123. *Mechanism and Stereochemistry of the Addition of Nitrogen Dioxide to Olefins.*

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The activity of bromotrichloromethane as a transfer agent in the reaction of nitrogen dioxide with *cyclo*hexene affords definite evidence of a free-radical mechanism.

The stereochemistry of addition of nitrogen dioxide radicals to *cyclo*hexene, 1-methyl*cyclo*hexene, and *cyclo*pentene has been determined by hydrolysis of the nitro-nitrite ester to nitro-alcohol, followed by hydrogenation under controlled conditions to the corresponding amino-alcohol of known configuration. On this basis 2-nitro*cyclo*hexyl nitrite (58% *trans*) and 2-nitro*cyclo*pentyl nitrite (84% *trans*) were produced with an excess of the *trans*-isomer; but the reaction with 1-methyl*cyclo*hexene was stereospecifically *trans*, yielding 1-methyl-*trans*-2-nitro*cyclo*hexyl nitrite. 2-Chloro*cyclo*hexyl nitrite (62% *trans*) and 2-nitro*cyclo*hexyl nitrite (62% *trans*) were formed non-stereospecifically in the reaction of nitryl chloride with *cyclo*hexene.

THE reaction of dinitrogen tetroxide with simple olefins[1] was first placed on a firm experimental basis by Levy and his collaborators.[2] At that time interest in the chemistry of the nitronium ion (NO_2^+) stimulated the hypothesis,[2,3] consistent with the facts then known of the orientation of the addition, that the reaction involved heterolytic addition of the tetroxide as $NO_2^+NO_2^-$. The products (*vic.*-dinitro-compounds and nitro-nitrite esters) contain not less than one $C{-}NO_2$ group, as required by an explanation involving attack by NO_2^+.

Later evidence has eroded this argument considerably. Addition to diphenylacetylene (tolane)[4] and to hex-3-yne[5] is non-stereospecific; this result is not expected from a heterolytic process. The orientation of addition to methyl acrylate[6] is contrary to the Markovnikov rule. These results however are readily understood in terms of a free-radical mechanism:[6]

$$NO_2 + {>}C{=}C{<} = {>}C(NO_2)\cdot\dot{C}{<} \qquad \ldots\ldots\ldots\ldots \quad (1)$$

$${>}C(NO_2)\cdot\dot{C}{<} + NO_2 = {>}C(NO_2)\cdot C(NO_2){<} \text{ and } {>}C(NO_2)\cdot C(ONO){<} \quad \ldots \quad (2)$$

Similar suggestions were advanced for the cognate reactions of nitric oxide,[7] dinitrogen trioxide,[8] and nitryl chloride[5,9] with simple olefins. We used transfer agents to detect free-radical intermediates in the reaction of *cyclo*hexene with nitrogen dioxide; the stereochemistry of the products of addition to *cyclo*hexene, 1-methyl*cyclo*hexene, and *cyclo*pentene was determined.

Addition to cyclo*Hexene in Presence of Bromotrichloromethane.*—Participation of transfer agents in the addition is suggested by the induced oxidation of the solvent when the reaction is carried out in a halogenocarbon medium,[2] and by the presence of a large proportion of bromine in the (unidentified) mixture of products from *cyclo*hexene and nitrogen dioxide in bromoform.[10] The reaction of *cyclo*hexene with nitrogen dioxide in mixed ether–bromotrichloromethane was studied in detail. Under "normal" conditions (no bromotrichloromethane) the products are 1 : 2-dinitro*cyclo*hexane and 2-nitro*cyclo*hexyl nitrite,[2] neither

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[1] Riebsomer, *Chem. Rev.*, 1945, **36**, 157.
[2] Levy and Scaife, *J.*, 1946, 1093, 1100; Levy, Scaife, and Wilder-Smith, *J.*, 1946, 1096; 1948, 52, Baldock, Levy, and Scaife, *J.*, 1949, 2627.
[3] Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, New York, 1953 p. 670.
[4] Campbell, Shavel, and Campbell, *J. Amer. Chem. Soc.*, 1953, **75**, 2400.
[5] Freeman and Emmons, *ibid.*, 1957, **79**, 1712.
[6] Schechter and Conrad, *ibid.*, 1953, **75**, 5610.
[7] Brown, *ibid.*, 1957, **79**, 2480.
[8] Schechter and Ley, *Chem. and Ind.*, 1955, 535.
[9] Schechter, Conrad, Daulton, and Kaplan, *J. Amer. Chem. Soc.*, 1952, **74**, 3052.
[10] Titov and Baryshnikova, *Doklady Akad. Nauk S.S.S.R.*, 1953, **91**, 1099.

of which was detected when the reaction was carried out in presence of the transfer agent (Table 1). As light was excluded, bromotrichloromethane can only have altered the character of the product in its capacity as a radical-transfer agent, and the total suppression of the " normal " products must mean that the heterolytic reaction, if it operates at all, is of very minor importance.

TABLE 1. *Products (moles %) of the reaction of* cyclo*hexene with bromotrichloromethane induced by nitrogen dioxide.*

1-Bromo-2-chloro*cyclo*hexane	30·9	2-Chloro*cyclo*hexyl nitrate	4·4	Trichloronitromethane ...	3·1
1-Bromo-2-nitro*cyclo*hexane	28·7	1-Nitro*cyclo*hexene	3·6	Nitrosyl chloride	Small
2-Chloro*cyclo*hexanol	27·7	*cyclo*Hexene nitrosite	1·6		

Apparently the primary reaction of bromotrichloromethane is with the 2-nitro*cyclo*hexyl radicals produced in step (1), forming 1-bromo-2-nitro*cyclo*hexane:

$$\mathrm{NO_2{\cdot}C_6H_{10}{\cdot} + BrCCl_3 = NO_2{\cdot}C_6H_{10}Br + {\cdot}CCl_3} \qquad . \; . \; . \; . \; . \; . \; (3)$$

The remaining products are explained by reactions initiated by trichloromethyl radicals. Although the association of trichloromethyl with olefins is well known,[11] its reaction in the present system is with nitrogen dioxide, *viz.*,

$$\mathrm{{\cdot}CCl_3 + NO_2 = CCl_3{\cdot}NO_2} \qquad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (4)$$

and

$$\mathrm{{\cdot}CCl_3 + NO_2 = CCl_3O{\cdot} + NO} \qquad . \; . \; . \; . \; . \; . \; . \; . \; . \; (5)$$

Trichloromethyl nitrite may be formed as a transient intermediate in step (5). It appears that the trichloromethoxy-radicals also decompose rapidly:

$$\mathrm{CCl_3O{\cdot} = Cl{\cdot} + Cl_2CO} \qquad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (6)$$

[Reaction (5) and (6) have been identified in the pyrolysis of trichloronitromethane.[12]] The chlorine atoms liberated are considered to initiate processes leading to the formation of 1-bromo-2-chloro*cyclo*hexane, 2-chloro*cyclo*hexanol, and 2-chloro*cyclo*hexyl nitrate (Table 1):

$$\mathrm{Cl{\cdot} + C_6H_{10} = ClC_6H_{10}{\cdot}} \qquad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (7)$$

$$\mathrm{ClC_6H_{10}{\cdot} + BrCCl_3 = ClC_6H_{10}Br + {\cdot}CCl_3} \qquad . \; . \; . \; . \; . \; . \; . \; (8)$$

$$\mathrm{ClC_6H_{10}{\cdot} + NO_2 = ClC_6H_{10}{\cdot}ONO} \qquad . \; . \; . \; . \; . \; . \; . \; . \; . \; (9)$$

Step (8) represents the formation of 1-bromo-2-chloro*cyclo*hexane in a transfer step, analogous to (3), from a 2-chloro*cyclo*hexyl free radical. The origin of 2-chloro*cyclo*hexanol and 2-chloro*cyclo*hexyl nitrate is thought to be the reaction (9), the nitrite ester first produced being either oxidised to nitrate or hydrolysed during isolation. In principle the steps (5), (6), (7), and (8) are self-supporting, but the yield of 1-bromo-2-chloro*cyclo*hexane roughly equals the combined yield of 2-chloro*cyclo*hexanol and its nitrate ester, and thus on the average this cycle of reactions occurs only once before termination by (4) and (9).

*cyclo*Hexene nitrosite formation is related to the accumulation of nitric oxide [eqn. (5)] in the later stages of reaction,

$$\mathrm{NO_2{\cdot}C_6H_{10}{\cdot} + NO = NO_2{\cdot}C_6H_{10}{\cdot}NO \longrightarrow Dimer}$$

(Nitric oxide itself does not attack a double bond at moderate temperature.[7, 13]) Pyrolysis of *cyclo*hexene nitrosite during the distillation of the reaction product was probably the main source of 1-nitro*cyclo*hexene.

Reaction of cyclo*Hexene with Nitrogen Dioxide in Ether.*—Up to this point the evidence is wholly favourable to Schechter and Conrad's mechanism,[6] represented by eqn. (1) and

[11] Cadogan and Hey, *Quart. Rev.*, 1954, **8**, 308.

[12] Gray, *Trans. Faraday Soc.*, 1955, **51**, 1367.

[13] Rabinovitch and Looney, *J. Chem. Phys.*, 1955, **23**, 2439.

(2). However an alternative to step (2) that would be equally acceptable is (2*a*). Under certain conditions (2) and (2*a*) are kinetically distinguishable.

$$NO_2{\cdot}C_6H_{10}{\cdot} + N_2O_4 = NO_2{\cdot}C_6H_{10}{\cdot}NO_2 \text{ (or } NO_2{\cdot}C_6H_{10}{\cdot}ONO) + NO_2 \quad . \; . \quad (2a)$$

Velocities of reaction were measured in ether solution at 5°: the degree of dissociation of dinitrogen tetroxide is then sufficiently small ($<1\%$, by direct measurement) for the real and the virtual (stoicheiometric) dinitrogen tetroxide concentration to be equated. As the union of nitrogen dioxide radicals is extremely fast,[14] it can be shown that the apparent order of reaction with respect to $[N_2O_4]$ will be between 0·5 and 1 if (2) is appropriate rather than (2*a*), and between 0 and 1 if the rôles are reversed. The limits are controlled by the relative speeds of the reverse of reaction (1) and of (2) or (2*a*).

With $[N_2O_4] = 0{\cdot}03$—$0{\cdot}1$M the reaction was approximately of the first order in $[N_2O_4]$, $k = 0{\cdot}008_9$ l. moles^{-1} sec.$^{-1}$ at 5°. (Similar kinetics apply to the reaction of nitrogen dioxide with ethylene and propene in the vapour phase at 160—260°, where the order with respect to *nitrogen dioxide* is 1·8.[15]) The fact that the reaction order with respect to tetroxide is near unity demonstrates that the reverse of reaction (1) is kinetically significant, in agreement with evidence that nitrogen dioxide catalyses the *cis–trans* isomerisation of olefins;[16] but it does not help to distinguish (2) from (2*a*), which would have been possible if the relative velocities had been such that the order was less than 0·5.

Reaction of cyclo*Hexene with Nitryl Chloride in Ether*.—Addition of nitrogen dioxide was also studied by letting nitryl chloride react with *cyclo*hexene. The composition of the product is summarised in Table 2, the experimental procedure being to allow hydrolysis of the nitrite esters to the corresponding hydroxy-compound to proceed before isolation. The formation of 1-chloro-2-nitro*cyclo*hexane, 1 : 2-dichloro*cyclo*hexane, and *cyclo*hexene nitrosite has been noted previously.[17] The reaction was conducted by distilling nitryl chloride in a current of oxygen into a solution of *cyclo*hexene in dry ether at 0°, the order of mixing of reagents being chosen to keep the concentration of nitryl chloride low and so to retard the reaction[18]

$$Cl{\cdot} + ClNO_2 = Cl_2 + NO_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (10)$$

which competes with *cyclo*hexene for the available chlorine atoms. However evidence presented later suggests that step (10) was important.

TABLE 2. *Products (moles %) of the reaction of nitryl chloride with* cyclo*hexene.*

1-Chloro-2-nitro*cyclo*hexane	41·6	2-Nitro*cyclo*hexanol	5·4
trans-1 : 2-Dichloro*cyclo*hexane	26·6	*cyclo*Hexen-3-ol	3·2
2-Chloro*cyclo*hexanol	6·2	*cyclo*Hexene nitrosite (?)	7·6
2-Chloro*cyclo*hexyl nitrate	6·4	1-Chloro-2-nitroso*cyclo*hexane (dimer) (?)	2·8

The composition of the product supports the partial mechanism suggested by Schechter and his co-workers[9] that initiation occurs by step (1) and is succeeded by

$$NO_2{\cdot}C_6H_{10}{\cdot} + ClNO_2 = NO_2{\cdot}C_6H_{10}Cl + NO_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (11)$$

Because 2-nitro*cyclo*hexanol, but not 1 : 2-dinitro*cyclo*hexane, was identified in the product, it appears that the former is not produced by the step (2) but by an alternative path to (11), namely

$$NO_2{\cdot}C_6H_{10}{\cdot} + ClNO_2 = NO_2{\cdot}C_6H_{10}{\cdot}ONO + Cl{\cdot} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (12)$$

2-Chloro*cyclo*hexanol must be derived from the initial attack of a chlorine atom, for the

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[14] Carrington and Davidson, *J. Phys. Chem.*, 1953, **57**, 418.

[15] Cottrell and Graham, *J.*, 1953, 556; 1954, 3644.

[16] Khan, *J. Chem. Phys.*, 1955, **23**, 2447.

[17] Price and Sears, *J. Amer. Chem. Soc.*, 1953, **75**, 3275.

[18] Volpe and Johnston, *ibid.*, 1956, **78**, 3903.

primary attack of nitrogen dioxide on an unsaturated system always establishes a C–N bond; [2, 5, 8] therefore the route to this product is the reaction (7) followed by

$$ClC_6H_{10}\cdot + ClNO_2 = ClC_6H_{10}\cdot ONO + Cl\cdot \quad . \; . \; . \; . \; . \; . \; . \; . \quad (13)$$

In principle the steps (1) and (11), as well as (7) and (13), are self-supporting in this system, but the opportunities for cross-linking and termination are too numerous for a probable chain-length to be evaluated. The stereochemical configuration (Table 3) of 2-chloro- and 2-nitro-*cyclo*hexanol isolated from the reaction is discussed below.

The formation of 1 : 2-dichloro*cyclo*hexane requires careful evaluation. If it is produced homolytically, the mechanism would presumably involve the steps (7) and (14):

$$ClC_6H_{10}\cdot + NO_2Cl = C_6H_{10}Cl_2 + NO_2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (14)$$

This is a possibility we cannot exclude. But the distinguishing feature of the reaction producing 1 : 2-dichloro*cyclo*hexane is that it is stereospecifically *trans* (see Experimental); therefore it appears more probable that the path to its formation is the reaction (10) followed by the normal, heterolytic addition of molecular chlorine. It is known that eqn. (10) represents a very fast step in the vapour-phase pyrolysis of nitryl chloride.[18]

The isolation of *cyclo*hex-2-enol suggests the abstraction of allylic hydrogen from *cyclo*hexene by a free radical. As this product is not formed from *cyclo*hexene and nitrogen dioxide we represent its formation by

$$C_6H_{10} + Cl\cdot = C_6H_9\cdot + HCl \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (15)$$

and

$$C_6H_9\cdot + NO_2 = C_6H_9\cdot ONO \longrightarrow C_6H_9\cdot OH$$

Stereochemistry.—The evidence relating to the stereochemistry of free-radical addition to double bonds is not extensive. Thermodynamic control operates in the photo-addition of bromotrichloromethane to *cis*- and *trans*-but-2-ene,[19a] in the copolymerisation of dichloroethylene with vinyl acetate,[20] and probably in the copolymerisation of but-2-ene with sulphur dioxide; [19b] in these reaction the lifetime of the intermediate radical apparently is sufficient for it to reach equilibrium among its conformations, and the composition of the product is the same from the *cis* and the *trans* isomer. On the other hand, addition of hydrogen bromide to *cis*- and *trans*-2-bromobut-2-ene is stereospecifically *trans* (the products are diastereoisomers of 2 : 3-dibromobutane [22d]) and that to 1-methyl-, 1-chloro-, and 1-bromo-*cyclo*hexene is almost quantitatively *trans*.[22a, b] Thiol-compounds and cyclic olefins give an excess of *trans*-addition, the proportion of *cis*-addition being kinetically controlled.[21, 22c] The data relating to the reaction of cyclic olefins are summarised Table 3, above the results now obtained. Apart from the results for the thiol-compounds the most striking feature of the Table is the non-stereospecificity of addition to *cyclo*hexene compared with the stereospecifically *trans*-reaction of its 1-substituted derivatives, a distinction that applies also to the examples of addition to but-2-ene [19] and 2-bromobut-2-ene [22d] mentioned above. This aspect is not explained satisfactorily by any of the theories [19, 21, 22] advanced so far.

The problem is exemplified by the reaction of nitrogen dioxide with *cyclo*hexene and 1-methyl*cyclo*hexene (Table 3), where the presence of a methyl substituent is sufficient to swing the addition from non-stereospecificity to *trans*-stereospecificity. Our interpretation involves four postulates. (*a*) It is supposed that the radical intermediate in the reaction is pyramidal at the odd-electron centre. This postulate, also favoured by Bordwell and Hewett,[21] implies that there are four distinguishable conformations of the

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[19] (*a*) Skell and Woodworth, *J. Amer. Chem. Soc.*, 1955, **77**, 4638; (*b*) Skell, Woodworth, and McNamara, *ibid.*, 1957, **79**, 1252.

[20] Mayo and Walling, *Chem. Rev.*, 1950, **46**, 191.

[21] Bordwell and Hewett, *J. Amer. Chem. Soc.*, 1957, **79**, 3493.

[22] (*a*) Goering, Abell, and Aycock, *ibid.*, 1952, **74**, 3588; (*b*) Goering and Sims, *ibid.*, 1955, **77**, 3465; (*c*) Goering, Relyea, and Larsen, *ibid.*, 1956, **78**, 348; (*d*) Goering and Larsen, *ibid.*, 1957, **79**, 2653.

intermediate, as in (Ia)—(Id); (*b*) that the particular conformation produced by the attack of the nitrogen dioxide radical on the olefin is that represented by (Ia); (*c*) that the speed of ring inversion, (Ia) $\rightleftharpoons$ (Ib) or (Ic) $\rightleftharpoons$ (Id), is slow compared with that of the second step for nitrogen dioxide addition. [This eliminates (Ib) and (Id) from consideration so far as the products are concerned.] Postulate (*d*) is a specific one mentioned later.

For the reaction of *cyclo*hexene with nitrogen dioxide, (*a*)—(*c*) permit the radical inversion (Ia) $\rightleftharpoons$ (Ic) (R = H) to be rapid compared with both the ring inversions and the second step of the addition; thus the intermediate has the opportunity to distribute itself at equilibrium between (Ia) and (Ic). The non-stereospecific reaction is attributed to the simultaneous reactions of the two forms in the second step of the addition. The inference that there is an element of thermodynamic control is in line with the evidence for thermodynamic control in additions to but-2-ene.[19]

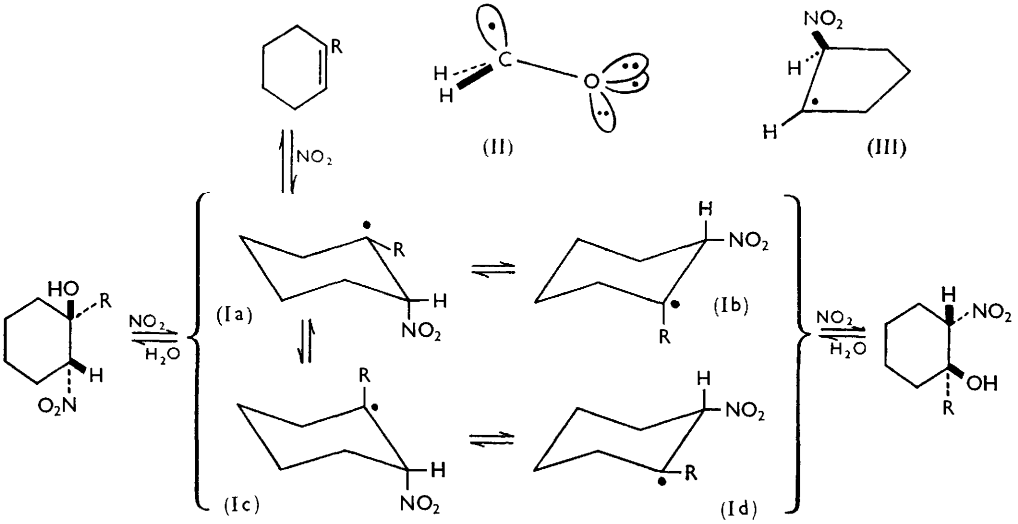

TABLE 3. *Stereochemistry of radical addition to cyclic olefins.*

Olefin	Adduct	Initiator	Product	*trans*-Addition (%)	Ref.
1-Methyl*cyclo*hexene	HBr	Br	1-Bromo-2-methyl*cyclo*hexane	~100	22 [a]
1-Methyl*cyclo*hexene	MeCOSH	MeCOS	2-Methyl*cyclo*hexyl thiolacetate	85	21
1-Bromo*cyclo*hexene	HBr	Br	1 : 2-Dibromo*cyclo*hexane	99·5	22 [b]
1-Chloro*cyclo*hexene	HBr	Br	1-Bromo-2-chloro*cyclo*hexane	99·7	22 [b]
1-Chloro*cyclo*hexene	H_2S	HS	2-Chloro*cyclo*hexanethiol	86—93	22 [c]
1-Methyl*cyclo*pentene	MeCOSH	MeCOS	2-Methyl*cyclo*pentyl thiolacetate	70	21
*cyclo*Hexene	N_2O_4	NO_2	2-Nitro*cyclo*hexanol	58	This paper
*cyclo*Hexene	NO_2Cl	NO_2	2-Nitro*cyclo*hexanol	62	„
*cyclo*Hexene	NO_2Cl	Cl	2-Chloro*cyclo*hexanol	62	„
1-Methyl*cyclo*hexene	N_2O_4	NO_2	1-Methyl-2-nitro*cyclo*hexanol	~100	„
*cyclo*Pentene	N_2O_4	NO_2	2-Nitro*cyclo*pentanol	84	„

The fourth postulate (*d*) is that, when R = Me, steric factors (especially the 1 : 3 repulsions) raise the energy of (Ic) considerably above that of (Ia), so that the lifetime of (Ic) is short in comparison with that of (Ia). {Possibly the potential energy rises continuously as the methyl group is displaced from the equatorial position [as in (Ia)] to the axial position (Ic), the steric repulsion being sufficient to eliminate the potential minimum in the conformation (Ic).} Consequently the reaction of methyl*cyclo*hexene will be associated with a very large excess of *trans* addition, that is, with a stereospecific reaction arising from kinetic control.

The assumption of a pyramidal radical needs careful qualification. Methyl radicals are planar, or nearly so.[23] However the diradical, excited electronic state of formaldehyde is pyramidal with the ethane-like configuration (II),[24] and examples are known of radical centres at the bridgehead of bicyclic compounds where the configuration must be pyramidal.[25] Our interpretation of this evidence is that an odd electron has no strong stereochemical preference; and that *a pyramidal configuration may be expected when the alternative planar configuration eclipses two bonds* or a bond and a non-bonding electron. Applied to *six-membered* ring radicals and to simple acyclic radicals from ethyl upwards, this hypothesis predicts a pyramidal configuration. For *five-membered* ring radicals there is no clear advantage in the pyramidal arrangement and the configuration may be planar. In this case the intermediate radical in the reaction of nitrogen dioxide with *cyclo*pentene has the configuration (III) with the valencies emanating from the odd-electron centre coplanar. Scale models show that there is an advantage for the second nitrogen dioxide radical to approach from the side opposite to the nitro-group already established, and this is sufficient to explain the excess of *trans* addition observed in the reaction (Table 3).

EXPERIMENTAL

Materials.—Dinitrogen tetroxide was prepared from lead nitrate–silver-sand at 500°: moisture and traces of nitric oxide were removed by several distillations over phosphoric oxide in a current of oxygen, and the product was condensed (−80°) as colourless crystals. Nitryl chloride was prepared by the standard method,[26] passed through sulphuric acid to remove dinitrogen tetroxide, dried, and collected as a pale yellow liquid: spectrophotometric analysis showed no nitrosyl chloride, $<3\%$ of chlorine, and traces of tetroxide.

*cyclo*Hexene, b. p. 83·5°, 1-methyl*cyclo*hexene, b. p. 107·4—108°, and *cyclo*pentene, b. p. 43—44°, were freed from hydroperoxides by refluxing them with cupric stearate [27] and purified by fractional distillation from sodium in a 25 cm. column.

Reaction of Dinitrogen Tetroxide with cyclo*Hexene–Bromotrichloromethane.*—Dinitrogen tetroxide (98 mmoles) was distilled (3 hr.) into a stirred solution of *cyclo*hexene (294 mmoles) and bromotrichloromethane (980 mmoles) in dry ether (150 ml.) at 0°. Preliminary separation in a film evaporator yielded an oil (i) and a volatile fraction (ii) composed mainly of ether and bromotrichloromethane. The oil (i) was washed with water, and the aqueous washings buffered to pH 5—6 with sodium hydrogen carbonate and extracted continuously with ether: fractionation of material from the ether extract yielded 2-chloro*cyclo*hexanol (14·1 mmoles), b. p. 79—80°/18 mm., and a less volatile fraction (0·3 g.) from which a little *trans-cyclo*hexane-1:2-diol, m. p. and mixed m. p. 99°, was isolated. The portion of (i) insoluble in water was dried azeotropically with benzene and separated by distillation in a 4″ Vigreux column into fractions (iii), b. p. 47—89°/0·7 mm. (the bulk boiled at 47—49°), and (iv), b. p. 94—108°/1·5 mm. The distillation was interrupted at intervals to extract *cyclo*hexene nitrosite, m. p. 153° (decomp.) (lit.,[2] m. p. 152°, decomp.) after crystallisation from ethyl acetate, which otherwise pyrolysed in the column to 1-nitro*cyclo*hexene and oxides of nitrogen. A portion of (iii) dissolved in light petroleum (b. p. 40—60°) and chromatographed over activated silica yielded 1-bromo-2-chloro*cyclo*hexane, b. p. 44°/0·6 mm., n_D^{20} 1·5167 (the *cis* and the *trans* isomer have n_D^{25} 1·5238 and 1·5173, respectively [22b]) (Found: C, 36·2; H, 5·21. Calc. for $C_6H_{10}BrCl$: C, 36·5; H, 5·10%): the second principal component of (iii) was 2-chloro*cyclo*hexanol, and the fraction was eventually combined with (v). Fraction (iv) was treated with 85% phosphoric acid, washed dried with benzene, and redistilled to yield a pale yellow oil from which *1-bromo-2-nitro*cyclo*hexane* (20·7 mmoles), m. p. 38·5—39° from light petroleum, $\lambda_{max.}$ 2780 (log $\varepsilon_{max.}$ 1·36), $\lambda_{min.}$ 2550 Å (1·22) in ethanol (Found: C, 35·0; H, 4·94; N, 6·60; Br, 38·2. $C_6H_{10}O_2NBr$ requires C, 34·6; H, 4·84; N, 6·73; Br, 38·4%), crystallised on standing. The content of the non-crystalline portion of (iv) was determined by infrared analysis: 1-bromo-2-nitro*cyclo*hexane (34·2 mmoles), 2-chloro*cyclo*hexyl nitrate (8·5 mmoles), 1-nitro*cyclo*hexene (6·8 mmoles), and 1-bromo-2-chloro*cyclo*hexane (2·5 mmoles):

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[23] Herzberg and Shoosmith, *Canad. J. Phys.*, 1956, **34**, 523.

[24] Brand, *J.*, 1956, 858.

[25] Kharasch, Englemann, and Urry, *J. Amer. Chem. Soc.*, 1943, **65**, 2428.

[26] Schechter and Kaplan, " Inorganic Syntheses," McGraw-Hill, London, 1952, Vol. IV, p. 52.

[27] George and Robertson, *Trans. Faraday Soc.*, 1946, **42**, 217.

this result checked satisfactorily with a Carius estimation of total halogen (83·5% of mixed silver halide. Calc. 84·6%).

Distillation of the volatile fraction (ii) yielded *cyclo*hexene (*ca.* 10 mmoles), bromotrichloromethane (460 mmoles), and a residual oil (v), b. p. 40—45°/0·8 mm., of 2-chloro*cyclo*hexanol and 1-bromo-2-chloro*cyclo*hexane. (iii) and (v) were united and the composition, measured by infrared analysis, was 2-chloro*cyclo*hexanol, 38·9 mmoles, and 1-bromo-2-chloro*cyclo*hexane, 56·5 mmoles. The recovered bromotrichloromethane fraction contained trichloronitromethane (~6 mmoles) and some nitrosyl chloride (1770 cm.$^{-1}$ band). The overall yield, based on dinitrogen tetroxide, was 69%.

Reaction of Nitryl Chloride with cyclo*Hexene.*—Nitryl chloride (295 mmoles) was distilled slowly in a current of oxygen into a stirred solution of *cyclo*hexene (324 mmoles) in dry ether (200 ml.) at 0°. Moisture was excluded. The solution became deep blue during the reaction and a white solid separated. Solvent was removed in a film evaporator and solid product (i) (3·96 g.) filtered off: the liquid product was dissolved in pentane and washed repeatedly with water. The residual water-insoluble oil (ii) from the pentane layer was dried azeotropically with benzene and the infrared spectrum recorded: comparison with reference spectra established the presence of 1-chloro-2-nitro*cyclo*hexane (102 mmoles), 2-chloro*cyclo*hexyl nitrate (15·6 mmoles), and *trans*-1 : 2-dichloro*cyclo*hexane (65·2 mmoles), the infrared analyses being in agreement with a Carius estimation of chlorine (27·2%. Calc. 27·5%). Distillation of (ii) gave a first fraction, b. p. 78—85°/15 mm., which was washed with 85% phosphoric acid and chromatographed in light petroleum over activated silica, yielding *trans*-1 : 2-dichloro*cyclo*hexane, b. p. 70—71°/12 mm., n_D^{19} 1·4904 (lit. n_D^{20} 1·4904,[28] 1·4910 [29]).

The aqueous washings (1·2 l.) were extracted with ether and the oil so obtained separated by distillation in a 4 in. column into three fractions: (iii) b. p. 68—76°/12 mm. (2·86 g.), (iv) b. p. 76—80°/12 mm. (0·45 g.), and (v) a mixture, b. p. 78—84°/0·25 mm., of *cis*- and *trans*-2-nitro*cyclo*hexanol (11·7 mmoles) distinguished by their infrared spectra. A portion of (iii) was fractionated in a small column (12 theoretical plates) into *cyclo*hexen-3-ol [b. p. 64—66°/11 mm., n_D^{16} 1·4858; phenylurethane, m. p. 106° (lit.,[30] m. p. 107°) (Found: C, 72·1; H, 7·2. Calc. for $C_{13}H_{15}O_2N$: C, 71·9; H, 7·0%); α-naphthylurethane, m. p. 155° (lit.,[30] m. p. 155°) (Found: C, 76·6; H, 6·0. Calc. for $C_{17}H_{17}O_2N$: C, 76·4; H, 6·4%)] and a mixture (identified by infrared absorption) of *cis*- and *trans*-2-chloro*cyclo*hexanol, b. p. 70—71°/11 mm. According to infrared analysis the composition of (iii) was *cyclo*hexen-3-ol, 7·9 mmoles; 2-chloro*cyclo*hexanol (by difference), 13·5 mmoles, in fair agreement with a Carius estimation (Cl, 19·7. Calc. 18·5%). The small fraction (iv) contained *cis* and *trans* isomers of 2-chloro*cyclo*hexanol (1·7 mmoles) and 2-nitro*cyclo*hexanol (1·6 mmoles).

The solid (i) was not positively identified. It was apparently a mixture of dimeric 1-chloro-2-nitroso*cyclo*hexane and 1-nitro-2-nitroso*cyclo*hexane (*cyclo*hexene nitrosite) and was analysed on this basis by Carius estimation (Cl, 6·1%). The overall yield was 83%, based on nitryl chloride.

Addition of Dinitrogen Tetroxide to cyclo*Hexene, 1-Methyl*cyclo*hexene, and* cyclo*Pentene.*—Dinitrogen tetroxide was distilled slowly in oxygen into a stirred solution of the olefin (1·1 equiv.) in dry ether at 0°. In experiments with *cyclo*hexene the method of isolation was that of Baldock, Levy, and Scaife.[2] With 1-methyl*cyclo*hexene and *cyclo*pentene it was an advantage to collect the involatile oil from a film evaporator in methanol at −80°; on warming to 0° the nitro-nitrite was converted into nitro-alcohol and methyl nitrite by trans-esterification, urea being added to destroy small amounts of nitrous acid liberated by hydrolysis. Concentration *in vacuo* yielded a mixture of dinitro-compound, nitro-alcohol, and nitro-nitrate ester, which was dissolved in benzene–light petroleum and extracted repeatedly with water: nitro-alcohol (and some nitro-nitrate) were recovered from the aqueous washings by extraction with chloroform. The purification and later treatment of the crude nitro-alcohol is described below.

A portion of the residual oil from the reaction with *cyclo*hexene was dried with benzene and chromatographed in benzene over activated silica. The product, an oil, crystallised on standing, yielding 1 : 2-dinitro*cyclo*hexane, m. p. 46° after crystallisation from chloroform–light petroleum (Found: C, 41·7; H, 5·5; N, 16·3. Calc. for $C_6H_{10}O_4N_2$: C, 41·4; H, 5·8; N, 16·1%). (Baldock, Levy, and Scaife [2] isolated this compound as an oil, b. p. 110—114°/<1 mm.). By analogy with the corresponding nitro-alcohol the crystals were probably the *trans*-isomer, but

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[28] Stevens and Grummitt, *J. Amer. Chem. Soc.*, 1952, **74**, 4876.

[29] Bohme and Schmitz, *Chem. Ber.*, 1955, **88**, 357.

[30] Clarke and Owen, *J.*, 1950, 2103.

the compound resisted hydrogenation under stereochemically unambiguous conditions and the configuration was not determined. The water-insoluble oil from the reaction with 1-methyl*cyclo*hexene crystallised after distillation, b. p. 110°/0·2 mm., yielding 1-*methyl*-trans-1 : 2-*dinitro*cyclo*hexane*, m. p. 90·5° after sublimation *in vacuo* or crystallisation from *cyclo*hexane (Found: C, 44·8; H, 6·1; N, 14·7. $C_7H_{12}O_4N_2$ requires C, 44·7; H, 6·4; N, 14·9%). The *trans* configuration was assigned on the basis of the stereospecifically *trans* character of the reaction producing the corresponding nitro-alcohol.

Stereochemical Configuration.—Nitrite ester hydrolysis occurs by O–N bond fission in all known cases,[31] and is assumed not to influence configuration. The configuration of the nitro-alcohols was determined by hydrogenation to the corresponding amino-alcohol of known or determinable configuration. Adams's catalyst equilibrates the stereoisomers of the nitro-alcohol and could not be used; but palladised charcoal was satisfactory.

2-*Nitro*cyclo*hexanol.*—Fractionation of the mixture of nitro-alcohols yielded a first fraction, b. p. 82·5°/1·3 mm., ν(C–OH) 974 cm.$^{-1}$ in chloroform, of *cis*-, and a final fraction, b. p. 88°/1·7 mm., of *trans*-2-nitro*cyclo*hexanol, ν(C–OH) 1074 cm.$^{-1}$, m. p. 46·5—47° (lit.,[2] m. p. 47—48°) after crystallisation from chloroform, $\lambda_{max.}$ 2790 (log $\varepsilon_{max.}$ 1·54), $\lambda_{min.}$ 2550 Å (1·29) in ethanol. The configuration of the *trans*-isomer was established by hydrogenation (Pd–charcoal) (85% yield) and benzoylation of the amino-alcohol (method of Leffler and Adams[32]; 93% yield), yielding *trans*-2-benzamido*cyclo*hexanol, m. p. and mixed m. p. 169° (lit.,[33] m. p. 171° corr.). Treated similarly, *cis*-2-nitro*cyclo*hexanol yielded *cis*-2-amino*cyclo*hexanol hydrochloride, m. p. 184° (lit.,[33] m. p. 185—187° corr.), and *cis*-2-benzamido*cyclo*hexanol, m. p. and mixed m. p. 183° (lit.,[33] m. p. 183—185° corr.).

The composition of the 2-nitro*cyclo*hexanol isolated from the reaction was determined by thermal analysis of the mixture of *cis*- and *trans*-2-benzamido*cyclo*hexanol produced by hydrogenation (Pd–charcoal) and benzoylation: *trans*, 58%; *cis*, 42%. The proportion of isomers resembled closely that of the equilibrium mixture of nitro-alcohols prepared by the neutralisation of a solution of 2-nitro*cyclo*hexanol in 5% sodium hydroxide with a 20% aqueous solution of urea acetate: to test whether equilibration had occurred during isolation from the preparation, *trans*-2-nitro*cyclo*hexanol, m. p. 46°, was dissolved in aqueous acid (0·1M), allowed to stand (2 hr. at 20°), and recovered after neutralisation by continuous extraction with ether. (These conditions were more extreme than in the actual isolation of crude nitro*cyclo*hexanol.) The product (91% recovery) had m. p. 43—46°, showing that epimerisation had not occurred under acid conditions.

1-*Methyl*-2-*nitro*cyclo*hexanol.*—The water-soluble product from the reaction of 1-methyl*cyclo*hexene crystallised on standing and was purified by sublimation *in vacuo* (85% recovery), yielding 1-*methyl*-trans-2-*nitro*cyclo*hexanol*, m. p. 72°, $\lambda_{max.}$ 2820 (log $\varepsilon_{max.}$ 1·82), $\lambda_{min.}$ 2560 Å (1·56) in ethanol, ν(C–OH) 992 or 928 cm.$^{-1}$ in chloroform (Found: C, 52·8; H, 7·9; N, 8·9. $C_7H_{13}O_3N$ requires C, 52·8; H, 8·2; N, 8·8%). The stereochemistry was established by hydrogenation (Pd–charcoal) to *trans*-2-amino-1-methyl*cyclo*hexanol (hydrochloride, m. p. 161·5°, undepressed by admixture with an authentic sample obtained by ammonolysis of 1 : 2-epoxy-1-methyl*cyclo*hexane. Mousseron and Granger[34] record m. p. 148—149°) which yielded on benzoylation[32] trans-2-*benzamido*-1-*methyl*cyclo*hexanol*, m. p. and mixed m. p. 180° (Found: C, 72·2; H, 8·2. $C_{14}H_{19}O_2N$ requires C, 72·1; H, 8·2%). A careful examination of the residues gave no evidence of products derived from the *cis*-nitro-alcohol.

The following experiments showed that there was no appreciable amount of *cis* $\rightleftharpoons$ *trans* interconversion of the isomers of the nitro-alcohol during isolation. (*a*) 1-Methyl-*trans*-2-nitro*cyclo*hexanol was dissolved in deuterium oxide containing DCl (2 × 10^{-4}M) and allowed to stand: no infrared absorption due to a C–D group was detected in the recovered material. (This covers the possibility of epimerisation of the nitro-alcohol in the aqueous phase during its extraction with water from the total mixture of products.) (*b*) The *trans*-nitro-alcohol was dissolved in methanolic hydrogen chloride (~10^2M) enriched with deuterium (2·25 atoms % of D), and allowed to stand (18 hr. at 20°). (The conditions here were considerably more exacting than in the actual isolation, where the methanolic solution from the film evaporator was kept for *ca.* 2 hr. only at 0°.) The recovered nitro-alcohol, analysed by

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[31] Allen, *J.*, 1954, 1968.

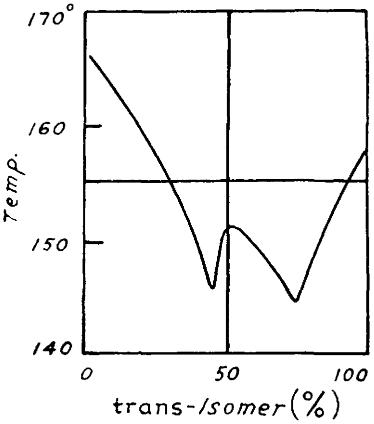
[32] Leffler and Adams, *J. Amer. Chem. Soc.*, 1937, **59**, 2255.

[33] Johnson and Schubert, *ibid.*, 1950, **72**, 2187.

[34] Mousseron and Granger, *Bull. Soc. chim. France*, 1947, 843.

determination of the deuterium content of the combustion water (we are indebted for this measurement to Miss A. W. P. Jarvie), contained 0·244 ± 0·005 atom % of D, corresponding to the exchange of 1·29 atoms of hydrogen. Therefore about 30% of the hydrogen of the $>CH{\cdot}NO_2$ group had exchanged under these conditions (exchange within the OH group accounts for 1·0 atom). The rate of exchange sets an upper limit to the rate of epimerisation of the nitro-alcohol; and as the exposure in the preparation was considerably less severe than under the test conditions for exchange we conclude, with a margin of safety, that epimerisation was not significant.

2-*Nitro*cyclo*pentanol.*—The water-soluble product from the reaction with *cyclo*pentene was dissolved in benzene and washed with aqueous sodium hydrogen carbonate to remove a carboxylic acid impurity, and the residual oil distilled. (Only 77% of the material distilled smoothly, even when the distillation was interrupted and the contents of the flask were extracted with chloroform; the remainder suffered a low-order explosion.) The distillate was a mixture of *cis*- and *trans*-2-nitro*cyclo*pentanol, b. p. 78—79°/0·25 mm., and was converted by hydrogenation (Pd–charcoal) and *p*-nitrobenzoylation [32] into the corresponding mixture of *cis*- and *trans*-2-*p*-nitrobenzamido*cyclo*pentanol (78% yield), from which the *trans* isomer, m. p. 157·5° (lit.,[35] m. p. 160° corr.), was isolated by crystallisation from aqueous ethanol. Confirmation was obtained by treatment with thionyl chloride,[35] yielding *cis*-2-*p*-nitrobenzamido*cyclo*pentanol, m. p. 165—166° (lit.,[35] m. p. 167° corr.). Finally, the composition of the mixture was established by thermal analysis of the mixed *cis*- and *trans*-2-*p*-nitrobenzamido*cyclo*pentanol: *trans*, 84%; *cis*, 16% (Figure).



Freezing-point diagram for cis- *and* trans-2-p-*nitrobenzamido*cyclo*pentanol, illustrating the formation of a* 1 : 1-*complex.*

Retention of the stereochemical integrity of the epimeric nitro-alcohols was assumed by analogy with the two previous cases.

Infrared Analyses.—The isomeric composition of the samples of 2-chloro*cyclo*hexanol and 2-nitro*cyclo*hexanol isolated from the reaction of *cyclo*hexene with nitryl chloride was determined by infrared analysis (in carbon disulphide) by use of bands identified in the reference spectra of the pure isomers as characteristic of the stereochemical configuration. Independent analyses for the isomers of 2-chloro*cyclo*hexanol were in good agreement.

Band	2-Chloro*cyclo*hexanol		Band	2-Nitro*cyclo*hexanol	
(cm.$^{-1}$)	*cis* (%)	*trans* (%)	(cm.$^{-1}$)	*cis* (%)	*trans* (%)
796	—	62·$_2$	862	—	62·$_3$
809	38·$_6$	—			

The specimen of 1 : 2-dichloro*cyclo*hexane isolated from the reaction with nitryl chloride showed no absorption due to the *cis* isomer (0·5 mm. liquid film).

When it was desired to estimate *cis* and *trans* isomers together the band chosen was common to both and had, so far as possible, the same intensity in the reference spectra of the individual isomers.

Velocity Measurements.—The velocity of reaction of nitrogen dioxide with *cyclo*hexene was

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[35] McCasland and Smith, *J. Amer. Chem. Soc.*, 1950, **72**, 2190.

determined in ether solution at 5° from the change of optical density at 4358 Å. At this wavelength light was absorbed by nitrogen dioxide but not by dinitrogen tetroxide.[36] With *cyclo*hexene in excess, the individual runs were of first order. To allow for the small degree of dissociation of dinitrogen tetroxide in these conditions, the slope of a plot of log (optical density) against time was identified with $k/(2 \times 2{\cdot}3)$, where k (sec.$^{-1}$) was the apparent first-order rate constant.

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[36] Hall and Blacet, *J. Chem. Phys.*, 1952, **20**, 1745.