Azo Compounds.[1] Oxidative Decomposition Products from 3,6-Dicyano-3,6-dimethylpiperidazine

C. G. OVERBERGER, G. KESSLIN,[2] AND N. R. BYRD

Polytechnic Institute of Brooklyn, Brooklyn, N. Y.

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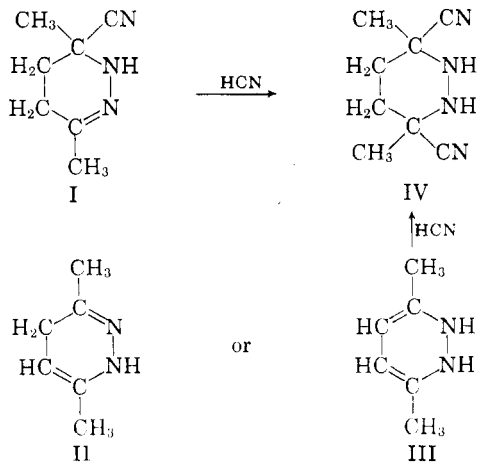
Two products were isolated from the abnormal oxidation of the cyclic hydrazine (IV). The formation of the cleavage product, methacrylonitrile, and the coupled product, *trans*-1,2-dicyano-1,2-dimethylcyclobutane, is consistent with a mechanism involving an intermediate 1,4-biradical. Although the stereochemical configuration of the cyclic hydrazine was not resolved, retention of configuration in the coupled product is believed to have resulted. A convenient one-step synthesis of the cyclic hydrazine is described.

Previous work on the oxidation of 3,6-dicyano-3,6-dimethylpiperidazine,[3] a cyclic analog of hydrazobisisobutyronitrile,[4] had not resulted in the expected formation of the cyclic azo compound. Instead, the authors observed nitrogen evolution and isolated a solid tentatively assigned the structure dicyanodimethylcyclobutane. This paper presents confirmation of the structure of the solid product formed with probable retention of configuration in the oxidative decomposition and describes the isolation of a second product, methacrylonitrile, resulting from the cleavage of an intermediate 1,4-biradical.

The cyclic hydrazine (IV) oxidized in this study has been prepared as described previously[3,5] with some modifications:



I IV II III

Addition of liquid hydrogen cyanide to I, II, or III is based on the method of Alderson and Robertson.[6] In the present study, it was found possible, and most convenient, to convert acetonylacetone directly to IV with sodium cyanide in aqueous sulfuric acid in more concentrated solution, adhering more closely to the method of Thiele and Heuser.[4] The tautomers II and III could also be converted to IV by the use of sodium cyanide and aqueous sulfuric acid. This modification avoids the tar formation sometimes noted by Byrd[7] in using liquid hydrogen cyanide, and the difficulty of purifying the cyclic hydrazine dinitrile.

The oxidation of the cyclic hydrazine with potassium permanganate in acetone at 0° resulted in quantitative nitrogen evolution and gave an oily solid upon evaporation of solvent. Only one product was obtained from the residue remaining after acetone evaporation. Similar results were obtained with bromine in ethanol. A quantitative hydrogenation of the residue after acetone removal indicated negligible hydrogen absorption, thus making unlikely the presence of linear unsaturated products in the residue.

Recrystallization of the residue yielded a solid whose analysis and acid equivalent conformed to the empirical formula $C_8H_{10}N_2$.[3] Its infrared spectrum was similar to that of one of the isomeric dinitriles isolated by Albisetti and co-workers[8] from the thermal dimerization of methacrylonitrile, exhibiting a nonconjugated C≡N absorption peak at 4.45 μ and having no C=C absorption peak in the 6-μ region. Quantitative hydrogenation over palladium-on-carbon resulted in negligible hydrogen absorption. Hydrolysis with 50% aqueous sulfuric acid resulted in the isolation of a crystalline solid which agreed in melting point with the Albisetti and co-workers diacid obtained from their dinitrile in a similar manner. These authors were not able to convert this diacid to its anhydride, as they were able to do with the diacid from their isomeric dinitrile by warming with acetyl chloride. This established the *trans* configuration of one of their

(1) This is the 38th in a series of papers concerned with the preparation and decomposition of azo compounds. For the previous paper in this series, see C. G. Overberger and Louis P. Herin, in press.

(2) A portion of a thesis submitted by G. Kesslin 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, N. R. Byrd, and R. B. Mesrobian, *J. Am. Chem. Soc.*, **78**, 1961 (1956).

(4) J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896).

(5) C. G. Overberger, T. B. Gibbs, Jr., S. Chibnik, P. Huang, and J. J. Monagle, *J. Am. Chem. Soc.*, **74**, 3290 (1952).

(6) W. L. Alderson and J. A. Robertson, U. S. Patent 2,469,358, May 10, 1949.

(7) N. R. Byrd, Ph.D. thesis, Polytechnic Institute of Brooklyn, June 1955.

(8) C. J. Albisetti, D. C. England, M. J. Hogsed, and R. M. Joyce, *J. Am. Chem. Soc.*, **78**, 472 (1956).

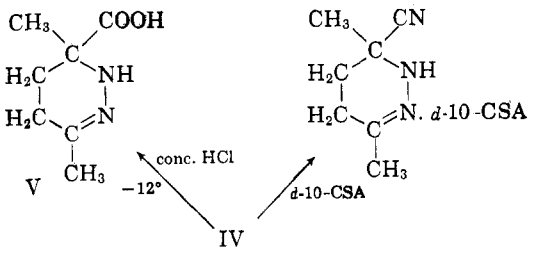
isomeric dinitriles which was found to be identical with the product of the present study. In addition, alkaline hydrogen peroxide hydrolysis of the solid dinitrile, by the Mooradian and Cloke[9] modification of the method of Radziszewski,[10] resulted in the isolation of its hitherto unreported diamide. This strongly suggests the structure of the solid product as *trans*-1,2-dicyano-1,2-dimethylcyclobutane.

Careful fractionation of the acetone removed from an oxidation reaction resulted in the isolation, in the end fraction, of a water-immiscible oil of distinctive odor. The presence of a conjugated nitrile absorption peak at 4.53 μ[11] in its infrared spectrum strongly suggested the presence of methacrylonitrile. By modifying the oxidation technique to the use of bromine in cold aqueous alkaline solution, again almost quantitative nitrogen was evolved. It was now possible to distil the methacrylonitrile as an azeotrope with water, and an approximately 30% yield of methacrylonitrile was obtained. Extraction of the aqueous residue with ether resulted in the isolation of an approximately 50% yield of crude coupled product. Thus, 80% of the products of oxidation are accounted for.

The boiling point, refractive index, and density of the liquid product agreed with the values reported[12] for methacrylonitrile. The infrared spectrum agreed with that of a pure commercial sample. In addition, alkaline hydrogen peroxide hydrolysis yielded methacrylamide, identical in melting point and mixture melting point with the amide obtained from authentic methacrylonitrile.

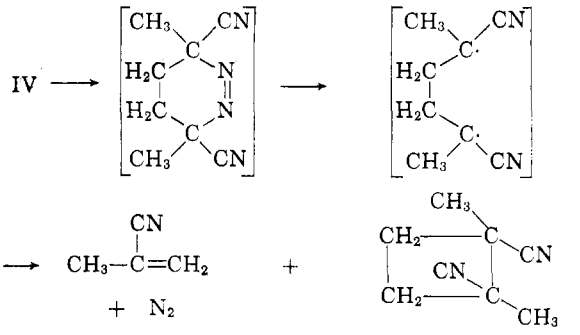
The isolation of purely *trans*-coupled product from the decomposition made it of interest to determine, if possible, the stereochemical configuration of the parent cyclic hydrazine (IV). This hydrazine may exist as the *trans* isomer which would consist of an enantiomorphic D,L-pair, or as the *meso-cis* isomer. Since the melting point of the cyclic hydrazine is sharp, when formed by any of the methods of preparation used, it is unlikely that it represents any mixture of isomers. An attempt was therefore made to directly resolve IV by means of its *d*-10-camphorsulfonic acid salt in ethanol. However, the crystalline salt obtained was that of the cyclic hydrazone (I), formed by the loss of a mole of hydrogen cyanide.

The attempt at resolution using dibenzoyl-*d*-tartaric acid also resulted in the formation of a hydrazone salt. An attempt to hydrolyze the cyclic hydrazine dinitrile (IV) to its analogous diacid, for resolution with an optically active base, resulted instead in the formation of 3-carboxy-3,6-dimethyl-2,3,4,5-tetrahydropyridazine (V):



The inability to resolve the cyclic hydrazine thus leaves the stereochemical configuration unresolved.

Stereochemistry and Mechanism of the Oxidation.—The fact that alkaline hypobromite oxidation of the 1,2-disubstituted cyclic hydrazine did not yield the cyclic azo analog of azobisisobutyronitrile (ABIN) may be ascribed to the instability of the required *cis*-configuration of the azo linkage in a six-membered ring[13-15] with tertiary substitution. It therefore decomposed with the quantitative evolution of nitrogen to give methacrylonitrile and dicyanodimethylcyclobutane. The decomposition of linear and cyclic azo compounds has been suggested as proceeding *via* a free radical mechanism.[13-17] The assumption that the decomposition of the hypothetical cyclic analog of ABIN proceeds *via* a free radical mechanism would lead to a 1,4-biradical:



The formation of methacrylonitrile is evidence that such a biradical has formed, since similar cleavages have resulted from 1,4-biradicals postulated as intermediates in the oxidative splitting of glycols[18,19] and in the decomposition of a six-membered ring azo compound.[15]

It is of interest to note, that the coupled products from the thermal decomposition of two stereopure seven- and eight-membered ring azo compounds[13,14] consisted of mixtures of *cis* and *trans* isomers, as compared to purely *trans* isomer obtained in the

(9) A. Mooradian and J. B. Cloke, *J. Am. Chem. Soc.*, **68**, 785 (1946).

(10) Br. Radziszewski, *Ber.*, **18**, 355 (1885).

(11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons Inc., New York, 1958.

(12) I. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, Vol. III. 1953.

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(17) C. G. Overberger, M. T. O'Shaughnessy, and H. Shalit, *ibid.*, **71**, 2661 (1949).

(18) W. A. Waters, "The Chemistry of Free Radicals," 2nd ed., Oxford University Press, New York, 1948, p. 229.

(19) R. Criegee, *Ber.*, **64**, 260 (1931).

present study. Thus stereoretention of configuration in the coupled product may have resulted from this low temperature oxidation, paralleling the results obtained in the decomposition of five-membered ring azo compounds[20] when conducted at 15° in the presence of sunlight. Such results would be consistent with the operation of a strong solvent cage effect preventing free rotation in the transition state or intermediate 1,4-biradical. An alternative explanation is that the *trans*-configuration of the coupled product is the most stable and the intermediate 1,4-biradical is free enough to assume the most stable configuration.

Experimental

All melting points are corrected.

Preparation of 3,6-Dimethyldihydropyridazine. The Low-Boiling and High-Boiling Tautomers.—The procedure used for this preparation is based on a modification of the method of Overberger[3,5] by which a mixture of tautomers are prepared.

To 114 g. (1.0 mole) of acetonylacetone in 1 l. of anhydrous ethanol was added 50 g. (1.0 mole) of hydrazine hydrate dissolved in 50 ml. of anhydrous ethanol over a 15-min. period at 7–15°. The mixture was heated to reflux for 30 min. and then allowed to cool to room temperature overnight. The solvent was removed at 35–40° under reduced pressure, and the clear, light yellow residue distilled through a 6-in. Vigreux column. Fraction 1, 41.5 g. (37.7%), b.p. 88–96°/20 mm., (n^{25}D 1.5082, 50°/1.4 mm., m.p. 32–33°, n^{25}D 1.5155[3]), was the low-boiling tautomer and developed needlelike crystals in the condenser and receiver during collection. Fraction 2, 41.5 g. (37.7%), b.p. 138–144°/4 mm., n^{25}D 1.5318 (115°/1.5 mm., n^{25}D 1.5340[3]), was the high-boiling tautomer.

Preparation of 3,6-Dicyano-3,6-dimethylpiperidazine. A. From Low-Boiling Tautomer.—This procedure is a modification of the method of Alderson and Robertson.[6] The difference resides in the use of aqueous sodium cyanide and sulfuric acid instead of liquid hydrogen cyanide.

To a solution of 41 g. (0.373 mole) of low-boiling tautomer and 58.8 g. (1.20 moles) of sodium cyanide in 400 ml. of water at 10–20° was added dropwise, with agitation, 34.4 ml. (0.615 mole) of 95% sulfuric acid (sp. gr., 1.84). After 30 min., the mixture was filtered to remove a gummy solid, and then allowed to stand at room temperature for 48 hr. The crystals which had precipitated were filtered, washed with water, and dried to give 14.6 g. (23.9%), m.p. 97.5–99.0° (gas). Extraction of the filtrate with methylene chloride, and evaporation of solvent, gave a residue which on slurrying with a minimum of ether yielded a second crop of crystals, 8.0 g. (13.1%), m.p. 99.0–100.0° (gas). The total yield of 3,6-dicyano-3,6-dimethylpiperidazine amounted to 37% (64%, 78–83°; 30.4%, 104.5° (gas)[3]; 99.0–99.9°.[5]

B. From High-Boiling Tautomer.—To a solution of 25 g. (0.227 mole) of high-boiling tautomer and 35.6 g. (0.727 mole) of sodium cyanide in 250 ml. of water at 20° was added dropwise, with agitation, 21.5 ml. (0.384 mole) of 95% sulfuric acid (sp.gr., 1.84) in 250 ml. of water. The mixture was allowed to stand 19 hr. at room temperature and then filtered. The crystalline cake, after washing with water and drying, weighed 21 g. Slurrying with 40 ml. of ether yielded off-white crystals, 18.1 g. (48.7%), m.p. 92–95° (gas). The filtrate from the reaction mixture was extracted with two 100-ml. portions of methylene chloride which, on evaporation, yielded a second crop of product, 5.8 g. (15.6%), m.p. 96–98° (gas). The total yield of crude dinitrile was 64.2%. Recrystallization from benzene–ether gave pure product, m.p. 99.0–100.0° (gas).

C. From Acetonylacetone.—This procedure is based on the method of Thiele and Heuser[4] for the preparation of azobisisobutyronitrile.

To a solution of 45.6 g. (0.40 mole) of acetonylacetone and 45.1 g. (0.920 mole) of sodium cyanide in 500 ml. of water at 25° was added 52 g. (0.40 mole) of hydrazine sulfate over a period of 20 min. The mixture was allowed to agitate 48 hr. at room temperature and then filtered. The crystalline product was washed well with water and air-dried, to yield 35.5 g. (54.1%), m.p. 97.5–99.5° (gas). A mixture melting point with cyclic dinitrile, m.p. 99.0–100.0°, prepared by known procedures,[3,5] gave a m.p. 98.0–99.5° (gas). Recrystallization from benzene–ether gave pure white crystals, m.p. 98.4–99.6°.

The infrared spectra of the cyclic dinitriles prepared by each of the above methods was identical with the compound prepared by known procedures.[3,5]

Attempted Optical Resolution of 3,6-Dicyano-3,6-dimethylpiperidazine. A. *Via* Basic Hydrazine. Formation of Hydrazone Salt.—To 3.28 g. (0.02 mole) of dicycanodimethylpiperidazine, the basic hydrazine dinitrile, in 50 ml. of 95% ethanol was added 4.64 g. (0.02 mole) of *d*-10-camphorsulfonic acid. The solution was evaporated at room temperature to leave 6.86 g. of solid residue (hydrogen cyanide odor). Recrystallization from 140 ml. of 1:1 methylene chloride–petroleum ether (b.p. 40–60°), with cooling to −12°, yielded the *d*-10-camphorsulfonic acid salt of 3-cyano-3,6-dimethyl-2,3,4,5-tetrahydropyridazine, 3.43 g. (46.4%), m.p. 121–125°. A second recrystallization gave 1.72 g. (23.3%), m.p. 123.2–125.4°.

Anal. Calcd. for $C_{17}H_{27}O_4N_3S$: C, 55.26; H, 7.37; N, 11.27; S, 8.68. Found: C, 55.62; H, 7.43; N, 11.61; S, 8.48.

The infrared spectrum showed absorption bands at 3.20 μ (NH), 4.0 μ and 5.0 μ (C=NH$^+$),[11] and 5.75 μ (C=O).

Regeneration of the free base from the salt, with aqueous sodium bicarbonate, yielded an oil which had an infrared spectrum similar to that of the cyclic hydrazone (I) prepared by a known method.[5]

A similar attempt at optical resolution using 1.09 g. (0.00665 mole) of basic cyclic hydrazine dinitrile and 2.5 g. (0.00665 mole) of dibenzoyl-*d*-tartaric acid monohydrate[21] yielded 3.20 g. of solid residue (hydrogen cyanide odor), m.p. 120–135°. Recrystallization from 12 ml. of chloroform yielded 1.53 g. of white crystals, m.p. 137.8–139.0°. Regeneration of the free base with aqueous sodium bicarbonate yielded an oil having an infrared spectrum very similar to that of the cyclic hydrazone (I). The solid was therefore assumed to be the dibenzoyl-*d*-tartaric acid salt of the cyclic hydrazone by analogy with the behavior of camphorsulfonic acid. No further characterization was attempted.

B. *Via* Dicarboxylic Acid Derivative. Formation of 3-Carboxy-3,6-dimethyl-2,3,4,5-tetrahydropyridazine.—The hydrolysis procedure for the cyclic hydrazine dinitrile is based on the method of Thiele and Heuser[4] for the preparation of the open chain analog.

A mixture of 5.0 g. (0.0304 mole) of 3,6-dicyano-3,6-dimethylpiperidazine and 50 ml. of concd. hydrochloric acid, made up at 0°, was kept at −12° for 48 hr. The solution was evaporated to dryness under reduced pressure, 50 ml. of water added, and the evaporation repeated. Another evaporation after the addition of 50 ml. of water, yielded a residue which was dissolved in 25 ml. of water. The aqueous solution of residue was continuously extracted with ether for 12 hr. Upon cooling to −10°, the ether extract yielded 1.0 g. (21.1%), m.p. 154–159°, of 3-carboxy-3,6-dimethyl-2,3,4,5-tetrahydropyridazine. Recrystallization from 100 ml. of ether yielded 0.66 g. (13.9%), m.p. 156.5–160.0°. Sublima-

(20) (a) K. L. Rinehart, Jr., and T. V. Van Auken, *J. Am. Chem. Soc.*, **82**, 5251 (1960); (b) C. G. Overberger and J. P. Anselme, *ibid.*, in press.

(21) C. L. Butler and L. H. Cretcher, *J. Am. Chem. Soc.*, **55**, 2605 (1933).

tion of 0.30 g., m.p. 156.5–160.0°, at 135°/0.3 mm., gave 0.22 g., m.p. 159.0–160.0°.

Anal. Calcd. for $C_7H_{12}O_2N_2$: C, 53.83; H, 7.74; N, 17.94; neut. equiv., 156.2. Found: C, 54.20; H, 7.67; N, 18.00; neut. equiv. 158.0.

The infrared spectrum showed bands at 2.96 μ (NH), 4.0 μ and 5.13 μ (amino acid), 5.92 μ (C=O), and 6.06 μ (C=N).[11]

Oxidation of 3,6-Dicyano-3,6-dimethylpiperidazine. A. With Potassium Permanganate in Acetone. Isolation of the Liquid and Solid Products.—To 11.0 g. (0.0672 mole) of cyclic hydrazine dinitrile (IV) dissolved in 250 ml. of acetone was added 15.0 g. (0.10 mole) of potassium permanganate in four portions over a 10-min. period at 5–10°, with vigorous agitation. During the course of 85 min. approximately 1470 ml. (98.2%) of nitrogen was evolved. The mixture was agitated 15 hr. longer and then filtered. The filtrate was evaporated free of solvent at 60°. The residual oil crystallized, on cooling to room temperature, to a deep orange mass, 5.01 g. (55.6%), m.p. 68–83° (42.8%, 40–48°[3]). Quantitative hydrogenation over 10% palladium-on-carbon[22] indicated negligible hydrogen uptake. Recrystallization from 50 ml. of petroleum ether (b.p. 40–60°) and 20 ml. of ether yielded, on cooling to −12°, white flakes of dicyanodimethylcyclobutane, 3.44 g. (38.2%), m.p. 86.2–88.4° (no yield, 87–88°[3]).

Careful refractionation of the acetone distillate through a 12-in. Vigreux column gave fraction 1, b.p. 56–60°/760 mm., fraction 2, 1.536 g., b.p. 65–90°/760 mm. Dilution of fraction 2 with water yielded 0.51 g. of an immiscible oil of characteristic odor and having an infrared spectrum showing an absorption peak at 4.53 μ (conj. C≡N).

B. With Bromine in Aqueous Alkali.—This procedure is a modification of the method employed by Thiele and Heuser[4] for the oxidation of the linear analog.

To 26.5 g. (0.1615 mole) of cyclic hydrazine dinitrile (IV) and 13.05 g. (0.326 mole) of sodium hydroxide dissolved in 750 ml. of water, was added 29.3 g. (0.163 mole) of bromine, at 7–10°, over a period of 1 hr. Stirring was continued for 1 hr. longer at 10° and the temperature then allowed to rise spontaneously to 18°. Approximately 95.5% of the theoretical nitrogen was evolved. The mixture was neutralized to *p*H 7 with bicarbonate, and then heated to distill an azeotropic mixture (74–75°) of water and oil. The upper oil layer weighed 6.48 g. (29.9%). Redistillation yielded 6.0 g. (27.7%), b.p. 89.6–90.6°/760 mm., $n^{20}D$ 1.3995, d^{20}_{20} 0.8010 (89.4–89.6°/757 mm., $n^{20}D$ 1.4013, d^{20}_4 0.7998.[12] The infrared spectrum of redistilled oil was identical with that of authentic methacrylonitrile showing bands at 4.53 μ (conj. C≡N) and 6.20 μ (conj. C=C).[11]

The aqueous residue left after azeotropic distillation of methacrylonitrile was cooled to 20° and saturated with ammonium sulfate causing precipitation of a white crystalline solid, 10.8 g. (49.9%), m.p. 79.0–85.0°. Recrystallization from petroleum ether (b.p. 40–60°) raised the melting point to 86.0–89.0°. A mixture melting point with dicyanodimethylcyclobutane prepared by permanganate oxidation, m.p. 86.2–88.4°, gave a m.p. 86.2–88.8°.

Alkaline Hydrogen Peroxide Hydrolysis of the Liquid Products.—This procedure is based on the method of Radziszewski[10] as modified.[9]

The liquid product, 0.51 g. (0.00762 mole), was mixed with 16 ml. of 10% hydrogen peroxide and 20 ml. of acetone at 0°, and 3 ml. of 10% sodium hydroxide was added. The mixture was allowed to stand at −12° for 13 hr., the acetone evaporated, and the aqueous residue saturated with ammonium sulfate and extracted with three 50-ml. portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate and the ether evaporated. The residue, 0.50 g. (77.2%), m.p. 82–95°, was a white crystalline solid. Recrystallization from 20 ml. of ether yielded methacrylamide, 0.28 g. (43.2%), m.p. 108.2–110.8° (102–106°[12]); 109–110°.[23] A mixture melting point with amide, m.p. 108.0–110.5°, prepared similarly from authentic methacrylonitrile, gave a m.p. 108.0–110.8°. The infrared spectrum was identical with authentic amide showing two bands at 2.95 μ and 3.15 μ, two bands at 6.0 μ and 6.2 μ, and a band at 7.10 μ, all typical of primary amides.[24]

Identity of the Solid Product.—The analysis of the solid product had previously been shown to conform to the empirical formula $C_8H_{10}N_2$.[3] In addition, the infrared spectrum was shown to contain no band for C=C absorption. Additional evidence is now presented to confirm its structural representation.

A. Acid Hydrolysis.—This procedure is based on a general method for nitrile hydrolysis.[25]

A mixture of 1.0 g. (0.00746 mole) of the solid product, m.p. 86–89°, 20 ml. of 50% sulfuric acid, and 0.40 g. of sodium chloride was refluxed for 1.5 hr. on an oil bath at 160°. The mixture was then cooled to 5° and filtered. The filter cake was washed with water and dried, to yield a white crystalline solid, 0.562 g. (43.2%), m.p. 230.8–234.0°. The filtrate was extracted with four 25-ml. portions of ether, the combined extracts dried over anhydrous magnesium sulfate, and the ether evaporated to leave a second crop of solid, 0.537 g. (41.3%), m.p. 204–229°. Recrystallization of the combined solids, 1.099 g., from aqueous methanol yielded white crystals of *trans*-1,2-dicarboxy-1,2-dimethylcyclobutane, 0.53 g. (40.7%), m.p. 237.6–238.6° (237–238°[8]). Neut. equiv., 86.1 (calcd.); 85.1 (found).

The infrared spectrum showed a strong band at 5.90 μ (C=O) and a broad band at 10.7 μ (OH deformation).[11]

B. Alkaline Hydrogen Peroxide Hydrolysis.—To 10 ml. of 10% hydrogen peroxide and 10 ml. of acetone at 0° was added 1.0 g. (0.00746 mole) of solid product, m.p. 86–89°, and then 2 ml. of 10% sodium hydroxide. The mixture was kept at −12° for 3 days. The fine, white needles that had precipitated were filtered, washed with water, and dried at 80° to yield a first crop of *trans*-1,2-dicarboxamido-1,2-dimethylcyclobutane, 0.346 g. (27.3%), m.p. 262.0–265.5° (sealed tube). Saturation of filtrate with ammonium sulfate precipitated a second crop, 0.675 g. (53.2%), m.p. 248–251°, which on vacuum sublimation at 165°/0.5 mm. yielded 0.568 g. (44.7%), m.p. 255–265.5°. Vacuum sublimation of first crop crystals did not change the melting point, 262.0–265.5°.

Anal. Calcd. for $C_8H_{14}O_2N_2$: C, 56.45; H, 8.29; N, 16.46. Found: C, 56.80; H, 8.14; N, 16.73.

The infrared spectrum showed two bands at 3.0 μ and 3.15 μ (NH), a doublet at 6.0 μ (C=O) and 6.2 μ (NH_2), and a band at 7.10 μ, all typical of primary amides.[24]

Acid hydrolysis of the diamide yielded diacid, m.p. 237.0–238.5°. A mixture melting point with the *trans* diacid obtained directly from *trans*-1,2-dicyano-1,2-dimethylcyclobutane, m.p. 237.6–238.6°, gave a m.p. 237.2–238.5°.

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