may have the same retention time. The component isolated from the dehydration mixture had an infrared spectrum which showed a non-conjugated unsaturated ester and a 1,1-disubstituted olefin with bands at 1725, 1650, 1420 and 897 cm^{-1} (27). This component might, therefore, be methyl 3-ethyl-3-butenate, which is a likely product to arise by the removal of the elements of water from methyl 3-methyl-3-hydroxy-pentanoate, though unexpected as a product from the pyrolysis of 4,5-dimethyl-3-carbomethoxy-2-pyrazoline. The physical properties did not correspond with any of those reported for possible structures. On the basis of this evidence component B is tentatively identified as methyl 3-ethyl-3-butenate, (VII).



VII

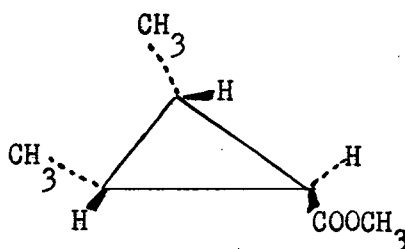
The analysis of component A provided the empirical formula

$C_7H_{12}O_2$, and its physical properties were in agreement with those reported for methyl trans-1,2-dimethylcyclopropane-3-carboxylate (20). The infrared spectrum of a sample of A showed absorption due to an ester carbonyl at 1715 cm^{-1} and the absence of absorption in the carbon-carbon double bond regions. Other bands appeared at 1365, 1302, 1165, 1095 and 1055 cm^{-1} which are in agreement with those reported for methyl trans-1,2-dimethylcyclopropane-3-carboxylate (20). The N.M.R. spectrum of a sample of A was consistent with the assignment of component A as methyl trans-1,2-dimethylcyclopropane-3-carboxylate, (VIII).



VIII

The analysis of component F provided the empirical formula $C_7H_{12}O_2$, and its physical properties corresponded with those reported for methyl cis-1,2-dimethylcyclopropane-trans-3-carboxylate (20). The infrared spectrum of a sample of F showed absorption due to the ester carbonyl at 1710 cm^{-1} and the absence of absorption in the carbon-carbon double bond frequency ranges. Bands at 1325, 1125, 1085 and 1040 were in agreement with those reported from the infrared spectrum of methyl cis-1,2-dimethyl cyclopropane-trans-3-carboxylate (20), and the N.M.R. spectrum of a sample of F sustained the identification of component F as methyl cis-1,2-dimethyl cyclopropane-trans-3-carboxylate, (IX).



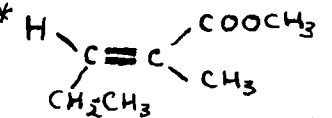
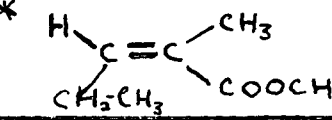
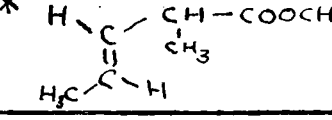


IX

B. 3,5-dimethyl-3-carbomethoxy-1-pyrazoline

Two of the five components isolated from the pyrolysis of this pyrazoline have received structural assignments, and the other three, none of which are reported in the literature, have been assigned tentative structures. A reproduction of the chromatogram obtained on vapour phase chromatographic analysis of the pyrolysis products is contained in Figure IV, and the results of the investigations of the components separated by vapour phase chromatography from the mixture of pyrolysis products are collected in Table 3.

The analysis of component K provided the empirical formula $C_7H_{12}O_2$, and its refractive index agreed with that reported for methyl cis-1,2-dimethylcyclopropane-1-carboxylate (26). The infrared spectrum of a sample of K showed absorption due to the ester carbonyl at 1703 cm^{-1} and the absence of absorption in the carbon-carbon double bond frequency ranges. Bands at 1453 , 1368 , 1308 and 1096 cm^{-1} corresponded with those reported from the infrared spectrum of methyl cis-1,2-dimethylcyclopropane-1-carboxylate (26). The N.M.R. spectrum of a sample of K was identical with the N.M.R. spectrum reported for methyl cis-1,2-dimethylcyclopropane-1-carboxylate (26), and component K is accordingly

Table 3

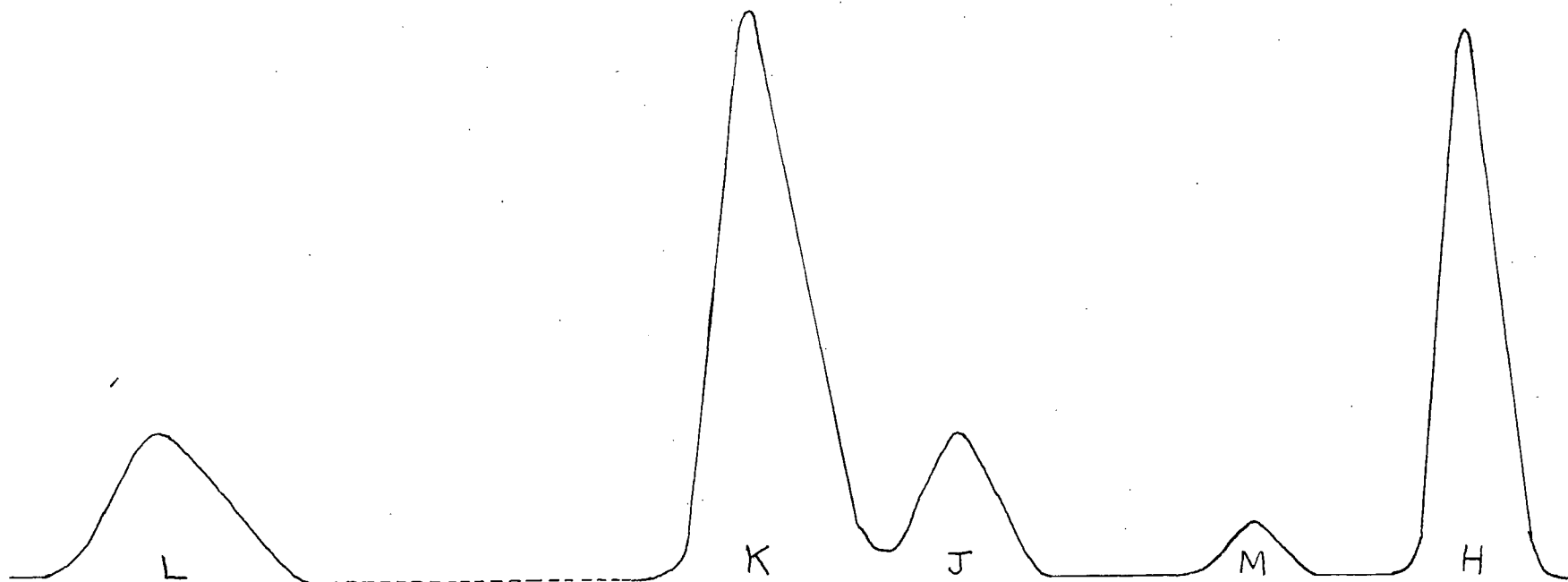
| Name of Compound | Structure | n_D | b.p. | Other evidence utilised (see text) |
|--|--|----------------------|--------|---|
| L - Methyl <u>trans</u> -2-methyl-2-pentenoate | *  | 1.4394 /24 | 156.0° | Analysis, N.M.R., infrared, equilibration studies |
| J - Methyl <u>cis</u> -2-methyl-2-pentenoate | *  | 1.4351 /24 | 143.0° | Analysis, infrared, equilibration studies |
| M - Methyl <u>trans</u> -2-methyl-3-pentenoate | *  | 1.4229 /23 | 139.0° | Analysis, infrared, equilibration studies |
| K - Methyl <u>cis</u> -1,2-dimethyl cyclopropane-1-carboxylate |  | 1.4314 /20 (a) | 145.0° | Analysis, N.M.R., infrared |
| H - Methyl <u>trans</u> -1,2-dimethyl cyclopropane-1-carboxylate |  | 1.4220 /27 (b) | 136.0° | Analysis, N.M.R., infrared |

* - tentative assignments

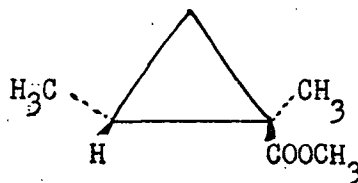
(a) - lit. (26) n_D^{25} 1.4289(b) - lit. (26) n_D^{25} 1.4218

Figure IV

Vapour phase chromatographic separation of the pyrolysis products from 3,5-dimethyl-3-carbomethoxy-1-pyrazoline on a 10-ft Dinonyl Phthalate column.

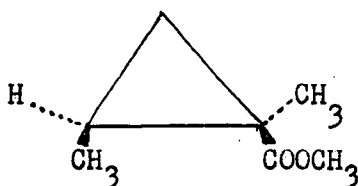


identified as methyl cis-1,2-dimethylcyclopropane-1-carboxylate, (X).



X

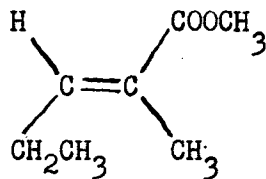
The analysis of component H provided the empirical formula $C_7H_{12}O_2$, and the refractive index of a sample was in agreement with that reported for methyl trans-1,2-dimethylcyclopropane-1-carboxylate (26). The infrared spectrum showed absorption due to the ester carbonyl at 1720 cm^{-1} and the absence of absorption in the carbon-carbon double bond frequency ranges. The N.M.R. spectrum of a sample of H was identical with the N.M.R. spectrum reported for methyl trans-1,2-dimethylcyclopropane-1-carboxylate (26), and component H is accordingly identified as methyl trans-1,2-dimethylcyclopropane-1-carboxylate, (XI).



XI

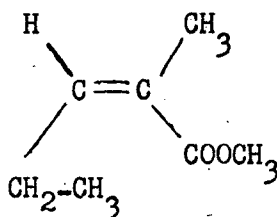
The analysis of component L provided the empirical formula $C_7H_{12}O_2$, and its infrared spectrum showed absorption bands at 1700, 1645 and 978 cm^{-1} , indicative of a trans conjugated unsaturated ester. The physical properties of component L did not correspond with any physical properties reported for possible structures. Equilibration studies showed that L occurred together with other methyl 2-methyl-pentenoates, and the

N.M.R. spectrum of a sample of L was consistent with its assignment as a methyl 2-methyl-2-pentenoate. These data allow of a tentative assignment of component L as methyl trans-2-methyl-2-pentenoate, (XII).



XII

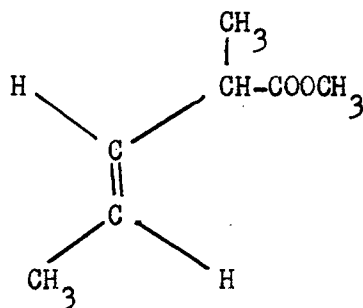
The analysis of component J provided the empirical formula $C_7H_{12}O_2$, and the infrared spectrum, with absorption bands at 1705 and 1641 cm^{-1} , indicated that J was a conjugated unsaturated ester. Equilibration studies on isomeric esters showed that J occurred together with other methyl 2-methyl-pentenoates. The sample of J isolated was insufficient for determining its N.M.R. spectrum and did not allow use of N.M.R. for the cis-trans assignments for L and J. J has a lower boiling point than methyl trans-2-methyl-2-pentenoate, XII, and this fact and the above data allow of a tentative assignment of component J as methyl cis-2-methyl-2-pentenoate, (XIII).



XIII

The analysis of component M provided the empirical formula $C_7H_{12}O_2$. The infrared spectrum of a sample of M showed absorption bands at 1725 and 967 cm^{-1} characteristic of a non-conjugated unsaturated

ester carbonyl group and a trans olefin; no bands, however, were found in the 1600-1700 cm^{-1} region. Equilibration studies on isomeric esters showed that component M occurred together with other methyl 2-methyl-pentenoates. These data indicate that component M is methyl trans-2-methyl-3-pentenoate, and the absence of an absorption band in the 1600-1700 cm^{-1} region of the infrared spectrum sustains this assignment, since the symmetry of the trans configuration of this ester would lower the intensity of absorption in the carbon-carbon double bond absorption region (27). Accordingly, component M is tentatively identified as methyl trans-2-methyl-2-pentenoate, (XIV).



XIV

C. Equilibration studies

Equilibrium values were determined by heating samples of isomeric unsaturated esters at 250° for two weeks. Equilibrium was reached by starting with two isomeric olefins isolated, in each case, from the pyrolysis of 4,5-dimethyl-3-carbomethoxy-2-pyrazoline and 3,5-dimethyl-3-carbomethoxy-1-pyrazoline. The equilibrium mixtures obtained were analysed by vapour-phase chromatography and the results of the analyses are collected in Table IV. From each of the pair of

Table 4

Equilibrium composition in % after equilibration at 250°

| Initial unsaturated ester | <u>α,β -Unsaturated ester</u> | | <u>β,γ -Unsaturated ester</u> | | Other |
|--|---|-------|---|-------|---------------------------------|
| | cis | trans | cis | trans | |
| Methyl <u>trans</u> -3-methyl-2-pentenoate | 14 | 48 | 13 | 18 | methyl 3-ethyl-3-butenolate 7 a |
| Methyl <u>trans</u> -3-methyl-3-pentenoate | 12 | 46 | 13 | 20 | methyl 3-ethyl-3-butenolate 9 a |
| Methyl <u>trans</u> -2-methyl-2-pentenoate | 12 | 47 | b | 15 | b |
| Methyl <u>trans</u> -2-methyl-3-pentenoate | 10 | 44 | b | 17 | b |

a - A new peak appeared in the chromatogram having one quarter the area of the methyl 3-ethyl-3-butenolate. It has not been identified, but may be due to methyl 3-methyl-4-pentenoate.

b - Two new peaks appeared in the chromatogram with compositions 16%, 18% and 10%, 11%. These have not been identified, but may be due to methyl cis-2-methyl-3-pentenoate and methyl 1-n-propyl acrylate.

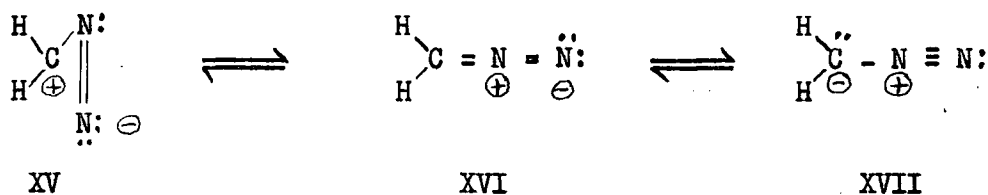
samples all of the unsaturated ester isomers isolated from the respective pyrolysis mixture occurred. This fact was taken as additional proof of the correctness of the assignments made, because isomerisations are only likely to occur within the basic structure of each group of esters: shifts of hydrogen are likely but shifts of methyl or other groups are extremely improbable under the conditions obtaining in the equilibrations studied.

Comparison of the equilibration results in Table IV with the pyrolysis results in Table I readily leads to the conclusion that the composition of the olefin portion of the pyrolysis product in general is not an equilibrium mixture. In general the equilibrium mixture is richer in the trans-unsaturated esters than is the pyrolysis mixture; the cis to trans ratio of the olefin portion of the pyrolysis product often approaching 1. This will be discussed in Section III.

Section III

DISCUSSION

Eistert (6) and Young and his co-workers (7) have suggested that the reactions of the carbon-carbon double bond with diazoalkanes are similar to reactions of the carbonyl group with diazoalkanes and that the mechanisms of the additions may be strictly compared. The pyrazoline synthesis proceeds by the addition of the lone electron pair of the α -carbon atom of the diazoalkane due to contributions of the formula XVII, of the three possible resonance hybrids (28):



to the double bond at the carbon β to the carbalkoxy or other activating group to yield a diazonium betaine (XVIII). This addition is illustrated in Figure V. An intermediate unstable addition product with the properties expected of a resonance-stabilised diazonium betaine such as XVIII has been isolated from the reaction of diazomethane and benzoquinone (29); on standing a pyrazoline is formed. The intermediate diazonium betaine can then undergo ring closure to a pyrazoline (XIX). The thermal decomposition of the pyrazoline, XIX, is believed to involve ring opening of the pyrazoline to give the diazonium betaine, XVIII, which then loses nitrogen to give either cyclopropane or olefin products (6, 7). It will be the purpose of this Section to discuss the merits of this suggestion

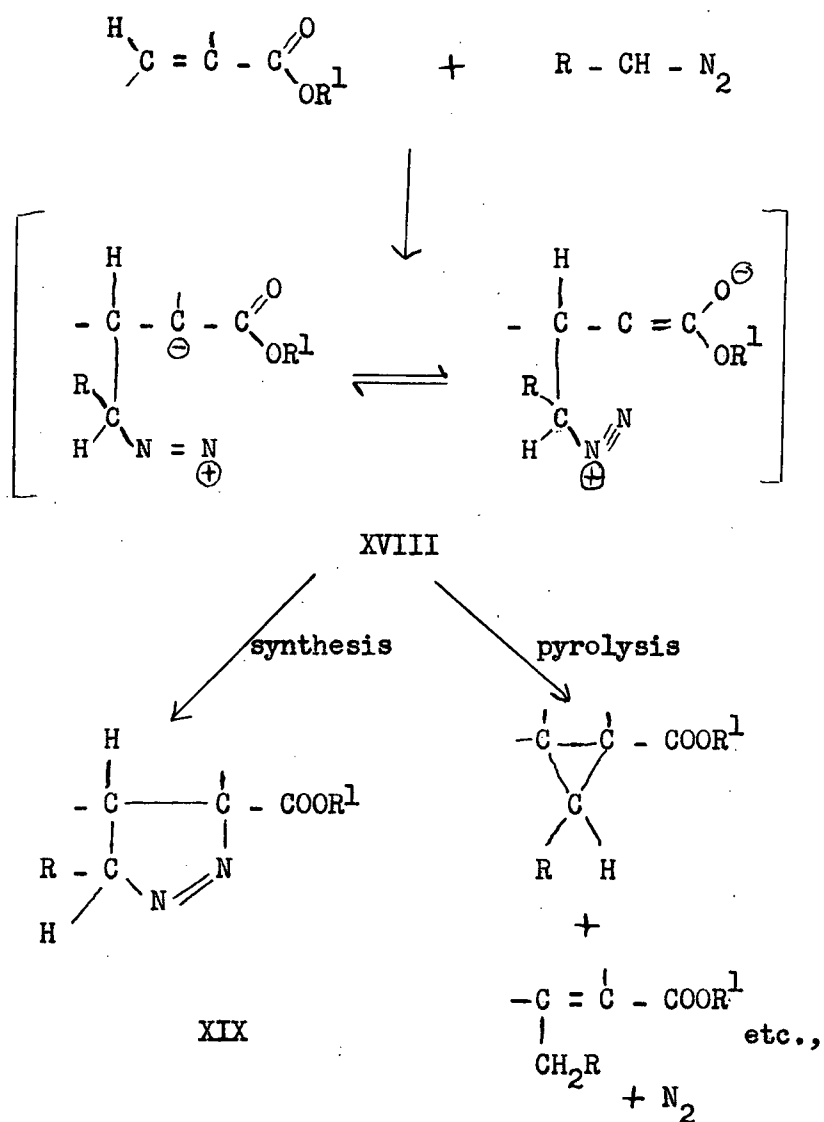


Figure V

Illustration of a possible mechanism for pyrazoline synthesis and pyrolysis

with particular reference to the synthesis and pyrolysis of 4,5-dimethyl-3-carbomethoxy-2-pyrazoline and 3,5-dimethyl-3-carbomethoxy-1-pyrazoline, and to suggest some extensions and alternatives to this mechanism.

Pyrazoline pyrolyses catalysed by light have been observed by a number of authors (16, 26, 34). This might suggest that a free radical mechanism, with homolytic cleavage of the carbon-nitrogen bond, is possible for pyrazoline decompositions, since most photochemical reactions are not very polar and often involve free radical intermediates. A non-polar mechanism for the thermal decompositions of pyrazolines is effectively ruled out on the basis of the evidence available. A large number of products of unpredictable composition would be expected from a free radical mechanism (35) and this has not been observed. Product composition from pyrazoline pyrolyses is strongly dependent on the nature, position and degree of substitution in the pyrazoline (5, 9, 18, 36): such observations are generally indicative of a non-radical mechanism. Since it is not possible to extrapolate data from the photochemical decompositions to thermal decompositions, the observations cited suggest that the initial cleavage of the carbon-nitrogen bond is heterolytic rather than homolytic for thermal decompositions of pyrazolines.

Several investigators have suggested that 1-pyrazolines should lose nitrogen more readily than 2-pyrazolines and have obtained strong evidence to support this suggestion (2, 5, 15-18). The pyrolyses of 3,5-dimethyl-3-carbomethoxy-1-pyrazoline (II) and 4,5-dimethyl-3-carbomethoxy-2-pyrazoline (I) provide further evidence to sustain this

postulate. The 1-pyrazoline (II) is readily pyrolysed in the liquid-phase at a much lower temperature than is the 2-pyrazoline. The vapour-phase pyrolysis of the 2-pyrazoline (I) has been shown to require a catalyst which is believed to promote tautomerisation of the 2-pyrazoline to the more readily pyrolysable 1-pyrazoline structure.

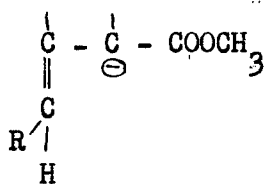
The mechanism proposed by Eistert (6) and Young and his co-workers (7) suggests that pyrazoline synthesis and decomposition proceeds through a common intermediate. Although there is no proof of this point it is suggestive that diazomethane has been observed to react with olefins under conditions for which a pyrazoline would be stable with loss of nitrogen during the reaction and direct formation of cyclopropanes and substituted olefins (7, 31, 32). Direct formation of cyclopropanes and substituted olefins has been observed even when the double bond of the reacting olefin was not activated by an electro-negative group (33), but generally there is no reaction (7, 32) between diazoalkanes and non-activated olefins. The observation that cyclopropane and olefin products are formed directly during the reaction of a diazoalkane and an olefin, without formation of an isolable pyrazoline, is strong evidence for the existence of a common intermediate for pyrazoline synthesis and pyrolysis.

The first steps in the pyrolysis of a pyrazoline may, therefore, be: tautomerisation, if necessary, of the Δ^2 -structure to the Δ^1 -structure, followed by rupture of the nitrogen-carbon bond between positions 2 and 3 of the pyrazoline and the formation of a diazonium betaine (XVIII). No evidence is available to clarify whether the diazonium betaine (XVIII) is an intermediate or an activated complex;

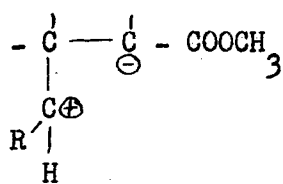
its exact nature may be dependent on the structure of the pyrazoline and the reaction conditions.

The loss of nitrogen from the diazonium betaine (XVIII) may take place in a concerted or step-wise manner, and present evidence indicates that the reactions determine which mechanism will prevail. Thermal decompositions of pyrazolines almost invariably lead to products with a cis to trans ratio approaching 1, as shown in Table 1 and reference 18. A cis to trans ratio of about 1 would be expected if both isomers were formed from the same high-energy intermediate for which the transition state to each olefin would be approximated by the intermediate rather than the product (37).

There are two possible step-wise mechanisms: bimolecular elimination of nitrogen to give the ion XX, or unimolecular elimination of nitrogen to give the zwitterion XXI.



XX



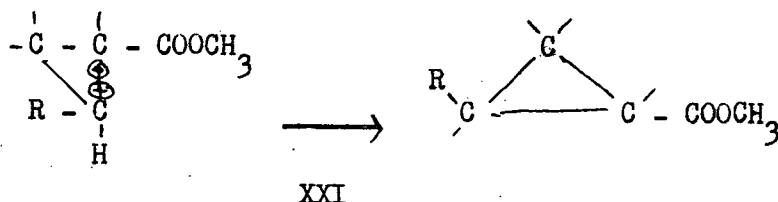
XXI

The percentage of β,γ -unsaturated ester formed in those pyrolyses studied seems remarkably constant and does not seem to be dependent on the relative stability of α,β and β,γ -unsaturated products, as may be seen from a comparison of the results compiled in Tables 1 and 4. Similar results have been reported in the literature (18). This fact may indicate that the β,γ -unsaturated product is formed from the same intermediate as the other products (18b). If the ion XX were a

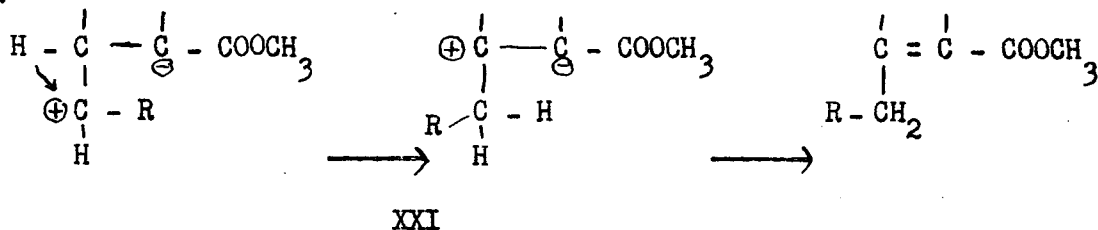
possible intermediate a wide variation in the percentage of β,γ -unsaturated product in the pyrolysis mixtures would be expected, since substituents in the original pyrazoline would have a strong influence on the formation of the ion XX. The presence of alkyl substituents at position 4 of the original pyrazoline would disfavour bimolecular elimination of nitrogen to give the ion XX. This may be compared to the Hofmann-type elimination in that alkyl substitution at the carbon β to the leaving group will reduce the acidity of the remaining β -hydrogens and retard bimolecular elimination (38). The percentage of β,γ -unsaturated esters in the pyrolysis products does not vary greatly when the reaction conditions are changed from the liquid phase to high dilution in the vapour phase. Reaction in the vapour-phase would be expected to reduce the effectiveness of a bimolecular mechanism, resulting in a relatively smaller percentage of β,γ -unsaturated esters in the pyrolysis products. The fact that this has not been observed, and the other observations already discussed provide strong evidence against the bimolecular eliminations of nitrogen from the diazonium betaine XVIII to give the ion XX.

Pyrolysis product composition and substituent effects indicate that the zwitterion XXI may play a significant role in the thermal decomposition of pyrazolines. The zwitterion, XXI would be a high energy transition state as required by the observed cis to trans ratio of the olefin product from the pyrolyses and it approximates the transition state for each isomer (39). Further, all the pyrolyses products observed could arise from the zwitterion XXI.

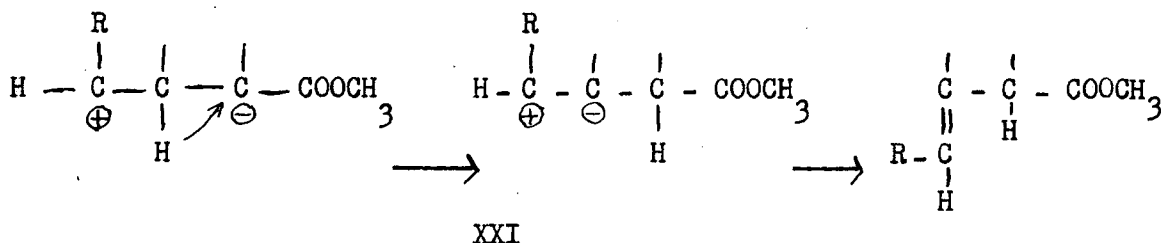
Ring closure of XXI would lead to cyclopropane product:



Anionic migration of hydrogen would lead to α,β -unsaturated esters:



Cationic migration of hydrogen would lead to β,γ -unsaturated esters:



Cationic migration of hydrogen would be extremely unfavourable unless electronegative groups were present at position 4 of the original pyrazoline to stabilise the negative charge (40). Where no such negative charge-stabilising groups are present the percentage of β,γ -unsaturated esters in the pyrolysis products would be expected to be relatively small, as has been observed with hydrogen, methyl or phenyl substitution at position 4 of the original pyrazoline (5, 7, 15, 18). None of these substituents would provide the necessary electronic influence to favour cationic migration.

All these possible products arising from the zwitterion XXI have been observed in the pyrolyseses of 4,5-dimethyl-3-carbomethoxy-2-

pyrazoline and 3,5-dimethyl-3-carbomethoxy-1-pyrazoline.

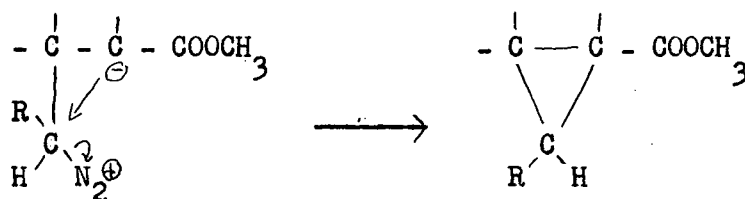
The influence of substituents in the original pyrazoline provides further evidence in support of the postulate that the zwitterion XXI is significant as an intermediate in the thermal decomposition of pyrazolines. The stability of the zwitterion XXI would be increased by alkyl substitution at the 5-position of the original pyrazoline because of the ability of alkyl groups to distribute positive charge by hyperconjugation and to stabilise the positive charge by the inductive effect (40). This enhanced stability of the carbonium ion would favour the formation of more olefin product and a more complex mixture of products (41). This has been observed for 4,5-dimethyl-3-carbomethoxy-2-pyrazoline (I) and for 5-methyl-3-carbomethoxy-2-pyrazoline (18).

The stabilising effect of an alkyl substituent at position 4 of the original pyrazoline on the carbonium ion produced by anionic migration of hydrogen in XXI, should mean that this anionic migration of hydrogen would be more favourable than ring closure of the zwitterion XXI. Pyrazolines substituted with an alkyl group in the 4-position would therefore be expected to give a yield of olefin product relatively higher than that from the pyrolysis of pyrazolines unsubstituted by an alkyl group at the 4-position. This has been observed for the pyrolysis of 4-methyl-3-carbomethoxy-2-pyrazoline, which yields only 4% of cyclopropane product compared to 29% of cyclopropane product from the pyrolysis of 5-methyl-3-carbomethoxy-2-pyrazoline (18).

The effect of an alkyl substituent at position 3 of the original pyrazoline would be to de-stabilise the negative charge of the

zwitterion XXI (40). The results indicate that the pyrolyseses of a 3-alkyl substituted pyrazolines yield a relatively higher proportion of cyclopropane product (5, 7, 18). The electro-positive alkyl group might increase the nucleophilicity of the negatively charged carbon of the zwitterion XXI, and might in consequence tend to increase the likelihood of ring-closure of XXI to give cyclopropane products.

Studies on the vapour-phase pyrolysis of alkyl-substituted pyrazolines (Table 1 and reference 18) have shown that there is an increase in the relative proportion of cyclopropane product under these conditions. It is difficult to reconcile this increase in cyclopropane product with the change in conditions if a step-wise mechanism for the pyrolyses were applicable, since there is no reason why reaction in the vapour-phase should increase the likelihood of ring closure over hydrogen migration for the zwitterion XXI. A concerted mechanism may be considered. An internal nucleophilic displacement of nitrogen from the diazonium betaine (XVIII) would lead directly to cyclopropane product:



XVIII

The effect of an alkyl substituent at the 3-position of the original pyrazoline might, as in the stepwise mechanism, increase the nucleophilicity of the negatively charged carbon. In the concerted mechanism, however, this effect might be greater since the stability of the betaine XVIII might be of less importance, particularly if it is a

transition state rather than an intermediate. Under the reaction conditions of vapour-phase pyrolysis it is unlikely that the betaine XVIII could be more than a very short-lived intermediate.

Protonation of the negatively-charged carbon of the betaine XVIII would be more favourable in the liquid-phase than in the vapour phase. This might offer an alternative explanation for the increase in cyclopropane product in the vapour phase.

A concerted elimination of nitrogen would be expected to lead to products with complete retention of configuration at carbons 4 and 5 of the original pyrazoline, and also at carbon 3 if the betaine XVIII had only transitory existence. This has never been observed in thermal decompositions of pyrazolines but has been observed in light catalysed decompositions (26). In this case the reaction was shown to proceed stereospecifically and to produce only cyclopropane product. It is possible that light catalysed decompositions under the conditions reported may proceed through a completely concerted mechanism, but conclusive evidence on this point is not available.

A probable overall mechanism may therefore be a combination of the concerted and step-wise mechanisms, with the step-wise mechanism prevailing under the conditions of liquid-phase pyrolyses and the concerted mechanism prevailing in the vapour-phase.

EXPERIMENTAL

Melting points and boiling points are uncorrected. Most boiling points were determined by the micro inverted capillary method. Infrared spectra were measured with a Perkin-Elmer Model 21 spectrometer using sodium chloride optics. N.M.R. spectra were recorded on a 40 Mc/s Varian spectrophotometer with field stabiliser VK 3506 and the methylene chloride and hexamethyl disiloxane used as external standards were observed to have respective values of 4.60 τ and 10.30 τ . The vapour chromatograph unit was an Aerograph model A-100-C.

N-Nitroso N-Ethyl Urea (42)

A solution of ethylamine hydrochloride (122.5g, 1.5 mole) and urea (300g, excess) in 500mls of water was refluxed gently for three hours and then vigorously for 15 minutes. After cooling the ethyl urea solution was divided into 0.25 mole portions and sodium nitrite (24g, excess) was dissolved. Each batch was cooled to -10° in an ice/salt bath and a mixture of concentrated sulphuric acid (24.5g, 0.25 mole) and 100g of ice was added with vigorous stirring at a rate sufficient to maintain the temperature of the reaction below 5° .

The nitrosoethyl urea, which separated as pale yellow crystals, was collected on a filter, washed with cold water to remove acid, and dried: m.p. $103-104^{\circ}$ with decomposition (lit. (43) m.p. 103°)
Yield (based on ethylamine hydrochloride) 35-65%.

Diazoethane (44)

To a well-stirred mixture of 250mls. of ether and 50mls. of 40% aqueous potassium hydroxide solution which was cooled to 0° in an Erlenmeyer flask, finely powdered N-nitroso N-ethyl urea (23.4g, 0.2 mole) was added as rapidly as the crystals would dissolve.

When the addition was completed, the deeply coloured orange ethereal layer was separated from the aqueous layer, washed once with water, and dried over pellets of potassium hydroxide. Yield: (estimated from the reaction with methyl crotonate) 65%.

4,5-Dimethyl-3-carbomethoxy-2-pyrazoline

A 1:1 solution by volume of methyl crotonate in ether was added slowly to an anhydrous diazoethane solution in ether until the orange colour of the diazoethane disappeared. The reaction was rapidly completed at room temperature, but the rate of addition of the methyl crotonate was controlled because of the evolution of heat by the reaction.

After removal of the ether by distillation, the residue was distilled in an atmosphere of nitrogen under reduced pressure, b.p. 101-102°/1.8 mm (lit. (2) b.p. 139-140°/14 mm.) Yield (based on methyl crotonate) 52%. The infrared spectrum (5% in chloroform) had bands at 3400, 1710 and 1557 cm^{-1} assigned to the N-H, C=O and C=N functions respectively. (45)

The viscous oil which was the primary distillation product crystallised very slowly to give colourless needle shaped crystals, m.p. 46-47°C. The pyrazoline autoxidises very rapidly in the presence of air and light to yield dark orange crystals, and finally colourless needles m.p. 134-136°C. The nature of the oxidation products has not been ascertained.

3,5-Dimethyl-3-carbomethoxy-1-pyrazoline

A 1:1 solution by volume of methyl methacrylate in ether was added slowly to a dry diazoethane solution in ether until the orange colour of the diazoethane disappeared. The pyrazoline formed almost immediately at room temperature.

After removal of the ether by distillation, the residue was distilled under reduced pressure, to yield a colourless liquid, b.p. 59°C/0.65 mm (lit. (5) b.p. 86-88°/2 mm). Yield (based on methyl methacrylate) 65%. The infrared spectrum (5% in chloroform) showed no absorption due to N-H or C=N; the ester carbonyl appeared at 1735 cm⁻¹.

Pyrolysis of 4,5-Dimethyl-3-carbomethoxy-2-pyrazoline

4,5-Dimethyl-3-carbomethoxy-2-pyrazoline (17g, 0.12 mole) was heated in a distillation apparatus in an oil bath. At a bath temperature of 170° pyrolysis was indicated by the evolution of gas and at 190° it became vigorous. Distillation yielded 12.0g (79%) of a colourless product boiling up to 165°. Six components were isolated by

vapour chromatography and were identified as indicated below, where boiling point, retention time in the vapour chromatogram using a 10-ft Dinonyl Phthalate column of 0.25-in. diameter with a helium flow rate of 67 cc/minute, and percentage of the total product determined by the weights of the paper cuts of the peaks are given. In all chromatographic analyses it is assumed that the thermal conductivities of the components are close enough to each other compared to helium to be assumed equal.

Methyl trans-3-methyl-2-pentenoate b.p. 160.0° , n_D^{25} 1.4424 (lit. (19) b.p. $79^{\circ}/50\text{mm}$, n_D^{20} 1.4446), 44.8 minutes, 25.5%. The infrared spectrum (5% in chloroform) showed bands at 1702 and 1647 cm^{-1} characteristic of an α, β -unsaturated ester (46). The N.M.R. spectrum (0.5 ml per ml of carbon tetrachloride) showed vinyl hydrogen signals at 4.55τ (singlet), ester methyl hydrogens at 6.36τ (singlet), methylene hydrogens at 7.73τ (quartet, $J = 7.0\text{cps}$) and alkyl methyl hydrogens at 7.70τ (singlet) and 8.66τ (triplet $J = 7.0\text{cps}$). These data are consistent with the trans α, β -unsaturated structure assigned to this compound (47).

Methyl cis-3-methyl-2-pentenoate: b.p. 151° , n_D^{23} 1.4409 (lit. (19) b.p. $74^{\circ}/50\text{mm}$, n_D^{20} 1.4420), 36.8 minutes, 26%. The infrared spectrum (5% in chloroform) showed bands at 1702 and 1645 cm^{-1} characteristic of an α, β -unsaturated ester (46). The N.M.R. spectrum (0.30 ml per ml of carbon tetrachloride) showed a vinyl hydrogen signal at 4.51τ (singlet), and peaks for the ester methyl hydrogens at 6.46τ (singlet), methylene hydrogens at 7.45τ (quartet $J = 6.9\text{cps}$), and alkyl methyl hydrogens at 8.22τ (singlet) and 8.19τ (triplet $J = 7.0\text{cps}$). These data are consistent with the cis α, β -unsaturated structure assigned to this compound (47).

Methyl trans-3-methyl-3-pentenoate: b.p. 150° , n_D^{21} 1.4323 (lit. (25) b.p. $74^{\circ}/50$ mm, n_D^{20} 1.4306) 33.6 minutes, 3%. Calculated for $C_7H_{12}O_2$: C, 65.49; H, 9.45. Found: C, 65.43; H, 9.51. No reason can be found for the discrepancy in the refractive index. A sample isolated from the synthesis mixture (see below) had n_D^{25} 1.4302. The infrared spectrum (5% in chloroform) showed bands at 1725 and (weak) 1665 cm^{-1} indicative of a non-conjugated ester and a carbon-carbon double bond (46). The N.M.R. spectrum (0.50 ml per ml of carbon tetrachloride) showed vinyl hydrogen signals at 4.67 τ (quartet $J = 7.0$ cps). Other peaks were due to the ester methyl hydrogens, 6.41 τ (singlet), the methylene hydrogens, 7.14 τ (singlet) and the methyl hydrogens, 8.33 τ (unequal doublet, $J = 7.2$ cps) (47). These data are consistent with the β, γ -unsaturated structure assigned to this ester, and the structure was confirmed by synthesis.

Methyl cis-3-methyl-3-pentenoate: b.p. $148^{\circ}C$, n_D^{20} 1.4321, 29.6 minutes, 2%. Calculated for $C_7H_{12}O_2$: C, 65.49; H, 9.45 Found: C, 65.65; H, 9.41. The infrared spectrum (10% in chloroform) showed absorption at 1725 and (weak) 1665 cm^{-1} indicative of a non-conjugated ester and a carbon-carbon double bond (46). The N.M.R. spectrum (0.33 ml per ml of carbon tetrachloride) showed vinyl hydrogen signals at 4.75 τ (quartet $J = 7.0$ cps), ester methyl hydrogens at 6.59 τ (singlet), methylene hydrogens at 7.18 τ (singlet) and methyl hydrogens at 8.52 τ (unequal doublet $J = 7.2$ cps). These data are consistent with the β, γ -unsaturated structure assigned to this compound (47), and the configuration was confirmed by synthesis (see below).

Methyl trans-1,2-dimethylcyclopropane-3-carboxylate: b.p. 143° , n_D^{25} 1.4241, (lit. (20) b.p. $40-50^{\circ}/20$ mm, n_D^{20} 1.4252), 26.0 minutes, 26.5%. Calculated

for $C_7H_{12}O_2$: C, 65.49%; H, 9.45%. Found: C, 65.40%; H, 9.35%. The infrared spectrum (10% in chloroform) showed absorption due to the ester carbonyl group at 1715 cm^{-1} and the absence of absorption in the 1600 to 1700 cm^{-1} region. Medium to strong bands also appeared at 1365, 1302, 1165, 1095 and 1055 cm^{-1} which were in agreement with the structure assigned to this compound (20). The N.M.R. spectrum (0.50 ml per ml of carbon tetrachloride) showed signals assigned to the ester methyl hydrogens at 6.49 τ (singlet) and the alkyl methyl hydrogens at 9.05 τ (singlet) (47).

Methyl cis-1,2-dimethylcyclopropane-3-trans-carboxylate: b.p. $150^\circ/759\text{mm}$, n_D^{18} 1.4330, (lit. (20) n_D^{20} 1.4306), 36.8 minutes, 16%. Calculated for $C_7H_{12}O_2$: C, 65.49%; H, 9.45%. Found: C, 65.65%; H, 9.41%. The infrared spectrum (10% in chloroform) showed absorption due to the ester carbonyl group at 1710 cm^{-1} and the absence of absorption in the 1600 to 1700 cm^{-1} region. Medium to strong bands also appeared at 1325, 1125, 1085 and 1040 cm^{-1} which were in agreement with the structure assigned to this compound (20). The N.M.R. spectrum (0.20 ml per ml of carbon tetrachloride) showed two peaks which were assigned to the ester methyl hydrogens at 6.42 τ (singlet) and the alkyl methyl hydrogens at 8.85 τ (singlet) (47).

Two other peaks were observed during vapour chromatographic analysis with retention times 22.8 minutes (0.3% of total product) and 28.2 minutes (0.8% of total product). The latter was also observed during the analysis of the mixture arising from the synthesis of the methyl 3-methyl-pentenoates, and was identified by a comparison of retention times as methyl 3-ethyl-3-butenate (see below). The former could not be isolated.

Vapour-Phase Pyrolysis of 4,5-Dimethyl-3-carbomethoxy-2-pyrazoline

The lower portion of a 50 cm x 25 mm glass tube was placed in a vertical position in a tube furnace 25 cm in length and heated to 250°. The tube was filled to 35 cm from its lower end with freshly ground 20-mesh fire-brick. The portion of the tube above the furnace was heated to 100° with a heating coil. The tube was fitted at the top with a pressure-equalised dropping funnel and at the bottom with two traps in series connected to a vacuum system. The traps were cooled with acetone-Dry Ice mixtures.

Five grams of a sample of the pyrazoline, b.p. 117°/2 mm, was added dropwise to the pyrolysis tube held at a pressure of 2 to 4 mm. Under these conditions 10% of the pyrazoline was not pyrolysed and was frozen out of the product. The pyrolysis product was analysed by vapour chromatography as in the analysis of the liquid-phase pyrolysis product and was found to contain: 15.5% of methyl trans-3-methyl-2-pentenoate, 14% of methyl cis-3-methyl-2-pentenoate, 1.5% of methyl trans-3-methyl-3-pentenoate, 2% of methyl cis-3-methyl-3-pentenoate, 43% of methyl trans-1,2-dimethylcyclopropane-3-carboxylate and 24% of methyl cis-1,2-dimethylcyclopropane-3-trans-carboxylate.

Isomerisation Studies on Methyl trans-3-Methyl-2-Pentenoate and Methyl trans-3-Methyl-3-Pentenoate

An ampoule containing 100 mg of Methyl trans-3-methyl-2-pentenoate and one containing 60 mg of methyl trans-3-methyl-3-pentenoate isolated from the pyrolysis mixture were heated in a furnace at 250°

for two weeks. The samples were analysed by vapour chromatography in the same manner as the product from the pyrolysis of 4,5-dimethyl-3-carbomethoxypyrazoline and was found to contain from methyl trans-3-methyl-2-pentenoate and methyl trans-3-methyl-3-pentenoate, respectively; methyl 3-ethyl-3-butenate 7%, 9%; methyl cis-3-methyl-3-pentenoate 13%, 13%; methyl trans-3-methyl-3-pentenoate 18%, 20%; methyl cis-3-methyl-2-pentenoate 14%, 12%; methyl trans-3-methyl-2-pentenoate 48%, 46%. A peak having the same retention time (22.8 minutes) as the unidentified peak observed in the vapour chromatographic analysis of the pyrolysis mixture was also observed, having a maximum area of 0.25 that of the methyl 3-ethyl-3-butenate. This may possible be due to the isomer methyl 3-methyl-4-pentenoate.

Pyrolysis of 3,5-Dimethyl-3-Carbomethoxy-1-Pyrazoline

3,5-Dimethyl-3-carbomethoxy- Δ^1 -pyrazoline (11g, 0.07 mole) was heated in a distillation apparatus in an oil bath. At a bath temperature of 90° pyrolysis was indicated by the evolution of gas and at 110° it became vigorous. Distillation yielded 8.0g (83%) of a colourless product boiling up to 150°. Five components were isolated by vapour chromatography and were identified as indicated below, where boiling point, retention time in the vapour chromatogram using a 10-ft Dinonyl Phthalate column of 0.25-in. diameter with a helium flow rate of 67 cc/minute, and percentage of the total product are given.

Methyl trans-2-methyl-2-pentenoate: b.p. 156°, n_D^{24} 1.4394, 58.0 minutes, 15%. Calculated for $C_7H_{12}O_2$: C, 65.49%; H, 9.45% Found: C, 65.27%;

H, 9.45%. The infrared spectrum (10% in chloroform) showed bands at 1700, 1645 and 978 cm^{-1} characteristic of a α, β -unsaturated ester (46). The N.M.R. spectrum (0.50 ml per ml of carbon tetrachloride) had a triplet in the olefin hydrogen region at 3.48τ ($J = 7.5\text{cps}$). Other peaks were due to the ester methyl hydrogens, 6.41τ (singlet), the methylene hydrogens, 7.94τ (multiplet), and the methyl hydrogens at 8.26τ (singlet) and 9.04τ (triplet $J = 7.3\text{cps}$). These data are consistent with the trans- α, β -unsaturated structure assigned to this compound (47).

Methyl cis-2-methyl-2-pentenoate: b.p. 143° , n_D^{24} 1.4351, 36.0 minutes, 10%. Calculated for $C_7H_{12}O_2$: C, 65.49%; H, 9.45%. Found: C, 65.23%; H, 9.46%. The infrared spectrum (10% in chloroform) showed bands at 1705 and 1641 cm^{-1} indicative of a conjugated unsaturated ester (46). There was no absorption in the region of 970 to 960 cm^{-1} in agreement with the cis structure assigned to this compound (46).

Methyl trans-2-methyl-3-pentenoate: b.p. 139° , n_D^{23} 1.4229, 31.6 minutes, 3%. Calculated for $C_7H_{12}O_2$: C, 65.49%; H, 9.45%. Found: C, 65.60%; H, 9.39%. The infrared spectrum (10% in chloroform) showed bands at 1725 and 967 cm^{-1} characteristic of a non-conjugated ester carbonyl group and a trans olefin (46), but no bands were found in the 1600 to 1700 cm^{-1} region possibly due to the symmetry of the double bond (27).

Methyl cis-1,2-dimethyl-cyclopropane-1-carboxylate: b.p. 145° , n_D^{20} 1.4314 (lit. (26) n_D^{25} 1.4289), 39.6 minutes, 45%. Calculated for $C_7H_{12}O_2$: C, 65.49%; H, 9.45%. Found: C, 65.60%; H, 9.51%. The infrared spectrum (10% in chloroform) showed absorption due to the ester carbonyl at 1703 cm^{-1} and the absence of olefinic bands in the 1700-1600 or

950-880 cm^{-1} regions (46). Medium to strong bands also appeared at 1453, 1368, 1308, and 1096 cm^{-1} which were in agreement with the structure assigned to this compound (26). The N.M.R. spectrum (0.50 ml per ml of carbon tetrachloride) was identical with the N.M.R. spectrum of an authentic sample of cis-1,2-dimethylcyclopropane-1-carboxylate (26), with signals at 6.41 τ (singlet), 8.81 τ (sextet $J = 6.5\text{cps}$) and 9.69 τ (quartet $J = 6.5\text{ cps}$).

Methyl trans-1,2-dimethylcyclopropane-1-carboxylate: b.p. 136° , n_D^{27} 1.4220 (lit. (26) n_D^{25} 1.4218), 26.4 minutes, 27%. Calculated for $\text{C}_7\text{H}_{12}\text{O}_2$: C, 65.49%; H, 9.45%. Found: C, 65.60%; H, 9.39%. The infrared spectrum (5% in chloroform) showed absorption due to the ester carbonyl at 1720 cm^{-1} and the absence of olefinic bands in the 1700-1600 or 950-880 cm^{-1} regions (46). The N.M.R. spectrum (0.50 ml per ml of carbon tetrachloride) was identical with the N.M.R. spectrum of an authentic sample of trans-1,2-dimethylcyclopropane-1-carboxylate (26), with signals assigned to the ester methyl hydrogens at 6.40 τ (singlet), and the cyclopropane hydrogens and methyl hydrogens at 9.08 τ (quintet $J = 6.9\text{cps}$) (47).

Vapour-Phase Pyrolysis of 3,5-Dimethyl-3-carbomethoxy-1-pyrazoline

The apparatus used was identical with that used for the pyrolysis of 4,5-dimethyl-3-carbomethoxy-2-pyrazoline except that pyrolysis was obtained without benefit of the pre-heating coil, and 5/8-in diameter pyrex beads were used in place of the catalyst. The pyrolysis tube was heated to 200-225 $^{\circ}$.

A sample of the pyrazoline, (1.2g) b.p. $54^{\circ}/0.5$ mm, was added dropwise to the pyrolysis tube held at a pressure of 2 to 4 mm. The pyrolysis product was analysed by vapour chromatography as in the analysis of the liquid-phase pyrolysis product and was found to contain 2% of methyl trans-2-methyl-2-pentenoate, 2.5% of methyl cis-2-methyl-2-pentenoate, 1% of methyl trans-2-methyl-3-pentenoate, 41.5% of trans-1,2-dimethyl-1-carbomethoxy-cyclopropane and 53% of cis-1,2-dimethyl-1-carbomethoxy-cyclopropane.

Isomerisation Studies on Methyl trans-2-Methyl-2-Pentenoate and Methyl trans-2-methyl-3-Pentenoate

Samples of methyl trans-2-methyl-2-pentenoate and methyl trans-2-methyl-3-pentenoate were heated at 250° for two weeks. Analysis of the product by vapour chromatography showed, respectively, methyl trans-2-methyl-2-pentenoate 47%, 44%; methyl cis-2-methyl-2-pentenoate 12% 10%; methyl trans-2-methyl-3-pentenoate 15%, 17%. In addition to these components two peaks which had not previously been observed appeared in the chromatogram with retention time 33.4 minutes (16%, 18%) and 38.2 minutes (10%, 11%). The first peak may possibly be due to methyl cis-2-methyl-3-pentenoate, and the second to methyl 1-n-propyl-acrylate. No further new peaks were observed when a Ucon Polar column was used.

Synthesis of Methyl 3-Methyl-2- and -3-Pentenoates

(a) Methyl 3-methyl-3-hydroxy valerate

The method used was an adaptation of the procedure of Kuhn, Köhler and Köhler (48). Methyl ethyl ketone (28.5g, 0.395 mole) in 90 ml anhydrous benzene and 60 ml anhydrous toluene was placed in a 1-litre three-necked flask fitted with a mechanical stirrer, an efficient reflux condenser and a pressure-equalised dropping funnel. All the apparatus was previously dried thoroughly and to the open end of the condenser was joined a calcium chloride drying tube in order to exclude water vapour during the course of the reaction. Activated 30 mesh zinc (49) (26g, 0.395 mole) was added to the benzene-toluene solution, and stirring commenced. A few drops of methyl bromoacetate (61g, 0.40 mole, excess) were added to the reactants, and the flask and contents warmed to initiate the reaction. When the benzene began to reflux heating was discontinued and the methyl bromoacetate added at a rate sufficient to maintain refluxing temperature. After the addition of all the methyl bromoacetate and the subsidence of the reaction the reactants were refluxed for a further hour. The reaction mixture was cooled, and cold dilute sulphuric acid was added in sufficient quantity to decompose the zinc adduct. The benzene-toluene layer separated from the aqueous layer, was washed with water and dried over sodium sulphate. Distillation under reduced pressure yielded a colourless oil, b.p. 33-34°/0.23 mm, n_D^{17} 1.4320 (lit. (47) b.p. 74-78° / 12 mm, $n_D^{17.5}$ 1.4310); yield 50%. The infrared spectrum (5% in chloroform) showed absorption due to the hydroxyl group at 3500 cm^{-1} and the ester carbonyl group at 1710 cm^{-1} (50).

(b) Methyl 3-methyl-2- and -3-pentenoates (51)

Methyl 3-methyl-3-hydroxy valerate (28g, 0.19 mole) and 3g phosphorus pentoxide were refluxed in 125 ml benzene for five hours. Distillation of the residue after removal of the solvent yielded 17g (70%) of a colourless oil boiling between 145-160°. Analysis by vapour phase chromatography showed five components, which, by comparison of their retention times, physical constants and infrared spectra, were proved to be identical with the following compounds isolated from the pyrolysis of 4,5-dimethyl-3-carbomethoxy-2-pyrazoline:

Methyl trans-3-methyl-2-pentenoate: b.p. 160°, n_D^{25} 1.4425, 19% of total product.

Methyl cis-3-methyl-2-pentenoate: b.p. 150°/758 mm, n_D^{17} 1.4431, 9% of total product.

Methyl trans-3-methyl-3-pentenoate: n_D^{25} 1.3202, 38% of total product.

Methyl cis-3-methyl-3-pentenoate: b.p. 148°, n_D^{25} 1.4307, 26% of total product.

The infrared spectra of all the above compounds were identical with those obtained from respective compounds isolated from the pyrolysis mixture.

Methyl 3-ethyl-3-butenate: retention time, (10-ft Dinonyl Phthalate column with a helium flow rate of 67 cc/minute) 28.4 minutes, b.p. 146°, n_D^{23} 1.4261, 8% of total product. The infrared spectrum (5% in chloroform) showed absorption due to the ester carbonyl group and the carbon-carbon double bond at 1725 and 1650 cm^{-1} respectively (46). Other bands appeared at 1420 and 897 cm^{-1} attributed to absorptions due to a 1,1-disubstituted olefin as is the frequency of the carbon-carbon double bond absorption (46).

These data are in agreement with the structure assigned to this compound.

The Absolute Configuration of Methyl cis-3-Methyl-3-Pentenoate

(a) 2,3-Dibromo-2-methyl-butyric acid (23)

A mixture of tiglic acid (30g, 0.3 mole) in 200 ml of anhydrous carbon tetrachloride and bromine (48g, 0.3 mole) was allowed to stand overnight and was then boiled under reflux until the solution was light orange. The solvent was removed by evaporation, and the solid residue was re-crystallized twice from ligroin to yield 63g (83%) of 2,3-dibromo-2-methyl-butyric acid, m.p. 85-88° (lit. (23) m.p. 82-88°).

(b) 2,3-Dibromo-2-methyl-butyryl chloride

2,3-dibromo-2-methyl-butyric acid (63g, 0.24 mole) and redistilled thionyl chloride (39g, excess) were added to a flask fitted with a reflux condenser provided with an outlet and a gas trap to remove evolved gases. The reactants were refluxed on a steam bath until there was no further evolution of gases and then for a further hour. Excess thionyl chloride was removed by distillation from a steam bath. Distillation of the residue under reduced pressure yielded 62g (86%) of a pale yellow liquid, b.p. 73-74°/14 mm. Calculated for $C_5H_7OBr_2Cl$: C, 21.54%; H, 2.51%. Found: C, 21.69%; H, 2.38%. The infrared spectrum (5% in carbon disulphide) showed two acid chloride carbonyl bands at 1780 and 1760 cm^{-1} due to the possibilities of rotational isomerism of the α -bromine atom with the carbonyl group (52).

(c) Methyl 2,3-dibromo-3-methyl-pentanoate

2,3-Dibromo-2-methyl-butyryl chloride was converted to methyl 2,3-dibromo-3-methyl-pentanoate by the Arndt-Eistert method (53). 2,3-Dibromo-2-methyl-butyryl chloride (36g, 0.12 mole) in an equal volume of anhydrous ether was added dropwise to a dry, well-stirred solution of diazomethane (13g, excess) in ether, (44) cooled in an ice-bath to 0-5°. A vigorous evolution of nitrogen occurred and, immediately after addition, the solid diazoketone began to separate slowly. The reactants were allowed to stand for 12 hours and the ether was then removed by evaporation. The crystalline diazoketone was washed with 10 ml of ice-cold ether to remove oily impurities and the ether decanted.

Anhydrous methanol (200 ml) was added to the diazoketone and the solution stirred and warmed on a water bath. Silver oxide (as a slurry in anhydrous methanol) was added in portions to the hot methanolic solution until it appeared that there was no further reduction of the silver oxide. The supernatant was tested with one drop of concentrated hydrochloric acid; the absence of an evolution of nitrogen indicated that all the diazoketone had reacted. After cooling, the methanol solution was decanted from the silver residues, filtered through alumina to remove colloidal silver and silver salts and the methanol removed by distillation. Distillation of the residue under reduced pressure yielded 18.6g (51%) of a pale yellow liquid b.p. 62-64°/0.9 mm, n_D^{23} 1.4509. Calculated for $C_7H_{12}O_2Br_2$: C, 28.44%; H, 3.55%. Found: C, 28.20%; H, 3.98%. The infrared spectrum (5% in carbon tetrachloride) showed absorption due to the ester carbonyl at 1747 cm^{-1} ; in addition bands

appeared at 1455 and 1440 cm^{-1} ascribed to the carbon-hydrogen deformation frequencies of the methylene and methyl groups respectively (54).

(d) Methyl cis-3-methyl-3-pentenoate

Methyl 2,3-dibromo-3-methyl-pentanoate was debrominated according to the method of Schubert, Rabinovitch, Larson and Sims (24a).

Methyl 2,3-dibromo-3-methyl-pentanoate (15.4g, 0.05 mole), 20 mesh zinc (0.2 g-atom) and 30 ml water were stirred in the dark for three hours. The temperature of the reaction mixture rose to about 50°, and, when it had cooled to room temperature, the reactants were extracted with ether and filtered. The ether layer was washed with water and dried over sodium sulphate. Removal of the solvent and fractional distillation under reduced pressure yielded 0.85g (14%) of a colourless liquid b.p. 52-54°/33 mm and 12g of unchanged methyl 2,3-dibromo-3-methyl-pentanoate, b.p. 108-110°/31 mm, indicating about 20% conversion. Vapour phase chromatographic analysis of the first fraction showed it to be 97% methyl cis-3-methyl-3-pentenoate, n_D^{25} 1.4306. The infrared spectrum (5% in carbon tetrachloride) had bands at 1725 and 1665 cm^{-1} due to the ester carbonyl group and the carbon-carbon double bond, respectively, of a non-conjugated ester (46). Medium to strong bands also appeared at 1379, 1355, 1322 and 1080 cm^{-1} both in the spectrum of this sample and in the infrared spectrum of a sample of methyl cis-3-methyl-3-pentenoate isolated from the pyrolysis mixture, but not present in that of the corresponding trans ester.

Synthesis of Methyl 2-Methyl-2- and -3-Pentenoates

(a) Methyl 3-keto-3-methyl-pentanoate (55)

Methyl propionate (26.7g, 0.3 mole), previously dried over calcium chloride and distilled from phosphorous pentoxide, and sodium methoxide (2.6g, 0.05 mole) were placed in a 50 ml flask under a 1-ft nichrome-spiral packed column fitted with a refluxing head. The entire apparatus was protected from atmospheric moisture by calcium chloride tubes. The reaction flask was heated in an oil bath at 100° , and the reaction mixture became homogenous within an hour. The column was operated at a jacket temperature of 65° , with slow take-off and frequent total reflux. A total of 10g of distillate was collected at a vapour temperature of $64-67^{\circ}$ during a reaction period of 12 hours. The residue on cooling set to a semi-solid cake. This cake was broken up, 30 ml of ether added and the slurry cooled in an ice-bath. An ice cold solution of 10 ml of glacial acetic acid in 20 ml of water was added in portions with stirring. Stirring was continued at ice-bath temperature until all the solid material had dissolved. The organic layer was separated and the aqueous layer twice extracted with 10 ml portions of ether. The combined ether solutions were washed once with water and dried over sodium sulphate. Removal of the drying agent and ether followed by distillation of the residue under reduced pressure through the spiral packed column referred to above yielded 15g (36%) of a colourless liquid, b.p. $70-71^{\circ}/8$ mm, n_D^{25} 1.4210 (lit.(55) b.p. $74-76^{\circ}/10$ mm, n_D^{25} 1.4211).

(b) Copper Chromite Catalyst (56)

Ammonium hydroxide was added to a solution of ammonium dichromate (25.2g, 0.1 mole) in 100 ml water until the colour changed from orange to yellow. After cooling to room temperature a solution of cupric nitrate trihydrate (8.32g, 0.2 mole) in 60 ml of water was added with stirring. The red-brown precipitate which appeared was filtered at the pump and dried overnight in an oven at 100-110°. The finely powdered brown solid was heated with a bunsen flame in a porcelain evaporating dish. Decomposition began almost immediately and the heat of the reaction was almost sufficient to complete the decomposition. When the spontaneous reaction subsided heating was recommenced and continued until there was no further evolution of white fumes and the solid was completely black and of a free-flowing consistency. The black solid was allowed to cool and suspended in 40 ml of 10% acetic acid, filtered with suction, washed thoroughly with water and dried in an oven at 100-110°. Yield 18.6g.

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