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

# Pyrazolines. IV. On the Mechanism of Decomposition and Conformational Analyses of 2-Pyrazolines[1]

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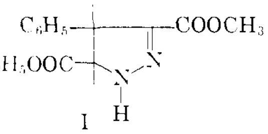
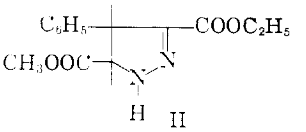
The two isomeric mixed methyl, ethyl diesters of 4-phenyl-2-pyrazoline-3,5-dicarboxylic acid have been synthesized and subjected to thermal decomposition. Upon partial decomposition, no detectable isomerization of either isomer to the other was observed, thus indicating that the first step in the thermal decomposition is slow. Geometrical configurations were assigned to the two esters on the basis of their decomposition products.

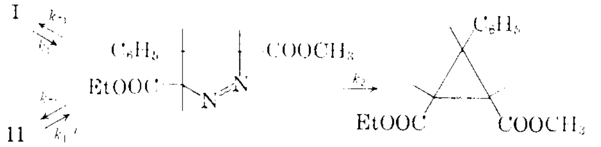
In two recent papers[1,2] evidence was presented which indicated that the thermal decomposition of 2-pyrazolines to cyclopropanes probably proceeds by initial tautomerization to the corresponding 1-pyrazoline followed by expulsion of nitrogen.

It was naturally of interest to determine the relative rates of the two steps suggested for this decomposition. A readily available pair of isomers which appeared especially suitable to a study of this type were the two isomeric mixed methyl, ethyl esters of 4-phenyl-2-pyrazoline-3,5-dicarboxylic acid.[3] From the reactions of methyl diazoacetate with ethyl cinnamate and ethyl diazoacetate with methyl cinnamate, Buchner and his co-workers[3] isolated two compounds to which they assigned structures I and II, respectively. Although they were not able to demonstrate conclusively the positions of the ester methyl and ethyl groups,[4] they did present conclusive evidence for the remaining gross structures.



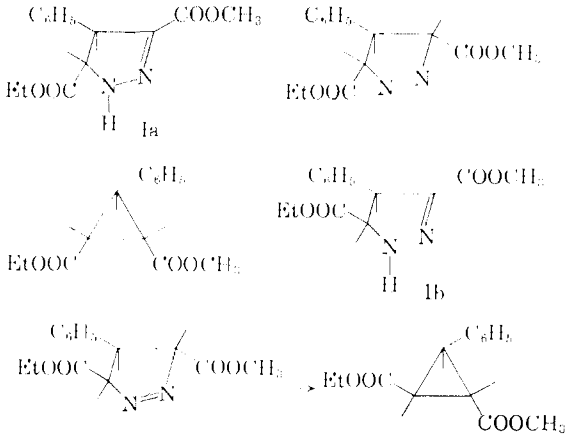


In view of the proposed reaction path for the decomposition of 2-pyrazolines it is apparent that I and II would lead to identical 1-pyrazolines as intermediates.



Consequently, a reaction path involving tautomerization followed by expulsion of nitrogen in which $k_{-1}$ is greater than $k_2$ should lead, upon partial decomposition (approximately one-half) of either pure ester, to an equilibrium mixture of the two isomeric starting esters. On the other hand, a reaction path involving slow tautomerization followed by nitrogen expulsion which is more rapid than reversal to the starting material ($k_2 > k_{-1}$) should lead, upon partial decomposition, to a nonequilibrium mixture of the two starting esters. The latter was indeed found to be the case. When either I or II was decomposed until approximately one-half the calculated nitrogen had been expelled, *only* the starting ester was isolated from the mixture (85 and 76% recovery of the calculated unreacted crude esters I and II, respectively) thus indicating little, if any, equilibration. It therefore became apparent that the tautomerization in the decomposition of these 2-pyrazolines is the slow step.

On the basis of this evidence and the previously demonstrated[1,2] notion that "the geometrical configuration of the primary cyclopropane resulting from the decomposition of a 2-pyrazoline is determined by the relative thermodynamic stabilities of the intermediate 1-pyrazolines," it became apparent at this point that the geometrical configurations of the two solid pyrazolines could be derived from an examination of the stereochemical consequences of their decomposition; *e.g.*, Ia would lead to predominately the di-ester of the *cis*-cyclopropanedicarboxylic acid whereas I-b would lead to predominately the *trans* isomer.



Samples of each solid (I and II) were therefore decomposed at 230°. The resulting products were then hydrolyzed to the di-acids and the acids converted to the dimethyl esters with diazomethane. The olefinic by-products present in the mixtures were then reduced to the saturated materials. This yielded reaction mixtures which could be analyzed readily by gas chromatography. It was found that the two solids gave essentially identical ratios of the *cis*- and *trans*-esters (I and II gave 65 ± 2% and 62 ± 2% of the *cis* isomer, respectively).

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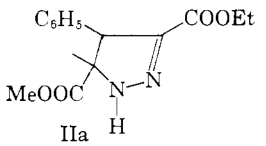
[1] For the previous paper, see W. M. Jones, THIS JOURNAL, **81**, 5153 (1959).

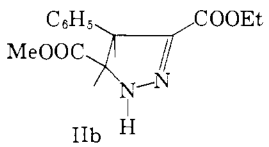
[2] W. M. Jones, *ibid.*, **80**, 6687 (1958).

[3] E. Buchner and H. Dessauer, *Ber.*, **26**, 259 (1893); E. Buchner and C. von der Heide, *ibid.*, **35**, 31 (1902).

[4] Employing nuclear magnetic resonance studies, the two compounds have, indeed, been shown to have the structures assigned by Buchner and Dessauer.[3] This investigation will be reported in detail in a forthcoming publication.

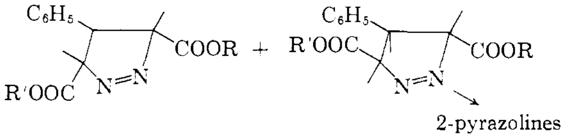
This predominance of the *cis*-cyclopropane led us to assign the same geometrical configurations to both I and II; Ia and IIa, respectively.


IIa


IIb

In view of the method of preparation of these 2-pyrazolines[3] as well as the generally assumed reaction path[5] it was apparent that Ia and IIa should not be the sole geometrical isomers present in the crude reaction mixtures. In an attempt to detect the presence of Ib and IIb the crude filtrates resulting from the removal of Ia and IIa from their respective reaction mixtures were examined further. Following thorough washing with hexane to remove unreacted starting materials, the filtrates were decomposed and worked up as described above. The resulting mixtures were then analyzed and found to contain predominately the *trans*-cyclopropane; 69 ± 2% and 59 ± 2% of the cyclopropane products from the decomposition of the filtrate from Ia and IIa, respectively, were the *trans* isomer. It was therefore apparent that the filtrates were rich in Ib and IIb. These results also further confirmed the suggestion that the first step in the decomposition path is the slow one.

$C_6H_5CH{=}CH{-}COOR + N_2CHCOOR' \longrightarrow$



## Experimental

**Mixed Methyl, Ethyl Esters of 4-Phenyl-2-pyrazoline-3,5-dicarboxylic Acid.**—The two mixed methyl, ethyl esters were prepared by the method of Buchner and co-workers[3]; I, m.p. 106–106.5°, reported m.p. 107°; II, m.p. 75–76°, reported m.p. 76°.

**Limited Decomposition of I.**—A sample of the pure pyrazoline I (0.378 g.) was heated at 230° until 44% of the calculated nitrogen had been evolved. The residue was cooled to room temperature and dissolved in ether. Cooling in ice gave 0.091 g. of a white compound, m.p. 103–105°. Evaporation of the filtrate to near dryness followed by cooling yielded a second crop of white crystals; 0.090 g., m.p. 92–97°. Recrystallization of each sample from ether gave pure I, m.p. 105–106°; admixture with starting material, m.p. 106–107°. The infrared spectra of both crude samples were virtually identical with the spectrum of the starting material.[6] The total yield corresponds to 85% recovery of the unreacted starting ester.

**Limited Decomposition of II.**—A sample of the more soluble, lower melting pyrazoline II (0.339 g.) was heated at 230° until 38% of the calculated nitrogen had been evolved. The sample was then cooled and dissolved in a small quantity of ether. Cooling yielded no solid. Seeding with pure I followed by cooling also yielded no solid material. Seeding with pure II gave 0.163 g. of white solid, m.p. 69–71°. Recrystallization from a little ether yielded pure II, m.p. 74–75°; admixture with pure starting material, m.p. 74–76°. The infrared spectrum of the crude material was virtually superimposable with that of the pure starting material.[6] This yield corresponds to 77% recovery of the unreacted starting ester.

**Total Decomposition of I.**—A sample of pure I (4.0 g.) was heated at 230–235° for 30 minutes. The residue was then distilled at 4 mm. (all material that distilled below 200° was collected) to give a colorless oil.

A sample of the distillate was then hydrolyzed by allowing it to remain for 2 days at room temperature in methanolic potassium hydroxide.[7] The resulting mixture was worked up in the usual manner to give a mixture of acids which was then treated with excess diazomethane in ether to give a mixture of dimethyl esters. After removal of the solvent, the residue was dissolved in ethyl acetate and reduced with hydrogen employing platinum oxide as the catalyst. After removal of the catalyst and the solvent, the residue was analyzed by gas chromatography using the procedure previously described.[8] Using integrated intensities, it was found that 65 ± 2% of the cyclopropane product was the *cis* isomer (the two carboalkoxy groups *cis*) and 35 ± 2% was the *trans*. In addition to the two peaks corresponding to the *cis* and *trans* isomers (retention times of 12.6 and 10.1 minutes, respectively), there was observed a small peak with a retention time of about 8.5 minutes. This presumably resulted from the saturated ester.

**Total Decomposition of II.**—A sample of pure II was decomposed and worked up exactly the same way as described above for I. Employing gas chromatography, it was found that 62 ± 2% of the cyclopropane product was the *cis* isomer and 38 ± 2% was the *trans*.

**Decomposition of the Residual Oil from the Preparation of I.**—After Compound I had been removed by filtration from the reaction of ethyl cinnamate with methyl diazoacetate, the filtrate was washed thoroughly with hexane. The residual viscous oil was then decomposed and worked up exactly the same way as described above for I. Analyses showed that 31 ± 2% of the cyclopropane product was the *cis* isomer and 69 ± 2% was the *trans*.

**Decomposition of the Residual Oil from the Preparation of II.**—After crystallization of II from the reaction of methyl cinnamate with ethyl diazoacetate was complete, the product was removed by filtration. The filtrate was then washed thoroughly with hexane and the residual viscous oil decomposed and worked up as described above. Analyses of the final mixture showed that 41 ± 2% of the cyclopropane product was the *cis* isomer and 59 ± 2% was the *trans*.

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[5] T. L. Jacobs in R. C. Elderfield, "Heterocyclic Compounds," John Wiley and Sons, Inc., New York, N. Y., Vol. 5, 1957, pp. 80–83.

[6] The spectra of the crude products resulting from partial decomposition of both I and II were compared at five different wave lengths, three at which I exhibits absorptions which are absent in II (6.50, 7.42 and 12.63 μ) and two at which II exhibits absorptions which are absent in I (7.26 and 7.50 μ). Due to either overlapping of absorptions or absorptions of low intensity, it was not possible to demonstrate conclusively the total absence of the other isomer; however, it was certainly conclusive that one isomer predominated over the other. From known mixtures, a safe estimate would be a maximum of 10% of the other isomer in even the crudest product.

[7] These conditions have been previously demonstrated to be so mild that neither ring opening nor isomerization of the cyclopropane occur.[1]

[8] W. M. Jones, THIS JOURNAL, **81**, 3776 (1959).