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.

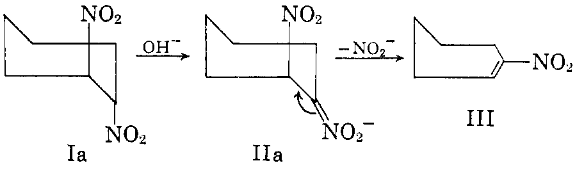
(2) A. T. Nielsen, *Chem. and Ind.* (London), 1358 (1957); (b) A. T. Nielsen, unpublished work.

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

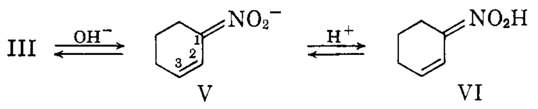
(4) H. Baldock, N. Levy, and C. W. Scaife, *J. Chem. Soc.*, 2627 (1949); by reaction with one mole-equivalent of sodium hydroxide this liquid has been reported to form III (55% yield) and 7.6% recovered (liquid) I.

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

Reaction of pure *trans*-1,2-dinitrocyclohexane (Ia) with one mole-equivalent of sodium hydroxide was found to produce pure 1-nitrocyclohexene (III) in over 82% yield; the proton magnetic resonance spectrum of the product indicated 3-nitrocyclohexene to be absent. Because of nonbonded electrical repulsion between the nitro groups it appears likely that Ia exists predominantly in the diaxial form in the solid state and in solution.[6] Elimination of nitrite ion by Ia occurs rapidly and may proceed through the mononitronate ion, IIa. Configuration IIa, with axial nitro group, would form initially, and also be preferred over its ring inversion isomer (IIb) because of electrical repulsions.[7a] Form IIb with equatorial nitro might be expected to react more slowly than IIa.[7b] It is possible that *cis*-1,2-dinitrocyclohexane (Ib) undergoes elimination to III less readily than does Ia.[4]



By reaction with excess sodium hydroxide, *trans*-1,2-dinitrocyclohexane (Ia), and 1-nitrocyclohexene (III) (λ_{max} 258 mμ, ϵ_{max} 5250)[8] readily form the same nitronate ion, V. Protonation of V leads immediately to the nitronic acid, VI, which disappears rapidly in neutral solution, ultimately producing the spectrum of III. The observed intensity of the resulting absorption band at 258 mμ indicates III to be the sole product. The nitronic acid → nitroalkane isomerization is known to proceed through the nitronate ion.[9,10] The formation of pure III is more rapid (complete in one hour) than one would anticipate for an isomerization proceeding through 3-nitrocyclohexene (VII).[11] One would expect proton removal from a 3-nitroalkene to be extremely slow in neutral solution at 25°. Exclusive protonation of V at C-3 is indicated, the transition state for formation of conjugated III probably being of much lower energy than that leading to VII. By again making the solution of reformed III basic, nitronate ion V is regenerated in its original concentration.



The rate of isomerization of VI to III was measured spectrophotometrically. No unusual enhanced stability of VI was noted; its half-life in neutral aqueous ethanol is estimated to be *ca.* fifteen minutes at 25°. By comparison, propane-1-nitronate ion (λ_{max} 237 mμ, ϵ 9700) under the same conditions forms a nitronic acid (λ_{max} 227 mμ) having a half-life of *ca.* twelve minutes (isomerization to 1-nitropropane). The rate of isomerization of ethane nitronic acid to nitroethane in water has been examined previously (half-life *ca.* forty minutes at 0°).[9,12] By comparison, the rate of isomerization of *aci*-phenylnitromethane to phenylnitromethane is much slower (half-life seventeen and one half hours at 0°).[12,13]

***cis*- and *trans*-1,3-dinitrocyclohexane** (VIIIb and VIIIa, respectively) react with 0.01 *M* 85% ethanolic sodium hydroxide solution to yield a bisnitronate ion, IX (λ_{max} 238 mμ, ϵ_{max} 20,300). The solution very slowly becomes yellow on standing at room temperature, forming nitrite ion. After sixty-six hours a strong absorption band is observed at 389 mμ (ϵ_{max} 13,300) and a band at 243 mμ (ϵ_{max} 3980); the true value of ϵ_{max} for the species absorbing at 389 mμ may be somewhat higher because of side reactions and/or incomplete reaction of IX. The bisnitronate ion (IX) is more stable in 0.001 *M* sodium hydroxide solution, but solutions of 0.1 *M* or greater hydroxide ion concentration lead immediately to yellow solutions absorbing at 389 mμ. Acidification of this solution (ϵ^{389}_{max} 13,300) gives absorption maxima at 309 mμ (ϵ 10,000) and 212 mμ (ϵ 10,100) (shoulder at 235 mμ, ϵ 5100); again, these values of ϵ_{max} may be low. The spectrum remains unchanged during sixteen hours and resembles that of a conjugated dialkylnitrodiene.

The ultraviolet spectrum of the substance having an absorption maximum at 309 mμ is that to be expected for 2-nitro-2,4-hexadiene (II); calculated

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[6] K. Kozima, K. Sakashita, and S. Maeda, *J. Am. Chem. Soc.*, **76**, 1965 (1954) report *trans*-1,2-dibromocyclohexane to exist solely in the diaxial form in the solid state and to be predominantly diaxial in carbon tetrachloride solution; *cf.*, M. T. Rogers and J. M. Cannon, *J. Phys. Chem.*, **65**, 1417 (1961). Direct evidence of nonbonded repulsion of nitro groups is found in *cis*-dinitroalkenes; T. E. Mead and L. B. Clapp, *J. Org. Chem.*, **23**, 921 (1958).

[7] (a) E. J. Corey, *J. Am. Chem. Soc.*, **76**, 175 (1954); (b) Evidence relating to this question is found in recent work of A. M. Wilson and N. L. Allinger, *ibid.*, **83**, 1999 (1961). *trans*-2(axial)-Chloro-4-*t*-butylcyclohexanone was reduced more readily than its isomer having equatorial chlorine indicating favored *transoid* elimination of chloride ion.

[8] (a) G. F. Bloomfield and G. A. Jeffrey, *J. Chem. Soc.*, 120 (1944), report λ_{max} *ca.* 250 mμ (log ϵ 3.75) for III; data reported graphically and solvent not stated; (b) By comparison, 2-nitro-2-butene has absorption maxima at 234 (ϵ 5600), 242 (ϵ 5800), and 250 mμ (ϵ 5600); (ethanol solvent); E. A. Braude, E. R. H. Jones, and G. G. Rose, *ibid.*, 1104 (1947).

[9] S. H. Maron and V. K. La Mer, *J. Am. Chem. Soc.*, **61**, 692 (1939).

[10] H. E. Zimmerman and T. E. Nevins, *ibid.*, **79**, 6559 (1957).

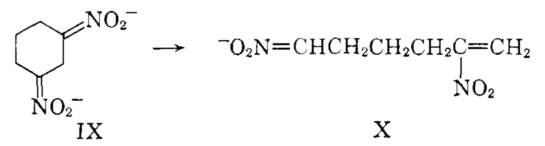
[11] (a) The ultraviolet spectrum of VII would be expected to resemble that of nitrocyclohexane (λ_{max} 278 mμ, ϵ_{max} 33; at 258 mμ, ϵ = 20). Pure VII has not been described, but others have prepared what appear to be impure samples of it; ref. 8a and H. Wieland, *Ann.*, **424**, 71 (1921); (b) The spectra of nitrocyclohexane and cyclohexene (which has no absorption maximum above 205 mμ) have been reported elsewhere; ref. 8a and G. Eglinton, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 2873 (1952).

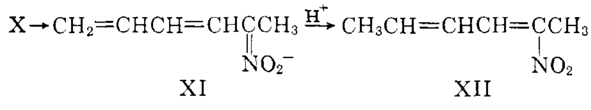
[12] K. H. Meyer and P. Wertheimer, *Ber.*, **47**, 2374 (1914).

[13] R. G. Cooke and A. K. Macbeth, *J. Chem. Soc.*, 1024 (1938).

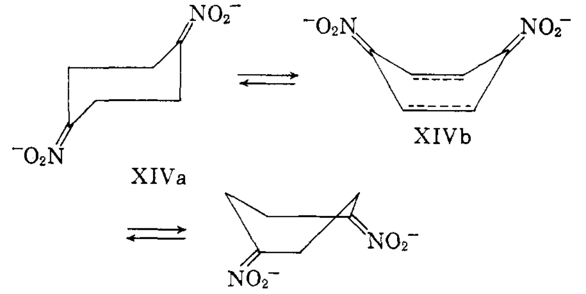
λ_{max} 210 + 35 + 65 = 310 mμ.[14,15] Regeneration of the nitronate ion of 2,6-dinitro-1-hexene (X, precursor of IX[5a]) followed at various stages by base attack, prototropic rearrangements, and elimination of nitrous acid,[15] would lead to nitronate ion XI (λ_{max} 389 mμ[14b]).

Protonation of XI would ultimately produce XII. Here, as in the case of V, protonation is believed to occur readily at the terminal position of the conjugated nitronate ion, thereby leading to a conjugated nitrodiene. The intervention of nonconjugated nitrodienes in the conversion XI→XII might be excluded as was 3-nitrocyclohexene (VII) from the conversion V→III (discussion above).


IX X


$$X \rightarrow CH_2{=}CHCH{=}CH\underset{\overset{\|}{NO_2^-}}{C}CH_3 \xrightarrow{H^+} CH_3CH{=}CHCH{=}\underset{\overset{|}{NO_2}}{C}CH_3$$
XI XII

In contrast to 1,2- and 1,3-dinitrocyclohexane, ***cis*- and *trans*-1,4-dinitrocyclohexane** (XIIIb and XIIIa, respectively) form a strongly absorbing, very stable bisnitronate ion (XIV); λ_{max} 238 mμ, ϵ_{max} 29,300 in 0.01 *M* 85% ethanolic sodium hydroxide solution. In solution this ion may contain a very few per cent of the boat form XIVb[6,16]; polarization of the central C—C bond with resulting increased p-orbital content might facilitate the inversion XIVa → XIVb,[2a,16,17] although strongly opposing non-bonded repulsions of the nitronate groups in XIVb would disfavor it. In view of the recent findings of Allinger and Freiberg[16b] boat-form XIVc might be favored over XIVa.



Reactions of protonation, chlorination, bromination, and methylolation of the ion XIV have been studied in some detail. Except for methylolation, these reactions are rapid, and the product composition, which is believed to be kinetically controlled, is a reflection of the stereochemical path of the reaction. Since the reaction products are formed in high yields (90–100%) in high purity and are immediately removed from solution by precipitation, no opportunity for their equilibration is allowed; it must be mentioned that such equilibration is highly unlikely, even in solution, under the reaction conditions employed. Configurations of each of the isomeric halogenation products has been established previously.[5a] Analyses of isomer mixtures were made by fractional crystallization and infrared measurements; the infrared spectra of the products revealed no OH or C=O stretching bands indicating absence of nitronic acids or Nef products. Results are summarized in Table I.

TABLE I

REACTIONS OF CYCLOHEXANE-1,4-BISNITRONATE ION (XIV)

Reactant	Product—cis and trans	Total yield, %	Per cent trans—Cryst'n. ca. ±5%	Per cent trans—Infrared ±1.5%
Acetic acid	XIII	100	50	45.5
Chlorine	XVI	97	63	60.5
Bromine	XVII	90	71	61.5[a]
Formaldehyde	XX	99	66	...

[a] Figure may be slightly low due to reaction during pressing of the potassium bromide disk (see Experimental).

The slight preference for formation of *cis*-1,4-dinitrocyclohexane (XIIIb) would appear to indicate some hindrance to protonation by axial hydrogens in the 3- positions, assuming protonation to occur on the mononitronate ion XVa in which orientation of the nitro group is equatorial.[18] Formation of nearly equal amounts of *cis* and *trans* products affirms the view that the nitronate ion is essentially planar (*sp*^{2}). A tetrahedral carbanion would be expected to lead principally to *trans* products, assuming it to exist in a chair conformation with equatorial nitro groups.

Chlorination or bromination of XIV leads to a mixture of *cis* and *trans* derivatives (90–97% yield) which were separated by fractional crystallization. The higher melting, less soluble isomers

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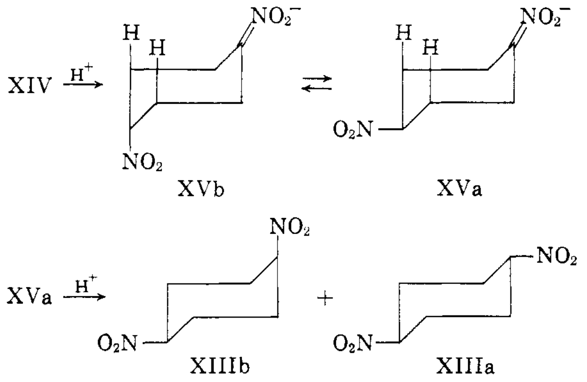
[14] (a) From the study of Braude, Jones, and Rose[8b] the following bathochromic absorption maxima wavelength shifts (mμ; ethanol solvent) are predicted for alkyl substitution in nitroolefins, $R_2C{=}C(R)NO_2$; α, 15; β, 20; α,β, 35; β,β, 45 ± 5 mμ; each added olefinic double bond, 65 mμ (*cf.* ref. 15). The parent nitroethylene itself would have an estimated λ_{max} of *ca.* 210 mμ. (b) By contrast, in nitronate ion spectra the effect of alkyl substitution is relatively small and irregular, although each added olefinic double bond produces a large bathochromic shift (50–80 mμ).[1,2b]

[15] H. Shechter and F. Conrad, *J. Am. Chem. Soc.*, **76**, 2716 (1954) report for 5-methyl-2-nitro-2,4-hexadiene λ_{max} 335 mμ (ϵ_{max} 11,700) and 230 mμ (ϵ_{max} 7700) in 95% ethanol solvent. They suggest that this substance arises from 2,5-dinitro-5-methyl-2-hexene by base-catalyzed elimination of nitrous acid.

[16] (a) For related discussions of 1,4-cyclohexanedione configurations see N. L. Allinger, *ibid.*, **81**, 5727 (1959) and C. G. Le Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.*, 3549 (1956); (b) N. L. Allinger and L. A. Freiberg, *J. Am. Chem. Soc.*, **83**, 5028 (1961).

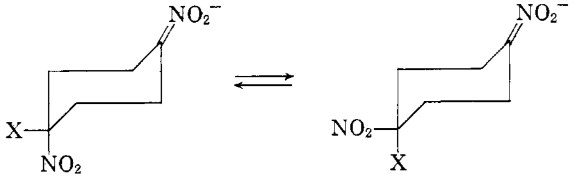
[17] C. G. Le Fèvre and R. J. W. Le Fèvre, *Chem. and Ind.* (London), 54 (1956).

[18] Hindrance by axial hydrogens has been reported in the base-catalyzed decarboxylation of 4-phenylcyclohexane-1,1-dicarboxylic acid. The decarboxylation, which proceeds through the enol, leads to 61% *cis*-4-phenylcyclohexane-1-carboxylic acid when the attacking base is collidine; H. E. Zimmerman and H. J. Giallombardo, *J. Am. Chem. Soc.*, **78**, 6259 (1956).



were identical with *trans*-1,4-dichloro-1,4-dinitrocyclohexane (XVIa) and *trans*-1,4-dibromo-1,4-dinitrocyclohexane (XVIIa) obtained previously[5a] by oxidation of the corresponding *trans* dinitroso compounds. The lower melting 1,4-dibromo-1,4-dinitrocyclohexane (XVIIb) proved to be identical with the *cis* isomer of this substance obtained previously.[5a] Analysis of the mixture of bromo isomers was complicated by a reaction of the *cis* isomer with the potassium bromide during preparation of the disks; the mixture may, in fact, contain about 70% *trans* isomer (see Experimental).

Assuming the halogenation reactions to proceed stepwise, the isomer ratio of epimeric 1,4-dihalo-1,4-dinitrocyclohexanes would be affected by the structure of the mononitronate ion intermediate. Since hindrance by axial hydrogens in the 3-position favors equatorial attack, structures XVIIIa and XIXa, with equatorial orientation of halogen, appear to be preferred over the ring-inversion isomers XVIIIb and XIXb. Rapid halogenation, or protonation, of the bisnitronate ion XIVa (chair-form) without intervention of mononitronate intermediates would favor formation of *trans* products in every case; boat-forms XIVb and XIVc would favor *cis* products. Reactions of mononitronate ions without the possibility of their prior ring inversion would lead to the same result. Since the product compositions are not overwhelmingly *trans* or *cis* and depend on the nature of the attacking reagent, it appears reasonable that the reactions of XIV proceed through mononitronate ions whose preferred configurations (XVa, XVIIIa, and XIXa) are determined by prior ring-inversion equilibria.



XVIIIa(x-a) XIXa(x-b)

XVIIb(x-a) XIXb(z-b)

The position of the equilibrium XVIIIa ⇆ XVIIIb is not known, but formation of 60.5% *trans* XVIa requires a minimum of 60.5% XVIIIa and 100% equatorial attack by chlorine. Exclusive equatorial attack would appear unlikely; more reasonably a lower figure, as for example 80%, would require 75% XVIIIa. Since the product composition of these reactions is determined by the amount of equatorial attack as well as by the position of equilibrium, it can be seen that the small increase (relative to chlorination) in the amount of *trans* product in the bromination reaction could actually represent a rather large amount of equatorial attack by bromine. For example, a figure of 65% *trans* XVIIa could be represented by 75% XIXa (with equatorial halogen) and 87% equatorial bromine attack. The relative amounts of equatorial isomers XVIII aand XIXa in the equilibrium cannot be accurately assessed. The preference for equatorial halogen over nitro may be due to greater interaction with adjacent equatorial hydrogens by nitro.[16] It is interesting to presume that bromine may more closely resemble nitro than chlorine in this respect,[6] thus leading to the result of less equatorial halogen for XIX (bromo) than XVIII (chloro). Neglecting for the moment the difference in bulk between chlorine and bromine, one would then conclude the amount of equatorial attack by bromine (relative to chlorine) to be somewhat greater than suggested in the above discussion.

Reaction of 1,4-bisnitronate ion XIV with excess formaldehyde led to a mixture of epimeric 1,4-bis-hydroxymethyl - 1,4 - dinitrocyclohexanes. These were separated by fractional crystallization to yield 66% of crude high-melting isomer [probably the *trans* form (XXa), m.p. 200–203°, when pure]. A small amount of a lower melting material, m.p. 140–143°, was isolated which is believed to be crude *cis* isomer (XXb). The methylolation reaction, in contrast to protonation and halogenation, is relatively slow. Since the ratio of epimeric products may to some extent be thermodynamically controlled by the equilibrium between XIV and formaldehyde, no attempt was made to determine more accurately the composition of the isomer mixture by infrared analysis.

Experimental[19]

1-Nitrocyclohexene (III) from *trans*-1,2-Dinitrocyclohexane (Ia).—The procedure of Baldock, Levy, and Scaife[4] was used with slight modifications. To a solution of 4.45 g. (0.0256 mole) of *trans*-1,2-dinitrocyclohexane (Ia), m.p. 45.5–46.5°,[20] in 25 ml. of ether was added a solution of 1.03 g. (0.0256 mole) of sodium hydroxide in 20 ml. of water. The mixture was stirred at 24° for 5.5 hr. The orange colored aqueous layer (*p*H *ca.* 8) was extracted with ether and the extracts combined with the ether layer. The ether solution was washed with dilute acetic acid and water and dried

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[19] Melting points were determined on a Kofler block and are uncorrected. Ultraviolet spectra were measured in 95% ethanol unless otherwise stated.

[20] A generous sample of 1,2-dinitrocyclohexane was provided by the Union Oil Co. of California.

TABLE II

ULTRAVIOLET ABSORPTION SPECTRA OF NITRONATE IONS IN 85% ETHANOLIC SODIUM HYDROXIDE SOLUTIONS

$\lambda_{\max}$ in mμ ($\epsilon_{\max}$ in parentheses)

Compound	Concn., $M \times 10^5$	Reaction Time, Min.	Sodium Hydroxide Concn., M		
			0.1	0.01	0.001
1-Nitrocyclohexene	14.3	5	238 (14,100) 284 (6230)	241 (11,780) 285 (4900)	247 (5800)
		11	238 (13,300) 284 (5880)	242 (11,280) 285 (5310)	244 (6230)
		120	240 (12,500) 286 (5700)	241 (11,000) 286 (5500)	242 (9000) 287 (5300)
trans-1,2-Dinitrocyclohexane	10.1	3	238 (11,900) 285 (4800)	238 (9950) 282 (4300)	260 (5450) shoulder
trans-1,3-Dinitrocyclohexane	6.1	4		238 (20,000)[a]	238 (12,600)
		24	247 (7700) 389 (8750)	238 (17,500)	238 (19,700)[b]
		3960		243 (3980) 389 (13,300)	238 (16,800) 390 (2130)
trans-1,4-Dinitrocyclohexane	4.36	5		238 (29,000)	
		2550		238 (26,000)	
Nitrocyclohexane	12.3	...[c]		237 (12,200)	238 (10,300)
1-Nitropropane	15.8	...[c]		237 (9700)	237 (8600)

[a] $\epsilon_{\max}$ 20,300 at 2 min. [b] $\epsilon_{\max}$ 19,900 at 110 min. [c] No significant change of these $\epsilon_{\max}$ values with time.

with magnesium sulfate. After removing the ether the residue was distilled through a short column to yield 2.67 g. (82%) of 1-nitrocyclohexane, b.p. 40° (0.08 mm.), and 0.22 g. of liquid residue and holdup (odor suggests the presence of additional nitrocyclohexene). Redistillation gave a sample b.p. 40° (0.06 mm.), n^{22}_{D} 1.5055, $\epsilon_{\max}^{258.5}$ 5250. The proton magnetic resonance spectrum (deuterochloroform solution) revealed a single vinyl proton strongly coupled to two equivalent protons (triplet); further splitting of this triplet into triplets due to weaker coupling to two equivalent protons was observed. No other type of vinyl proton was evident in the spectrum indicating the absence of 3- and 4-nitrocyclohexene.

Reaction of *trans*-1,2-Dinitrocyclohexane (Ia) and 1-Nitrocyclohexene (III) with Sodium Hydroxide.—A solution of 1-nitrocyclohexene in 85% ethanolic sodium hydroxide (0.01 M) reveals absorption maxima at 241 and 285 mμ. The rate of formation of these maxima decreases with decreasing hydroxide ion concentration. In 0.1 M sodium hydroxide solution *trans*-1,2-dinitrocyclohexane produces the same spectrum as III; nitrite ion is rapidly produced simultaneously (starch–potassium iodide test). Data are summarized in Table II.

Neutralization of the 0.01 M sodium hydroxide solution of III with an equivalent amount of 0.1 N hydrochloric acid gave an absorption maximum at 265 mμ ($\epsilon_{\max}$ 7500 after 3 min.). A hypsochromic shift in the absorption maximum and a decrease in the extinction coefficient was observed at 25°; absorption maxima, molecular extinction coefficients, and times observed (average of two determinations) were: 264 mμ, 7000, 8 min.; 263 mμ, 6500, 13 min.; 262 mμ, 6050, 19 min.; 260 mμ, 5750, 26 min.; 258 mμ, 5250, 60, and 360 min. By plotting these data graphically and extrapolating to zero time, an extinction coefficient of 8000 is obtained for the species absorbing at 265 mμ; the half-life of this material is calculated to be 15 ± 2 min. When the solution was again made basic (0.01 M with sodium hydroxide) absorption maxima at 242 mμ (ϵ 10,300) and 282 mμ (ϵ 3000) were observed. Again neutralizing the solution with hydrochloric acid regenerated the species absorbing at 265 mμ (ϵ 7400 after 3 min.) which changed to 258 mμ (ϵ 6000) after 82 min.

1-Nitropropane in 0.01 M 85% ethanolic sodium hydroxide produced an absorption maximum at 237 mμ (ϵ 10,300). Neutralization with hydrochloric acid led to an absorption maximum at 223 mμ (ϵ 9500 after 1.5 min.); the intensity of this absorption decreased with time as follows: ϵ 7950, 5 min.; 6450, 8 min.; 5450, 11 min.; 3970 16 min.; and 2650, 27 min. After 27 min. a shoulder, but no maximum at 223 mμ was observed. By extrapolation to zero time the molecular extinction coefficient at 223 mμ was calculated to be 10,500. 1-Nitropropane itself has weak absorption in ethanol at this wave length ($\epsilon \cong 300$). From these data the half-life of the species absorbing at 223 mμ is calculated to be *ca.* 12 min. at 25°.

Ultraviolet Spectra of Nitronate Ions.—The ultraviolet spectra of *trans*-1,4- and 1,3-dinitrocyclohexane in 85% ethanolic sodium hydroxide solution are summarized in Table II. The corresponding *cis* isomers have essentially identical spectra under the same conditions. It was found that 1,4-dinitrocyclohexane was quite stable in 0.01 N sodium hydroxide solution, but that the 1,3-isomer was not. The latter compound in basic solution readily produced a yellow color, $\lambda_{\max}$ 389 mμ (ϵ 13,300 after 66 hr.); nitrite ion was also formed (starch–iodide test). The true maximum value of the extinction coefficient for the 389 mμ band is not known. When the yellow solution was neutralized with 0.1 N hydrochloric acid absorption maxima appeared at 309 mμ (ϵ 10,000), 237 mμ (shoulder, ϵ 5100), and 212 mμ (ϵ 10,100); the true values of $\epsilon_{\max}$ may be somewhat higher than those calculated here.

Reactions of Cyclohexane-1,4-bisnitronate Ion (XIV). A. Protonation. *cis*- and *trans*-1,4-Dinitrocyclohexane (XIIIb and XIIIa).—A 0.71-g. sample of *trans*-1,4-dinitrocyclohexane (XIIIa), m.p. 168–169.5° was dissolved in a mixture of 20 ml. of ethanol and 20 ml. of N sodium hydroxide by stirring for 45 min. After chilling to 5° the mixture was acidified by adding all at once a solution of 1.5 ml. of acetic acid in 15 ml. of water. After chilling 29 hr. and filtering there was obtained 0.71 g. of material, m.p. 100–145°. Crystallization from ethanol gave 0.35 g., m.p. 160–163° (principally *trans*-1,4-dinitrocyclohexane XIIIa) and evaporation of the filtrate gave 0.35 g. m.p. 88–92°, principally *cis*-1,4-dinitro-cyclohexane (XIIIb); recrystallization of the latter from carbon tetrachloride gave needles, m.p. 89–90°, of pure XIIIb.

To secure a more accurate analysis of the mixture of *cis*- and *trans*-1,4-dinitrocyclohexane an infrared procedure, similar to that described by Zimmerman and Giallombardo,[18] was employed. Bands at 11.78 and 11.20 μ were selected for the analysis; absorbances were corrected by subtracting the absorbance value at 10.5 μ (usually *ca.* 0.08). A 7-mg. sample was thoroughly ground and mixed with 2.0 g. of potassium bromide. From the expressions $A'_m = c_c A'_c +$

$c_tA'_t$ and $A''_m = c_cA''_c + c_tA''_t$, equation 1 was derived for the ratio of *cis* to *trans* isomers, c_c/c_t.

$$\frac{c_c}{c_t} = \frac{A''_mA'_t - A''_tA'_m}{A'_mA''_c - A'_cA''_m} \qquad (1)$$

where c_c = Concentration of *cis* isomer in the mixture, c_t = Concentration of *trans* isomer in the mixture, A'_m = Absorbance of mixture at λ', A''_m = Absorbance of mixture at λ'', A'_c = Absorbance of pure *cis* isomer at λ', A''_c = Absorbance of pure *cis* isomer at λ'', A'_t = Absorbance of pure *trans* isomer at λ', A''_t = Absorbance of pure *trans* isomer at λ''.

Observed absorbances (corrected) for *trans*-1,4-dinitrocyclohexane were 0.90 at 11.2 μ (A'_t) and 0.005 at 11.8 μ (A''_t) and for the *cis* isomer 0.23 at 11.2 μ (A'_c) and 0.77 μ at 11.8 μ (A''_c). Known mixtures of pure *cis* and *trans* isomers were prepared and the mixtures analyzed using equation 1. For example, a known mixture containing 60.0% *cis*-1,4-dinitrocyclohexane and 40.0% of the *trans* isomer produced values of A''_m and A'_m of 0.455 and 0.485, respectively. Substituting in equation 1 leads to a calculated value of 60.1% *cis*. Values for other known mixtures (observed values in parentheses) were 80 (80.4), 40 (40.4), and 20 (19.2). The analysis of the unknown mixture obtained above by protonation indicated 56.0% *cis*. The protonation was repeated three times under similar conditions to yield mixtures which analyzed 54.6, 53.2, and 54.4% *cis* (average of all four values, 54.5 ± 1.5%).

B. Chlorination. *cis*- and *trans*-1,4-Dichloro-1,4-dinitrocyclohexane (XVIb and XVIa).—A 0.7-g. (0.0040 mole) sample of *trans*-1,4-dinitrocyclohexane was dissolved in 20 ml. of ethanol and 10 ml. of *N* aqueous sodium hydroxide. Chlorine gas was passed into the solution for a few minutes until no further precipitation was noted; the solution was then chilled. Filtration gave 0.9112 g. (93% yield) of a mixture of *cis*- and *trans*-1,4-dichloro-1,4-dinitrocyclohexane, m.p. 125–188°; in another run the yield was 97%. Crystallization of an 0.86-g. aliquot of the mixture from ethanol (seeding with pure *trans* isomer) gave 0.54 g., m.p. 183–191°, containing principally *trans* isomer, XVIa; recrystallization gave coarse crystals of pure *trans*-1,4-dichloro-1,4-dinitrocyclohexane (XVIa), m.p. 191–192°. When mixed with a sample of this material, m.p. 190–191°, obtained previously by oxidation of *trans*-1,4-dichloro-1,4-dinitrocyclohexane,[5a] the melting point was not depressed. Evaporating to dryness the filtrate remaining after removing the crude *trans* isomer gave 0.32 g., m.p. 120–130°, containing principally the *cis* isomer, XVIb. Recrystallization of the latter from cyclohexane gave hexagonal plates of pure *cis*-1,4-dichloro-1,4-dinitrocyclohexane (XVIb), m.p. 121–122°, which was used for analysis.

Anal. Calcd. for $C_6H_8Cl_2N_2O_4$: C, 29.65; H, 3.32; Cl, 29.17; N, 11.52. Found: C, 30.00; H, 3.86; Cl, 29.16, N, 11.44.

The mixture of chlorination products obtained was analyzed using the infrared technique. Infrared bands at 11.8 and 10.1 μ were used and absorbances were corrected by subtracting the absorbance at 9.5 μ (*ca.* 0.10). Samples of mg. were mixed and ground with 2 g. of potassium bromide. Absorbance values for pure *cis* and *trans* isomers at 11.8 μ were 0.54 for *cis* and 0.00 for *trans*, and at 10.1 μ, 0.01 for *cis* and 0.34 for *trans*. Known mixtures were prepared giving analyses accurate to ±1%. The unknown mixture above and that from another run gave analyses of 40.2 and 38.8% *cis*.

C. Bromination. *cis*- and *trans*-1,4-Dibromo-1,4-dinitrocyclohexane (XVIIb and XVIIa).—*trans*-1,4-Dinitrocyclohexane (0.50 g.) was dissolved in a solution of 15 ml. of ethanol and 12 ml. of *N* aqueous sodium hydroxide solution and treated with 1.0 g. of bromine. The precipitate which formed immediately was washed with ethanol to yield 0.85 g. (89%), m.p. 155–201°; in another run the yield was 91%. Crystallization from ethanol gave 0.60 g., m.p. 190–205°, of crude *trans*-1,4-dibromo-1,4-dinitrocyclohexane (XVIIa); recrystallization from ethanol gave XVIIa, m.p. 211–214° dec. When mixed with a sample of this material, m.p. 211–214°, obtained previously by oxidation of *trans*-1,4-dibromo-1,4-dinitrosocyclohexane,[5a] the melting point was not depressed. From the filtrate, by recrystallization from carbon tetrachloride, 0.16 g. of *cis*-1,4-dibromo-1,4-dinitrocyclohexane was isolated, m.p. 159–160°, which was used for analysis.

Anal. Calcd. for $C_6H_8Br_2N_2O_4$: C, 21.71; H, 2.43; Br, 48.15; N, 8.44. Found: C, 21.61; H, 2.65; Br, 48.44; N, 8.17.

The mixture of bromination products was analyzed by the infrared technique. Strong absorption at 11.8 μ was found to be characteristic of the *cis* isomer, and at 10.1 μ for the *trans* isomer, as was the case for the corresponding dichloro compounds. Samples of 5 mg. were mixed and ground with 2 g. of potassium bromide. Absorbance values for the *trans* compound were 0.24 at 10.1 μ and 0.04 at 11.8 μ. The duration of grinding and pressing (80,000 p.s.i.) affected the intensity of the absorption of the *cis* isomer, particularly at 11.8 μ. Prolonged grinding and a 2-min. pressing time gave an absorbance value of 0.37 at 11.8 μ and 0.05 at 10.1 μ. Using a minimum amount of grinding and a 10-sec. pressing, absorbance values of 0.50 at 11.8 μ and 0.05 at 10.1 μ were obtained. By correcting for what appears to be some *trans* in the *cis* isomer, and, extrapolating to zero pressing time a plot of values obtained at various times, an absorbance of *ca.* 0.7 is obtained for 5 mg. of XVIIb. A similar correction for the *trans* isomer XVIIIa gives a value of 0.25 at 10.1 μ. Known mixtures of *cis* and *trans* isomers were prepared and analyzed to give the following results (observed values in parentheses): 25.0 (25.6), 35 (34.6), 50 (50.2), 60 (61.5), and 75 (73.6). Two mixtures of unknown composition, including the one described above, were analyzed to give values of 38.5 and 38.6% *cis* isomer, XVIIIb.

D. Methylolation. 1,4-Bishydroxymethyl-1,4-dinitrocyclohexane (XX).—A 0.52 g. (0.003 mole) sample of *cis*-1,4-dinitrocyclohexane was dissolved in a solution of 0.5 g. of sodium bicarbonate, 20 ml. of ethanol, and 3 ml. of water and 6 ml. of formalin added (1.8 g., 0.06 mole of formaldehyde). The mixture was alternately allowed to remain at room temperature and chilled to produce precipitates which were removed as successive crops. After 10 days there was isolated 0.692 g. of diol, m.p. 155–195° (98.5%); the yield was 0.24 g., m.p. 155–195°, after 1 day. (By using a solution of 1,4-dinitrocyclohexane containing 5.7 mole-equivalents of sodium hydroxide and a 500-fold molar excess of formaldehyde, similar results were obtained; 81% yield, m.p. 148–200°, after 5 days.) The 0.692-g. sample was recrystallized from ethanol to yield 0.454 g., m.p. 185–200°; recrystallization gave 0.22 g. of XXa as needles, m.p. 200–203° dec.

Anal. Calcd. for $C_8H_{14}N_2O_6$: C, 41.02; H, 6.03; N, 11.96. Found: C, 41.22; H, 5.70; N, 12.13.

The mother liquor remaining from the above crystallization was fractionally crystallized, first from ethanol and then from chloroform, to yield 20 mg. of small crystals, m.p. 140–143°, believed to contain principally the low-melting diol.

Anal. Calcd. for $C_8H_{14}N_2O_6$: C, 41.02; H, 6.03; N, 11.96. Found: C, 42.81; H, 5.57; N, 11.64.

The diacetyl derivative of the high-melting diol (m.p. 200–203°) was prepared by reaction with excess acetic anhydride and sulfuric acid catalyst at room temperature for 15 hr., 83% yield, m.p. 163–164°; recrystallization from ethanol gave flat prisms of **1,4-bisacetoxymethyl-1,4-dinitrocyclohexane,** m.p. 163–165°.

Anal. Calcd. for $C_{12}H_{18}N_2O_8$: C, 45.28; H, 5.70; N, 8.80. Found: C, 45.21; H, 5.79; N, 8.73.

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