tic sample of the 2-*cis* acid prepared by the Reformatsky reaction.

The dimethyl ester of the 4-carboxy acid was obtained by action of diazomethane on the crude diacid from the condensation. The reaction mixture was added to water and the aqueous layer extracted with ether. Acidification of the aqueous layer precipitated an oil which partially solidified. This, with diazomethane, gave an oil (65%), b.p. 135°/0.05 mm., which solidified and was recrystallized from methanol–water, m.p. 57–57.5°; λ_{max} 288 mμ; ϵ 4220 (methanol).

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 72.03; H, 7.11.

Saponification of the diester with potassium hydroxide in ethanol under reflux gave a crude solid diacid which was recrystallized from benzene–petroleum ether. This product melts at 116–118°, solidifies, and remelts at 191–193°, λ_{max} 287.5 mμ, ϵ 4050 (methanol).

Anal. Calcd. for $C_{32}H_{32}O_8$: C, 70.57; 5.92; neut. equiv., 136.1, mol. wt., 554. Found: C, 70.44; H, 6.08; neut. equiv., 135; mol. wt. (ebull. toluene), 510 ± 5%.

Vacuum drying of the acid m.p. 116°; 191° at 76° for 10 hr. gave a product showing no melting at 116°; m.p. 191°. There are no differences in the ultraviolet, n.m.r., or infrared between these two compounds.

Anal. Calcd. for $C_{32}H_{32}O_8$: C, 70.57; H, 5.92; neut. equiv., 136.1; mol. wt. 554. Found: C, 70.44; H, 6.08; neut. equiv., 135.5; mol. wt. (ebull. toluene), 558. ± 5%.

The ultraviolet absorption measurements were made with a Beckman DK-2 recording spectrometer in the solvents (spectrograde) stated. The infrared absorption measurements were made with a Baird double beam recording spectrometer with sodium chloride optics and in chloroform (0.04 g./ml.) or as potassium bromide pellets. The n.m.r. measurements were made with a Varian high resolution (Model HR-4302) spectrometer with 60-Mc. oscillator with superstabilizer and field homogeneity control. The calibrations were made by the side band technique at several frequencies. Tetramethylsilane was used as an internal reference standard. Data for the acids were obtained in pyridine solutions; the esters in the carbon tetrachloride at about 15% concentration. Values are given in τ units.[8] Microanalyses by Micro Tech Laboratories, Skokie, Ill. Melting points are not corrected. The acids melt with gas evolution and are best used comparatively at controlled rates of heating.

Acknowledgment.—The authors gratefully acknowledge partial support of this research under Grant NSF G-11108 from the National Science Foundation. One of us (T. H. Crawford) is grateful for a National Science Foundation Cooperative Graduate Fellowship (1959–1961) and two (P.F.G.N and H.C.P.) are grateful for Fulbright Travel Grants in support of postdoctoral appointments. The authors also acknowledge grants from the Atomic Energy Commission AT-(40–1)-229 and AT-(40–1)-2025; National Institutes of Health H-4952; from the Lilly Co.; and from the Mead Johnson and Co. which made possible purchase of the n.m.r. spectrometer and accessories used in this study.

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[8] G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

The Isomeric Dinitrocyclohexanes. I. Synthesis of Epimeric 1,3- and 1,4-Dinitrocyclohexanes[1]

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1,4-Dinitrocyclohexane (II) has been prepared by peroxytrifluoroacetic acid oxidation of 1,4-cyclohexanedione dioxime (I) and by sodium borohydride reduction of *cis*- or *trans*-1,4-dibromo-1,4-dinitrocyclohexane (VII). Oxidation of *trans*-1,4-dibromo-1,4-dinitrosocyclohexane (IIIa) by peroxytrifluoroacetic acid affords *trans*-VII. Incidental to the synthetic work the stereochemistry of the isomers of dibromo compounds IIIa and VII and the corresponding dichloro compounds has been established. 1,3-Dinitrocyclohexane has been prepared by peroxytrifluoroacetic acid oxidation of 1,3-cyclohexanedione dioxime and by reaction of 2,6-dinitrohexyl acetate with sodium methoxide. Both epimers of II and IX have been prepared.

Recent years have marked rapid progress in the development of synthetic methods for preparing nitroalkanes and conformational analysis of cyclohexane compounds. It was of interest to extend this knowledge to the preparation of the isomeric dinitrocyclohexanes and to establish the configurations of the six possible isomers. Two of these, of unknown configuration, have been described previously.[2–5]

1,2-Dinitrocyclohexane is prepared by adding dinitrogen tetroxide to cyclohexene.[2–4] The product, a liquid,[2] probably is a mixture of epimers; one (m.p. 46°) has been separated from the mixture.[3,4] One isomer of 1,4-dinitrocyclohexane is formed, in trace amounts, as a by-product of vapor-phase nitration of cyclohexane.[5] No synthesis of 1,3-dinitrocyclohexane has previously been re-

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[1] Presented at the 138th National American Chemical Society Meeting, New York, N. Y., September 12, 1960.

[2] H. Baldock, N. Levy, and C. W. Scaife, *J. Chem. Soc.*, 2627 (1949).

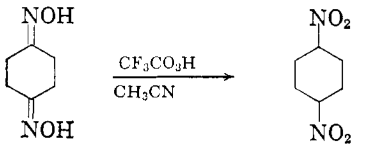
[3] J. C. D. Brand and I. D. R. Stevens, *ibid.*, 629 (1958).

[4] (a) R. W. Long, U. S. Patent 2,551,027, May 1, 1951; *Chem. Abstr.*, **45**, 7293 (1951); (b) T. F. Doumani and R. W. Long, U. S. Patent 2,580,742, January 1, 1952; *Chem. Abstr.*, **46**, 8675 (1952); (c) T. F. Doumani, C. S. Coe, and E. C. Attane, Jr., U. S. Patent 2,622,205, December 9, 1952; *Chem. Abstr.*, **47**, 10552 (1953).

[5] E. H. Schmorr, *J. Org. Chem.*, **24**, 868 (1959).

ported. The present work describes methods of preparing both epimers of 1,3- and 1,4-dinitrocyclohexane.

1,4-Dinitrocyclohexane.—Several methods of synthesizing 1,4-dinitrocyclohexane (II) were examined. Best was oxidation of 1,4-cyclohexanedione dioxime (I) by peroxytrifluoroacetic acid using a modified Emmons' procedure.[6] This synthesis of II appears to be the first reported oxidation of a dioxime to a dinitro compound. The product isolated was a mixture of epimers (44% yield) which could be separated by fractional crystallization (IIa, m.p. 169–170° and IIb, m.p. 89–90°). The high-melting isomer, the major component, was found to be identical with the 1,4-dinitrocyclohexane (m.p. 174°) obtained by nitration of cyclohexane.[5]

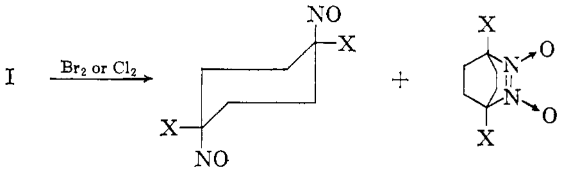


I II (Epimers)

A second synthesis of II from I involved the conversion of I to 1,4-dibromo-1,4-dinitrosocyclohexane (IIIa) and oxidation of the latter to 1,4-dibromo-1,4-dinitrocyclohexane (VII) which was reduced to II with sodium borohydride. The stereochemistry of the epimers of IIIa and VII has been studied.

A study of the bromination and chlorination of I, made earlier by Piloty and Steinbock,[7] has been re-examined and extended. These authors found that bromination of I in aqueous pyridine led to two isomers of $C_6H_8Br_2N_2O_2$, one an unstable blue solid, m.p. 89°, which decomposed at room temperature within a few days (*trans*-1,4-dibromo-1,4-dinitrosocyclohexane, IIIa, 10% yield). The other product (IVa, obtained in smaller amounts) was colorless, less soluble in the same solvents, but more stable; m.p. 125° with decomposition. We have found that by brominating I in aqueous dimethylformamide, in the presence of sodium bicarbonate buffer at 0°, IIIa is formed rapidly in good yield (73% yield of crude product).

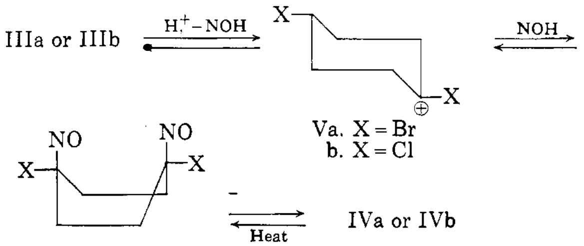
Chlorination of I by the procedure of Piloty and Steinbock gave the best yields of dichlorodinitroso derivatives. In concentrated hydrochloric acid I reacts to produce a 68% yield of blue *trans*-1,4-dichloro-1,4-dinitrosocyclohexane (IIIb), m.p. 108°, and 10% of colorless IVb, m.p. 165°; IIIb is much more stable than IIIa and keeps at 0° for long periods. Colorless IVa and IVb are stable at room temperature.[8]



Blue colorless

IIIa. X = Br IVa. X = Br
b. X = Cl b. X = Cl

Blue *trans*-IIIb undergoes an interesting acid-catalyzed isomerization to colorless IVb in acetic acid solution saturated with hydrochloric acid (35% yield after four days; no *trans*-IIIb remains after this time).[7] Acid-catalyzed isomerization of IIIa to IVa is also observed (see discussion below). The reaction may proceed through cations V and nitroxyl, leading to *cis*-1,4-dihalo-1,4-dinitrosocyclohexanes (VI) which couple internally to IV. Formation of IVb from VIb reverses on heating in acetic acid or acetonitrile solution; a blue color which appears fades on cooling.



Va. X = Br
b. X = Cl

Blue (*cis*)
VIa. X = Br
b. X = Cl

Oxidation of *trans*-dihalodinitrosocyclohexanes (IIIa and IIIb) to the corresponding dinitro compounds, in good yield, proceeds readily with peroxytrifluoroacetic acid. Reaction occurs rapidly in methylene chloride solution at room temperature and gives higher yields than oxidation by nitric or chromic acids.[7,9] Instability of IIIa made its purification difficult; large losses resulted. To avoid this problem, a cold methylene chloride extract of the crude reaction product was conveniently employed in the immediately ensuing peroxytrifluoroacetic acid oxidation step. There resulted (from I) a 31% over-all yield of 1,4-dibromo-1,4-dinitrocyclohexane (VII) as a mixture of isomers.

Crystallization of this mixture of 1,4-dibromo-1,4-dinitrocyclohexane isomers led principally to one, m.p. 211–214°, in addition to a smaller amount of a more soluble isomer, m.p. 160°. On the other hand, Piloty and Steinbock by oxidizing IIIa under more vigorous conditions (hot nitric acid, or chromic acid in acetic acid) obtained a 1,4-dibromo-1,4-

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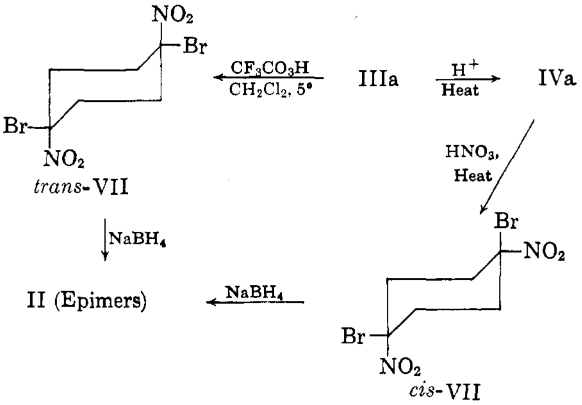
[6] W. D. Emmons and A. S. Pagano, *J. Am. Chem. Soc.*, **77**, 4557 (1955).

[7] O. Piloty and H. Steinbock, *Ber.*, **35**, 3101 (1902).

[8] The characteristic N—O stretching frequency (1580 cm.$^{-1}$) found in the infrared spectrum of IIIb was absent in that of IVb (N—O bands at 1395 and 1340 cm.$^{-1}$, potassium bromide). The problem of infrared band assignments of nitrosoalkanes and their dimers, including IIIb and IVb, has been studied. (a) W. Lüttke, *Z. Elektrochem.*, **61**, 302, 976 (1957); (b) B. G. Gowenlock, H. Spedding, J. Trotman, and D. Whiffen, *J. Chem. Soc.*, 3927 (1957).

[9] D. C. Iffland and G. X. Criner, *J. Am. Chem. Soc.*, **75**, 4047 (1953).

dinitrocyclohexane, m.p. 158° (2% over-all yield from I). Their procedure produced much decomposition of starting material, leading to oxides of nitrogen (rapid decomposition of IIIa). It is reasonable that their reaction conditions caused some transformation of IIIa to IVa, as discussed above. These different results appear to arise because of important differences in reaction conditions. In our experiments, relatively mild conditions of rapid oxidation would be expected to permit oxidation of IIIa without its extensive decomposition or isomerization; thus, the product should be *trans*-VII (structure assigned to the high-melting isomer). Since IVa is quite stable in hot acid solution whereas IIIa is not, vigorous oxidation conditions would be expected to lead primarily to *cis*-VII (structure assigned to the low-melting isomer). (The dihalodinitro compounds are reasonably stable to the action of hot acids.) Oxidation to *cis*-VII does not necessarily occur directly with the bicyclic form IVa, but probably with the monocyclic *cis* dinitroso form, VIa, slowly generated by heating IVa.



Oxidation of *trans*-1,4-dichloro-1,4-dinitrosocyclohexane (IIIb) in methylene chloride solution with peroxytrifluoroacetic acid led principally to *trans* - 1,4 - dichloro - 1,4 - dinitrocyclohexane (VIII) (84% yield of isomer mixture). Piloty and Steinbock, employing chromic acid in warm acetic acid, reported 25% yield of a product, m.p. 178°, after recrystallization. Crystallization of our isomer mixture led to a compound, $C_6H_8Cl_2N_2O_4$, m.p. 191–192°, representing at least two thirds of the total reaction product. The low-melting isomer (*cis*-VIII) evidently is formed in quite small amounts; although not isolated in the present experiment, it has been prepared by chlorination of the bisnitronate ion of II which produces both epimers of VIII, m.p. 121 and 191°.[10b] As in the case of the corresponding bromo derivative, IIIa, our mild oxidation procedure is believed to lead principally to the high-melting isomer (*trans*-VIII). The product, m.p. 178°, obtained by Piloty and Steinbock may be a mixture of isomers containing mainly the *trans* form. Since IIIb is much more stable than IIIa, the chloro compound evidently is oxidized to produce relatively more of the *trans* dinitro derivative than is the bromo compound.

Sodium borohydride reduction of either *cis*- or *trans*-1,4-dibromo-1,4-dinitrocyclohexane (VII) led to 1,4-dinitrocyclohexane (II, mixture of epimers) in 63% yield in each case. Although this yield might be increased, the direct oxidation of I by peroxytrifluoroacetic acid must be considered a better method of preparing II. 1,4-Dichloro-1,4-dinitrocyclohexane (VIII) is obtained from I in good over-all yield (65% yield of isomer mixture) but its reduction to II with sodium borohydride failed, the starting material being largely recovered.

Attempts to synthesize 1,4-dinitrocyclohexane by displacement reactions were unsuccessful. *cis*- or *trans*-1,4-dibromocyclohexane failed to react with silver nitrite; *trans*-1,4-cyclohexanediol *bis-p*-toluenesulfonate with sodium nitrite in dimethyl sulfoxide or dimethylformamide gave no 1,4-dinitrocyclohexane. The procedures employed, similar to those of Kornblum and co-workers,[11,12] give good yields of nitro compounds from most primary and secondary halides except bromo- or iodocyclohexane. This exceptional behavior may be a result of crowding by axial hydrogens and the presence of a large leaving group in an equatorial position which hinders attack; the low nucleophilicity of nitrite ion is a contributing factor.

1,3-Dinitrocyclohexane.—Two syntheses of 1,3-dinitrocyclohexane (IX) have been developed, but each method gave poor yields. The convenient peroxytrifluoroacetic acid oxidation procedure for preparation of 1,4-dinitrocyclohexane from oxime I was not as successful when applied to 1,3-cyclohexanedione dioxime (X); much decomposition resulted with formation of oxides of nitrogen and water-soluble compounds. By operating at 60–70° for a relatively short reaction time a 6% yield of IX (mixture of epimers) from X was isolated from the water-insoluble material, an oil which decomposed on attempted distillation. Crystallization of the mixture of 1,3-dinitrocyclohexane epimers led to the less soluble, higher melting form, m.p. 58° (IXa). The low-melting isomer (IXb, m.p. 32°) was conveniently obtained by refluxing IXa with ethanolic sodium bicarbonate solution. To confirm their structures IXa and IXb were each reduced to 1,3-diaminocyclohexane.[10a] Attempts to prepare IX from X by the procedure of Iffland and Criner[9] were unsuccessful.

A second synthesis of IX, starting with 1,5-dinitropentane, follows a new method of preparing

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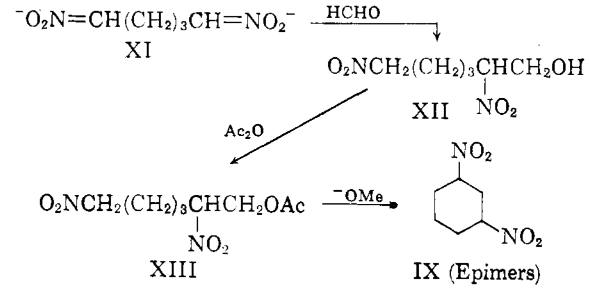
(10) (a) A. T. Nielsen, Paper II of this series, *J. Org. Chem.*, **27**, 1908 (1962); (b) Paper III, *ibid.*, **27**, 2001 (1962).

(11) N. Kornblum, H. O. Larson, R. K. Blackwood, D. D. Mooberry, E. P. Oliveto, and G. E. Graham, *J. Am. Chem. Soc.*, **78**, 1497 (1956).

(12) N. Kornblum, B. Taub, and H. E. Ungnade, *ibid.*, **76**, 3209 (1954).

acyclic 1,3-dinitroalkanes.[13] Rapid methylolation of the bisnitronate ion (XI) with one mole-equivalent of formaldehyde led to 2,6-dinitro-1-hexanol (XII, 44% yield) and some 2,6-dinitro-1,7-heptanediol; the alcohol could not be distilled without decomposition. The acetate (XIII) was distillable, however.[14] Reaction of a dilute methanolic solution of XIII with one mole-equivalent of sodium methoxide gave IX (principally the high-melting isomer) in 5% yield; an additional amount (< 15%) of the low-melting isomer, inseparable from 1,5-dinitropentane and other substances, may have formed. The reaction leads principally to undistillable material. The 1,5-dinitropentane (formed in 25% yield) could arise by acyl-oxygen fission of XIII and release of formaldehyde.



Experimental[15]

Peroxytrifluoroacetic Acid Oxidation of 1,4-Cyclohexanedione Dioxime (I) to Epimeric 1,4-Dinitrocyclohexanes (II).—To 1.42 g. (0.01 mole) of 1,4-cyclohexanedione dioxime,[16] 12.6 g. of sodium bicarbonate, 2 g. urea, and 175 ml. of acetonitrile were added, with vigorous stirring during 1 hr. a solution of 1.4 ml. of 85% hydrogen peroxide, 7.7 ml. of trifluoroacetic anhydride, and 20 ml. of acetonitrile. The temperature was maintained at 75–79° during the addition and 50 min. thereafter. Volatile materials were removed under reduced pressure and the residue diluted with 250 ml. of cold water. After chilling overnight the mixture was filtered to yield 0.76 g. (44%) of a mixture of epimeric 1,4-dinitrocyclohexanes, m.p. 130–170°. Two recrystallizations from ethanol gave 0.34 g. of 1,4-dinitrocyclohexane (IIa), m.p. 168–170°. A third recrystallization gave a sample, m.p. 169–170°, used for analysis. When mixed with a sample of 1,4-dinitrocyclohexane (m.p. 169–170° in our hands) kindly furnished by Dr. E. H. Schmorr of the DuPont Co., the melting point was not depressed (reported,[5] m.p. 174°); the infrared spectra of the two samples were identical.

Anal. Calcd. for $C_6H_{10}N_2O_4$: C, 41.38; H, 5.79; N, 16.09. Found: C, 41.23; H, 6.08; N, 15.54.

In another experiment, 5.56 g. of the crude reaction mixture of 1,4-dinitrocyclohexane isomers, m.p. 120–170°, was separated by fractional crystallization, first from ethanol and later from carbon tetrachloride to give 0.68 g. of the low-melting epimer, IIb, m.p. 89–90°.

Anal. Calcd. for $C_6H_{10}N_2O_4$: C, 41.38; H, 5.79; N, 16.09. Found: C, 41.44; H, 5.42; N, 16.38.

Peroxytrifluoroacetic Acid Oxidation of *trans*-1,4-Dibromo-1,4-dinitrosocyclohexane (IIIa).—To 1.42 g. (0.01 mole) of 1,4-cyclohexanedione dioxime (I) and 4.2 g. of sodium bicarbonate in 20 ml. of dimethylformamide and 100 ml. of water was added 3.2 g. (0.02 mole) of bromine, dropwise, with ice bath cooling and stirring, during 5 min. After the mixture had been shaken for several minutes to complete the reaction, the blue nitroso compound which precipitated was extracted three times with 25-ml. portions of methylene chloride. The extract was washed with water, dried with anhydruus sodium sulfate for 40 min. (in the refrigerator), and filtered.

The cold blue solution of the *trans* nitroso compound was used immediately for the next step. It was added during 40 min., with stirring at room temperature, to a solution of 1.5 ml. of 85% hydrogen peroxide and 8 ml. of trifluoroacetic anhydride in 20 ml. of methylene chloride. The volatile materials were removed by concentrating *in vacuo*, and the residue was diluted with water. The mixture was filtered and the precipitate washed with water and alcohol to yield 1.02 g. (31% from I) of *cis*- and *trans*-1,4-dibromo-1,4-dinitrocyclohexane isomers, m.p. 160–175°. Two recrystallizations from ethanol gave 0.34 g., m.p. 197–205°. Three additional recrystallizations gave an analytical sample of *trans*-1,4-dibromo-1,4-dinitrocyclohexane (*trans* VII), m.p. 211–214° dec.

Anal. Calcd. for $C_6H_8Br_2N_2O_4$: C, 21.71; H, 2.43; Br, 48.15; N, 8.44. Found: C, 21.72; H, 2.45; Br, 47.88; N, 8.18.

From the filtrate, by crystallization from carbon tetrachloride, a small amount of *cis*-1,4-dibromo-1,4-dinitrocyclohexane was isolated (*cis*-VII), m.p. 160–163°; reported for one isomer of VII, m.p. 158°[7]; 159–160°.[10b]

Reduction of 1,4-Dibromo-1,4-dinitrocyclohexane (VII) to 1,4-Dinitrocyclohexane (II).—The following procedure was adapted from one of Iffland and Criner.[9] A solution of 0.34 g. of *trans*-1,4-dibromo-1,4-dinitrocyclohexane in 150 ml. of ethanol was treated with a solution of 0.38 g. of sodium borohydride in 15 ml. of 60% ethanol. After standing at room temperature for 30 min., the mixture was acidified with dilute acetic acid and concentrated *in vacuo* to remove solvent. The residue was diluted with water and filtered to yield 0.11 g. (63%) of a mixture of epimeric 1,4-dinitrocyclohexanes, m.p. 110–145°. By refluxing this material with a solution of 1 ml. of saturated ethanolic sodium bicarbonate and 4 ml. of ethanol for 5 hr., it was all converted into the high-melting isomer, m.p. 167–170°. A recrystallization from chloroform gave a sample, m.p. 169–170°, which when mixed with authentic 1,4-dinitrocyclohexane (m.p. 169–170°) melted at 168–169°.

A sample of *cis*-1,4-dibromo-1,4-dinitrocyclohexane also was reduced by means of the above procedure; 1,4-dinitrocyclohexane was again formed, in the same yield (63%), and was identical with the sample isolated above.

Peroxytrifluoroacetic Acid Oxidation of *trans*-1,4-Dichloro-1,4-dinitrosocyclohexane (IIIb).—A solution of 0.63 g. (0.003 mole) of blue *trans*-1,4-dichloro-1,4-dinitrosocyclohexane,[7] m.p. 108–110°, in methylene chloride was oxidized in the manner described above for 1,4-dibromo-1,4-dinitrosocyclohexane to yield 0.61 g. (84%) of crude *trans*-1,4-dichloro-1,4-dinitrocyclohexane, m.p. 165–180°. Recrystallization from ethanol gave 0.41 g., m.p. 189–190°; a second recrystallization raised the melting point to 190–191°.

Anal. Calcd. for $C_6H_8Cl_2N_2O_4$: C, 29.65; H, 3.32; Cl, 29.17; N, 11.52. Found: C, 29.39; H, 3.32; Cl, 29.00; N, 11.58.

An attempt to reduce *trans*-1,4-dichloro-1,4-dinitrocyclohexane to 1,4-dinitrocyclohexane with sodium borohydride, by the procedure employed above with 1,4-dibro-

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[13] H. Feuer and R. Miller, *J. Org. Chem.*, **26**, 1348 (1961).

[14] The crude reaction product was reacted with acetic anhydride to produce XIII and some 1,7-diacetoxy-2,6-dinitroheptane (XIV, formed from 2,6-dinitro-1,7-heptanediol). In one case an attempt to distill XIV resulted in rapid formation of *ca.* two mole-equivalents of acetic acid and a nitroolefin, $C_7H_{10}N_2O_4$, possibly 2,6-dinitro-1,6-heptadiene. Recently E. S. Zonis and V. V. Perekalin [*J. Applied Chem. USSR*, **33**, 1427 (1960)] prepared 2,5-dinitro-1,5-hexadiene by deacetoxylation of 1,6-diacetoxy-2,5-dinitrohexane.

[15] Melting points were determined on a Kofler hot stage and are uncorrected. Infrared spectra of liquids were determined neat. Ultraviolet spectra were measured in 95% ethanol solvent.

[16] The oxime was prepared by the procedure of A. Baeyer and W. A. Noyes, *Ber.*, **22**, 2168 (1899).

mo-1,4-dinitrocyclohexane, gave recovered starting material only.

Attempted Syntheses of 1,4-Dinitrocyclohexane.—Attempts were made to synthesize 1,4-dinitrocyclohexane by displacement reactions. *trans*-1,4-Dibromocyclohexane, m.p. 112–114°[17] (2.5 g.), and silver nitrite (2.8 g.) in ether (50 ml.) were stirred at 0–25° for 18 hr. to yield 68% recovered *trans* dibromide. A few milligrams of material, m.p. 59–62° (needles from aqueous ethanol), was isolated, but not investigated. In a similar experiment the liquid *cis*-1,4-dibromocyclohexane[17] failed to yield a crystalline product.

trans-1,4-Cyclohexanediol bis-*p*-toluenesulfonate, m.p. 150–151°,[18] (8.48 g.), sodium nitrite (5.5 g.), urea (10 g.), and phloroglucinol (0.5 g.) were dissolved in 100 ml. of dimethyl sulfoxide and the solution allowed to stand at 25–31° for 69 hr. After pouring into water (1 l.) and chilling there was isolated 2.4 g. of crude starting material, m.p. 130–148°; a recrystallized sample, m.p. 154–155°, when mixed with the starting material did not depress the melting point. A similar experiment with cyclohexyl *p*-toluenesulfonate led to recovered ester (72%) and material having the odor of cyclohexene; by changing the solvent to dimethylformamide similar results were obtained.

1,3-Dinitrocyclohexane (IX) from 1,3-Cyclohexanedione Dioxime (X).—To 7.1 g. (0.05 mole) of 1,3-cyclohexanedione dioxime,[19] 65 g. of sodium bicarbonate, 10 g. of urea, and 650 ml. of acetonitrile was added, with stirring during 30 min., a solution of 7 ml. of 85% hydrogen peroxide, 38.5 ml. of trifluoroacetic anhydride, and 50 ml. of acetonitrile. The temperature was maintained at 60–70° during the addition. The reddish brown mixture was concentrated under reduced pressure (bath temperature 50–60°) to remove most of the solvent. The residue was diluted with 250 ml. of cold water and the mixture chilled overnight. A small precipitate (0.12 g., m.p. 145°) was filtered and the filtrate extracted with five 50-ml. portions of methylene chloride. The combined extracts were washed with saturated sodium bicarbonate solution and dried with magnesium sulfate; the solvent was removed to yield 2.15 g. of a dark red oil. (In another experiment an attempt to distil the oil *in vacuo* resulted in decomposition of most of it.) Chromatography of the oil on alumina, eluting with carbon tetrachloride–chloroform mixtures and chloroform gave 1,3-dinitrocyclohexane isomers, 0.53 g. (6%) as a yellow oil; strong infrared band at 1540 cm.$^{-1}$ (NO_2 stretching); absorption in the OH, C=O and C=N stretching regions was absent (spectrum that of 1,3-dinitrocyclohexane isomers). Crystallization from ethanol gave 0.26 g., m.p. 30–52°; recrystallization gave 0.09 g., m.p. 54–58° of high melting 1,3-dinitrocyclohexane (IXa). When mixed with a sample (m.p. 55–58°) obtained from 2,6-dinitrohexyl acetate (see below) the melting point was not depressed. Other products which were isolated in small amounts from the product mixture are under continued investigation.

Equilibrium of 32 mg. of the above high-melting IXa by refluxing with saturated sodium bicarbonate (5 ml.) for 4 hr. gave 14.3 mg., m.p. 30–35°. Recrystallization from ethanol gave needle-shaped prisms of the low-melting isomer of 1,3-dinitrocyclohexane, (IXb), m.p. 30–32°.

Anal. Calcd. for $C_6H_{10}N_2O_4$: C, 41.38; H, 5.79. Found: C, 42.12; H, 6.14.

Attempts to convert 1,3-cyclohexanedione dioxime (X) to 1,3-dinitrocyclohexane by the procedure of Iffland and Criner[9] were unsuccessful. Bromination by the procedure described for 1,4-cyclohexanedione dioxime gave a green precipitate which failed to yield a crystalline product on reaction with peroxytrifluoroacetic acid. Attempts to prepare a blue nitroso compound by reaction of X with bromine by a variety of procedures were unsuccessful. Reaction of bromine with a solution of 1,3-dinitrocyclohexane in 0.03 *M* sodium hydroxide failed to yield a solid bromonitro derivative.

2,6-Dinitro-1-hexanol (XII).—1,5-Dinitropentane[20] (50.8 g., 0.314 mole) was stirred at 0–5° with a solution of 25.6 g. (0.628 mole) of sodium hydroxide (98% assay) in 300 ml. of water for 1 hr. Formalin (30.5 g. of 37% solution, 0.376 mole of formaldehyde) was added all at once to the vigorously stirred solution. Stirring was continued for 15 min. at 7–10° when a cold solution of 50 ml. of acetic acid in 150 ml. of water was added all at once. After stirring for 30 min., the mixture was extracted three times with methylene chloride. The combined extracts were washed with saturated sodium bicarbonate solution and water and dried over magnesium sulfate. All volatile materials were removed at 50° *in vacuo* to yield 38.2 g. of a pale yellow oil, n^{25}D 1.4745.

Anal. Calcd. for $C_6H_{12}N_2O_5$: C, 37.50; H, 6.29; N, 14.58. Found: C, 37.28; H, 6.30; N, 15.40.

The oil could not be distilled without decomposition, at pressures below 1 mm. The **1-naphthylurethan** derivative was prepared (70% yield, crude) and recrystallized from ethanol, m.p. 99–100°.

Anal. Calcd. for $C_{17}H_{19}N_3O_6$: C, 56.50; H, 5.30; N, 11.63. Found: C, 56.22; H, 5.17; N, 11.66.

The elemental analysis for nitrogen, the yields of urethan and acetate derivatives (see below) indicate the above crude formylation product to contain approximately 70% 2,6-dinitro-1-hexanol (44% over-all yield). The impurities are most likely unchanged 1,5-dinitropentane and some 2,6-dinitro-1,7-heptanediol. 2,5-dinitro-1-pentanol has been prepared from 1,4-dinitrobutane by the same procedure in the same yield.

2,6-Dinitrohexyl Acetate (XIII).—A solution of 33.0 g. of the above crude 2,6-dinitro-1-hexanol in 300 ml. of acetic anhydride containing 1 ml. of concd. sulfuric acid, was allowed to stand at room temperature for 16.5 hr. One liter of water was then added and the mixture stirred vigorously for 5 min.; the temperature rose to 54°. After cooling to room temperature the mixture was extracted three times with methylene chloride and the combined extracts washed twice with saturated sodium bicarbonate solution, and dried. Concentration to remove volatile materials gave 38.8 g. of crude acetate as a pale yellow oil. Distillation of a 21.4-g. aliquot portion through a short-path still, under nitrogen at 0.1 mm., gave the following fractions: (1) b.p. 110–138°, n^{23}D 1.4619, 5.5 g.; (2) b.p. 138–148°, n^{23}D 1.4629, 10 g., mainly 2,6-dinitrohexyl acetate; (3) b.p. 148–173°, n^{23}D 1.4788, 2.3 g.; (4) undistillable residue, 2.7 g. Fraction 2 was redistilled; b.p. 144–146° (0.1 mm.), n^{25}D 1.4620, and this material used for analysis.

Anal. Calcd. for $C_7H_{14}N_2O_6$: C, 37.84; H, 6.35. Found: C, 37.50; H, 6.29.

Fraction 1, n^{25}D 1.4605, had infrared and NMR spectra agreeing closely with that of 1,5-dinitropentane, and a weaker carbonyl band than fraction 2 indicating the presence of a small amount of acetate.

In another run redistillation of 25.2 g. of acetylated product gave 18.2 g. of crude acetate (XII, fraction 5), b.p. 126–169° (< 0.1 mm.), n^{23}D 1.462. Continuing the distillation caused the residue to decompose to yield 8.86 g. (fraction 6, believed to be mainly 2,6-dinitro-1,6-heptadiene), b.p. 139–158° (0.2–0.55 mm.), n^{23}D 1.4788, and 2.3 g. of residue. Redistillation of fraction 6 gave 4.10 g. (fraction 7, used for analysis), b.p. 140–141° (0.6 mm.), n^{23}D 1.4816 (bath temperature 174–180°) before the residue began to fume off; infrared bands of fraction 7 at 3150 (vinyl CH) and 1515 cm.$^{-1}$ (conjugated NO_2 stretching) and 950 cm.$^{-1}$ (=CH out-of-plane deformation); ultraviolet absorption band at 212 mμ (ϵ 6600) and shoulder at 237 mμ (ϵ 4400).

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(19) G. Merling, *Ann.*, **278**, 21 (1894).

(20) H. Feuer and G. Leston, *Org. Syntheses*, **34**, 39 (1954). 1,5-Dibromopentane was substituted for 1,5-diiodopentane to give a 48% yield of 1,5-dinitropentane, b.p. 141° (1.0 mm.), n^{25}D 1.4600.

Anal. Calcd. for $C_7H_{10}N_2O_4$: C, 45.16; H, 5.41; N, 15.05. Found: C, 45.19; H, 6.00; N, 15.14.

The yield of $C_7H_{10}N_2O_4$, fraction 6, would require formation of 5.71 g. (0.095 equivalent) of acetic acid from a diacetate precursor, $C_{11}H_{18}N_2O_8$. The weight loss during the distillation was 5.77 g. and the liquid (6.0 g.) in the Dry Ice trap, having acetic acid odor, was found by titration with 0.1 *N* sodium hydroxide to contain 0.0754 equivalent of acid (corresponding to 4.54 g. of acetic acid).

A 1.74-g. sample of fraction 7 when treated with methanolic methoxide in the manner described below failed to yield 1,3-dinitrocyclohexane.

1,3-Dinitrocyclohexane (IX) from 2,6-Dinitrohexyl Acetate (XIII).—To 4.68 g. (0.02 mole) of 2,6-dinitrohexyl acetate in 500 ml. of absolute ethanol was added a solution of sodium methoxide [prepared from 0.46 g. sodium (0.02 g.-atom) dissolved in 20 ml. of methanol] and the solution allowed to stand at room temperature for 15.5 hr. To the yellow solution was added 2 ml. of acetic acid and the methanol was removed *in vacuo*. The residue was diluted with water and the mixture extracted with methylene chloride; the extracts were washed with sodium bicarbonate solution and dried. Removal of volatile material gave 3.38 g. of red oil which was distilled to yield 1.23 g. (fraction A) b.p. 132–136° (0.15 mm.) and 1.93 g. of black, undistillable residue. Fraction A was dissolved in 15 ml. of hot ethanol and chilled to yield 0.13 g. of crystalline 1,3-dinitrocyclohexane, m.p. 45–58°. Three recrystallizations from ethanol gave prisms of high-melting 1,3-dinitrocyclohexane, m.p. 57–58°, which was used for analysis.

Anal. Calcd. for $C_6H_{10}N_2O_4$: C, 41.38; H, 5.79; N, 16.09. Found: C, 41.27; H, 5.72; N, 16.30.

The filtrates remaining from crystallization of fraction A, above, were combined and distilled to yield 0.8 g., (fraction B), b.p. 110–116° (0.03 mm.), $n^{24}\mathrm{D}$ 1.4720; the material turned orange on standing. From an ethanol solution of a 0.34-g. aliquot of this liquid 0.02 g. of crystals was isolated, m.p. 50–59°; total yield of crude, crystalline 1,3-dinitrocyclohexane, 0.177 g. (5%). In ethanolic sodium hydroxide solution (0.1 *M*) fraction B had $\lambda_{\max}$ 239.5 mμ (ϵ 13,000), 385 mμ (ϵ 3300); in ethanol a shoulder appeared at 275 mμ (ϵ 137) and a strong band below 230 mμ; the infrared spectrum showed a strong band at 1540 cm.$^{-1}$ (NO_2), very weak OH and C=O absorption (1720 cm.$^{-1}$); no vinyl CH absorption at 3100 cm.$^{-1}$ was observed. The infrared spectrum has features of a mixture of 1,5-dinitropentane and 1,3-dinitrocyclohexane. The distilled reaction product from another run (3.3 g.) chromatographed on alumina gave (2.1 g., 25% yield) of 1,5-dinitropentane, $n^{25}\mathrm{D}$ 1.4667, having no OH or C=O bands and a strong NO_2 band at 1540 cm.$^{-1}$ (infrared and proton magnetic resonance spectra identical with that of authentic 1,5-dinitropentane).

The Isomeric Dinitrocyclohexanes. II. Stereochemistry[1]

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The stereochemistry of the five known isomeric dinitrocyclohexanes has been established by two independent methods. Iron and acetic acid reduction of the crystalline isomer of 1,2-dinitrocyclohexane (Ia), obtained by addition of dinitrogen tetroxide to cyclohexene, led to *trans*-1,2-diaminocyclohexane (II). Hydrogenation with platinum and acetic acid was more effective for reduction of both epimers of 1,3-dinitrocyclohexane (IVa and IVb) and 1,4-dinitrocyclohexane (IIIa and IIIb) to the corresponding diamines, with a high degree of configuration retention in each case. Equilibration of 1,3- and 1,4-dinitrocyclohexane epimers with ethanolic sodium bicarbonate led to the diequatorial isomer as the principal product in each case, and these results are in agreement with the hydrogenation data.

The stereochemistry of the dinitrocyclohexanes has not been investigated previously. In recent years advances in conformational analysis of cyclohexane ring compounds have been rapid, and it became of interest to apply and extend this knowledge to the isomeric dinitrocyclohexanes.

Five of the six possible dinitrocyclohexanes have been prepared. The syntheses of *cis*- and *trans*-1,3- and 1,4-dinitrocyclohexane are described in the first paper of this series.[2] One of the isomers of 1,2-dinitrocyclohexane, of unknown stereochemistry, has been prepared by the addition of dinitrogen tetroxide to cyclohexene.[3]

In the present work the stereochemistry of the five known isomeric dinitrocyclohexanes has been established by two independent methods. With each isomer stereospecific reduction led to the corresponding diaminocyclohexane of known stereochemistry. Equilibration experiments (with 1,3- and 1,4-dinitrocyclohexanes) in ethanolic sodium bicarbonate solution produced the expected diequatorial isomer in each case, and these results are in agreement with the reduction data.

1,2-Dinitrocyclohexane.—The problem of establishing stereochemistry in optically active nitroalkanes has been examined previously by Kornblum and co-workers.[4,5] They found *l*-2-nitrooctane to be reduced with iron and acetic acid with less than 18% racemization. We have found this procedure to be effective in reducing the crystalline isomer of 1,2-dinitrocyclohexane (Ia), m.p. 46°, to known *trans*-1,2-diaminocyclohexane (IIa), thus establishing the *trans* stereochemistry of Ia. The

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[1] Presented, in part, at the 138th National American Chemical Society Meeting, New York, N. Y., September 12, 1960.

[2] A. T. Nielsen, *J. Org. Chem.*, **27**, 1993 (1962).

[3] References cited in footnotes 3 and 4, ref. 2.

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