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.), $n^{24}D$ 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 λ_{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, $n^{25}D$ 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).

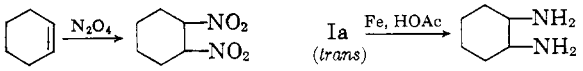
[3] References cited in footnotes 3 and 4, ref. 2.

[4] N. Kornblum and L. Fishbein, *J. Am. Chem. Soc.*, **77**, 6266 (1955).

[5] N. Kornblum, W. D. Gurowitz, H. O. Larson, and D. E. Hardies, *ibid.*, **82**, 3099 (1960).

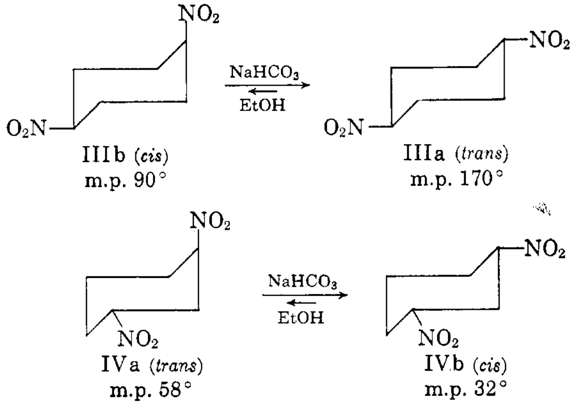
diamine, isolated in 88% yield, was of high purity (m.p. 19–20°, after a single distillation).[6,7,8a]

Establishment of the *trans* stereochemistry of crystalline 1,2-dinitrocyclohexane (Ia, m.p. 46°) is of interest in relation to the identity of the *cis* isomer (Ib) which might also form by addition of dinitrogen tetroxide to cyclohexene.[8] As yet, pure *cis*-1,2-dinitrocyclohexane has not been described; it is very likely a liquid at room temperature. The 2-nitrocyclohexan-1-ols produced by addition of dinitrogen tetroxide to 1-methylcyclohexene and cyclohexene form with 100% and 58% *trans* addition, respectively.[8a] Thus, by considering the proposed radical mechanism and stereochemistry of this reaction[8a,9] one might expect dinitrocyclohexane formation from cyclohexene to produce a mixture of epimers.[10]



I (Epimers a and b) IIa (*trans*)

The stereochemistry of the epimeric **1,3- and 1,4-dinitrocyclohexanes** was established first by equilibration experiments. An ethanolic sodium bicarbonate solution of the low-melting (90°) isomer of 1,4-dinitrocyclohexane (IIIb) after heating under reflux for five hours produced quite pure high-melting (170°) isomer, IIIa. Pure IIIa was essentially unchanged by this treatment. Based on the melting point of the crude product, the equilibrium overwhelmingly favors the high-melting form; the *trans* (diequatorial) structure is therefore assigned to IIIa. A similar treatment of the high-melting (58°) isomer of 1,3-dinitrocyclohexane (IVa) led to a mixture containing *ca.* 80% of the low-melting (32°) isomer, IVb; equilibration of IVb produced *ca.* 17% of crude IVa. The crystallization data and melting point behavior thus indicate the equilibrium to favor IVb, which is assigned the *cis* (diequatorial) structure. Some decomposition accompanies these epimerization reactions; yields of 1,3- and 1,4-dinitrocyclohexane isomer mixtures were 68% and 78%, respectively. The 1,3-isomer is relatively more sensitive to base attack.[10b] The stereochemistry of each epimer has been established independently by stereospecific hydrogenation to the corresponding diamine of known configuration.



IIIb (*cis*) m.p. 90°
IIIa (*trans*) m.p. 170°
IVa (*trans*) m.p. 58°
IVb (*cis*) m.p. 32°

When the iron and acetic acid reduction procedure,[4,5] successfully used with *trans*-1,2-dinitrocyclohexane, was applied to *trans*-1,4-dinitrocyclohexane (IIIa) only traces of *trans*-1,4-diaminocyclohexane could be isolated. Several modifications in procedure did not improve the results.

The stereospecific reduction of 1,4- and 1,3-dinitrocyclohexane isomers was achieved by hydrogenation in acetic acid solvent with platinum catalyst. When reductions were conducted on a millimole scale at one atmosphere, reduction to the diamine (isolated as the dihydrochloride) was quantitative. Uptake of hydrogen was initially rapid (four mole-equivalents were absorbed in *ca.* one hour); the remaining two mole-equivalents needed for complete reduction were absorbed more slowly, requiring two to four additional hours. In one instance (with IIIa) it was found that hydrogenation ceased entirely after uptake of four mole-equivalents of hydrogen; however, it was possible to complete the hydrogenation to the diamine by adding more catalyst. These observations suggest an initial rapid reduction to the bishydroxylamine, followed by a slow hydrogenolysis to the diamine.[2,11] Although oximes may result

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(6) Reported for IIa: m.p. 14.8° and b.p. 80–82° (12 mm.) by (a) F. M. Jaeger and J. A. van Dijk, *Proc. Acad. Sci. Amsterdam*, **39**, 384 (1936); *Chem. Abstr.*, **30**, 6341 (1936) and (b) F. M. Jaeger and L. Bijkerk, *Proc. Acad. Sci. Amsterdam*, **40**, 12 (1937); *Chem. Abstr.*, **31**, 4960 (1937).

(7) *cis*-1,2-Diaminocyclohexane (IIb) is described as a liquid, b.p. 92–93° (18 mm.); V. G. Iashunskii, *J. Gen. Chem. USSR*, **28**, 1361 (1958).

(8) (a) J. C. D. Brand and I. D. R. Stevens [*J. Chem. Soc.*, 629 (1958)] obtained 1,2-dinitrocyclohexane as a liquid by adding dinitrogen tetroxide to cyclohexene (ether, 0°). From the liquid, by chromatography, it was possible to separate crystalline Ia (yield not stated) which they suggested had the *trans* configuration. However, they were unable to reduce the substance under stereochemically unambiguous conditions and the configuration was not established; (b) T. F. Doumani and R. W. Long, U. S. Patent 2,551,027, May 1, 1951 [*Chem. Abstr.*, **45**, 7293 (1951)] separated 27% Ia from the liquid 1,2-dinitrocyclohexane obtained by adding dinitrogen tetroxide to cyclohexene.

(9) H. Shechter and F. Conrad, *J. Am. Chem. Soc.*, **75**, 5610 (1953).

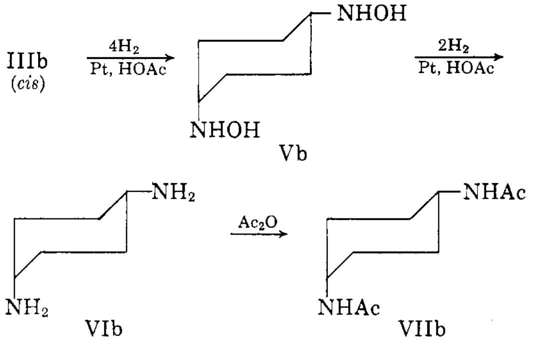
(10) (a) The following observation may be pertinent. H. Baldock, N. Levy, and C. W. Scaife [*J. Chem. Soc.*, 2627 (1949)] treated the liquid 1,2-dinitrocyclohexane (obtained from cyclohexene and dinitrogen tetroxide) with one mole-equivalent of sodium hydroxide to produce 1-nitrocyclohexene (55% yield) and 7.6% unchanged 1,2-dinitrocyclohexane (liquid, possibly Ib). By employing their procedure with pure *trans* IA we obtained 1-nitrocyclohexene in over 82% yield. The explanation of these different yields may be the presence in the liquid of IB which failed to undergo facile nitrite elimination to 1-nitrocyclohexene; (b) *cf.*, Paper III of this series, A. T. Nielsen, *J. Org. Chem.*, **27**, 2001 (1962).

(11) The reported rapid absorption of two mole-equivalents of hydrogen by 1,3-cyclohexanedione dioxime, followed by very slow reduction to the diamine suggests a 1,3-bishydroxylamine intermediate; F. R. Hewgill and P. R. Jefferies, *J. Chem. Soc.*, 805 (1956). Many examples of reduction of nitro compounds to hydroxylamines are known; H. B. Hass and E. F. Riley, *Chem. Rev.*, **32**, 390 (1943). Catalytic hydrogenation of nitroalkanes to hydroxylamines (palladium–barium sulfate, 69–98% yields) has been reported to proceed rapidly (2–20 minutes) in the presence of acetic or oxalic acid; E. Schmidt, A. Ascherl, and L. Mayer, *Ber.*, **58**, 2430 (1925).

from reduction of nitroalkanes under certain conditions,[12] they cannot be intermediates in the present reduction because of the stereospecificity observed.

It was of concern to determine the degree of stereospecificity of the hydrogenation. Kornblum and co-workers[4,5] observed that hydrogenation of optically active 2-nitrooctane in acetic acid solvent resulted in some racemization (less than 25%) whereas in ethanol solvent complete racemization occurred. Their results with optically active α-phenylnitromethane were less satisfactory[4,5]; lower yields of amine and more racemization were observed.

To test the reliability of our hydrogenation procedure for establishing stereochemistry of the dinitrocyclohexanes, the thermodynamically less stable *cis*-1,4-isomer (IIIb) was selected for careful study. The diamine dihydrochloride, obtained in 94% yield, was conveniently converted into *cis*-1,4-diacetamidocyclohexane (VIIb) as the principal product, without isolating the bishydroxylamine (Vb) or the diamine (VIb). Fractional crystallization of the acetylated reduction product indicated the hydrogenation procedure to occur with 75–90% retention of configuration. The reduction procedure, when carried through to the diacetyl derivative with pure *trans*-1,4-dinitrocyclohexane led to *trans*-1,4-diacetamidocyclohexane (IXa) as the sole isolable product. In another experiment, the known *trans* diamine (VIIIa) itself was isolated, m.p. 72°.



Stereospecific reduction was observed with the thermodynamically less stable *trans*-1,3-dinitrocyclohexane, IVa. The diamine produced gave *trans*-1,3-diacetamidocyclohexane (Xa) as the only product, identical with an authentic sample.[13] Hydrogenation of *cis*-1,3-dinitrocyclohexane (IVb) gave only *cis*-1,3-diacetamidocyclohexane (XIb) which also was identical with an authentic sample.[13]

Experimental[14]

***cis*- and *trans*-1,3- and 1,4-Dinitrocyclohexane.—Epimerization Experiments.**—A 30.8-mg. sample of the low-melting isomer of 1,4-dinitrocyclohexane (IIIb, *cis*), m.p. 88–89.5°, was refluxed with 5 ml. of saturated ethanolic sodium bicarbonate solution for 5 hr. After removing the solvent, diluting the residue with water and filtering, there was obtained 24 mg. (78%) of material containing principally the high-melting isomer, m.p. 162–166° (IIIa, *trans*-1,4-dinitrocyclohexane). A sample of the pure *trans* isomer, m.p. 169–169.5°, when treated in a similar manner gave a product, m.p. 165–167°.

A 100-mg. sample of the high-melting isomer of 1,3-dinitrocyclohexane (IVa, *trans*), m.p. 55–58°, was refluxed with 10 ml. of the ethanolic sodium bicarbonate solution for 5 hr. The solution was concentrated to a small volume and chilled to yield a total of 68.4 mg. of crystals, m.p. 25–39°, in successive crops. Recrystallization from ethanol led to 13.6 mg. m.p. 48–54°; the remainder melted at 25–36°. In another run (32 mg. of IVa, m.p. 57–58°, refluxed 4 hr. with 5 ml. of saturated ethanolic sodium bicarbonate solution), there was obtained 14.3 mg., m.p. 30–35°. Recrystallization gave *cis*-1,3-dinitrocyclohexane, IVb, as needles, m.p. 30–32°. A 0.54-g. sample of crude *cis* isomer, IVb, when equilibrated in a similar manner produced 0.09 g. of crude *trans* IVA, m.p. 45–60°.

Reduction of *trans*-1,2-Dinitrocyclohexane (Ia) to *trans*-1,2-Diamino-cyclohexane (IIa).[15]—A 1.74-g. (0.01 mole) sample of *trans*-1,2-dinitrocyclohexane (Ia), m.p. 45.5–46.5°,[16] was refluxed with 5.3 g. of iron powder and 40 ml. acetic acid for 1.5 hr. The mixture was diluted with 100 ml. of water and made alkaline with sodium hydroxide. The mixture was extracted continuously with ether for 75 hr. to yield 1.0 g. (88%) of *trans*-1,2-diaminocyclohexane, m.p. 12–14°; on distillation it gave b.p. 79–80° (12 mm.), m.p. 19–20°.[6]

The dibenzenesulfonyl derivative was prepared in quantitative yield, m.p. 154–154.5°; reported for derivative of IIa, m.p. 153–155°[6a] and of *cis*-IIb, m.p. 165–166°.[7]

Anal. Calcd. for $C_{18}H_{32}N_2O_4S_2$: C, 54.80; H, 5.62; N, 7.10; S, 16.26. Found: C, 55.47; H, 5.61; N, 7.08; S, 16.28.

When the above reduction procedure was applied to *trans*-1,4-dinitrocyclohexane only a few crystals of impure *trans*-1,4-diaminocyclohexane, m.p. 65–70°, could be isolated.[17] Several modifications of the procedure failed to increase the yield. The hydrogenation procedure described below was found to be satisfactory.

Hydrogenation of *trans*-1,4-Dinitrocyclohexane (IIIa) to *trans*-1,4-Diaminocyclohexane (VIIIa).—A 0.1013-g. sample of *trans*-1,4-dinitrocyclohexane dissolved in 10 ml. of acetic acid was hydrogenated with platinum catalyst at 25° (702 mm.). Four mole-equivalents of hydrogen was absorbed in *ca.* 45 min. and two additional mole-equivalents after a total reaction time of 3.5 hr., at which time hydrogen uptake practically ceased. In another run hydrogenation ceased after the absorption of four mole-equivalents of hydrogen; after addition of more platinum oxide hydrogenation was continued until a total of six mole-equivalents of hydrogen was absorbed. The platinum was filtered and dry hydrogen chloride passed into the filtrate to precipitate the hydrochloride salt; removal of the solvent *in vacuo* gave *trans*-1,4-diaminocyclohexane dihydrochloride, 0.107 g. (98% yield). A portion of the dihydrochloride was treated with

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[12] (a) J. v. Braun and E. Danziger, *Ber.*, **46**, 103 (1913); (b) T. Urbanski and M. Slon, *Compt. rend.*, **204**, 870 (1937); (c) K. Johnson and E. F. Degering, *J. Am. Chem. Soc.*, **61**, 3194 (1939).

[13] Samples of *cis*- and *trans*-1,3-diacetamidocyclohexane were kindly furnished by Dr. Hewgill. These substances were made from *cis*- and *trans*-1,3-diaminocyclohexanes, which in turn were prepared from the corresponding dicarboxylic acids by Schmidt reactions, known to proceed with retention of configuration.[11]

[14] Melting points were determined on a Kofler hot stage and are uncorrected.

[15] Adapted from the procedure of Kornblum and Fishbein.[4]

[16] Sample generously furnished by Union Oil Co. of Calif. R. W. Long reports m.p. 46.4°, U. S. Patent 2,551,027, May 1, 1951; *Chem. Abstr.*, **45**, 7293 (1951).

[17] *trans*-1,4-Diaminocyclohexane, prepared by T. Curtius and R. Stangassinger, was reported to melt at 72–73°; diacetyl derivative m.p. >300°; *J. prakt. Chem.*, [2] **91**, 1 (1915).

excess concd. sodium hydroxide solution and heated in a small sublimation apparatus under reduced pressure to yield long needles of *trans*-1,4-diaminocyclohexane, m.p. 72°.[17] The amine reacts with carbon dioxide of the air extremely rapidly to form a solid white carbonate.

Reaction of the diamine with acetic anhydride led to ***trans*-1,4-bisacetamidocyclohexane (IXa)**; rectangular prisms from ethanol, m.p. 310–315° dec. with formation of needles near 230°).[17]

Anal. Calcd. for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15. Found: C, 60.48; H, 8.97.

***cis*-1,4-Diacetamidocyclohexane (VIIIb).**—A 0.0987-g. sample of *cis*-1,4-dinitrocyclohexane (IIIb), m.p. 88–90°, was hydrogenated by the above procedure and converted into the diamine dihydrochloride (94% yield). The diamine was liberated by adding a few drops of concd. sodium hydroxide solution. Without isolating the diamine it was converted into its diacetyl derivative by refluxing with excess acetic anhydride for 1.5 hr. The reaction mixture was concentrated to dryness and the residue was sublimed at 150–170° (0.1 mm.). The sublimate was fractionally crystallized from acetone to yield 7.1 mg., of less soluble crystals, m.p. 265–287°, believed to be crude *trans*-1,4-diacetamidocyclohexane, IXa[17] (6.3% yield), and 73.7 mg. of crude *cis*-1,4-diacetamidocyclohexane, VIIb, m.p. 170–205° (65.5% yield from IIIb). Crystallization of this latter material from acetone gave 20 mg., m.p. 202–207°, and recrystallization gave 10 mg. of small white needles, m.p. 208–209°, used for analysis.

Anal. Calcd. for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15. Found: C, 60.37; H, 8.83.

Hydrogenation of *cis*- and *trans*-1,3-Dinitrocyclohexane. *cis*- and *trans*-1,3-Diacetamidocyclohexane.—*trans*-1,3-Dinitrocyclohexane (IVa), m.p. 55–57°, was hydrogenated by the procedure used with 1,4-dinitrocyclohexane and the resulting diamine converted into its diacetyl derivative. After sublimation, the diacetyl derivative was crystallized once from acetone to give pure ***trans*-1,3-diacetamidocyclohexane (Xa)**, m.p. 221–222°; when mixed with an authentic sample of this substance, m.p. 220–220.5°, the melting point was not depressed (reported m.p. 220–221°).[11,13] The substance crystallizes from acetone in clusters of spear-shaped crystals, which near 200° become needle-like prisms and finally near the melting point change to flat prisms.

cis-1,3-Dinitrocyclohexane (IVb) was hydrogenated and converted into its diacetamido derivative in a similar manner. Crystallization of the sublimate from ethyl acetate–ethanol gave ***cis*-1,3-diacetamidocyclohexane (XIb)** as feathery needles, m.p. 262°; when mixed with an authentic sample, m.p. 262°, the melting point was not depressed (m.p. reported, 262–263°).[11,13]

Anal. Calcd. for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15; N, 14.13. Found: C, 60.31; H, 9.21; N, 14.15.

The Isomeric Dinitrocyclohexanes. III. Chemistry of the Nitronate Ions

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The three isomeric dinitrocyclohexanes exhibit different chemical behavior in sodium hydroxide solution. With one mole-equivalent of sodium hydroxide *trans*-1,2-dinitrocyclohexane (Ia) forms 1-nitrocyclohexene (III). Both Ia and III react with excess hydroxide ion to form cyclohexene 3-nitronate ion (V). The nitronic acid of V rapidly forms only III in aqueous ethanol solution. 1,3-Dinitrocyclohexane (VIII) forms a bisnitronate ion (IX) which reacts with hydroxide ion to form the nitronate ion of a conjugated nitrodiene, possibly 2-nitro-2,4-hexadiene (XII). 1,4-Dinitrocyclohexane (XIII) forms a very stable bisnitronate ion (XIV) which on protonation leads to a mixture of XIII epimers containing 54.5% of the *cis* isomer. Chlorination, bromination, and methylolation of XIV lead to high yields of 1,4-disubstituted epimer mixtures containing 60–70% *trans* isomers. The stereochemistry of these reactions is discussed.

In basic solution nitroalkanes form relatively stable nitronate ions, $RCH{=}NO_2^-$, which are characterized by strong ultraviolet absorption in the range 220–250 mμ.[1] α,ω-Dinitroalkanes having nitro groups separated by more than three carbon atoms form stable bisnitronate ions, but 1,2-dinitroethane and, less readily, 1,3-dinitropropane are destroyed by hydroxide ion.[2] Alicyclic mononitroalkanes form stable nitronate ions.[1,3] The present work is a study of the chemical behavior of the isomeric dinitrocyclohexanes in basic solution—*i.e.*, reactions of the resulting nitronate ions.

The three isomeric dinitrocyclohexanes exhibit different chemical behavior in sodium hydroxide solution. The 1,2- and, less readily, the 1,3-isomer are destroyed by hydroxide ion, whereas the 1,4-isomer forms a rather stable bisnitronate ion. An understanding of these reactions has been assisted by examination of the ultraviolet spectra of the resulting nitronate ions.

1,2-Dinitrocyclohexane (I), prepared by addition of dinitrogentetroxide to cyclohexene, is described as a liquid[4] which is probably a mixture of epimers.[5b]

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(1) H. Shechter, P. W. K. Flanagan, J. G. Traynham, and F. T. Williams, Jr., Abstracts of the 136th National American Chemical Society Meeting, Atlantic City, N. J., September 13–18, 1959; Paper No. 53, p. 33P; article to be published; we wish to thank Professor Shechter for providing us with a copy of this paper prior to its publication.

(2) A. T. Nielsen, *Chem. and Ind.* (London), 1358 (1957); (b) A. T. Nielsen, unpublished work.

(3) M. F. Hawthorne, *J. Am. Chem. Soc.*, **79**, 2510 (1957).

(4) H. Baldock, N. Levy, and C. W. Scaife, *J. Chem. Soc.*, 2627 (1949); by reaction with one mole-equivalent of sodium hydroxide this liquid has been reported to form III (55% yield) and 7.6% recovered (liquid) I.

(5) (a) A. T. Nielsen, Paper I of this series, *J. Org. Chem.*, **27**, 1993 (1962); (b) Paper II, *ibid.*, **27**, 1998 (1962).