examples, *cis*-2-butene-1,4-diol itself (21) and its 2,3-dimethyl derivative (23) both have low $\Delta\nu$'s (130, and 90 cm.$^{-1}$, respectively) and very weak bonded peaks (free/bonded intensity ratios 5.5 and 4.1). The unsymmetrical character of 2-methyl-*cis*-2-butene-1,4-diol (22) evidently is propitious for hydrogen bonding, since both $\Delta\nu$ (148 cm.$^{-1}$) and the free/bonded intensity ratio (2.1) are improved.

Free/Bonded Intensity Ratios—When a proton donor and a proton acceptor group are placed at different ends of a hydrocarbon chain, ring formation through intramolecular association is opposed by the natural tendency of the chain to adopt a linear, zig-zag conformation. With α,ω-diols proton donor and acceptor groups are both moderately strong; the hydrogen bond between them is sufficiently energetic to ensure that association persists to a large measure even in 1,4-diols, but intramolecular hydrogen bonding falls off drastically in 1,5-diols. Although strictly not directly comparable, the free/bonded intensity ratios of terminal diols give a convincing indication of this: Ethylene glycol = 1.3, propane-1,3-diol = 2.0,[7] butane-1,4-diol (1) = 2.6, and pentane-1,5-diol = *ca.* 40.[1]

Any conformational effect which would facilitate ring formation should increase the percentage of molecules engaged in intramolecular hydrogen bonding and decrease the free/bonded intensity ratio. Ordinarily nonbonded skew butane type repulsions would tend to favor the adoption of a *trans* conformation for the butane-1,4-diol chain; this nonbonding conformation competes with hydrogen bond ring formation. If the hydroxymethylene groups of a 1,4-diol are attached to a ring, the nonbonding conformation is not possible; considerably reduced free/bonded intensity ratios are observed for almost all monocyclic and bicyclic diols (Table I). Molecules with more than one bonded peak (such as 33–36, 39, 40, and 41) display higher ratios for each, but both peak areas should be added together to make a more valid comparison. Alkyl groups also generally reduce the free/bonded intensity ratios. A single substituent, such as methyl (2), permits the butane chain to adopt an orientation favoring hydrogen bonding without increase in nonbonded repulsions; the C_4-carbon can as easily be *trans* to the methyl group at C_2 as *trans* to the C_1 carbon. The "*gem*-dialkyl effect"—the heightened tendency toward ring formation of alkyl chains bearing alkyl substituents, especially when geminal—has its chief origin in such steric influences.[7] The trend is best illustrated here by comparing planimeter peak area ratios, A_f/A_b, for the series: butane-1,4-diol (1), 1.0; 2-methylbutane-1,4-diol (2), 0.6; and 2,2-dimethylbutane-1,4-diol (3), 0.35. In most of the other more complicated molecules, substituents also favor intramolecular hydrogen bonding. Compound 4 appears to be anomalous in this respect. We make no claim to understanding the fine details of substituent effects. Perhaps the pronounced nonbonded interactions in these molecules, many of them quite crowded, vitiate simple analysis.

One further influence of substituents is noteworthy; they seem to favor the adoption of more than one conformation and two peaks often appear in the spectra. This influence is seen most clearly in the series 1, 2, 3, but we do not have an entirely satisfying explanation.

Extensions of this work to 1,5- and 1,6-diols have been completed, and the results will appear shortly.[1] Further illustrations of the effects described above are even more dramatically exemplified in longer chain molecules.

Acknowledgments.—We wish to thank Dr. J. Meinwald, Dr. A. G. Cook, Dr. A. T. Blomquist, Dr. J. Sicher, and Dr. N. L. Allinger for supplying compounds used in this research. Partial support of this project by a grant from the National Science Foundation to P. R. S. is acknowledged with appreciation.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN 1, N. Y.]

Azo Compounds.[1] Five-Membered Cyclic Azo Compounds. Their Stereospecific Decomposition

BY C. G. OVERBERGER AND JEAN-PIERRE ANSELME[2]

RECEIVED AUGUST 20, 1963

Two cyclic five-membered azo compounds, 3,5-diphenyl-1-pyrazoline and 3,5-bis-(*p*-chlorophenyl)-1-pyrazoline, have been prepared. Their stereospecific decomposition to the corresponding *trans*-1,2-diarylcyclopropanes is reported and the mechanism of the decomposition is discussed.

Introduction

Five-membered ring azo compounds (1-pyrazolines), having an α-hydrogen and capable of rearranging to a conjugated system, usually isomerize to the more stable 2-pyrazolines.[3] However, as a part of our general studies of cyclic azo compounds, we decided to synthesize 3,5-diphenyl-1-pyrazoline (I, Ar = C_6H_5) and study its chemistry. There were no previous authenticated reports of stable 1-pyrazolines of this type. The mechanism of the decomposition of both 1- and 2-pyrazolines has been the subject of a controversy which is still not settled at present. It was hoped that the decomposition of 3,5-diphenyl-1-pyrazoline would shed some light on the problem.

Results and Discussion

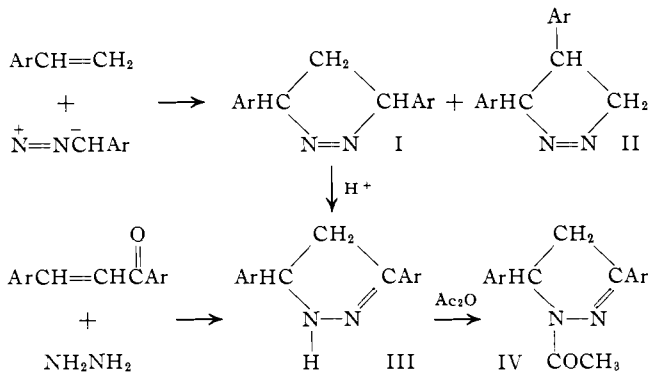
One of the most general methods for the synthesis of 1-pyrazolines consists in the addition of an olefin to a diazoalkane. The reaction of styrene with phenyldiazomethane resulted in the formation of a white crystalline solid which melted with decomposition. The infrared spectrum had no absorption indicating the presence of –N–H and had a sharp peak of moderate intensity at 1548 cm.$^{-1}$, assigned to the azo linkage. The product from the thermal decomposition was pure *trans*-1,2-diphenylcyclopropane. The structure of the pyrazoline was confirmed by its isomerization to 3,5-diphenyl-2-pyrazoline (III, Ar = C_6H_5) isolated as its N-acetyl derivative (IV, Ar = C_6H_5). It was identical

(1) (a) This is the 43rd in a series of papers concerned with the preparation and the decomposition of azo compounds. For the previous paper in this series, see C. G. Overberger, J-P. Anselme, and J. R. Hall, *J. Am. Chem. Soc.*, **85**, 2752 (1963). (b) For a preliminary report of this work, see C. G. Overberger and J-P. Anselme, *ibid.*, **84**, 869 (1962).

(2) This paper comprises a portion of a dissertation submitted by Jean-Pierre Anselme in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

(3) T. L. Jacobs in R. Elderfield, "Heterocyclic Compounds," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 72.

with the N-acetyl derivative prepared from 3,5-diphenyl-2-pyrazoline.



This indicated that indeed β-addition[4] of phenyldiazomethane to styrene had occurred to give 3,5-diphenyl-1-pyrazoline (I, Ar = C_6H_5), although a small amount of what may be the 3,4-isomer II (Ar = C_6H_5) was isolated. In order to test the generality of the reaction and of the decomposition, 3,5-bis-(*p*-chlorophenyl)-1-pyrazoline (I, Ar = *p*-ClC_6H_4) was prepared from *p*-chlorophenyldiazomethane and *p*-chlorostyrene. It also underwent thermal decomposition with the sole formation of *trans*-1,2-bis-(*p*-chlorophenyl)-cyclopropane.

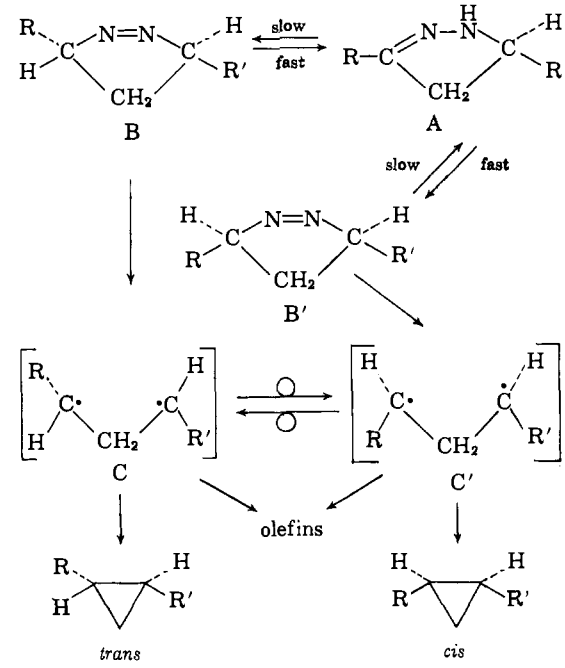
The addition of diazoalkanes to olefins has been viewed as a *cis* addition[5] and was shown to be a stereoselective reaction.[4] From steric considerations, it was assumed that the addition of the aryldiazomethanes to the styrenes had resulted in the formation of the *trans*-1-pyrazolines (I). It was subsequently shown that indeed the 3,5-substituents were *trans*.[6]

The stereospecific decomposition of I to the corresponding *trans*-1,2-diarylcyclopropanes is to be contrasted with the mixture of products formed from the thermal decomposition of 3,7-diphenyl-1,2-diaza-1-cycloheptene[7] and of 3,8-diphenyl-1,2-diaza-1-cyclooctene.[8] The base-catalyzed decomposition of 2-pyrazolines at high temperatures, though extensively used for the synthesis of cyclopropanes, very often gives a mixture of the *cis* and *trans* isomers as well as the corresponding olefins.[3] Rinehart and Van Auken[4,9] have shown that, at low temperatures, *cis*- and *trans*-3-carbomethoxy-3,4-dimethyl-1-pyrazolines gave the corresponding cyclopropanes with very little formation of olefin. Similar results were obtained by Swiss workers.[10]

Van Auken and Rinehart[4] have discussed the mechanism of the decomposition of 1-pyrazolines. The core of the problem seems to reside in the step during which stereospecificity may be retained or lost. Walborsky and Pitt[11] have recently questioned the validity of the free radical mechanism for the thermal decomposition of 1-pyrazolines.

Electron spin resonance studies of the photolytic decomposition of I at 77°K. in a Nujol or Fluorolube matrix[12] have indicated the presence of a free radical in each case (free spin value). No evidence was found for a triplet state. This result seems consistent with the exclusive formation of the *trans*-1,2-diarylcyclopropanes, since if a triplet state were formed, the coupling should not be stereospecific.[4] The photolytic decomposition of 3,5-diphenyl-1-pyrazoline at 15° gave *trans*-1,2-diphenylcyclopropane as the sole product, a result identical with that of the thermal decomposition. Coupled with the e.s.r. studies, this would suggest a free radical mechanism for the thermal decomposition of 3,5-diaryl-1-pyrazolines.

Thus, using the free radical mechanism as a working hypothesis, the various steps in the decomposition of pyrazolines can be depicted by the scheme



The stereospecific decomposition of the *trans*-3,5-diaryl-1-pyrazolines indicated that, at least in the 3,5-diaryl compounds, the lack of stereospecificity of the cyclopropanes resulting from the base-catalyzed decomposition of the corresponding 2-pyrazolines did not result during the conversion of B to C (or B′ to C′). Since it was shown that the cyclopropanes were stable under the conditions of the decomposition, the formation of the mixture of *cis*- and *trans*-cyclopropanes must be due to the nonstereoselective isomerization of the 2-pyrazolines to the 1-pyrazolines (A → B and B′). A similar *general* conclusion was reached by Jones,[13] although the results of Rinehart and Van Auken have conclusively shown that such a *general statement* is not always valid. Inspection of the scheme for the decomposition suggested a more generally applicable theory, namely that the stereochemistry of the resulting cyclopropanes and the extent of olefin formation will be determined by the structure and the stability of the intermediate biradicals (C or C′) at the temperature of the decomposition.

The nonstereospecific decomposition of the seven- and eight-membered ring azo compounds has been previously compared to that of 3,5-diphenyl-1-pyrazoline (I, Ar = C_6H_5). The rate of decomposition of I (Ar = C_6H_5) at 80° was 526 times faster than that of 1-azo-bis-1-phenylpropane (see Table I). Models of the 1-pyrazolines had indicated that the planar configuration of the five-membered azo ring induced a considerable amount of angle strain. This would weaken the C—N bonds and furthermore, the planarity of the C—N=N—C system in the ground state would greatly facilitate

(4) T. V. Van Auken and K. L. Rinehart, *J. Am. Chem. Soc.*, **84**, 3736 (1962).

(5) R. Huisgen, H. Stangl, H. J. Sturm, and H. Wagenhofer, *Angew. Chem.*, **73**, 170 (1961).

(6) C. G. Overberger, J-P. Anselme, and J. R. Hall, *J. Am. Chem. Soc.*, **85**, 2752 (1963).

(7) C. G. Overberger and J. G. Lombardino, *ibid.*, **80**, 2317 (1958).

(8) C. G. Overberger and I. Tashlick, *ibid.*, **81**, 217 (1959).

(9) K. L. Rinehart and T. V. Van Auken, *ibid.*, **82**, 525 (1960).

(10) K. Kocsis, P. D. Ferrini, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **43**, 2178 (1960).

(11) H. M. Walborsky and C. G. Pitt, *J. Am. Chem. Soc.*, **84**, 4831 (1962).

(12) We wish to thank Dr. A. M. Trozzolo of Bell Telephone Co. for obtaining these spectra for us.

(13) W. M. Jones, *J. Am. Chem. Soc.*, **82**, 3136 (1960), and previous papers.

the decomposition. This was entirely borne out by the remarkably low activation energy for the decomposition. It was found to be 11.6 kcal./mole compared to that of the seven- and eight-membered ring azo compounds, 29.7 and 36.7 kcal./mole, respectively (see Table I). The low activation energy may also explain the stereospecificity observed during the decomposition to the cyclopropanes.

TABLE I

KINETIC DATA OF CYCLIC AZO COMPOUNDS

	Rate constant k, sec.$^{-1}$, 80°	Rel. rate	Energy of activ. E_a, kcal./mole
1-Azo-bis-1-phenylpropane[8]	1.9×10^{-6}	1	32.3
3,5-Diphenyl-1-pyrazoline	1.0×10^{-3}	526	11.6
3,7-Diphenyl-1,2-diaza-1-cycloheptene[7]	4.3×10^{-4}	268	29.7
3,8-Diphenyl-1,2-diaza-1-cyclooctene[8]	3.5×10^{-8}	0.02	36.7

The base-catalyzed decomposition of 3,5-bis-(*p*-chlorophenyl)-2-pyrazoline (III, Ar = *p*-ClC_6H_4) at 200° was reported to give *trans*-1,2-bis-(*p*-chlorophenyl)-cyclopropane, m.p. 83–83.5°.[14,15] There was no mention of the formation of the *cis* isomer. While it is true that the m.p. of the crude solid obtained from the decomposition was about 80°, it was found that, by careful work-up of the various filtrates (see Experimental section), the *cis* isomer was isolated as a low melting solid, m.p. 50–52°. The assignment of configuration was confirmed by their n.m.r. spectra (see Table II).

TABLE II

N.M.R. DATA OF 1,2-DIARYLCYCLOPROPANES[a]

	Aromatic protons			Benzylic protons		
	cis	*trans*	*c–t*	*cis*	*trans*	*c–t*
1,2-Diphenylcyclopropane[b]	3.04	2.87	0.17	7.55	7.87	−0.32
1,2-Bis-(*p*-chlorophenyl)-cyclopropane	3.08	2.73	0.35	7.63	7.90	−0.27

[a] Given in τ-values and taken in CCl_4 at 60 Mc. [b] D. Y. Curtin, *et al.*, *J. Am. Chem. Soc.*, **83**, 4838 (1961); **84**, 863 (1962).

Experimental[16]

3,5-Diphenyl-1-pyrazoline.—To 525 ml. of an ether solution of phenyldiazomethane, prepared by oxidation with 300 g. of mercuric oxide of an ether solution of benzalhydrazone (from 106 g. of benzaldehyde and 66 g. of anhydrous hydrazine in 600 ml. of ether), was added over a period of 1 hr. 35 g. (0.336 mole) of styrene in 90 ml. of ether. Throughout the reaction the flask was wrapped with a piece of aluminum foil. The following day the reaction mixture remained red in color. About 200 ml. of the solvent was removed *in vacuo*. The flask then was immersed in an ice bath and the reaction mixture allowed to stir. The total reaction time was 36 hr. After thorough cooling of the flask in an ice bath for 2 hr., the precipitate was washed with ice-cold ether to remove the red color. The total yield of crude product after work-up of the first and second filtrates was 17.7 g. (23.7%), m.p. 107–109° dec. Two recrystallizations from warm methanol, followed by drying *in vacuo* over phosphorus pentoxide at room temperature, gave the pure product as shiny white flakes, m.p. 109–110° dec. The ultraviolet spectrum had a single peak, λ_{max}^{EtOH} 329 mμ (ϵ_{max} 291). The infrared spectrum was very similar to that of 3,7-diphenyl-1,2-diaza-1-cycloheptene[7] and of 3,8-diphenyl-1,2-diaza-1-cyclooctene,[8] showing a sharp medium band at 1548 cm.$^{-1}$ [6] (—N=N—).

Anal. Calcd. for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35. Found: C, 81.04; H, 6.28.

1-Acetyl-3,5-diphenyl-2-pyrazoline.—A solution of 0.14 g. (0.6 mmole) of 3,5-diphenyl-1-pyrazoline in 5 ml. of acetic anhydride and a catalytic amount of *p*-toluenesulfonic acid was stirred for 1 hr. at room temperature. It was then heated for an additional hour with continued stirring. The excess acetic anhydride was removed by heating *in vacuo*. To the residual brown oil was added 25 ml. of 3:1 ethanol–water mixture with heating. Upon cooling, there was obtained about 0.10 g. of cream-colored grains, m.p. 125–125.5°. This product was identical with the compound prepared by the reaction of 3,5-diphenyl-2-pyrazoline with acetic anhydride,[14] mixture m.p. 125–128°. The infrared spectra were identical and had a strong carbonyl absorption at 1650 cm.$^{-1}$.

trans-**1,2-Diphenylcyclopropane.**—A solution of 0.23 g. (1.0 mmole) of 3,5-diphenyl-1-pyrazoline in 10 ml. of benzene was heated under reflux until the evolution of nitrogen had stopped. The solvent was removed *in vacuo* and pure *trans*-1,2-diphenylcyclopropane was obtained as a colorless oil, $n^{23}D$ 1.5987 ($n^{20}D$ 1.5995[17] prepared by base-catalyzed decomposition of 3,5-diphenyl-2-pyrazoline). The n.m.r. spectrum was identical with that reported by Curtin, *et al.*[17]

3,5-Bis-(*p*-chlorophenyl)-1-pyrazoline.—A solution of *p*-chlorophenyldiazomethane in ether was prepared in a manner similar to that described for phenyldiazomethane from 140.5 g. (1.0 mole) of *p*-chlorobenzaldehyde and 64 g. (1.9 moles) of anhydrous hydrazine. From this solution, by addition of 42.2 g. (0.30 mole) of *p*-chlorostyrene in 100 ml. of ether, was obtained after 1 day 24 g. (27%) of 3,5-bis-(*p*-chlorophenyl)-1-pyrazoline, m.p. 118–119° dec. Recrystallization from hot methanol gave colorless needles, m.p. 120–121° dec. after drying *in vacuo* over phosphorus pentoxide. The ultraviolet spectrum had a single peak, λ_{max}^{EtOH} 327 mμ (ϵ_{max} 680). The infrared spectrum had the characteristic sharp medium band at 1543 cm.$^{-1}$ (—N=N—).[6]

Anal. Calcd. for $C_{15}H_{12}Cl_2N_2$: C, 61.87; H, 4.29; Found: C, 61.84; H, 4.26.

1-Acetyl-3,5-bis-(*p*-chlorophenyl)-2-pyrazoline.—A solution of 0.1 g. (0.3 mmole) of 3,5-bis-(*p*-chlorophenyl)-1-pyrazoline in 10 ml. of acetic anhydride and a catalytic amount of *p*-toluenesulfonic acid was allowed to stand at room temperature for 3 days. The slightly yellow solution was evaporated *in vacuo* with heating on a steam bath and the residue dissolved in ethanol, heated with charcoal, filtered, and allowed to cool. The slightly brownish crystals were recrystallized from ethanol; m.p. 108–109°, identical with the product obtained from the reaction of 3,5-bis-(*p*-chlorophenyl)-2-pyrazoline with acetic anhydride,[14] mixture m.p. 108–110°. The infrared spectra were identical and had a strong carbonyl absorption at 1650 cm.$^{-1}$.

trans-**1,2-Bis-(*p*-chlorophenyl)-cyclopropane.**—A solution of 0.468 g. (1.5 mmoles) of 3,5-bis-(*p*-chlorophenyl)-1-pyrazoline in 10 ml. of toluene was heated on the steam bath for 2 hr., after which time the evolution of nitrogen had ceased. A practically quantitative yield of *trans*-1,2-bis-(*p*-chlorophenyl)-cyclopropane, m.p. 83–83.5°, was obtained after evaporation of the solvent. The n.m.r. spectrum had a symmetrical quadruplet centered at 2.76 τ, a triplet centered at 7.90 τ, and a quadruplet at 8.60 τ and was identical with the spectrum of the high melting isomer (m.p. 83–83.5°), obtained from the base-catalyzed decomposition of 3,5-bis-(*p*-chlorophenyl)-2-pyrazoline, mixture m.p. 83–83.5°.

Base-Catalyzed Decomposition of 3,5-Bis-(*p*-chlorophenyl)-2-pyrazoline. *cis*- **and** *trans*-**1,2-Bis-(*p*-chlorophenyl)-cyclopropane.**—The pyrazoline obtained from 17.5 g. (0.0633 mole) of *trans*-*p*,*p*′-dichlorobenzalacetophenone and 10 ml. of anhydrous hydrazine was decomposed immediately after isolation by heating at about 200° in the presence of a catalytic amount of powdered potassium hydroxide.[14,15] The crude pyrolysis product was taken up in ether, the ether layer separated, washed successively with water, a dilute solution of hydrochloric acid, finally with water and dried over sodium sulfate. The solvent was removed under vacuum and the resulting oil chilled. The m.p. of the crude product was about 80°. Recrystallization of the product from ethanol gave pure *trans*-1,2-bis-(*p*-chlorophenyl)-cyclopropane, m.p. 83–83.5°. The n.m.r. spectrum consisted of a symmetrical quadruplet centered at 2.73 τ (aromatic protons), a triplet at 7.90 τ (benzylic protons), and a quadruplet at 8.60 τ.

Concentration of the mother liquor from the *trans* isomer gave a second crop of solid with a lower melting point. This process was repeated five times to give the pure *cis*-1,2-bis-(*p*-chlorophenyl)-cyclopropane, m.p. 50–52° (from ethanol–water). The n.m.r. spectrum was similar to that of the *trans* isomer except for the position of the bands. It had a symmetrical quadruplet centered at 3.08 τ (aromatic protons), a triplet at 7.63 τ (benzylic protons), and a quadruplet at 8.67 τ.

Anal. Calcd. for $C_{15}H_{12}Cl_2$: C, 68.45; H, 4.60. Found: C, 68.66; H, 4.78.

Kinetics.—Spectro grade xylene was used as solvent for the decomposition and the rate constants were calculated from the plots of nitrogen evolved against time.

(14) M. Hamada, *Botyu Kagaku*, **21**, 22 (1956).

(15) V. Biro, W. Voetgli, and P. Lauger, *Helv. Chim. Acta*, **37**, 2230 (1954).

(16) The melting points are uncorrected. The n.m.r. spectra were run in carbon tetrachloride at 60 Mc. with tetramethylsilane as an internal standard.

(17) D. Y. Curtin, *et al.*, *J. Am. Chem. Soc.*, **83**, 4838 (1961); **84**, 863 (1962).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA, IOWA CITY, IOWA]

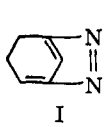
Reactions of 1,3-Cyclohexanediones with Hydrazine: A Novel Pyridazinopyridazine Synthesis as a Result of Oxidation Promoted by Steric Strain

BY J. K. STILLE AND R. ERTZ[1]

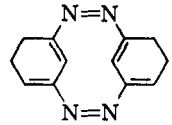
RECEIVED SEPTEMBER 5, 1963

The reactions of 1,3-cyclohexanedione and 5,5-dimethyl-1,3-cyclohexanedione with excess hydrazine hydrate produce 1,4,5,8-bis-trimethylenepyridazino[4,5-*d*]pyridazine and 1,4,5,8-bis-β,β-dimethyltrimethylenepyridazino[4,5-*d*]pyridazine, respectively. The mechanism of this reaction was demonstrated to involve formation of the cyclic azine and subsequent air oxidation to the aromatic pyridazine structure. This reaction represents a novel method of pyridazine formation.

The reaction of 1,3-cyclohexanedione with excess hydrazine hydrate has been reported[2] to afford a product $C_6H_6N_2$, whose structure was reported to be either 1,3-azo-1,3-cyclohexadiene (I) or its dimer II. It is evident that I is an unlikely candidate for the $C_6H_6N_2$



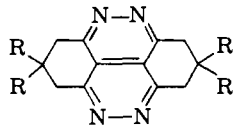
I



II

compound and the formation of II would involve azine formation, tautomerization, and finally oxidation of the hydrazo tautomer to the azo compound. Further, it is unusual that such a facile isomerization and oxidation in the formation of II would take place to the exclusion of cyclic azine formation, since the formation and isolation of cyclic azines from diketones are the usual modes of reaction.[3] Under certain conditions acetonylacetone reacts with hydrazine hydrate to form an associated dimer of a dimethyldihydropyridazine,[4] but this is a special case of the reaction with diketones.

The reaction of 1,3-cyclohexanedione with hydrazine hydrate does indeed form a light yellow, crystalline compound, whose elemental analysis and molecular weight verified the $C_{12}H_{12}N_4$ compound described earlier. The infrared spectrum of this compound failed to reveal the characteristic C=N or N=N stretching and only a weak maximum at 1625 cm.$^{-1}$, which could be ascribed to the C=C moiety, was observed. The ultraviolet spectrum confirmed the absence of N=N absorption and showed a complicated absorption spectrum in the 250–310 mμ range. This spectral data and the n.m.r. spectrum established 1,4,5,8-bistrimethylenepyridazino[4,5-*d*]pyridazine (III, R = H) as the product of the reaction of 1,3-cyclohexanedione with hydrazine hydrate. The

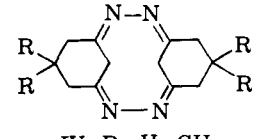


III, R = H, CH_3

quintet centered at 7.67 τ (relative to tetramethylsilane) was assigned to the four internal methylene protons; the areas of the components of the quintet were the expected 1:3:5:3:1. The triplet centered at 6.6 τ was assigned to the eight equivalent methylene protons; the areas of the components of the triplet approximated a 1:2:1 ratio. The relative number of triplet to quintet protons was 2:1.

Further support of the pyridazine structure (III, R = H) was gained by an investigation of the product of the reaction of 5,5-dimethyl-1,3-cyclohexanedione with excess hydrazine hydrate. The infrared spectrum of this product showed no absorption associated with the C=N or N=N moiety. The ultraviolet spectrum failed to reveal the characteristic N=N absorption, but showed again a complicated absorption spectrum between 250 and 310 mμ. This spectral data and the n.m.r. spectrum established 1,4,5,8-bis-β,β-dimethyltrimethylenepyridazino[4,5-*d*]pyridazine (III, R = CH_3) as the product of the reaction of 5,5-dimethyl-1,3-cyclohexanedione with hydrazine hydrate. The singlet at 8.83 τ (relative to tetramethylsilane) was assigned to the twelve methyl hydrogens and the singlet at 6.72 τ corresponded to the eight methylene hydrogens. The relative number of methyl protons to methylene protons was 3:2.

The formation of III (R = H, CH_3) presumably proceeds through the intermediate IV which contains two azine linkages, yet compounds containing two



IV, R = H, CH_3

azine linkages formed in the condensation of acyclic diketones with hydrazine are stable enough to be isolated from the reaction mixture.[3] This would indicate that the intermediate IV must have a special reactivity associated with it and is not stable under the conditions of the reaction. Models of IV show that the hydrogens on the two internal methylene groups are no greater than 1.2 Å. apart, the van der Waals radius for hydrogen. Thus, because of the close proximity of the two internal methylene groups, IV, in the presence of an oxidizing agent, dehydrogenates with bond formation to produce the pyridazine III, and thereby relieves the strain imposed. It is significant that cyclodecapentaene, which is forced into the same type of steric crowding, has never been isolated, although its transitory existence has been indicated.[5] Several examples of this type of oxidation involving bond formation to afford the same ring system have been described in the

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(4) C. G. Overberger, N. R. Byrd, and R. B. Mesrobian, *J. Am. Chem. Soc.*, **78**, 1961 (1956).

(5) M. Avram, C. D. Nentizescu, and E. Marica, *Ber.*, **90**, 1857 (1957).