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Pyrazolines. VII. The Stereochemistry of the Thermal Decomposition of 5-Phenyl-1-pyrazolines[1]

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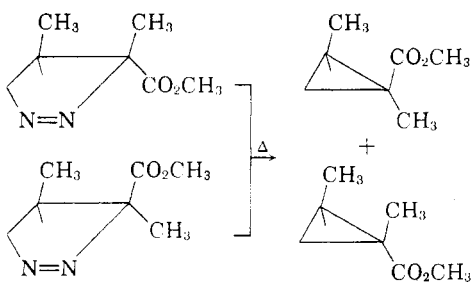
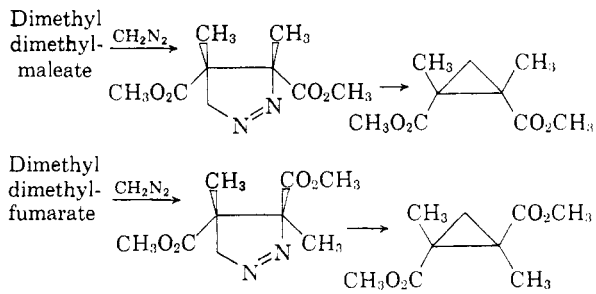
Two of the four possible 5-phenyl-3-methyl-3,4-dicarbomethoxy-1-pyrazolines have been isolated in pure form and subjected to thermal decomposition. Although only small yields of cyclopropane actually resulted from these decompositions, under the conditions which did yield some cyclopropane the decompositions were partially stereospecific; the 1-pyrazoline with the two carbomethoxy groups *trans* giving exclusively the cyclopropane with the carbomethoxy groups *trans* and the 1-pyrazoline with the two carbomethoxy groups *cis* giving a mixture of cyclopropanes consisting of 75% of the isomer with the two carbomethoxy groups *cis* and 25% of the isomer with the two carbomethoxy groups *trans*. The stereochemistry of the two isolated cyclopropanes was determined by chemical tests, NMR., and alternate syntheses from appropriate 2-pyrazolines.

There exists in the literature evidence that the often presumed[2-4] general stereospecificity of the decomposition of 1-pyrazolines to cyclopropanes might well be far from general. For example, it was recently reported by Rinehart and van Auken[5] that the thermal decomposition of the 1-pyrazolines resulting from the reaction of diazomethane with methyl tiglate and methyl angelate led to "essentially equal amounts" of geometrically isomeric cyclopropanes.



Furthermore, it has been shown[1] that the 1-pyrazolines resulting from the reaction of diphenyldiazomethane with dimethyl citraconate[6] and dimethyl mesaconate, upon thermal decomposition, both give, within experimental error, exclusively the cyclopropane product in which the two carboalkoxy groups are *trans* again a case of nonstereospecific thermal decomposition of a 1-pyrazoline.

These observations are to be contrasted with the observations of von Auwers and Konig[4] in which they found that the 1-pyrazolines resulting from the reaction of diazomethane with the dimethyl esters of dimethylmaleic acid and dimethylfumaric acid gave, upon thermal decomposition, almost exclusively cyclopropanes which had the same geometrical configurations as the original diesters. From these observations it has been most reasonably presumed that the geometrical integrity of the starting diester was maintained throughout the sequence of reactions.



Furthermore, they found that thermal decomposition of the pyrazolines resulting from the reaction of diazomethane with dimethyl mesaconate and dimethyl citraconate also gave different cyclopropanes of configurations which lead to the same conclusion with regard to the stereochemistry of the decomposition of the 1-pyrazolines.

Thus, it is obviously impossible to predict, *a priori*, whether the thermal decomposition of a 1-pyrazoline will occur stereospecifically, partially stereospecifically, or with no preference whatsoever.

This conclusion is of particular interest to us as our investigations of the stereochemistry of the thermal decomposition of certain 2-pyrazolines[3,7] have led us to suggest that the stereochemistry of the predominant cyclopropane resulting from the decomposition of a 2-pyrazoline can be predicted by assuming that the decomposition proceeds in such a way as to give predominantly the thermodynamically more stable 1-pyrazoline followed by stereospecific decomposition of the 1-pyrazoline to

(1) For the previous paper, see W. M. Jones and W. T. Tai, *J. Org. Chem.*, **27**, 1030 (1962). Based upon a theses submitted by W. T. Tai in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) For a discussion of this subject, see T. L. Jacobs in R. C. Elderfield, "Heterocyclic Compounds," Wiley, New York, Vol. 5, 1957, Chapter 2.

(3) W. M. Jones, *J. Am. Chem. Soc.*, **81**, 5153 (1959); **80**, 6678 (1958).

(4) K. von Auwers and F. Konig, *Ann.*, **496**, 252 (1932).

(5) K. L. Rinehart, Jr., and T. V. van Auken, Abstracts of Papers, American Chemical Society Meeting, New York, September 11–16, 1960, p. 96-P.

(6) J. van Alphen, *Rec. trav. chim.*, **62**, 334 (1943).

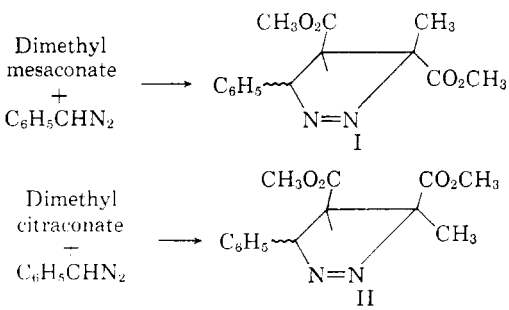
(7) W. M. Jones, *J. Am. Chem. Soc.*, **82**, 3136 (1960).

cyclopropane. Thus, it has become obvious that, as the decomposition of certain 1-pyrazolines is not stereospecific, this rule should not hold for all 2-pyrazolines, unless, of course, the decomposition of 2-pyrazolines does not proceed, as has been suggested,[3,7,8] *via* the 1-pyrazoline and this rule successfully predicts the stereochemistry of the decomposition simply by coincidence.

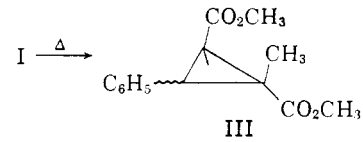
We felt that one approach toward gaining further information along this line was to examine the stereochemistry of the decomposition of 1-pyrazolines which are as similar as possible in structure to those from which the above rule was derived. To report the results of an examination of the stereochemistry of the decomposition of one pair of such 1-pyrazolines is the purpose of this paper.

RESULTS AND DISCUSSION

In an attempt to examine the decomposition of a 1-pyrazoline that was as nearly analogous to the 5-phenyl-2-pyrazolines from which the aforementioned conclusions were derived, it was decided to attempt to synthesize the stereoisomeric 3-methyl-3,4-dicarbomethoxy-5-phenyl-1-pyrazolines. Dimethyl mesaconate and dimethyl citraconate were therefore treated with phenyldiazomethane. Only one isomeric 1-pyrazoline was isolated in pure form from each reaction mixture; however, as we were primarily interested in whether or not total equilibration occurred during the decomposition, this was sufficient for our purposes. The fact that there is virtually no doubt but that the formation of 1-pyrazolines from the reaction of diazomethanes with α,β-unsaturated esters is stereospecific[1-5,9] led us immediately to assign structures I and II to the products resulting from the reaction with dimethyl mesaconate and dimethyl citraconate, respectively.

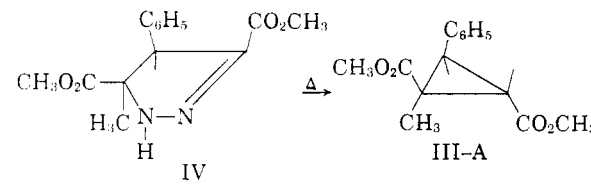


Thermal decomposition of the *trans*-1-pyrazoline (I) was effected in the melt at 180–185°. Gas-liquid partition chromatography (g.l.p.c.) analysis of the crude reaction product showed, in addition to several peaks of very short retention time, only one peak in the region (approximately thirteen minutes under our conditions) which we later found to be the cyclopropane region. Work-up of the crude reaction mixture yielded a material which exhibited all of the anticipated properties of the *trans*-cyclopropane (III).



The *trans* configuration of the two carboalkoxy groups was ascertained by hydrolysis of the diester to the diacid followed by attempts to close thermally the diacid to the anhydride. At temperatures as high as 230°, only the starting acid sublimed. That epimerization had not occurred during hydrolysis was demonstrated by re-esterifying with diazomethane to the starting ester.

Furthermore, the geometrical configuration of the phenyl ring was elucidated by examining the stereochemistry of the decomposition of the 2-pyrazoline IV. Thus, whether or not the decomposition of a 2-pyrazoline proceeds *via* the 1-pyrazoline, we have found[3,7] that the stereochemistry of the predominant cyclopropane resulting from the thermal decomposition of 5-carboalkoxy-2-pyrazolines can be predicted by assuming that the reactant initially tautomerizes to give predominantly the thermodynamically favored 1-pyrazoline which then decomposes stereospecifically to the cyclopropane. Thus, it was possible to predict that the decomposition of IV should give predominantly III-A:



The 2-pyrazoline (IV) was therefore synthesized from the reaction of methyl diazoacetate with the methyl ester of *cis*-α-methyl cinnamic acid. Thermal decomposition of the crude 2-pyrazoline gave a mixture in which the predominant cyclopropane (72% of the cyclopropane products by g.l.p.c.; also, the only cyclopropane isolated) was identical in every way with the cyclopropane resulting from the decomposition of the *trans*-1-pyrazoline (I). Thus, there could be little doubt but that the phenyl ring in the cyclopropane (III) was *trans* to the methyl group and that the stereochemistry was that pictured in IIIa.

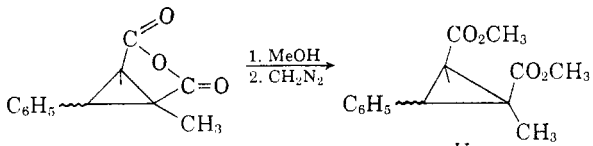
Finally, consistent with the assigned structure for III in which the two cyclopropane ring hydrogens are *trans*, the NMR spectrum of the cyclopropane was found to exhibit a coupling constant for the two ring hydrogens of 7.2 c.p.s.[10]

(8) S. G. Beech, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, 4686 (1952).

(9) K. L. Rinehart, Jr., and T. V. van Auken, *J. Am. Chem. Soc.*, **82**, 5251 (1960).

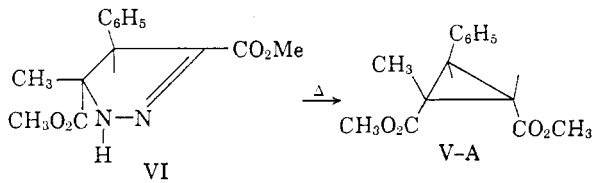
(10) G. L. Closs and L. E. Closs, *ibid.*, **82**, 5723 (1960).

Thermal decomposition of the 1-pyrazoline with the two carbomethoxy groups *cis* (II) was then examined. However, when this material was decomposed at its melting point (137°) until nitrogen evolution ceased, initial attempts to isolate a cyclopropane failed. In view of the difficulty encountered in the isolation of this 1-pyrazoline and in order to have material for standardizing the g.l.p.c., we decided to attempt the synthesis of the cyclopropane with the two carbomethoxy groups *cis* by an alternate route. This was accomplished by effecting the reaction of phenyldiazomethane with citraconic anhydride followed by thermal decomposition of the resulting pyrazoline. This led to the cyclopropane anhydride which was then opened with methyl alcohol and the corresponding half-acid was then esterified with diazomethane. This gave a material which was different in every way from the *trans*-cyclopropane (IIIa) and exhibited a retention time of *ca.* eighteen minutes (as compared with a retention time of thirteen minutes shown by the *trans*-isomer). Assignment of the



V

configuration of the phenyl of this cyclopropane as *cis* to the methyl group resulted from an examination of the decomposition of the pure 2-pyrazoline (VI) resulting from the reaction of methyl diazoacetate with the methyl ester of *trans*-α-methyl cinnamic acid. It was found that over 90% of the cyclopropane product resulting from this de-



VI V-A

composition was identical in every way with the *cis*-cyclopropane (V) synthesized from the anhydride. Again, the *trans*-assignment of the two cyclopropane hydrogens was confirmed by the NMR spectrum in which it was found that the two ring hydrogens exhibited a coupling constant of 6.9 c.p.s.[10]

With this information at hand, we felt that we were finally in a position to examine intelligently the thermal decomposition of the *cis*-1-pyrazoline (II). Much to our surprise, when this material was heated above its melting point (137°) until no further gas evolution was observed and the resulting product passed through the vapor fractometer, there were observed no peaks in the ten- to thirty-minute region. Attempts were therefore made to find conditions under which the *cis*-1-pyrazoline would yield the cyclopropane. The decomposition was effected at temperatures ranging from 140–260°. The decompositions were also run by refluxing the pyrazoline in xylene, mesitylene, and decalin. In no case could any cyclopropane be detected by g.l.p.c. analysis of the crude reaction mixture. However, it was finally found that when the *cis*-1-pyrazoline was introduced into a test-tube which had been preheated to 280°, the decomposition gave some cyclopropane.[11] G.l.p.c. analysis of the crude reaction mixture showed that, although the decomposition gave only a low yield of cyclopropanes (ca. 8%), the cyclopropane product was definitely predominately the *cis*-cyclopropane Va; the mixture consisting of 75% of the *cis*-isomer (Va) and 25% of the *trans*-material.

Attempts were then made to effect decomposition of the *trans*-1-pyrazoline to cyclopropane under the same conditions. Unfortunately, under these conditions, the *trans*-pyrazoline gave no detectable cyclopropane. Thus, there apparently exists a rather narrow range of conditions under which cyclopropane formation in these systems competes at all with whatever side reactions may be taking place. Finally, it was found that the two cyclopropanes were thermally stable under the drastic conditions required to convert the *cis*-1-pyrazoline to cyclopropane.

Thus, in conclusion, it can be stated that despite the fact that only small yields of cyclopropanes were observed from the decomposition of each of these 1-pyrazolines, under the conditions employed, cyclopropane formation from the two pyrazolines certainly does not proceed entirely through a common intermediate. Concerning the stereospecificity of the reaction, it can only be concluded that the reaction is, at best, partially stereospecific with respect to the carbon–carbon bond between the number three and four members of the heterocyclic ring. Furthermore, no conclusions can be reached regarding possible rotation around the carbon-carbon bond between the four and five members of the ring; however, there is no evidence to date that would indicate that, during the decomposition of a 1-pyrazoline, free rotation might be allowed around one bond and restricted around the other.

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(11) Although our primary interest was the stereochemistry of the formation of cyclopropane from this 1-pyrazoline, we were naturally curious as to just why no cyclopropane was formed under most of the conditions tried. Although no extensive attempts were made to solve this problem, one observation was made which suggests a possible solution. When the 1-pyrazoline was only partially decomposed and the infrared spectrum of the crude reaction mixture examined it was found that quite a strong N—H absorption had developed. Thus, the most probable complicating side reaction is tautomerization to 3-phenyl-4,5-dicarbomethoxy-5-methyl-2-pyrazoline (or, possibly, the corresponding 3-pyrazoline) followed by decomposition to uncharacterized products.

EXPERIMENTAL[12]

Preparation of benzaldehyde hydrazone. To an ice-cooled solution of anhydrous hydrazine (64.0 g., 2.0 moles) was added dropwise with stirring a solution of 106 g. (1.0 mole) of benzaldehyde in 300 ml. of ether. After the addition of the benzaldehyde, the resultant solution was dried over solid sodium hydroxide for 3 or 4 days until the solution became reddish brown. The solution was then filtered and the solvent and excess hydrazine were removed on a water bath with an aspirator. The residue was distilled at reduced pressure to give 72.0 g. (60%) of colorless distillate, b.p. 12 mm. 134–136°; reported[13] b.p. 14 mm. 140°.

Phenyldiazomethane. Phenyldiazomethane was synthesized from benzaldehyde hydrazone by the general method of Staudinger and Gaule.[14] In a typical preparation, 50 g. (0.458 mole) of benzaldehyde hydrazone was suspended in 500 ml. of pentane. With vigorous stirring 100 g. of red mercuric oxide was added over a 2.5-hr. period. After the addition of the mercuric oxide was complete, the reaction mixture was stirred for an additional 30 min. The mixture was then filtered and the residue was washed with 50 ml. of pentane. The washing was combined with the filtrate. An aliquot of the filtrate was titrated with a solution of maleic anhydride using the loss of color of the phenyldiazomethane as the end-point. From this the yield of phenyldiazomethane was estimated at 38%.

Preparation of 3-methyl-cis-3,4-dicarbomethoxy-5-phenyl-1-pyrazoline (II). To 14.8 g. (0.0939 mole) of dimethyl citraconate was slowly added 300 ml. of a cold solution of 11.1 g. (0.0939 mole) of phenyldiazomethane. The resultant solution was shaken well and placed in the refrigerator. After three days at this temperature, a mass of white and yellow solid had separated. The solids were removed by filtration and washed several times with pentane until the washings were only slightly yellow. The solid was then washed with ether to remove the remaining yellow color. The remaining white solid weighed 18.40 g., m.p. 104–109°. The solid was quite unstable in the air. Upon standing in the air for 3 or 4 hr., the solid changed to a brown, viscous oil. It was also unstable in warm methanol, chloroform, and carbon tetrachloride solution; turning yellow upon standing in any of these solvents.

The white solid with a m.p. of 104–109° (15.65 g.) was dissolved in 800 ml. of ether. Most of the ether was allowed to evaporate slowly at room temperature. The colorless crystals which formed were separated from the remaining yellow oil by filtration. This material, after washing with a little ether, weighed 3.05 g., m.p. 130° with decomposition. Recrystallization from cold methanol gave 1.30 g. of white crystals, m.p. 137° with decomposition. The infrared spectrum was devoid of absorption in the 3-μ region.

Anal. Calcd. for $C_{14}H_{16}N_2O_4$: C, 60.90; H, 5.80. Found: C, 60.93; H, 5.83.

Preparation of 3-methyl-trans-3,4-dicarbomethoxy-5-phenyl 1-pyrazoline (I). To 24.5 g. (0.155 mole) of dimethyl mesaconate was slowly added an ice-cold solution of 18.3 g. (0.155 mole) of phenyldiazomethane in 220 ml. of pentane. The resultant solution was thoroughly mixed and placed in a refrigerator. After 3 days, a mass of white solid contaminated with orange and yellow precipitate had separated. The solids were removed by filtration and the resultant residue washed with pentane until the washings were only slightly yellow. Further washing with a little ether gave 38.5 g. of white solid which melted at 63° (began evolving bubbles at 65°).

Pure 1-pyrazoline was isolated by dissolving the white solid in ether (*ca.* 5 ml. per g. of solid) and allowing the solution to remain at 0° for several days. In a good run, 10 g. of of the crude solid would deposit about 1 g. of pure pyrazoline, m.p. 175° with decomposition. Recrystallization from acetone did not raise the m.p. The infrared spectrum of this material showed no absorption in the 3-μ region.

Anal. Calcd. for $C_{14}H_{16}N_2O_4$: C, 60.90; H, 5.80; N, 10.14. Found: C, 61.02; H, 5.69; N, 10.08.

Preparation of 1-methyl-cis-1,2-dicarbomethoxy-3-phenylcyclopropane (V). To 30 g. (0.268 mole) of citraconic anhydride was added an equimolar amount of phenyldiazomethane in 500 ml. of pentane. The reaction mixture was placed in the refrigerator overnight. The next day, the white solid (contaminated with some yellow solid) was removed, dried in a vacuum desiccator, and decomposed at 90–100° to give 28.8 g. of product. A 12.0-g. portion of the product was then refluxed in methanol for 6 hr. After refluxing, the solvent was removed with an aspirator. The residue was then treated with an excess of diazomethane in ether and the ether removed on a steam bath. The resulting residue was dissolved in acetone and treated with a slight excess of aqueous potassium permanganate solution. After the precipitated manganese dioxide was removed by filtration, water was added to the filtrate followed by extraction with ether. The ether was washed with water and dried over sodium sulfate. Following removal of the ether, the residue was distilled to give 3.2 g. of a colorless liquid, b.p. 6 mm. 160–162°. The distillate showed no reaction with potassium permanganate solution. The NMR spectrum showed a coupling constant for the ring hydrogens of 6.9 c.p.s.

Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.78; H, 6.45. Found: C, 67.62; H, 6.72.

1-Methyl-trans-1,2-dicarbomethoxy-3-phenylcyclopropane (III). The crude reaction product resulting from the reaction of phenyldiazomethane with dimethyl mesaconate was distilled at reduced pressure. In a typical run, distillation of 43 g. of the crude material gave 14 g. of material boiling from 175–190° at 13 mm. Chromatography of 1 g. of this material over 40 g. of acid-washed alumina and eluting with a mixture of 20% ether and 80% hexane and collecting 50-ml. cuts gave in the combined third through seventh cuts 0.375 g. of residue. This residue was dissolved in hexane and cooled at 0° overnight to give 0.320 g. of white solid. Recrystallization several times from methanol-water gave 0.250 g. of white crystals, m.p. 41.5–43°. This product showed no reaction with permanganate and the NMR spectrum showed a coupling constant for the ring hydrogens of 7.2 c.p.s.

Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.78; H, 6.45. Found: C, 68.16; H, 6.49.

Hydrolysis and attempted ring closure of the trans-cyclopropane (III). A sample of the *trans*-cyclopropane was dissolved in 5 ml. of 5% potassium hydroxide in methanol and the mixture was allowed to remain at room temperature for four days. The mixture was then poured into water and acidified. The turbid solution was extracted with ether. The ether solution was washed with water and dried over sodium sulfate. Removal of the ether gave 0.54 g. of white solid, m.p. 104–110°. Recrystallization from methanol–water gave colorless crystals, m.p. 113–115°.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.46; H, 5.46. Found: C, 65.75; H 5.64.

A small amount of the diacid was converted to its dimethyl ester with diazomethane. The infrared spectrum, melting point, and mixed melting point with pure *trans*-cyclopropane proved that no isomerization had occurred during the hydrolysis.

An attempt to close the diacid to the anhydride failed. Upon heating the acid at 200–230° at 30 mm. in a sublimation apparatus, only unchanged acid sublimed, m.p. 113–115°; mixed with pure acid, m.p. 113–115°.

3,5-Dicarbomethoxy-4-phenyl-5-methyl-2-pyrazoline (VI). To 24.1 g. (0.137 mole) of the methyl ester of *trans*-α-methyl

(12) Melting points are uncorrected. Nuclear magnetic resonance spectra were determined in carbon tetrachloride solution employing a Varian 4300-2 high-resolution spectrometer, operating at 56.4 mc.

(13) T. Curtius and L. Pflug, *J. prakt. Chem.*, [2], **44**, 535 (1891).

(14) H. Staudinger and A. Gaule, *Ber.*, **49**, 1906 (1916).

cinnamic acid[15] was added 13.70 g. (0.137 mole) of methyl diazoacetate[16] prepared by the diazotization of methylglycine hydrochloride.[17] The resultant yellow solution was heated at 90–95° for 3 days. The reaction mixture was dissolved in ether and passed through a column packed with 200 g. of acid-washed alumina. The resulting eluent was evaporated to dryness and the residue (33.0 g.) distilled under nitrogen at 4.9 mm. to remove unchanged methyl α-methylcinnamate. The residue remaining after removal of all material boiling up to 160° was recrystallized from carbon tetrachloride to give 4.6 g. of colorless crystals, m.p. 113–116°. Repeated recrystallizations form carbon tetrachloride gave a colorless material, m.p. 114.5–115°. Significant infrared absorptions appeared at 2.95, 5.71, 5.81, and 6.41 μ.

Anal. Calcd. for $C_{14}H_{16}N_2O_4$: C, 60.90; H, 5.80; N, 10.14. Found: C, 60.91; H, 5.97; N, 10.20.

3,5-Dicarbomethoxy-4-phenyl-5-methyl-2-pyrazoline (IV). To 2.93 g. (17.6 moles) of the methyl ester of *cis*-α-methyl cinnamic acid[18] was added 1.76 g. (17.6 moles) of methyl diazoacetate. The resultant solution was heated at 80–85° for 4 days. The solution was then distilled at 5 mm. to remove unchanged cinnamate. All material which boiled up to 106° was removed. The residue (1.75 g.) showed significant infrared absorptions at 2.99, 5.70, 5.80, 6.15, and 14.25 μ. Because of the difficulty encountered in synthesis of the starting *cis*-cinnamic acid, decomposition studies were made on the crude 2-pyrazoline without attempting to isolate its pure form.

General procedure for g.l.p.c. analyses. A Perkin-Elmer Model 154-B vapor fractometer, operating at 188–192° and 25 p.s.i. and utilizing an 18-foot coiled 1/4-inch copper tube packed with 30–60 mesh Tide detergent (obtained from F and M Scientific Corp.) was employed for analyses of the decomposition products.

Before the column was used for analyses, it was "baked" in the heating chamber for about 18 hr. at a temperature of 180–190° and a helium pressure of 10 p.s.i. to remove excess liquid phase from the detergent packing. The liquid phase comes off initially in a discontinuous fashion, finally leveling off to a constant flow which continues throughout the operational life of the column. If not removed prior to the column's use, this initial effluent causes an erratic pattern of thermistor response which interferes with the analyses.

The column was standardized, not only with known mixtures of *cis*- and *trans*-cyclopropanes (V and III) but also against an internal standard of 4-*t*-butylcyclohexanone. Peak areas were employed. In analyzing the reaction products, a weighed amount of 4-*t*-butylcyclohexanone was added to a known weight of sample and the mixture dissolved in chloroform. This made possible a calculation of the absolute amount of cyclopropane in a sample.

Under the experimental conditions the retention time of *trans*- and *cis*-cyclopropanes ranged from 13 to 16 min. and 15 to 18 min., respectively. For this reason, a check was made on each run by adding either pure *cis*- or *trans*-cyclopropane to a portion of the reaction mixture and comparing its chromatogram with that of the crude sample.

Decomposition of 3-methyl-cis-3,4-dicarbomethoxy-5-phenyl-1-pyrazoline (II). G.l.p.c. analyses of the reaction product showed that no cyclopropane was formed when the *cis*-pyrazoline (II) was decomposed at several different temperatures ranging from 140–260°. Refluxing the *cis*-pyrazoline in xylene, mesitylene, or decalin also did not give any detectable cyclopropane. However, some cyclopropane was formed under the following conditions.

A sample of 0.240 g. of pure *cis*-pyrazoline (II) was introduced into a test tube which had been preheated to 280°. It was allowed to remain between 280 and 290° until nitrogen evolution had ceased. The residue weighed 0.180 g. From g.l.p.c. analysis, it was found that the mixture contained approximately 6% by weight of the *cis*-cyclopropane (V) and approximately 2% of the *trans*- material (III).

Decomposition of 3-methyl-trans-3,4-dicarbomethoxy-5-phenyl-1-pyrazoline (I). A sample of 0.0823 g. of the *trans*-pyrazoline (I) was decomposed at 180–185° until nitrogen evolution ceased. The residue weighed 0.0784 g. Analysis by g.l.p.c. showed that the residue contained approximately 12% of the *trans*-cyclopropane (III) and no detectable amount of the *cis*- isomer (V). The *cis*-cyclopropane was also found to be absent in the decomposition product of the crude *trans*-1-pyrazoline.

Attempts to decompose the *trans*-1-pyrazoline under the same conditions as those employed for the decomposition of the *cis* isomer failed to give any detectable quantity of any cyclopropane.

Both the *cis*- and *trans*-cyclopropanes (V and III) were heated at 280° for ten minutes and the resulting material analyzed by g.l.p.c. No detectable isomerization had occurred in either case.

Decomposition of 3,5-dicarbomethoxy-4-phenyl-5-methyl-2-pyrazoline (VI). A sample of 0.617 g. of the 2-pyrazoline (VI) was decomposed at 240–260° until 53.50 ml. of nitrogen had been evolved. Analysis of the crude decomposition product by g.l.p.c. showed it to contain approximately 79% of the *cis*-cyclopropane (V) and approximately 8% of other materials with retention times in the region of the *trans*-cyclopropane. Although the *cis*-cyclopropane was actually isolated in good yield from the crude reaction product by solution chromatography as previously described for the *trans*-cyclopropane (III), the actual presence of *trans*-cyclopropane was not proved. In fact, the chromatogram of the crude reaction product had the appearance of a mixture of *cis*- and *trans*-cyclopropanes containing a contaminant with a retention time just between these two peaks; leading to a smearing of the peak that would normally be assigned to the *trans*-isomer. Although this might well be either olefin or another of the possible isomeric cyclopropanes, the major peak was definitely the *cis*-cyclopropane which was sufficient for our purposes.

The isolated *cis*-cyclopropane was identified by its infrared spectrum and mixed m.p.

Decomposition of crude 3,5-dicarbomethoxy-4-phenyl-5-methyl-2-pyrazoline (IV). A sample of 1.19 g. of the crude 2-pyrazoline (IV) was decomposed in an oil bath between 220 and 250° until 89.80 ml. of nitrogen had been evolved. The decomposition product (0.94 g.) was analyzed by g.l.p.c. and found to contain approximately 23% of the *trans*-cyclopropane (III) and approximately 9% of materials with retention times similar to the *cis*-cyclopropane. The major cyclopropane product, the *trans* material (III) was isolated from the decomposition product by solution chromatography over acid washed alumina in the same manner as previously described to give an 11% yield of pure product. Its identity with authentic material was confirmed by infrared spectra and mixed melting point.

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(15) L. Edeleano, *Ber.*, **20**, 619 (1887).

(16) N. E. Searle, *Org. Syntheses*, **36**, 26 (1956).

(17) T. Curtis and F. Goebel, *J. prakt. Chem.*, (2), **37**, 150 (1888).

(18) R. Stoermer and G. Voht, *Ann.*, **409**, 54 (1915).