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

Pyrazolines. II. The Stereochemical Consequences of High Temperature Reactions of Diazomethanes with Olefins and α,β-Unsaturated Esters[1]

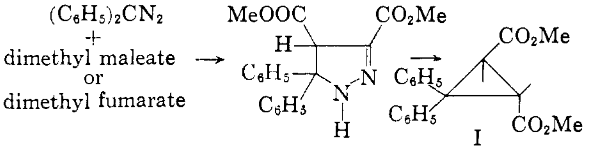
BY W. M. JONES

RECEIVED NOVEMBER 22, 1958

The stereochemical consequences of the high temperature (180–200°) reactions of diphenyldiazomethane and phenyldiazomethane with dimethyl maleate and dimethyl fumarate have been examined. Neither reagent showed any stereospecificity in its reactions. On the other hand, under identical conditions the reaction of ethyl diazoacetate with *cis*- and *trans*-stilbene was found to be stereospecific. Reasonable reaction paths which are consistent with these observations are discussed.

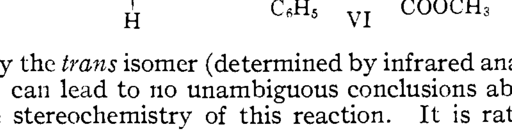
The stereochemical consequences of the low temperature reactions of diazomethanes with olefins and α,β-unsaturated carbonyl compounds have been investigated under a variety of conditions[2,3] and several reaction paths have been proposed to explain the results.[1,3,4] On the other hand, the high temperature reactions (180–200°) of this type which are accompanied by instantaneous loss of nitrogen have received no comparable examination. We therefore felt that it would be interesting to examine the stereochemical consequences of the reactions of various diazomethanes with both of these types of compounds.

Reactions with Dimethyl Maleate and Dimethyl Fumarate.—The first reaction which we elected to examine was that of diphenyldiazomethane with dimethyl maleate and dimethyl fumarate. Our selection hinged on the fact that van Alphen[5] had previously investigated the reaction of dimethyl fumarate and maleate with diphenyldiazomethane at low temperature and found them to both give the same 2-pyrazoline which, upon thermal decomposition, gave a high yield of the single cyclopropane with the carbomethoxy group *trans* (I).



We found that, at temperatures over 180°, diphenyldiazomethane reacted smoothly with both dimethyl maleate and dimethyl fumarate with essentially instantaneous loss of nitrogen and the diphenyldiazomethane color. Since one complicating factor was the possibility that, under the conditions of the reaction, dimethyl maleate might isomerize to dimethyl fumarate, the reactions were run with an excess of the starting ester and the product analyzed for dimethyl maleate, dimethyl fumarate and cyclopropane products. The amount and nature of the unreacted olefinic esters were determined by gas chromatographic analysis using 4-*t*-butylcyclohexanone as an internal standard. The approximate amount and nature of the cyclopropane products of the reactions were determined by elution chromatography over acid-washed alumina. From the reaction of the diazomethane with dimethyl fumarate, 94% of the starting ester was accounted for, 78% as unreacted dimethyl fumarate and 16% as the pure cyclopropane (71% yield based on reacted dimethyl fumarate). Only the *trans*-cyclopropane (I) was isolated, no trace of the *cis* isomer being found. From the reaction of diphenyldiazomethane with dimethyl maleate under the same conditions and analyzed in the same way, 64% of unreacted dimethyl maleate and less than 1% of dimethyl fumarate were found. Elution chromatography of the reaction mixture gave a 70% yield (based on reacted ester; accounting for 25% of the starting ester) of the *trans*-cyclopropane, thus accounting for 91% of the starting ester. In addition, the elution chromatography gave some tetraphenylethylene, benzophenone azine, about 11% (based on reacted ester) of the 2-pyrazoline and, finally, a little very viscous oil which gave positive test for unsaturation. In no fraction were we able to detect any of the *cis* isomer II. To eliminate the possibility that the *cis*-cyclopropane had been formed and had isomerized during the heating or during the chromatography, pure samples were subjected to each of these conditions and recovered unchanged. Thus, the high temperature reaction of diphenyldiazomethane with dimethyl maleate, is, at most, 20% stereospecific and probably much less.

The reactions of phenyldiazomethane with dimethyl maleate and dimethyl fumarate were also examined. Unfortunately the reaction of phenyldiazomethane with dimethyl maleate at high temperature gave results which were clouded by extensive isomerization of dimethyl maleate to dimethyl fumarate. Since it has been demonstrated[1] that the thermal decomposition of the dimethyl ester of 5-phenyl-2-pyrazoline-3,4-dicarboxylic acid (either geometrical isomer) yields only the cyclopropane product with the carbomethoxy groups *trans* (VI), the observation that, at high temperature, both dimethyl fumarate and dimethyl maleate gave only the *trans* isomer (determined by infrared analysis) can lead to no unambiguous conclusions about the stereochemistry of this reaction. It is rather curious that the phenyldiazomethane mixtures cata-



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[1] For the previous paper, see W. M. Jones, THIS JOURNAL, **80**, 6687 (1958).

[2] For an excellent review of this subject, see T. L. Jacobs in R. C. Elderfield, "Heterocyclic Compounds," John Wiley and Sons, Inc., New York, N. Y., Vol. 5, 1957, Chapter 2.

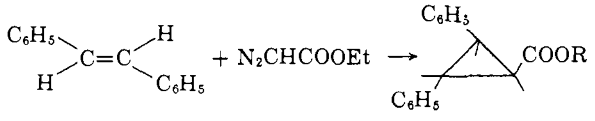
[3] (a) W. von E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, THIS JOURNAL, **78**, 3224 (1956); (b) W. von E. Doering and P. La Flemme, *ibid.*, **78**, 5447 (1956); (c) H. M. Frey, *ibid.*, **80**, 5005 (1958).

[4] Reference **2**, p. 82.

[5] J. van Alphen, *Rec. trav. chim.*, **62**, 210 (1943).

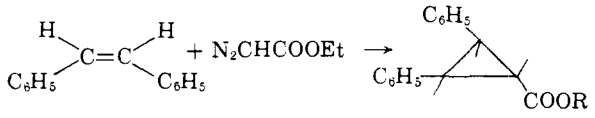
lyzed the isomerization of dimethyl maleate to dimethyl fumarate; however, here again, no real conclusions can be drawn since the phenyldiazomethane could not be purified and was therefore certainly contaminated with foreign substances.

Reactions with *cis*- and *trans*-Stilbene.—Since the reaction of a diazomethane with an olefin might well proceed by a path different from a similar reaction with an α,β-unsaturated carbonyl compound, the reaction of ethyl diazoacetate with *cis*- and *trans*-stilbene was investigated. These reactions were effected between 180 and 200° and, as reported by Burger and co-workers[6] for the same reaction at somewhat lower temperatures, only one cyclopropane product was isolated from each reaction. Thus, *trans*-stilbene was found to give a 33% yield (based on non-recovered stilbene) of the *trans*-cyclopropane (VIIa) and no isolatable quantity of the *cis* isomer.



VIIa, R = H
b, R = Et

cis-Stilbene, on the other hand, gave an 18% yield of the *cis*-cyclopropane (VIII) (isolated as the amide) and no isolatable quantity of the *trans* isomer.

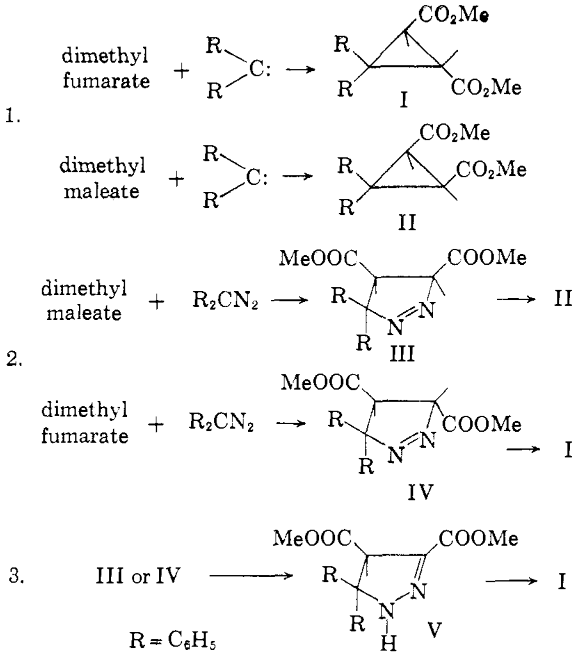


VIIIa, R = H
b, R = Et

Isolation of unreacted stilbenes from each reaction indicated that there had been no detectable amount of isomerization of either olefin.

Discussion.—Previous investigations of cyclopropane formation from olefins and diazomethanes and their proposed reaction paths[1-3,5,7] suggest at least three likely possibilities for describing the over-all path of the high temperature reaction of diphenyldiazomethane with dimethyl maleate and dimethyl fumarate (Chart I).

CHART I



Of the three suggested paths, path 1 appears at once unlikely in view of the recently demonstrated electrophilic nature of carbenes[8] and the relatively non-nucleophilic nature of this type of double bond. Since carbene reactions have been demonstrated to be stereospecific[3,9] the lack of stereospecificity of the reaction of diphenyldiazomethane with dimethyl maleate and dimethyl fumarate would appear to verify exclusion of the carbene reaction as a reasonable path. However, in view of the fact that most of the investigations of the stereochemical consequences of carbene reactions with double bonds were conducted at room temperature or below, we felt that the stereospecificity of high temperature carbene reactions should be examined. The results of the high temperature reactions of ethyl diazoacetate with *cis*- and *trans*-stilbene[10] would indicate that, even at temperatures of 180–200°, the stereospecificity of carbene reactions is maintained. Path 1 is therefore a very unlikely possibility for the high temperature reaction of diphenyldiazomethane with dimethyl maleate and dimethyl fumarate.

Path 2 also apparently becomes untenable on the basis of the non-stereospecific nature of the reaction. However, of the previously demonstrated[7] two stereospecific steps in the proposed path, only the decomposition of the 1-pyrazoline was examined under conditions comparable to those employed in these experiments (the first step was conducted at 0°). Thus, two reasonable explanations for the stereochemical consequences of this reaction are: (a) some modification of path 2 which involves either a non-stereospecific first step or perhaps an intermediate which never actually closes to form the 1-pyrazoline[11] or (b) path 3 which involves a rapid tautomeric equilibrium between the 1- and 2-pyrazolines preceding loss of nitrogen. We are presently engaged in experiments which we hope will distinguish between these possibilities.

Experimental[12]

The Reaction of Diphenyldiazomethane with Dimethyl Fumarate.—Dimethyl fumarate (6.0 g.) was heated to 180° under dry nitrogen in an oil-bath. To this was added, dropwise, 4.1 g. of the diphenyldiazomethane residue (dried over Na_2SO_4) resulting from the oxidation of benzophenone

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[6] A. Burger, D. G. Markees, W. R. Nes and W. L. Yost, THIS JOURNAL, **71**, 3307 (1949).

[7] K. von Auwers and F. Konig, *Ann.*, **496**, 27, 252 (1932).

[8] W. von E. Doering and W. A. Henderson, Jr., THIS JOURNAL, **80**, 5274 (1958).

[9] P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956); P. S. Skell and A. Y. Garner, *ibid.*, **78**, 3409 (1956).

[10] Stereospecific reactions of ethyl diazoacetate with olefins are generally believed to proceed *via* the carbene (*e.g.*, see ref. 9). This appears especially reasonable in view of the nucleophilic nature of the normal olefinic double bond.

[11] W. G. Young, L. J. Andrews, S. L. Lindenbaum and S. J. Cristol, THIS JOURNAL, **66**, 810 (1944).

[12] Melting points are uncorrected. Microanalyses were done by Drs. G. Weiler and S. B. Strauss, of 164 Banbury Road, Oxford, England.

hydrazone.[13] The addition was effected at such a rate as to maintain a pot temperature of 180–190°. Nitrogen was evolved and the deep red color of the diphenyldiazomethane disappeared the instant it came into contact with the hot ester. The reaction mixture was then cooled and the solid and liquid which had collected in the condenser and Dry Ice trap were added to the mixture. This gave a total of 8.9 g. of orange residue. A 1.33-g. aliquot of the residue was then treated with 30 ml. of a 10% ether–pentane mixture. Filtration gave 0.255 g. of the pure *trans*-ester I, m.p. 174–174.5°. Recrystallization from methanol did not raise the melting point. *Anal.* Calcd. for $C_{19}H_{18}O_4$: C, 73.53; H, 5.81. Found: C, 73.25; H, 5.88.[14]

The filtrate was then chromatographed over 40 g. of alumina which had been washed with HCl, distilled water and finally dried at 140° for 24 hours. The chromatogram was developed with 10% ether–pentane mixture to give, in addition to dimethyl fumarate, 0.039 g. of tetraphenylethylene, 0.147 g. of benzophenone azine, 0.055 g. of I and some unidentifiable oil. Gas chromatographic analyses (see below) of the crude product showed it to contain 4.64 g. of unreacted dimethyl fumarate and no detectable amount (less than 1%) of dimethyl maleate.

The Reaction of Diphenyldiazomethane with Dimethyl Maleate.—In the same apparatus described for the reaction with dimethyl fumarate, 5.0 g. of dry dimethyl maleate was heated to 180° under nitrogen. To this was added, dropwise, 8.0 g. of dry diphenyldiazomethane. During the addition, again nitrogen evolution and loss of the diphenyldiazomethane color were virtually instantaneous. This gave 11.61 g. of an orange oil. Working up a 1.50-g. aliquot of this residue in the same manner described above gave, from the original ether–pentane mixture, 0.18 g. of I, m.p. 173–175°. Chromatography over acid-washed alumina gave unreacted dimethyl maleate; tetraphenylethylene; 0.061 g. of the 2-pyrazoline, m.p. 136–141° dec., reported[5] m.p. 142°; benzophenone azine; 0.17 g. of I; and, finally, 0.10 g. of unidentified unsaturated oil. In no cut during the chromatography was there any trace of the *cis*-ester II.[15] A sample of the crude reaction mixture was analyzed by gas chromatography. It was found that the crude reaction mixture contained 3.2 g. of dimethyl maleate and no detectable amount of dimethyl fumarate.

Except for a somewhat higher percentage of decomposition products and no 2-pyrazoline, virtually no difference was observed when this reaction was effected at 200–210°.

Reaction of Dimethyl Fumarate with Phenyldiazomethane.—To 4.0 g. of dimethyl fumarate heated under nitrogen to 190° in an oil-bath was added, dropwise, crude phenyldiazomethane mixture (from the oxidation of benzaldehyde hydrazone)[16] until 470 ml. of nitrogen had been evolved. Cooling to room temperature gave 8.47 g. of orange residue. Gas chromatographic analysis of a portion of this mixture showed it to contain 0.91 g. of dimethyl fumarate and no detectable quantity of dimethyl maleate. Sublimation of a weighed portion (0.61 g.) of the crude reaction mixture was effected at 160° and 30 mm., conditions which had been independently demonstrated to effectively remove both the *cis*-[17] and the *trans*-cyclopropane esters. Infrared analysis of the sublimate (0.46 g.) showed it to contain no detectable (less than 10%) quantity of the *cis* isomer and quite an appreciable quantity of the *trans* isomer VI. Recrystallization from hexane gave 0.128 g. of VI contaminated with a little benzaldehyde azine (infrared) or approximately 61% of that calculated. Recrystallization from hexane gave pure VI, m.p. 82–83°, no depression upon admixture with authentic *trans*.[1]

The Reaction of Dimethyl Maleate with Phenyldiazomethane.—To 4.0 g. of dimethyl maleate heated under nitrogen to 190° in an oil-bath was added, dropwise, crude phenyldiazomethane until 400 ml. of nitrogen had been evolved. Cooling the reaction mixture gave 7.71 g. of red residue. Gas chromatographic analysis of a portion of this mixture showed it to contain 1.3 g. of dimethyl fumarate and, at most, 0.2 g. of dimethyl maleate. (A small peak was observed with the same retention time as dimethyl maleate; however, its shape was quite different. From the odor of the eluted gas, this was probably a little benzaldehyde.) Sublimation of 0.66 g. of this residue at 170° and 32 mm. until nothing further sublimed out gave 0.40 g. of yellow oily solid. Infrared analysis of this showed it to contain only benzaldehyde azine, olefin and the *trans*-ester VI. No detectable quantity (less than 10%) of the *cis*-ester was present. Recrystallization from hexane gave 0.16 g. of slightly contaminated VI (infrared indicated a little azine). Recrystallization from hexane gave pure VI, m.p. 82–83°.

Analyses of the Crude Reaction Mixtures for Dimethyl Maleate and Dimethyl Fumarate.—Since it was difficult to prevent extensive losses of unreacted dimethyl maleate and fumarate while evaporating the elution chromatography cuts to dryness, the crude reaction mixtures were analyzed for unreacted ester by gas chromatography techniques. Analyses were effected in a Perkin–Elmer model 154-B vapor fractometer at 190°, using an 18-ft. column packed with 60–80 mesh synthetic detergent granules, generously furnished by the Proctor and Gamble Co. Dimethyl maleate and dimethyl fumarate peak intensities were calibrated against 4-*t*-butylcyclohexanone. The crude reaction mixture was then analyzed by dissolving a known weight of the mixture and a known weight of 4-*t*-butylcyclohexanone in a little chloroform and chromatographing at 190°. By comparing the intensities of the dimethyl maleate and dimethyl fumarate peaks with the 4-*t*-butylcyclohexanone peak, absolute amounts of these materials were obtained. One disadvantage of this type of analysis was the non-volatile material which was injected into the instrument causing tube stoppage. In actual practice, we found that occasional cleaning with a little acetone, of the tube leading to the column, prevented any appreciable trouble.

The Reaction of Ethyl Diazoacetate with *trans*-Stilbene.—In the same apparatus described for the reaction of diphenyldiazomethane with dimethyl fumarate, 10.0 g. (55.5 millimoles) of *trans*-stilbene was heated to 180° under nitrogen. Ethyl diazoacetate (6.35 g., 55.5 millimoles) was added dropwise at such a rate as to maintain the temperature between 180 and 200°. During the addition, the mixture turned deep brown and 1330 ml. (54 millimoles) of nitrogen was collected. The reaction mixture was then hydrolyzed by refluxing for 6.5 hours with 100 ml. of 5% ethanolic sodium hydroxide. The ethanol was removed *in vacuo* and the residue treated with hot water and filtered. The filter cake was washed several times with hot water and then dried to give 6.15 g. of light tan *trans*-stilbene, m.p. 124–125°; mixed with pure *trans* stilbene, m.p. 124–125.5°.

The deep red aqueous filtrate remaining after removal of unreacted stilbene was then acidified with concentrated HCl and allowed to stand overnight. The resulting dark red solid was worked up by the method of Hager and Smith[18] by dissolving it in 10 ml. of hot 10% NaOH, adding 10 ml. of hot water and cooling in the refrigerator until precipitation was complete. Filtration followed by washing with a little cold water gave the light yellow sodium salt of VIIIa and a deep red filtrate. The salt was dissolved in water and acidified to give 1.68 g. (33% of theor.) of VIIa, m.p. 150–152. Recrystallization from ethanol–water gave pure VIIa, m.p. 155–157°, reported[16] m.p. 157–157.80; amide m.p. 126–127.5°, reported[6] m.p. 127.5°.

The deep red filtrate obtained by filtering the sodium salt of VIIa was worked up as described below. None of the amide of VIIIa could be isolated.

The Reaction of Ethyl Diazoacetate with *cis*-Stilbene.—In the same apparatus described for the reaction of diphen-

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[13] L. I. Smith and K. L. Howard, *Org. Syntheses*, **24**, 53 (1944).

[14] van Alphen[5] reported the melting point of the dimethyl ester of *trans*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid to be 158°. Although our melting point is 16° higher than reported, the compound gives the proper analysis and has all of the properties of the anticipated cyclopropane. Hydrolysis gave a diacid, m.p. 292°, reported by van Alphen, m.p. 290°. Upon thermal decomposition of 5,5-diphenyl-3,4-dicarbomethoxy-2-pyrazoline, m.p. 141° dec., reported[5] m.p. 142° dec., again, only the 175° ester was isolated. That this ester cannot be the *cis* isomer was demonstrated by its synthesis from the anhydride (see below). In a private communication from Dr. van Alphen, we unhappily learned that samples of his compounds as well as his notes were lost during the war. Dr. van Alphen suggested that this anomaly might be explained by either a misprint or possibly polymorphism.

[15] Synthesized for comparison by the method of van Alphen,[5] m.p. 71–72°, reported m.p. 72°.

[16] H. Staudinger and A. Gaule, *Ber.*, **49**, 1906 (1916).

[17] The *cis*-ester was prepared for comparison by the method of E. Buchner and H. Dessauer, *ibid.*, **26**, 258 (1893); **25**, 1147 (1892); m.p. 61–61.5°, reported m.p. 63°.

[18] G. P. Hager and C. I. Smith, *J. Am. Pharm. Assoc.*, **41**, 193 (1956).

yldiazomethane with dimethyl fumarate, 10.0 g. (55.5 millimoles) of *cis*-stilbene was heated to 180° under nitrogen. Ethyl diazoacetate (6.35 g., 55.5 millimoles) was added dropwise at such a rate as to maintain the temperature between 180 and 200°. During the addition, the mixture turned deep brown and 1310 ml. (53 millimoles) of nitrogen was collected. The reaction mixture was then hydrolyzed by refluxing for 6.5 hours with 100 ml. of 5% ethanolic sodium hydroxide. The ethanol was removed *in vacuo* and the residue treated with hot water and filtered. No solid remained on the filter paper. The filtrate was extracted with chloroform to give a light yellow $CHCl_3$ layer and a deep red aqueous layer. The chloroform layer was dried and distilled to give 5.85 g. of unreacted *cis*-stilbene. There was virtually no residue from the distillation indicating the absence of *trans*-stilbene. The aqueous layer was acidified with concd. HCl to give a deep brown oil. This was separated and dissolved in 10 ml. of hot 10% NaOH; 10 ml. of hot water was added and the mixture was cooled in the refrigerator. Filtration gave no solid material. In view of the insolubility of the sodium salt of VIIa (less than 0.30 g. of acid saturates 20 ml. of cold 5% NaOH) the reaction apparently led to, at most, 6% of the *trans*-ester, and probably much less.

The filtered aqueous solution was then diluted to 150 ml. and 5% HCl was added slowly with vigorous stirring until the deep red color had disappeared and a light brown solution remained. The aqueous layer was separated by decantation from the almost black oil which had separated and then acidified to *p*H 1. The mixture was extracted with benzene, dried and the benzene removed *in vacuo* to give 3.2 g. of light brown, very viscous oil. This oil was refluxed for 1 hr. with an excess of $SOCl_2$, cooled and poured into rapidly stirred ice and ammonium hydroxide. The brown precipitate was filtered, dried and extracted in a Soxhlet for two days with benzene. The benzene was removed and the residual solid washed with a little cold benzene to give 0.97 g. (18% yield) of the amide of the *cis*-acid VIIIa, m.p. 193–204°. Recrystallization from ethanol–water gave the pure colorless amide, m.p. 213.5–215.5°, reported[6] m.p. 212–215°. The infrared spectra of the impure and the recrystallized materials were virtually superimposable.

The amide was converted to its corresponding acid VIIIa in the following way: To a mixture of 0.5 g. of the crude amide in 10 ml. of acetic acid was added a fourfold excess of sodium nitrite followed by 20 drops of concentrated HCl. After the initial evolution of gas had subsided (*ca.* 2 min.) the mixture was warmed on a steam-cone until no more gas evolved, after which it was poured into 50 ml. of water. Filtration followed by recrystallization from ethanol–water gave 0.2 g. of colorless solid, m.p. 145–147°. Several recrystallizations from ethanol–water gave the colorless acid, m.p. 152.5–154.5°; admixture with the *trans*-acid VIIa, m.p. 122–138°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.73; H, 5.99.

GAINESVILLE, FLA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

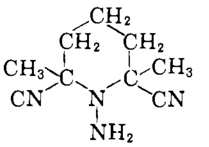
Azo Compounds. XXX.[1] Decomposition Products Obtained from the Oxidation of 1-Amino-2,6-dicyano-2,4,6-trimethylpiperidine. The Abnormal Oxidation

BY C. G. OVERBERGER, GEORGE KESSLIN AND PAO-TUNG HUANG[2]

RECEIVED NOVEMBER 22, 1958

Oxidation of 1-amino-2,6-dicyano-2,4,6-trimethylpiperidine yielded two products. One product was shown to be *cis*-1,2-dicyano-1,2,4-trimethylcyclopentane by conversion to a bicyclic derivative, 3-imino-3a,5,6a-trimethylcyclopenta(c)pyrrolidine-1-one. The second product was demonstrated to be 2,6-dicyano-4-methylheptene-2. Conformational considerations are consistent with a concerted nitrogen elimination mechanism for the formation of the cyclic oxidation product as has been proposed previously for related oxidations.

A previous paper in this series[3] has described the isolation and proof of structure of the oxidation products of 3,7-dicyano-3,7-dimethylhomopiperidazine, subsequently shown to be instead, 1-amino-2,6-dicyano-2,6-dimethylpiperidine (I).[4]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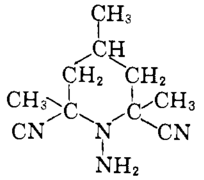
II

Three products were isolated. Two of these were shown to be *cis*- and *trans*-1,2-dicyano-1,2-dimethylcyclopentanes, isolated in 16–26 and 3.9% yields, respectively. The third product, isolated in 28–38%, yield, was demonstrated to be 2,6-dicyanoheptene-2. This paper describes the isolation and proof of structure of the oxidation products of the homologous 1-amino-2,6-dicyano-2,4,6-trimethylpiperidine (II) and correlates the previous results.

Discussion

Besides the physical and chemical evidence available in support of the structure of its homolog I,[4] additional experimental confirmation of structure II has been obtained. Deamination of II resulted in the quantitative evolution of nitrogen and the isolation of 2,6-dicyano-2,4,6-trimethylpiperidine (III). The infrared spectrum of III indicated the loss of one of the twin NH stretching frequencies in the 3μ region, and of the NH_2 bending frequency at $6.07\ \mu$, exhibited by II.

Oxidation of II with bromine at 0–5° gave two isomeric products (IV) and V). Quantitative hydrogenation of the crude oxidation mixture indicated the presence of 80% of the linear unsaturated isomer IV. Its isolation was achieved in 11% yield by crystallization or in 41.9% yield as mono- and diamide derivatives from the alkaline hydrogen peroxide hydrolysis of the crude oxidation mixture. The saturated cyclic isomer V could not be isolated directly from the crude oxidation mixture by distillation, sublimation or chromatography. Since

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[1] This is the 30th in a series of papers concerned with the preparation and reactions of azo and diazo compounds. For the previous paper in this series, see C. G. Overberger and A. V. DiGiulio, THIS JOURNAL, **81**, 2154 (1959).

[2] A portion of a thesis submitted by Pao-tung Huang in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

[3] C. G. Overberger, P. Huang and T. B. Gibbs, Jr., THIS JOURNAL, **75**, 2082 (1953).

[4] C. G. Overberger and B. S. Marks, *ibid.*, **77**, 4097 (1955).