Equimolar amounts of 2-bromo-4-nitrophenylhydrazine[23] and cyclohexanone were mixed for 5 min. in warm ethanol to form the cyclohexanone arylhydrazone; the resulting solution was added to an excess of 1:9 aqueous sulfuric acid. The acid mixture was heated under reflux for 6 hr. and then cooled. The precipitated cyclization product was recrystallized from ethanol to give yellow plates of XI, m.p. 227–234°. The tetrahydro compound was dissolved in sulfur-free xylene with the calculated amount of chloranil and heated under reflux until a test for unchanged chloranil was negative (24–48 hr. were required). The solvent and quinol were removed from the product, which was recrystallized from ethanol to yield yellow plates, m.p. 247–248° (XI).

Anal. Calcd. for $C_{12}H_7BrN_2O_2$(VIIb): C, 49.51; H, 2.42. Calcd. for $C_{12}H_{11}BrN_2O_2$(XI): C, 48.81; H, 3.73. Found: (run 1) C, 48.20; H, 3.83; (run 2) C, 48.16; H, 3.73; (run 3) C, 48.89; H, 3.73.

B. *Pyrolysis of* XII.[22] The carbazole was prepared by adding 1.5 g. of XII in small portions to 150 ml. of sulfuric acid-washed, distilled kerosene heated to 175–185°. Gas was evolved throughout the addition; after two additional min. at 175–185° the mixture was cooled and the olive-green solid which precipitated (1.05 g., 76%) was collected and recrystallized three times from ethanol. After sublimation the solid melted at 210–211°. Principal infrared absorption: 3350, 1600, 1520 and 1330, 1460 and 1380, 890, 750 cm.$^{-1}$

Anal. Calcd. for $C_{12}H_7BrN_2O_2$: C, 49.51; H, 2.42; N, 9.63. Found: C, 49.81, 50.01; H, 2.52, 2.48; N, 9.63.

(23) W. Davies, *J. Chem. Soc.*, 715 (1922).

Acknowledgment. We wish to thank Miss Jane Swan and Mrs. Kathryn Baylouney for the microanalyses, Mr. W. R. Feairheller, Jr., for his assistance in obtaining infrared spectra, and Professor E. R. Lippincott for his help in interpreting the spectra.

COLLEGE PARK, MD.

Notes

Pyrazolines. VI. The Stereochemistry of the Thermal Decomposition of 5,5-Diphenyl-1-pyrazolines[1]

W. M. JONES AND WUN-TEN TAI

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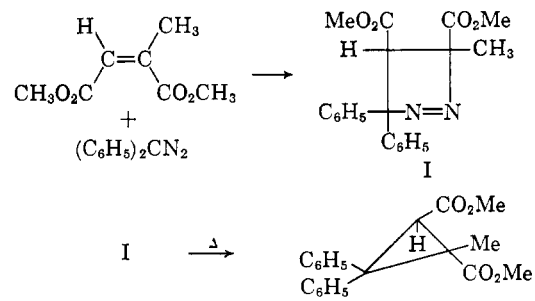
For some time there has existed the idea that the thermal decomposition of 1-pyrazolines to their corresponding cyclopropanes occurs with a real degree of stereoselectivity.[2] However, as early as 1943, van Alphen[3] reported an observation which, when it came to our attention, caused us to doubt that the stereoselectivity of these decompositions was as general as had been presumed.[4]

Van Alphen found that the decomposition of the 1-pyrazoline resulting from the reaction diphenyldiazomethane with dimethyl citraconate gave a cyclopropane product in which the two carbomethoxy are *trans*. From this observation, the



obvious question requiring answer was whether this loss of stereospecificity occurred during the formation of the 1-pyrazoline or during its conversion to the cyclopropane. To report the results of an examination of this problem is the purpose of this note.

As van Alphen[3] reported a stable 1-pyrazoline from the reaction of dimethyl citraconate with diphenyldiazomethane, the obvious extension of his work which needed examination was the corresponding reaction with dimethyl mesaconate. This reaction was therefore effected and it was found that an excellent yield of a 1-pyrazoline was isolated. A sample of the material reported by van Alphen was then synthesized and it was found that the two 1-pyrazolines were, indeed, quite different. As these materials were quite stable to recrystallization conditions and neither showed

(1) For the previous paper, see W. S. Brey, Jr., and W. M. Jones, *J. Org. Chem.*, **26**, 1912 (1961). Based upon a thesis submitted by W. T. Tai in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

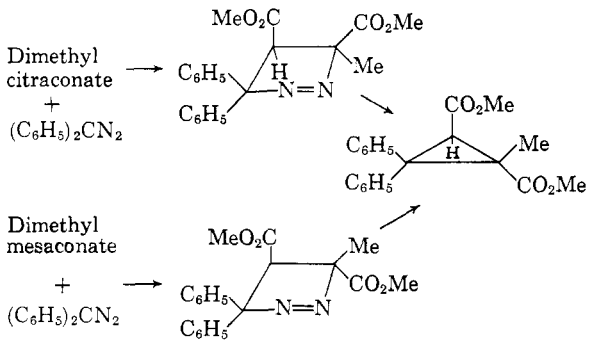
(2) For example, see T. L. Jacobs in R. C. Elderfield, *Heterocyclic Compounds*, Wiley, New York, Vol. 5, 1957, p. 80; and the previous papers in this series.

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

(4) As we made this observation and after this work was begun, Rinehart and van Auken (see the Abstracts of Papers given at the American Chemical Society meeting in New York, September 11–16, 1960, p. 96P) reported an examination of the thermal decomposition of the two pyrazolines resulting from the reaction of diazomethane with methyl tiglate and methyl angelate. They found that these decompositions were nonstereospecific. This is most surprising in view of the similarity between their system and the two systems examined by von Auwers and Konig [K. von Auwers and F. Konig, *Ann.*, **496**, 252 (1932)].

any trace of an N—H absorption in their infrared spectra, there can be little doubt that the double bond is between the two nitrogens in each isomer. Furthermore, although the two carbomethoxy groups in the two isomers have most likely retained the geometrical relationship of their precursor diesters, the fact that they are geometrical isomers is sufficient for the point in which we were primarily interested—the stereochemistry of their decomposition to cyclopropanes.

The two 1-pyrazolines were then decomposed slightly above their melting points and it was found that both gave, within experimental error, the same reaction mixture. Furthermore, the product was, so far as we could detect, exclusively the dimethyl ester of 3,3-diphenyl-1-methylcyclopropane-1,2-dicarboxylic acid in which the two carboalkoxy groups are trans.[3]



Thus, in the case examined by van Alphen, formation of the 5,5-diphenyl-1-pyrazoline is apparently stereospecific, and the loss of stereospecificity in this reaction series actually occurs during the decomposition step.

EXPERIMENTAL[5]

Preparation of 3-methyl-cis-3,4-dicarbomethoxy-5,5-diphenyl-1-pyrazoline. To 10 g. (0.0556 moles) of dimethyl citraconate[6] was added 10.8 g. (0.0556 moles) of crystalline diphenyldiazomethane[7] obtained from the oxidation of benzophenone hydrazone. The resultant solution was allowed to remain at room temperature with occasional shaking for one week. The slightly pink mixture was then filtered and the resulting solid was washed with ether. Three recrystallizations from methyl alcohol gave 8.4 g. (43.0% yield) of colorless solid, m.p. 124° dec., reported m.p. 123° dec. The infrared spectrum showed no absorption in the 3-μ region.

Anal. Calcd. for $C_{20}H_{20}N_2O_4$: C, 68.18; H, 5.68; N, 7.95. Found: C, 67.81; H, 5.95; N, 8.08.

Decomposition of 3-Methyl-cis-3,4-dicarbomethoxy-5,5-diphenyl-1-pyrazoline. A sample (0.237 g., 0.663 mole) of the pyrazoline was heated at 125° (just above its melting point) until nitrogen evolution had ceased. The decomposition product, a white solid, weighed 0.217 g. (equivalent to 0.670 mole of the corresponding cyclopropane). Recrystallization of the product from ethyl alcohol gave colorless needles, m.p. 114–115° (reported m.p. 115°), which did not decolorize potassium permanganate solution. The infrared spectrum of the crude material and the recrystallized material were virtually identical.

Preparation of 3-methyl-trans-3,4-dicarbomethoxy-5,5-diphenyl-1-pyrazoline. To 10 g. (0.0556 mole) of dimethyl mesaconate was added 10.8 g. (0.0556 mole) of diphenyldiazomethane. The resultant solution was mixed thoroughly and allowed to remain at room temperature for 1 week. The resulting greenish solid was washed well with ether and recrystallized from methanol to yield 9.1 g. (46.4%) of white crystals; m.p. 104° dec. The infrared spectrum showed no absorption in the 3-μ region.

Anal. Calcd. for $C_{20}H_{20}N_2O_4$: C, 68.18; H, 5.68; N, 7.95. Found: C, 68.28; H, 5.71; N, 8.22.

Decomposition of 3-methyl-trans-3,4-decarbomethoxy-5,5-diphenyl-1-pyrazoline. A sample of 0.192 g. (0.546 mmole) of of the 1-pyrazoline was heated above its melting point until nitrogen evolution had ceased. The decomposition product, a white solid, weighed 0.177 g. (corresponding to 0.545 mmole of the cyclopropane). Recrystallization of the product from methyl alcohol yielded colorless, crystalline needles, m.p. 115°. Admixture with the decomposition product from 3-methyl-cis-3,4-dicarbomethoxy-5,5-diphenyl-1-pyrazoline showed no depression in melting point. Furthermore, the infrared spectra of the two crude reaction products were identical and the infrared spectrum of the crude reaction product and the recrystallized product were identical.

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF FLORIDA
GAINESVILLE, FLA.

(5) Melting points are uncorrected.
(6) W. H. Perkin, *Ber.*, **14**, 2541 (1881).
(7) L. I. Smith and K. L. Howard, *Org. Syntheses*, **24**, 53 (1944).

Intramolecular Hydrogen Abstraction in a Primary Alkoxy Radical

E. L. JENNER

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It has been established that the Hoffman-Löffler-Freytag reaction, in which an *N*-haloamine is converted to the corresponding pyrrolidine, is a free-radical chain process depending on the intramolecular abstraction of a δ-hydrogen atom by a nitrogen free radical.[1] Recently a similar intramolecular hydrogen abstraction has been observed in the decomposition of long-chain tertiary hypochlorites.[2–5] It was reported that no analogous intramolecular reaction was observed

(1) E. J. Corey and W. R. Hertler, *J. Am. Chem. Soc.*, **82**, 1657 (1960).
(2) F. D. Greene, M. L. Savitz, H. H. Lau, D. Osterholtz, and W. M. Smith, *J. Am. Chem. Soc.*, **83**, 2196 (1961).
(3) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **83**, 2207 (1961).
(4) M. Akhtar and D. H. R. Barton, *J. Am. Chem. Soc.*, **83**, 2213 (1961).
(5) J. S. Mill and V. Petrov, *Chem. & Ind.* (London), 946 (1961).