Ethyl 2-Acetamido-2-cyano-4-methylhexanoate.—Using the condensation procedure for the intermediate described above, 1.54 g. of sodium, 200 ml. of ethanol, 11.3 g. of ethyl acetamidocyanoacetate and 12.5 g. of 2-methyl-1-bromobutane were allowed to react to yield 14 g. of crude product, which, after recrystallization from water, had a m.p. of 100–101°.

Anal. Calcd. for $C_{12}H_{20}N_2O_3$: C, 59.98; H, 8.39; N, 11.66. Found: C, 60.20; H, 8.76; N, 11.57.

Hydrolysis of this product by the procedure described above gave a sample of 2-amino-4-methylhexanoic acid which was identical with the material characterized above.

2-Methyl-2-butene-1-ol.—To a solution of 26.2 g. of tiglaldehyde dissolved in 100 ml. of methanol was added, with external cooling, 4 g. of sodium borohydride in 200 ml. of methanol. After the addition was complete, the reaction mixture was allowed to come to room temperature, and was finally heated for 30 minutes on a steam-cone. The solution was then reduced to about one-half the original volume and acidified with concentrated hydrochloric acid to about *p*H 3, after which 250 ml. of water was added and the resulting solution was extracted three times with 75-ml. portions of ether. The combined ether phase was washed with potassium carbonate solution, and dried over anhydrous potassium carbonate. After removal of the solvent, the residue was fractionally distilled to yield 15 g. of product, b.p. 136–139°, $n^{24}D$ 1.440.[13]

2-Bromomethyl-2-butene.—A mixture of 40 g. of 2-methyl-2-butene-1-ol and 5 ml. of pyridine was cooled in an isopropyl alcohol–Dry Ice-bath and 24 ml. of phosphorus tribromide was added slowly, after which the reaction mixture was allowed to warm to room temperature and finally stirred overnight. Upon the addition of water, an organic phase which separated was recovered, and the resulting aqueous phase was extracted with ether. The combined organic phases were washed with dilute sodium hydroxide followed by water, and finally dried over calcium sulfate. After removal of the solvent, the residue was fractionally distilled to yield 48 g. of lachrymatory product, b.p. 43–47° (44 mm.).

Anal. Calcd. for C_5H_9Br: C, 40.29; H, 6.09. Found: C, 40.17; H, 6.20.

Ethyl 2-Acetamido-2-cyano-4-methyl-4-hexenoate.—To a solution of 7 g. of sodium dissolved in 250 ml. of ethanol, 50 g. of ethyl acetamidocyanoacetate was added, and then 48 g. of 2-bromomethyl-2-butene, and the reaction mixture was stirred at room temperature for three days. After filtration, the filtrate was reduced to a small volume *in vacuo*, and upon the addition of water to the residue an oil formed which solidified upon standing. This solid was subsequently crystallized from ethanol–water to yield 40.6 g. of product, m.p. 95–96°.

(13) A. Guillemonat, *Compt. rend.*, **200**, 1416 (1935), reported a b.p. of 136–138°, $n^{24}D$ 1.441, for this compound prepared through a different procedure.

Anal. Calcd. for $C_{12}H_{18}N_2O_3$: C, 60.48; H, 7.61; N, 11.76. Found: C, 60.49; H, 7.49; N, 11.86.

2-Acetamido-4-methyl-4-hexenoic Acid.—A mixture of 31 g. of ethyl 2-acetamido-2-cyano-4-methyl-4-hexenoate and 100 ml. of 10% sodium hydroxide was heated to reflux in a stainless steel beaker for two days. The resulting reaction mixture was treated with Darco G-60, filtered, and the filtrate was acidified with concentrated hydrochloric acid to yield a precipitate. The solid finally was crystallized from water to yield 6 g. of product, m.p. 112–113°.

Anal. Calcd. for $C_9H_{15}NO_3$: C, 58.36; H, 8.16; N, 7.56. Found: C, 58.44; H, 8.40; N, 7.81.

2-Amino-4-methyl-4-hexenoic Acid.—A mixture of 7 g. of ethyl 2-acetamido-2-cyano-4-methyl-4-hexenoate and 100 ml. of 20% sodium hydroxide was heated to reflux in a stainless steel beaker for 92 hours. The reaction mixture was neutralized with hydrochloric acid, treated with Darco G-60, and finally evaporated to dryness *in vacuo*. The solid residue was extracted continuously with ethanol for 72 hours using a Soxhlet extractor and, upon cooling, the alcohol extract yielded some solid material which was discarded. Addition of ether to the alcohol solution precipitated 2.6 g. of solid which was taken into water, the inorganic salts were removed with acetone, and the filtrate was evaporated to dryness *in vacuo*. The resulting residue was dissolved in 10 ml. of water and placed on a column containing an intimate mixture of 100 g. of Darco G-60 and 100 g. of Celite. The column was subsequently washed with 800 ml. of water, after which the ninhydrin active material was eluted with 50% ethyl alcohol. The alcohol eluate was evaporated to dryness to yield a yellow-colored solid which was crystallized from ethanol–acetone–water to yield 150 mg. of product, m.p. 219° dec.

Anal. Calcd. for $C_7H_{13}NO_2$: C, 58.72; H, 9.15; N, 9.78. Found: C, 58.39; H, 9.54; N, 9.53.

Hydrogenation of the above compound gave a product which was identical with 2-amino-4-methylhexanoic acid in several paper chromatographic solvent systems.

Lactone of 2-Amino-4-methyl-4-hexenoic Acid.—A mixture of 1.6 g. of ethyl 2-acetamido-2-cyano-4-methyl-4-hexanoate and 10 ml. of concentrated hydrochloric acid was heated to reflux for about 18 hours, after which the reaction mixture was reduced to dryness *in vacuo*. The residue was freed of residual hydrochloric acid by the repeated addition and evaporation of ethyl alcohol. The resulting solid was taken up in ethanol, and the insoluble material was discarded. Upon the addition of ether to the alcohol solution a precipitate formed which was subsequently crystallized from ethanol–ether to yield 160 mg. of material, m.p. 147–48°.

Anal. Calcd. for $C_7H_{13}NO_2 \cdot HCl$: C, 46.77; H, 7.86; N, 7.80. Found: C, 46.52; H, 7.80; N, 8.01.

Using 65% pyridine as the solvent, the R_f of the lactone above was 0.90, whereas that of the corresponding unsaturated amino acid was 0.80.

AUSTIN, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF FLORIDA]

Pyrazolines. III. The Stereochemistry of the Decomposition of 2-Pyrazolines[1]

BY W. M. JONES

RECEIVED MARCH 28, 1959

The stereochemical consequences of the thermal decomposition of the two isomeric 3,4-dicarbomethoxy-5-phenyl-2-pyrazolines (I and II) were investigated. The major cyclopropane product was found to have a different geometrical configuration from the primary cyclopropane product resulting from the thermal decomposition of 3,5-dicarbomethoxy-4-phenyl-2-pyrazoline (VII), thus vitiating the commonly accepted theory that the geometrical configuration of the cyclopropane product resulting from the decomposition of a 2-pyrazoline is determined by its relative thermodynamic stability. The geometrical configurations of these 2-pyrazolines and a consistent path for their decomposition are discussed.

One of the classic methods employed for the synthesis of cyclopropanes is the decomposition of 1- or 2-pyrazolines.[2] Although the thermal decomposition of 1-pyrazolines has been clearly shown to occur stereospecifically,[3,4] the decomposition of 2-pyrazolines has been reported to give a mixture of the possible stereoisomeric cyclo-

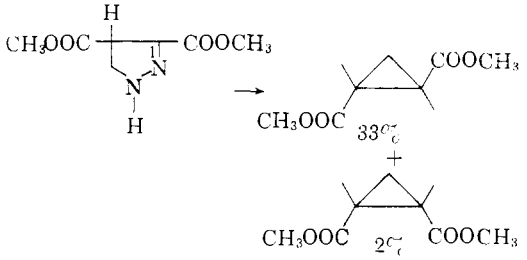
(1) Preceding paper, W. M. Jones, THIS JOURNAL, **81**, 3776 (1959).

(2) For an excellent discussion of pyrazolines, see T. L. Jacobs in R. C. Elderfield, "Heterocyclic Compounds," John Wiley and Sons, Inc., New York, N. Y., Vol. 5, 1957, Chapter 2.

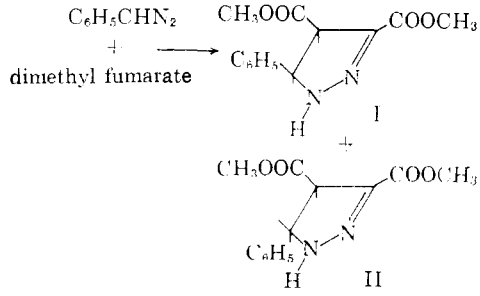
(3) K. von Auwers and F. Konig, *Ann.*, **496**, 27 (1932).

(4) *Ibid.*, **496**, 252 (1932).

propanes. For example, von Auwers[4] found that the decomposition of the dimethyl ester of 2-pyrazoline-3,4-dicarboxylic acid yielded, among other products, 33% *trans*-1,2-dicarbomethoxycyclopropane and 2% of the *cis* isomer. The predominance of the *trans* isomer over the *cis* and other observations of a similar nature[5] have led to the general assumption that the geometry of the predominant cyclopropane product resulting from the decomposition of a 2-pyrazoline is determined by its relative thermodynamic stability.[6]

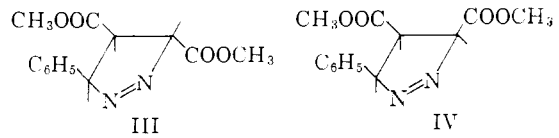


In the course of an investigation of the high temperature reaction of phenyldiazomethane with dimethyl fumarate and dimethyl maleate,[1] we found it necessary to demonstrate the stereochemistry of the decomposition to cyclopropanes of the dimethyl esters of the two isomeric 5-phenyl-2-pyrazoline-3,4-dicarboxylic acids (I and II). The syntheses of the two pyrazolines were accomplished by adding an ethereal solution of phenyldiazomethane to a cold solution of dimethyl fumarate. Upon standing at ice temperature, the pyrazoline to which we have assigned structure I crystallized out as white needles. Evaporation of the filtrate to dryness gave a very viscous oil whose infrared spectrum indicated the presence of a 2-pyrazoline (absorptions at 2.98, 5.75, 5.85 and 6.43 μ) and benzaldehyde azine. Since the spectrum in the fingerprint region was quite different from that anticipated for a mixture of the crystalline pyrazoline (I) and benzaldehyde azine, we concluded that the oil must be primarily the geometrical isomer of I (II).

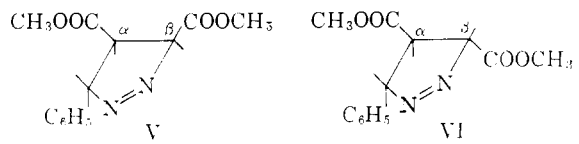


The geometrical configurations of these isomers were assigned as a result of the products obtained from the reaction of phenyldiazomethane with dimethyl maleate. Upon effecting this reaction under conditions identical with those employed for the reaction with dimethyl fumarate, only a viscous, uncrystallizable oil was obtained. The infrared spectrum of this oil was found to be identical with that of the oil isolated from the action of phenyldiazomethane on dimethyl fumarate. It therefore became apparent that, whereas dimethyl fumarate gave a mixture of the two geometrical isomers of 3,4-dicarbomethoxy-5-phenyl-2-pyrazoline, dimethyl maleate gave predominantly, if not exclusively, only one of these isomers.

This rather surprising difference in the ratio of geometrical isomers is most likely due to a difference in the steric requirements for the formation of the isomeric 1-pyrazolines which tautomerize to the observed products. An examination of molecular models shows that the two carbomethoxy groups of dimethyl maleate cannot assume the same degree of coplanarity as is possible in the dimethyl fumarate molecule.[7] Thus, the stereospecific reaction[3,4] of phenyldiazomethane with the ester to give the 1-pyrazoline with the phenyl *cis* to the adjacent carbomethoxy group would be less likely in the reaction with dimethyl maleate than in the reaction with dimethyl fumarate (III favored over IV). This difference in isomer ratio might



even be further enhanced by interaction between the phenyl and the carbomethoxy group on the carbon beta to the diazomethane carbon, an effect which would be present in the reaction with dimethyl fumarate but absent in the reaction with dimethyl maleate (V favored over VI). Both of



these considerations lead to the conclusion that the white, crystalline 2-pyrazoline has the geometrical configuration pictured in I and the oil that which is pictured in II.

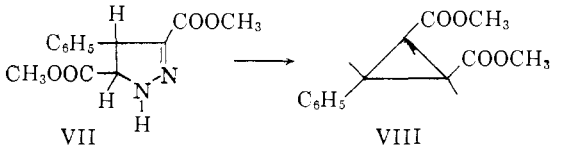
Each of these 2-pyrazolines then was thermally decomposed. In view of Buchner's earlier investigations of the decomposition of the dimethyl ester of 4-phenyl-2-pyrazoline-3,5-dicarboxylic acid (VII) to give as its sole cyclopropane product that isomer in which the carboalkoxy groups are *cis*[8] (VIII), and in view of the notion that the geometry of the predominant cyclopropane product is determined by its relative thermodynamic stability,[6] we expected the decomposition of one or both of the 2-pyrazolines I and II to give the *cis*-cyclopropane VIII. To our surprise, however, rather than yielding the anticipated cyclopropane,

(5) *E.g.*, J. van Alphen, *Rec. trav. chim.*, **62**, 210 (1943); E. Buchner and H. Witter, *Ann.*, **273**, 239 (1893).

(6) *E.g.*, ref. 1, p. 80; L. L. McCoy, THIS JOURNAL, **80**, 6568 1958).

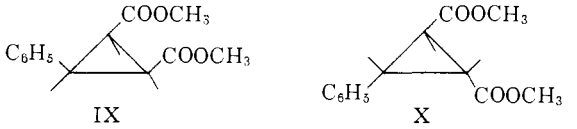
(7) The non-coplanarity of the carboxyl groups of maleic acid in solution has been postulated previously to explain its high first dissociation constant (M. Crawford, *Chemistry & Industry*, 797 (1953)). The substitution of a methyl group for a hydrogen would certainly be expected to further enhance this non-coplanarity.

(8) (a) E. Buchner and H. Dessauer, *Ber.*, **26**, 258 (1893); **25**, 1147 (1892); (b) also see: F. Feist and C. A. Chen, *ibid.*, **59B**, 2707 (1926); W. Haerdi and J. F. Thorpe, *J. Chem. Soc.*, **127**, 1237 (1925); E. Buchner and L. Perkel, *Ber.*, **36**, 3774 (1903); E. Buchner, *ibid.*, **21**, 2637 (1888).



VII VIII

each pyrazoline gave the same new white solid material, m.p. 83° (X), and a small amount of a very viscous oil. The infrared spectrum and the chemical reactions of the oil indicated that it was most likely the anticipated olefin (positive $KMnO_4$ reaction, strong absorption at 6.20 mμ, etc.). The infrared spectrum of the white solid showed a strong carbonyl absorption at 5.80 mμ and was devoid of absorption between 6.0 and 6.4 μ. It also gave no reaction with potassium permanganate and bromine, properties which are typical of cyclopropanes.[9] Thus, it was concluded that the white solid must be a geometrical isomer of VIII (IX or X). That its configuration is actually that



IX X

pictured in X was demonstrated conclusively by two means: (a) The di-acid was found to be quite resistant to thermal ring-closure; even above 200° the acid simply sublimed unchanged. (b) Partial resolution of the di-acid was effected with brucine. The resulting acids were converted to their dimethyl esters (for ease of purification) with diazomethane. Two esters were obtained, $[\alpha]^{20}D$ +42.3° and $[\alpha]^{20}D$ −20.40°.

The rather surprising observation that Buchner's cyclopropane VIII was not our product led us to examine more closely the thermal decomposition of both pyrazolines I and II as well as the pyrazoline VII reported by Buchner.[7a]

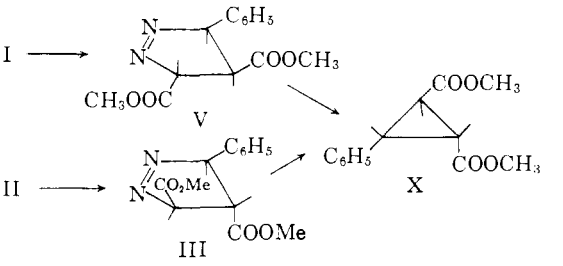
The infrared spectra of the decomposition products of both I and II showed the presence of the *trans*-cyclopropane X and an olefin, but no detectable sign of the *cis* isomer. In an earlier communication[10] an upper limit of 10% was estimated for the amount of *cis* actually present. Since that time, we have found by gas chromatography of these mixtures that a small amount of the *cis* isomer is indeed present. Unfortunately, a quantitative determination of the amount was not possible due to the interference of an unidentified foreign substance. However, the gas chromatography did verify the conclusion that the *trans* cyclopropane X is the predominant isomer resulting from the thermal decomposition of both I and II.

On the other hand, the thermal decomposition of Buchner's pyrazoline VII gave a reaction mixture which, after reduction of the double bond, could be quantitatively separated by gas chromatography into its individual components. By this technique it was found that 69% of the cyclopropane product was the *cis* isomer VIII and 31% was the *trans*.

(9) E. Buchner, *Ann.*, **284**, 197 (1895).

(10) W. M. Jones, THIS JOURNAL, **80**, 6687 (1958).

As pointed out in an earlier communication,[10] one path which is compatible with these observations involves an initial tautomerization of the 2-pyrazoline to the thermodynamically favored 1-pyrazoline followed by stereospecific decomposition to the cyclopropane.[2,3] Thus, initial tautomerization of I and II to the ircorresponding thermodynamically favored 1-pyrazolines (adjacent groups *trans*) would lead to V and III, respectively. Stereospecific decomposition of either of these pyrazolines would lead to the observed predominant *trans*-cyclopropane X. On the other hand, if it is



V III

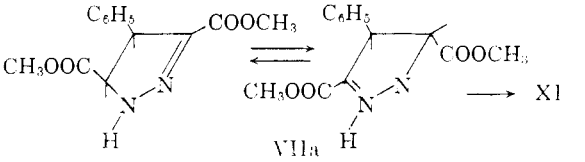
assumed that Buchner's pyrazoline has the geometrical configuration shown in VIIa, initial tautomerization would give mostly XI and stereospecific decomposition would then give the observed predominant product VIII.[11]

Experimental[12]

Phenyldiazomethane.—Phenyldiazomethane was prepared by the method of Staudinger and Gaule[13] employing red, rather than yellow, mercuric oxide. The crude mixture was found to contain 20–25% phenyldiazomethane. Since the primary contaminant was found to be benzaldehyde azine, a material which would not be expected to interfere with the desired reactions, the unstable mixture was used without attempting to purify it further.

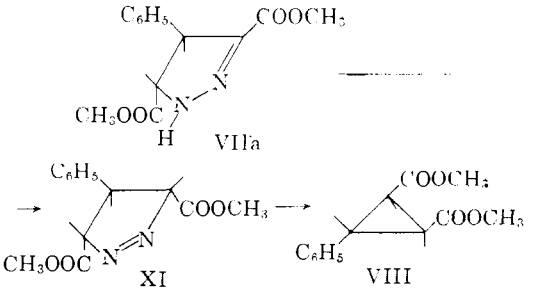
3,4-Dicarbomethoxy-5-phenyl-2-pyrazolines (I and II).—In a typical run, 1.0 g. of dimethyl fumarate was dissolved in 50 ml. of anhydrous ether. The solution was cooled in an ice-bath and 4.5 ml. of crude phenyldiazomethane was added. The mixture was cooled overnight, during which

(11) Even if Buchner's pyrazoline has the other geometrical configuration it could still decompose to the observed product by the same path. Thus, if the decomposition proceeds by a rapid tautomeric equilibrium followed by a relatively slow loss of nitrogen, the thermodynamically favored 1-pyrazoline (XI) would still obtain.



VIIa

This possibility is being investigated.



VIIa XI VIII

(12) All melting points are uncorrected. Microanalyses were done by Drs. G. Weiler and S. B. Straus, of 164 Banbury Rd., Oxford, England.

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

interval a white solid separated. Filtration followed by washing with ether yielded 0.66 g. (36%) of colorless needles, m.p. 130–132° (I). Recrystallization from methanol failed to appreciably affect the melting point; significant infrared absorptions: 3.01, 5.74, 5.83 and 6.38 μ.

Anal. Calcd. for $C_{13}H_{14}N_2O_4$: C, 59.53; H, 5.38; N, 10.69. Found: C, 59.74; H, 5.38; N, 10.75.

The filtrate, after the removal of I, still had a slightly red color, thus indicating the presence of an excess of phenyldiazomethane. When this filtrate was evaporated to dryness, a yellow oil (II) remained. Attempts to crystallize this oil were futile, yielding only small amounts of benzaldehyde azine. The infrared spectrum of this oil indicated the presence of benzaldehyde azine and a pyrazoline; significant infrared absorption: 2.98 (N–H), 5.75 (unconjugated ester), 5.85 (conjugated ester) and 6.43 μ (carbon–nitrogen double bond).[14,15] In the fingerprint region, the spectrum of the oil was found to be quite different from that of I.

Reaction of Phenyldiazomethane with Dimethyl Maleate.—The conditions employed for the reaction with dimethyl fumarate were exactly reproduced. After the ethereal solution had remained overnight in the refrigerator, the solution was still red and no solid had separated. The solution was allowed to remain at this temperature until most of the color had disappeared. (After two weeks, no further change was observed.) The light pink reaction mixture then was evaporated to dryness *in vacuo* to give a very viscous light yellow oil. The infrared spectrum of this oil was identical with the spectrum of the oil recovered from the reaction of phenyldiazomethane with dimethyl fumarate.

Decomposition of I.—A sample of 0.45 g. of I was heated at 220° until gas evolution had ceased. The mixture was then cooled to 160° and sublimed at 30 mm.[16] to give 0.32 g. of a colorless oily solid. The infrared spectrum of this material in the fingerprint region showed that there was no detectable quantity of the *cis*-cyclopropane VIII. Recrystallization from hexane gave 0.18 g. of pure X, m.p. 82–83°; significant infrared absorptions: 5.80; no absorption between 6.0 and 6.4 μ.

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found: C, 66.59; H, 5.85.

The hexane filtrate was evaporated to dryness to give a viscous, colorless oil (strong absorption at 6.20 μ indicative of an olefin; this was confirmed with the usual chemical tests).

The colorless oily solid was also analyzed by gas chromatography using a 12-ft. column of 60–80 mesh commercial detergent[17] in a Perkin–Elmer model 154-B vapor fractometer at 230° at an internal pressure of 30 p.s.i. and a recorder range of 1. Under these conditions, and injecting chloroform solutions containing about 2–5 mg. of known mixtures, the *trans* and *cis* isomeric cyclopropanes were cleanly separated, showing retention times of 10.1 and 12.6 minutes respectively. Unfortunately, there was some unidentified contaminant present in the crude reaction mixture which had a retention time between the two isomeric cyclopropanes and prevented resolution of the *cis*-cyclopropane peak. Thus, although the *trans* isomer X was clearly the predominant product it was not possible to determine accurately the percentage of *cis* isomer present. Reduction of the crude reaction mixture made virtually no difference in the retention time of this contaminant.

Decomposition of II.—The light yellow oil from the reaction of 1.0 g. of dimethyl maleate with phenyldiazomethane was distilled at 120 mm. in an oil-bath at 280°. A light yellow oil distilled over a large temperature range. A small portion of this oil was analyzed by gas chromatography and found to give a chromatogram which, in the 8–15 minute region, was virtually identical with that reported above for the chromatography of reaction product resulting from the decomposition of I. There was observed one other peak with a retention time of 24 minutes which presumably resulted from benzaldehyde azine. The remainder of the light yellow oil was dissolved in hot hexane and cooled at room temperature overnight. The benzaldehyde azine which recrystallized was removed by filtration. The filtrate was cooled at 0° and filtered to give 1.03 g. of light yellow solid, m.p. 69–79°; infrared showed absorptions characteristic of X and a little benzaldehyde azine. There was no detectable quantity of the *cis* isomer VIII. Recrystallization from hexane gave pure Xa, m.p. 82–83°. The filtrate was evaporated to dryness to give 0.4 g. of a yellow, uncrystallizable oil. Infrared showed absorptions at 5.78 and 6.15 μ.

Hydrolysis of X.—The *trans*-cyclopropane X was hydrolyzed by allowing it to stand in methanolic potassium hydroxide at room temperature for two or three days. The resulting mixture was worked up in the usual way. The acid was fairly soluble in water and therefore was isolated by extraction with ether. Recrystallization from a small amount of water gave pure material, m.p. 173.5–174°.

Anal. Calcd. for $C_{11}H_{10}O_4$: C, 64.17; H, 4.89. Found: C, 64.13; H, 4.87.

A small amount of the di-acid was converted to its dimethyl ester with diazomethane. Its melting point and mixed melting point with pure X proved that no isomerization had occurred during the hydrolysis. All attempts to close the di-acid to the anhydride failed. For example, upon heating the acid at 200–230° and 30 mm. in a sublimation apparatus, only unchanged acid sublimed out; m.p. 173–174°, mixed with pure acid, no depression.

A mixture of the pure acid from X with the acid from VIII (m.p. 172–173.5°, reported[7,8] 175°) exhibited a melting range of 139–156°.

Resolution of *trans*-3-Phenylcyclopropane-1,2-dicarboxylic Acid.—To a solution of 0.47 g. of the acid in 3 ml. of acetone was added 1.06 g. of brucine. The solution was warmed until solution was complete. Cooling overnight yielded a negligible amount of solid material. However, it was found that upon the addition of more acetone, a solid did separate. A total of 15 ml. of acetone was added and the mixture allowed to remain in the ice-box for three days. Filtration yielded 0.725 g. of white solid. No attempt was made to purify this further.

Decomposition with dilute acid followed by ether extraction, drying and removal of the ether gave a sample of impure acid which was converted directly to the dimethyl ester with diazomethane. The ester then was purified by recrystallization from hexane, m.p. 78–80°, $[\alpha]^{20}D$ −20.4°, in methanol. The filtrate from the removal of the solid salt was taken to dryness and worked up in the same manner to give *d*-dimethyl ester, m.p. 76–78°, $[\alpha]^{20}D$ 42.3°.

Decomposition of 4-Phenyl-3,5-dicarbomethoxy-2-pyrazoline.—This pyrazoline was prepared by the method of Buchner and Dessauer.[8a] Its decomposition was affected by distillation at 27 mm. to give a colorless oil, b.p. 204–208°. The infrared spectrum of this oil was rather difficult to interpret, presumably because of a masking effect of the olefinic contaminant. The fingerprint region did indicate the presence of the *cis*-cyclopropane VIII, but it was not possible to arrive at any real conclusions about the presence of the *trans* isomer X. Gas chromatography therefore was employed to determine the ratio of *cis*- to *trans*-cyclopropanes. Using the techniques described above, it was found that resolution of all peaks was not possible due to interference of the olefin (retention time of approximately 11.5 minutes). However, when the crude reaction mixture was reduced (Pt, EtOAc), all peaks were satisfactorily resolved and it was found that 69 ± 2% of the cyclopropane product was the *cis* isomer VIII and 31 ± 2% was the *trans* product X.

GAINESVILLE, FLA.

(14) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 213, 153, 232.

(15) The infrared spectra of I, II and VII in KBr (II as the liquid) showed absorptions around 2.90–2.95 mμ (shoulders) with very strong absorptions at 3.06–3.07 mμ. In dilute chloroform, however, they each exhibited a single absorption at the expected[14] wave length.

(16) These conditions were independently shown to be sufficient to remove both VIII and X.

(17) This material was graciously donated by the Procter and Gamble Co. of Cincinnati, Ohio.