PYRAZOLINES. PART II[1]

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ABSTRACT

Product analysis has been carried out on the pyrolysis reaction in the liquid and vapor phase of 4- and 5-methyl-3-carbomethoxy-Δ^2-pyrazolines and 3-methyl-3-carbomethoxy-Δ^1-pyrazoline. The proportion of cyclopropane product was found to be greater than earlier reports had indicated and was higher for the vapor-phase pyrolysis than for the liquid-phase reaction. Vapor-phase pyrolysis of Δ^2-pyrazolines was found to require a catalyst, such as potassium hydrogen phosphate, which is believed to make possible the transformation of the Δ^2-pyrazoline into the pyrolyzable Δ^1-pyrazoline.

The pyrolysis of carbalkoxypyrazolines and related compounds has been shown to be a useful synthetic method for the preparation of derivatives of cyclopropane only in a limited number of cases. The method is particularly useful when there are carbalkoxy groups in the pyrazoline nucleus at positions 3 and 4 (1–5) and when there is an alkyl substituent and carbalkoxy substituent at the 3 position (1, 6, 7). For example, von Auwers (1) reported that 3-methyl-3-carbomethoxypyrazoline gave a product which contained 63% of methyl 1-methylcyclopropanecarboxylate and that 3,4-dicarbomethoxy-4-methylpyrazoline gave methyl 1-methylcyclopropane-1,2-dicarboxylate as the sole product. In general it has also been found that 3-carbomethoxypyrazolines with alkyl substitution at the 4 or 5 positions yield no cyclopropane product.

Recently we reported (8) that 3-carbomethoxy-Δ^2-pyrazoline yields a product which contains 32% of methyl cyclopropanecarboxylate. In a continuation of this work the 4- and 5-methyl-3-carbomethoxy-Δ^2-pyrazolines and 3-methyl-3-carbomethoxy-Δ^1-pyrazoline have been found to yield products containing cyclopropane derivatives. Upon further investigation of the pyrolysis reaction we have found that the proportion of cyclopropane derivative in the product is increased considerably when the pyrolysis is carried out in the vapor phase. For example, under these conditions 3-carbomethoxy-Δ^2-pyrazoline yields a product which contains 62% of methyl cyclopropanecarboxylate, an increase of 30% over the liquid-phase reaction.

The results of the pyrolysis of the three isomeric methyl-3-carbomethoxypyrazolines is shown in Table I and illustrated in Chart I. The liquid-phase pyrolyses were carried out by heating the pyrazoline in a distillation apparatus to a temperature at which nitrogen evolution was rapid and distillation of the product occurred as it was formed. The vapor-phase pyrolyses were carried out by dropping the liquid pyrazoline on beads or other packing material in a vertical tube heated to about 200° and connected to a vacuum system which maintained a pressure of 2 to 5 mm in the tube. The Δ^1-pyrazoline readily pyrolyzed when a glass bead packing was used but the Δ^2-pyrazolines were unchanged even with the beads at 500° unless the tube was charged with a catalyst (potassium hydrogen phosphate was used) to promote transformation of the Δ^2-pyrazoline to the Δ^1-form. This observation may be taken as further evidence that it is the Δ^1-form of the pyrazoline which pyrolyzes and not the Δ^2-form. Jones (9) and Beech *et al.* (10) have also obtained strong evidence in support of this postulate.

It is not possible to determine with certainty whether pyrolysis in the tube is occurring in the vapor phase or on the surface of the packing material. The catalyst, potassium

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TABLE I

Product analysis from pyrazoline pyrolyses

Substituent in 3-carbomethoxy-pyrazoline	Phase	Proportion of components in the product in %				
		Cyclo-propane	α,β-Unsaturated ester		β,γ-Unsaturated ester	
			cis	trans	cis	trans
None	Liquid	32	30	31	7	
	Vapor	62	20	12	6	
3-Methyl	Liquid	65	15	15	5*	
	Vapor	85	7	4	4	
4-Methyl	Liquid	4	88		8	
	Vapor	26	62		12	
5-Methyl	Liquid	29	23*	43*	—	5
	Vapor	74†	12	10	—	4

*These compounds have not been previously reported and are tentatively identified from their N.M.R. and infrared spectra.

†Chromatography through a dinonyl phthalate or Ucon Polar column did not effect separation of the cis and trans esters. Infrared analysis of the acid obtained from the ester by hydrolysis indicated it to be 40% cis and 60% trans.

hydrogen phosphate, when added to the liquid-phase pyrolysis of 3-carbomethoxy-Δ^2-pyrazoline gives a lower yield of product which has approximately the same composition as the normal liquid-phase pyrolysis product. Because of this fact and since the boiling points of the pyrazolines at 2.5 mm are below the temperature at which pyrolysis occurs it is assumed that the pyrolysis takes place in the vapor phase. Further studies are now underway to determine the effect of catalyst, temperature, and pressure on the vapor-phase pyrolysis and to develop the method as a synthetic route to cyclopropane derivatives.

The pyrazolines used in the pyrolysis studies were prepared by the addition of diazomethane to the appropriate α,β-unsaturated ester. 3-Methyl-3-carbomethoxy-Δ^1-pyrazoline is a colorless liquid whereas the 4- and 5-methyl and the unsubstituted 3-carbomethoxypyrazolines are low-melting colorless solids which readily become straw-colored in the presence of air. The latter three are assigned the Δ^2-structure resulting from conjugation of the double bond with the ester carbonyl on the basis of their infrared spectra, which show N—H stretch and a conjugated carbonyl absorption.

The products from the pyrazoline pyrolyses were isolated by vapor chromatography and were identified from their physical properties. Three of these products (methyl 2-methyl-3-butenoate and methyl *cis*- and *trans*-2-pentenoate) have not previously been reported and the structures are tentatively assigned from the analysis, N.M.R., and infrared data and from the fact that each occur in equilibrium studies on known isomeric olefins. The evidence for these assignments is given in the experimental section.

The composition of the olefin portion of the pyrolysis product is in general not an equilibrium mixture as can be seen by a comparison of the equilibrium results in Table II with the pyrolysis results in Table I. The equilibrium values were determined by heating olefin samples at 250° for 2 weeks. The equilibrium was reached in each case by starting with two isomeric olefins and the equilibrium mixtures were analyzed by vapor chromatography. In general the olefin product from the pyrolysis reaction is richer in the *cis*-α,β-unsaturated olefin than is the equilibrium.mixture and in many cases the cis-to-trans ratio approaches 1. A ratio of about 1 would be expected if both olefins 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 (11).

TABLE II
Equilibrium composition in % after equilibration at 250° C

	α,β-Unsaturated ester		β,γ-Unsaturated ester	
Initial olefin	cis	trans	cis	trans
Methyl *trans*-crotonate (8)	12	83	5	
Methyl *cis*-crotonate (8)	12	84	4	
Methyl tiglate	14	84	2	
Methyl 2-methyl-3-butenoate	14	82	4	
Methyl senecioate	84		16	
Methyl 3-methyl-3-butenoate	86		13	
Methyl *trans*-2-pentenoate	7	47	—*	46
Methyl *cis*-2-pentenoate	7	48	—*	45

*A new peak appeared in the chromatogram having one-half the area of the *cis*-2-pentenoate but was not identified.

The percentage of β,γ-unsaturated ester formed in the various reactions studied thus far seems remarkably constant and does not seem to be dependent on the relative stability of α,β- and β,γ-unsaturated products. This may mean that the β,γ-unsaturated product is also formed from the same intermediate from which the other products are formed and possibly by a proton migration (12).

The change in product composition between the liquid-phase reaction and the vapor-phase reaction is quite interesting and may make the vapor-phase reaction a feasible method for the preparation of a number of cyclopropane derivatives not readily available at the present time. The effect of the phase on the reaction may indicate that at least part of the olefin product in the liquid phase is formed by a bimolecular process which is reduced in favor of unimolecular processes in the high dilution of the vapor phase. It is therefore possible that high dilution in a solvent may also be useful for the preparation of cyclopropane derivatives where reaction in the vapor phase is not possible.

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 stabilizer VK 3506 and the methylene chloride used as an external standard was observed to have a value of 4.60 τ. The vapor chromatograph unit was an Aerograph model A-100-C.

Methyl-3-carbomethoxypyrazolines

The pyrazolines were prepared from diazomethane plus methyl methacrylate, diazomethane plus methyl crotonate, and diazoethane plus methyl acrylate. Ether solutions of the diazoalkane were prepared from the corresponding nitrosourea by treatment with 40% potassium hydroxide and were dried over potassium hydroxide but were not distilled. The α,β-unsaturated ester was added slowly to the ether solution until the color of the diazoalkane disappeared. The reaction to form the 4-methyl derivative took several hours but the 3- and 5-methylpyrazolines formed almost immediately at room temperature. These pyrazolines have been reported previously (1) but the following physical constants were not included in the report. The yields given are based on the reagent used in lowest molar quantity indicated in parentheses after the yield.

3-Methyl-3-carbomethoxy-Δ^1-pyrazoline: b.p. 89°/1.5 mm, yield 57% (nitrosourea).

The infrared spectrum (10% in chloroform) showed no absorption due to N—H or C=N. The ester carbonyl appeared at 1734 cm^{-1}.

4-Methyl-3-carbomethoxypyrazoline: b.p. 98/1.2 mm, m.p. 26–27°, yield 35% (nitrosourea). The infrared spectrum (10% in chloroform) had bands at 3400, 1705, and 1566 cm^{-1} assigned to the N—H, C=O, and C=N functions (13).

5-Methyl-3-carbomethoxypyrazoline: b.p. 96°/1 mm, m.p. 37–38°, yield 77% (methylacrylate). The infrared spectrum (10% in chloroform) had bands at 3420, 1706, and 1568 cm^{-1} assigned to the N—H, C=O, and C=N functions (13).

Pyrolysis of 3-Methyl-3-carbomethoxy-Δ¹-pyrazoline

3-Methyl-3-carbomethoxy-Δ^1-pyrazoline (10 g, 0.07 mole) was heated in a distillation apparatus in an oil bath. At a bath temperature of 110° pyrolysis was indicated by the evolution of a gas and at 150° it became vigorous. Distillation yielded 7.0 g (88%) of a colorless product boiling up to 141°. Four components were isolated by vapor chromatography and were identified as indicated below where boiling point, refractive index, retention time in the vapor chromatogram using a 10-ft Ucon Polar 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 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 tiglate: b.p. 137–139°, n_D^{24} 1.4353 (lit. (14) b.p. 139.4–139.6°, n_D^{20} 1.4370), 29.1 minutes, 15%.

Methyl angelate: b.p. 127–128°, n_D^{20} 1.4320 (lit. (14) b.p. 127.6–127.8°, n_D^{20} 1.4321), 19.5 minutes, 15%.

Methyl 1-methylcyclopropanecarboxylate: b.p. 122.5–123° (lit. (15) b.p. 121–123°), n_D^{24} 1.4198, 17.9 minutes, 65%.

Methyl 2-methyl-3-butenoate: b.p. 115–116°, n_D^{24} 1.4091, 13.3 minutes, 5%. Calc. for $C_6H_{10}O_2$: C, 63.11; H, 8.84. Found: C, 62.81; H, 8.79. The physical constants for the isomer methyl α-ethylacrylate are b.p. 122–123° and n_D^{20} 1.4243 (14). The structure was confirmed from the infrared spectrum (10% in carbon tetrachloride), which showed absorption at 1740 cm^{-1} and 1640 cm^{-1} indicative of a non-conjugated ester and a carbon–carbon double bond (16). The N.M.R. spectrum (0.20 ml per ml of carbon tetrachloride) had a complex multiplet in the olefin hydrogen region with peaks at 4.14, 4.36, 4.57, 4.82, 4.89, 5.22, and 5.27 τ. Other peaks were due to the ester methyl, 6.42 (singlet), the tertiary hydrogen, 6.88 (quartet with $J \simeq 7$ c.p.s.), and the alkyl methyl, 8.83 (doublet with $J \simeq 7.2$ c.p.s.) (17).

Vapor-Phase Pyrolysis of 3-Methyl-3-carbomethoxy-Δ¹-pyrazoline

The lower portion of a 50 cm×25 mm tube was placed in a vertical position in a tube furnace 25 cm in length and heated to 200°. The tube was filled to 35 cm from its lower end with $\frac{5}{8}$ in. diameter pyrex beads. 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-equalized 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.

Two grams of 3-methyl-3-carbomethoxypyrazoline, b.p. 89°/1.5 mm, was added dropwise to the pyrolysis tube held at a pressure of 2 to 5 mm. The pyrolysis product was analyzed by vapor chromatography as in the analysis of the liquid-phase pyrolysis product and was found to contain 4% of methyl 2-methyl-3-butenoate, 85% of methyl 1-methylcyclopropanecarboxylate, 7% of methyl angelate, and 4% of methyl tiglate.

Isomerization Studies on Methyl Tiglate and Methyl 2-Methyl-3-butenoate

Ampoules containing 100 mg of methyl tiglate and methyl 2-methyl-3-butenoate isolated from the pyrolysis mixture were heated in a furnace at 250° for 2 weeks. The samples were analyzed by vapor chromatography in the same manner as the product from the pyrolysis of 3-methyl-3-carbomethoxypyrazoline and was found to contain from methyl tiglate and methyl 2-methyl-3-butenoate, respectively, methyl 2-methyl-3-butenoate 2%, 4%; methyl angelate 14%, 14%; and methyl tiglate 84%, 82%. The only new peak which might possibly be due to the isomer methyl α-ethylacrylate was a peak at 11.7 minutes, which showed a maximum area of 0.5 that of the methyl 2-methyl-3-butenoate. Analysis with a dinonyl phthalate column failed to show any new peaks.

Vapor-Phase Pyrolysis of 3-Carbomethoxy-Δ^2-pyrazoline

The apparatus used was identical with that used for the pyrolysis of 3-methyl-3-carbomethoxy-Δ^1-pyrazoline except that the pyrolysis tube above the furnace was heated with heating tape to 90° and the 15-cm portion of the tube in the center of the tube furnace was packed with potassium hydrogen phosphate. Pyrolysis of a 2-g sample yielded a colorless product which was shown by vapor chromatographic analysis (8) to contain methyl vinylacetate 6%, methyl *cis*-crotonate 20%, methyl cyclopropanecarboxylate 62%, and methyl *trans*-crotonate 12%.

Pyrolysis of 3-Carbomethoxypyrazoline in the Presence of Potassium Hydrogen Phosphate

In a distillation apparatus was placed 5.2 g of 3-carbomethoxy-Δ^2-pyrazoline and 1.5 g of potassium hydrogen phosphate and the mixture was heated in an oil bath to 190°. Analysis of the distillate (1.8 g, 44%) (8) showed methyl vinylacetate 6%, methyl cyclopropanecarboxylate 27%, methyl *cis*-crotonate 35%, and methyl *trans*-crotonate 32%.

Pyrolysis of 4-Methyl-3-carbomethoxy-Δ^2-pyrazoline

4-Methyl-3-carbomethoxy-Δ^2-pyrazoline (23 g, 0.15 mole) was pyrolyzed in a distillation apparatus at 190° in a similar manner to that described for 3-methyl-3-carbomethoxy-Δ^1-pyrazoline to give 15 g (80%) of a colorless product boiling up to 138°. Three components were isolated by vapor chromatography and identified as indicated below where boiling point, refractive index, retention time in the vapor chromatogram using a 10-ft Ucon Polar column of 0.25-in. diameter with a helium flow rate of 67 cc/minute, and percentage of the total product are given.

Methyl senecioate: b.p. 136°, n_D^{24} 1.4368, 31.2 minutes, 88%. This sample was identical in all respects with an authentic sample prepared by the procedure of Wagner (18).

Methyl 3-methyl-3-butenoate: b.p. 125°, n_D^{23} 1.4171 (lit. (18) b.p. 41°/27 mm, n_D^{20} 1.4168), 21.2 minutes, 8%.

Methyl 2-methylcyclopropanecarboxylate: —, n_D^{23} 1.4220, 26.8 minutes, 4%. The infrared and N.M.R. spectra of this compound were identical with those of the sample isolated from the pyrolysis of 5-methyl-3-carbomethoxypyrazoline.

Vapor-Phase Pyrolysis of 4-Methyl-3-carbomethoxy-Δ^2-pyrazoline

The pyrolysis was carried out at 225° by the procedure described for the vapor-phase pyrolysis of 3-carbomethoxy-Δ^2-pyrazoline. Under these conditions 10% of the pyrazoline was not pyrolyzed and was frozen out of the product. Analysis of the product by vapor chromatography showed that the product contained methyl senecioate 62%, methyl 2-methylcyclopropanecarboxylate 26%, and methyl 3-methyl-3-butenoate 12%.

Isomerization Studies on Methyl Senecioate and Methyl 3-Methyl-3-butenoate

Samples of methyl senecioate and methyl 3-methyl-3-butenoate were heated at 250°

for 2 weeks. Analysis of the product showed, respectively, methyl senecioate 84%, 87%; and methyl 3-methyl-3-butenoate 16%, 13%.

Pyrolysis of 5-Methyl-3-carbomethoxy-Δ^2-pyrazoline

5-Methyl-3-carbomethoxy-Δ^2-pyrazoline (5.0 g, 0.33 mole) was pyrolyzed in a distillation apparatus at 190° in a similar manner to that described for 3-methyl-3-carbomethoxy-Δ^1-pyrazoline to give 3.0 g (80%) of a colorless liquid boiling up to 142°. Four components were isolated and identified as indicated below where boiling point, refractive index, retention time in the vapor chromatogram using a 10-ft Ucon Polar column at 100° with a helium flow rate of 45 cc/minute, and percentage of the total product are given.

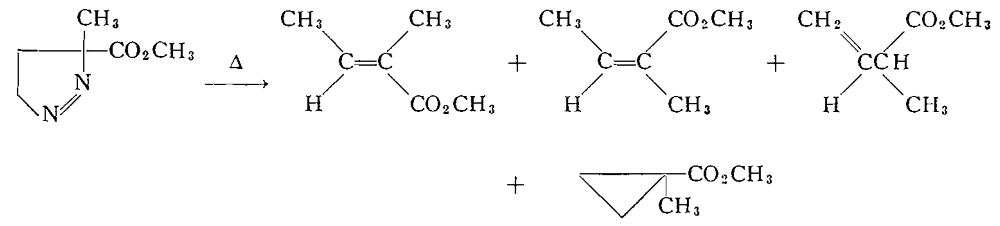
Methyl *trans*-2-pentenoate: b.p. 142°, n_D^{21} 1.4315, 37.2 minutes, 43%. Calc. for $C_6H_{10}O_2$: C, 63.11; H, 8.84. Found: C, 62.90; H, 8.91. The infrared spectrum (10% in carbon tetrachloride) showed bands at 1712, 1662, and 981 cm^{-1} characteristic of a *trans*-α,β-unsaturated ester (16). The N.M.R. spectrum (0.5 g per cc of carbon tetrachloride) showed vinyl hydrogen signals at 3.16 τ (sextet with $J_{trans} \simeq 16$ c.p.s. and $J_{CH_2} \simeq 6.4$ c.p.s.) and 4.41 τ (doublet), ester methyl hydrogens at 6.50 τ (singlet), methylene hydrogens at 7.78 τ (multiplet), and alkyl methyl hydrogens at 9.05 τ (triplet $J \simeq 7.2$ c.p.s.). These data are consistent with the *trans*-α,β-unsaturated structure assigned to this compound (17).

Methyl *cis*-2-pentenoate: b.p. 128°, n_D^{20} 1.4281, 23.6 minutes, 23%. Calc. for $C_6H_{10}O_2$: C, 63.11; H, 8.84. Found: C, 62.91; H, 9.14. The infrared spectrum (10% in carbon tetrachloride) showed bands at 1723 and 1643 cm^{-1} characteristic of an α,β-unsaturated ester (16). The N.M.R. spectrum (0.5 g per cc of carbon tetrachloride) was similar to that of the trans ester except for the value of the vinyl splitting constant, which was smaller in magnitude. Signals were found at 3.89 τ (sextet $J_{cis} \simeq 11.6$ c.p.s. and $J_{CH_2} \simeq 6.8$ c.p.s.), 4.46 τ (doublet), 6.55 τ (singlet), 7.56 τ (multiplet), and 9.23 τ (triplet $J \simeq 7.2$). These data are consistent with the *cis*-α,β-unsaturated structure assigned to this compound (17).

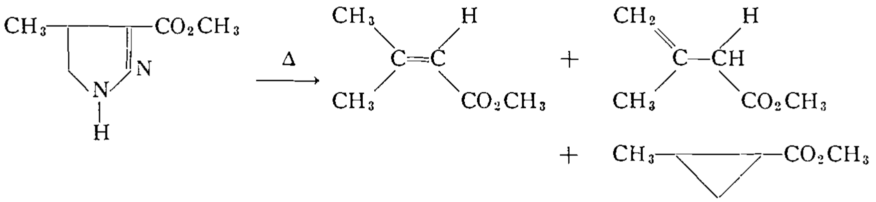
Methyl 2-methylcyclopropanecarboxylate: b.p. 130°, n_D^{20} 1.4228, 27.2 minutes, 29%. Calc. for $C_6H_{10}O_2$: C, 63.11; H, 8.84. Found: C, 63.28; H, 8.76. Hydrolysis with 10% sodium hydroxide of a 2-g sample obtained from a large-scale pyrolysis run, from which the olefin product was removed by oxidation with potassium permanganate, gave 1 g of 2-methylcyclopropanecarboxylic acid, b.p. 190–191° (lit. (19) b.p. 190–191°), n_D^{26} 1.4381. The infrared spectrum (10% in carbon disulphide) showed bands at 1174 cm^{-1} and 1013 cm^{-1} characteristic of the cis and trans acids, respectively, as well as the other prominent bands reported for these acids (20). The mixture was analyzed by the baseline method of Heigl (21) using the bands at 1174 and 1013 cm^{-1} and the spectra of the pure cis and trans acids kindly provided by D. E. Applequist and A. H. Peterson and was found to be 40% cis and 60% trans.

Methyl *trans*-3-pentenoate: b.p. 137°, n_D^{21} 1.4220 (lit. (22) b.p. 128°/625 mm, n_D^{20} 1.4217), 30.4 minutes, 5%. No reason can be found for the discrepancy in the boiling point. A sample isolated from the isomerization mixture (see below) had a boiling point of 136°. The infrared spectrum (10% in carbon tetrachloride) showed bands at 1740 and 970 cm^{-1} characteristic of a trans olefin and an ester but no bands were found in the 1600 to 1700 cm^{-1} region possibly due to the symmetry of the double bond (16). The N.M.R. spectrum (0.3 g per cc of carbon tetrachloride) showed bands at 4.62 τ (multiplet), 6.46 τ (singlet), 7.12 τ (broad), and 8.50 τ (broad) as would be expected for the assigned

3-Methyl-3-carbomethoxy-Δ1-pyrazoline



4-Methyl-3-carbomethoxy-Δ2-pyrazoline



5-Methyl-3-carbomethoxy-Δ2-pyrazoline

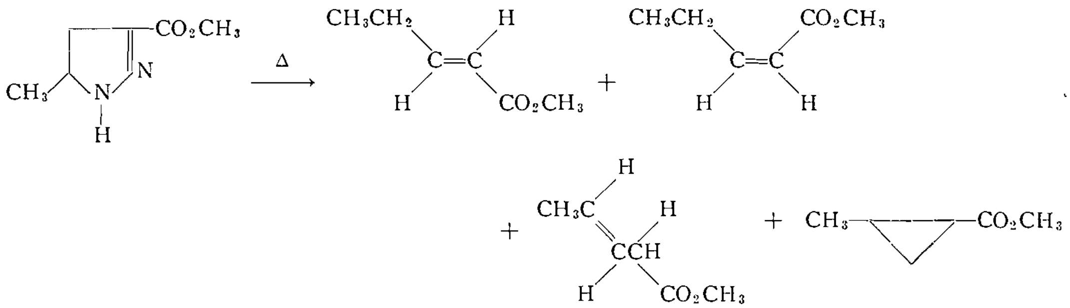


CHART I.

structure with broadening of the signals due to the large amount of long-range splitting possible (23).

Vapor-Phase Pyrolysis of 5-Methyl-3-carbomethoxy-Δ2-pyrazoline

The pyrolysis was carried out at 225° by the procedure described for the vapor-phase pyrolysis of 3-carbomethoxy-Δ2-pyrazoline. Analysis of the product showed the presence of methyl *trans*-2-pentenoate 10%, methyl *cis*-2-pentenoate 12%, methyl 2-methylcyclopropanecarboxylate 74%, and methyl *trans*-3-pentenoate 4%.

Isomerization Studies on Methyl trans-2-Pentenoate and Methyl cis-2-Pentenoate

Samples of methyl *trans*-2-pentenoate and methyl *cis*-2-pentenoate were heated at 250° for 2 weeks. Analysis of the product showed, respectively, methyl *cis*-2-pentenoate 7%, 7%; methyl *trans*-2-pentenoate 47%, 48%; and methyl *trans*-3-pentenoate 46%, 45%. In addition to these components a peak which had not previously been observed appeared in the chromatogram at 20.8 minutes. This peak was approximately one half of the area of that for methyl *cis*-2-pentenoate and might possibly be due to methyl *cis*-3-pentenoate. No new peaks were found when a dinonyl phthalate column was used.

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