Photolysis of Nitroso-compounds. Part IV.† 1-Chloro-1-nitrosocyclohexane and Other Geminal Chloro-nitroso-compounds

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Detailed studies of the photolysis of 1-chloro-1-nitrosocyclohexane are presented. Photolysis in methanol solutions gave hydrochloric acid, methyl nitrite, 1,1-dimethoxycyclohexane, cyclohexanone, and cyclohexanone oxime. 1-Methoxycyclohexene and 6-hydroxyimino-1-methoxycyclohexene were minor products. Photolysis in aprotic solvents afforded 1-chlorocyclohexene, cyclohexanone, and 1,1-dichlorocyclohexane with small amounts of α-chlorocyclohexanone and 1-chloro-1-nitrocyclohexane at low concentrations whereas at high concentrations substantial amounts of cyclohexanone oxime were found. Evidence based on the variation of product distribution with solvent, concentration, and added radical scavengers is presented, which shows that the primary photochemical step consists in C–NO bond cleavage in all solvents. α-Chloronitrones are postulated as intermediates. The importance of solvolysis and other secondary ionic reactions is emphasised. Other studies of the photolysis of geminal chloronitrosoadamantane, 3-chloro-3-nitrosopentane, and 2-chloro-2-nitrosobutane in alcohols are briefly re-examined in the light of the proposed mechanism. In none of these cases have we found any evidence for a carbonyl-like photoreduction.

THE photoximation of cyclic alkanes with nitrosyl chloride has been shown to provide an economical large scale route to cycloalkanone oximes, important inter-

mediates for the manufacture of polyamides.[1-3] One of the problems that severely limit an economical operation of the process consists in the formation of tarry, light-absorbing films that reduce the product quantum yields.

† Part III, B. G. Gowenlock, G. Kresze, and J. Pfab, *Tetrahedron*, 1973, **29**, 3587.

[1] E. Müller, H. Metzger, D. Fries, U. Heuschkel, K. Witte, E. Waidelich, and G. Schmid, *Angew. Chem.*, 1959, **71**, 229.

[2] M. Pape, *Fortschr. Chem. Forsch.*, 1967, **7**, 559.

[3] E. Müller, 'Melliand Textilberichte,' Heidelberg, 1963, vols. 5 and 6, pp. 484 and 596.

As long ago as 1937, Hammick[4] observed that the photolysis of 1-chloro-1-nitrosocyclohexane in ether and benzene produced an ill-defined, brown, insoluble gum. On the other hand it has been shown that 1-chloro-1-nitrosocyclohexane is formed in secondary dark reactions by chlorination of cyclohexanone oxime during the Tübingen process[5] or by the action of an excess of nitrosyl chloride upon the oxime product[2] during the Toyo–Rayon process.[6]

Thus it appeared that the formation of geminal chloronitroso-compounds during photoximation not only results in direct lowering of the oxime yield but also in the formation of light-absorbing lamp deposits by its concomitant photolysis. The possible economic significance of these facts is not reflected in studies of the photolysis of 1-chloro-1-nitrosocyclohexane. Three brief studies are available[4,7,8] and the mechanistic conclusions appear to us to be based on insufficient experimental data.

RESULTS

The absorption spectrum of (I) in the visible region is virtually identical with the spectra of other geminally sub-

(I)
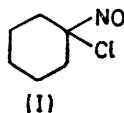
stituted nitroso-compounds and has been described.[8] In our re-examination we found that the n–π^* transition † exhibits vibrational fine structure in cyclohexane as solvent with two maxima, λ_{max} 652 (ε 21·7) and 641 nm (21·8) whereas the published spectrum for cyclohexane solution does not show fine structure and only one maximum, λ_{max} 655 nm (ε 22·0).[8] Other geminal halogeno-nitroso-compounds[9] and 1-cyano-1-nitrosocyclohexane[10] also exhibit fine structure of their n–π^* transitions in this region of the spectrum. Apart from the loss of fine structure and a slight hypsochromic shift in ethanol the absorption spectrum of (I) in the visible region is little affected by changes in solvent.

Photolysis of Compound (I) *in Alcohols.*—The photolysis of (I) with excitation of the n–π^* transition proceeded smoothly in degassed, dilute alcohol solutions and gave colourless, homogeneous solutions. The u.v. spectra of the resulting solutions indicated the formation of alkyl nitrites corresponding to the alcohol employed by the characteristic banded absorption in the near-u.v. region. Analyses for HCl formed gave yields close to 100%. Varying amounts of cyclohexanone oxime, 1,1-dimethoxycyclohexane, cyclohexanone, and small amounts of 1-methoxycyclohexene were observed. Gas evolution was absent in dilute solutions and negligible in concentrated solutions. Table 1 shows analytical results obtained from a series of runs at varying initial concentrations of (I) in methanol.

The analyses are hampered by the instability of the photolysed solutions. Thus upon standing in the dark methyl nitrite disappears with concomitant formation of

secondary products which absorb below 400 nm. Concentrated solutions of (I) require long exposure times even at high light intensity. The nitrite disappears rapidly in the dark and the solutions turn dark brown. The two photoproducts, cyclohexanone oxime and methyl nitrite, were shown to react in methanol in the presence of HCl to

TABLE 1

Products of the photolysis of compound (I) in methanol for various initial concentrations c_0

		Yields in mole per 100 mole of (I)					
$10^{-2}c_0/M$	t/min	A	B	C	D	E	F
1·96	6	2	29	51	20	39	98
10·7	25	3·5	19	18	40		+
40·4	40	3·8	3·5	22	47		+
123	50	0·7	1·1	23	49		+
5 *		13	28	16	22	160	+

* Products of the reaction of (I) with nitric oxide in the dark. t = Time required for complete photolysis. A = 1-Methoxycyclohexene. B = 1,1-Dimethoxycyclohexane. C = Cyclohexanone. D = Cyclohexanone oxime (hydrochloride). E = Methyl nitrite. F = HCl. + = Present.

form cyclohexanone and its dimethyl acetal, which are at equilibrium with each other and methanol or water respectively. Plots of methyl nitrite and product yields of this reaction *versus* time[10] indicated that both methyl nitrite and cyclohexanone are consumed in a secondary reaction.

By addition of triethylamine prior to photolysis secondary dark reactions could be prevented. The much simpler results obtained in this case are presented in Table 2. They indicate that the stoicheiometry of product formation is 0·5 mole of nitrite, 0·5 mole of oxime, 0·5 mole of cyclohexanone acetal, and 1 mole of HCl (as triethylammonium salt) per mole of photolysed nitroso-compound in the absence of secondary dark reactions. The final product distribution is, however, as Table 2 shows, only obtained after a sufficiently long time between completed photolysis and analysis.

TABLE 2

Dependence of the product distribution obtained by photolysis of a $9·5 \times 10^{-2}M$ solution of compound (I) in methanol in the presence of triethylamine on the time t between completed photolysis and analysis *

t/min	A	B	C	D	E
15	9·2	11	9		
40	3·2	41	1		49
85	1·7	47	1		
120	1	48	1	48	

* Yields of A—E in mole per 100 moles of (I) A—E = Product designations of Table 1.

Photolysis of Compound (I) *in Aprotic Solvents.*—The photolysis of concentrated aprotic solutions proceeded with precipitation of insoluble resins and formation of cyclohexanone and its oxime, HCl, and little N_2O. The product sums were unsatisfactory (see Experimental section). The photolysis of dilute solutions of (I), however, proceeded smoothly and gave a spectrum of products entirely different

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† This designation has been adopted from ref. 9 and references therein.

[4] D. Ll. Hammick and M. W. Lister, *J. Chem. Soc.*, 1937, 489.
[5] E. Müller, *Pure Appl. Chem.*, 1968, **16**, 153.
[6] Y. Ito, *Bull. Chem. Soc., Japan*, 1956, **29**, 227.
[7] S. Mitchell, K. Schwarzwald, and G. K. Simpson, *J. Chem. Soc.*, 1941, 602.

[8] E. Müller, H. Metzger, and D. Fries, *Chem. Ber.*, 1954, **87**, 1449.
[9] G. Kresze, N. M. Mayer, and J. Winkler, *Annalen*, 1971, **747**, 172.
[10] J. Pfab, Ph.D. Thesis, Technische Universität München, 1972.

from that obtained in methanol or in concentrated aprotic solutions. The main products (Table 3) were 1-chloro-cyclohexene, cyclohexanone, and 1,1-dichlorocyclohexane. Cyclohexanone oxime was virtually absent in all dilute solutions with the exception of ether, where it precipitated as the hydrochloride.

TABLE 3

Products and yields of the photolysis of compound (I) at initial concentrations c_0 in mole per 100 mole of (I)

Solvent	CHCl₃	Cyclo-hexane[a]	CCl₄[b]	C₆H₆	DPB[c]	Cyclo-hexene	Et₂O
$10^{-2}c_0$/M	1·0	5·5	2·4	2·3	2·3	4·8	7·8
A	16	16	14 (1)	13	16	10	1·7
B	26	25	20 (51)	27	24	22	18
C	36	41	35 (36)	39	35	30	1·2
D	4·0	0·8	4·3 (1)	4·0	?	1·2	0·8
E	4·4	4·8	2·3 (9·2)	3·6	?	2·8	1·0
F	1 (1)	4 (3)	—	—	—	8·5 (5)	—
G	—	3	—	—	—	?	30
H	+	+	+ (—)	+	+	+	+

[a] Undegassed solution. [b] Yields in parentheses refer to oxygen-saturated solution. [c] 1,4-Di-isopropylbenzene. ? = Product could not be determined because of solvent interference. + = Present. — = absent. A = 1-Chlorocyclohexene. B = Cyclohexanone. C = 1,1-Dichlorocyclohexane. D = α-Chlorocyclohexanone. E = 1-Chloro-1-nitrocyclohexane. F = Sum of unknown products with the number of products in parentheses. G = Cyclohexanone oxime (hydrochloride). H = Insoluble precipitate.

Dissolved O_2 in CCl_4 solution increased the yield of cyclohexanone from 20 to 51% and that of 1-chloro-1-nitro-cyclohexane from 2·3 to 9·2% at the expense of 1-chloro-cyclohexene (Table 3, column 3). Results of the photolysis of (I) in the presence of several other potential radical scavengers are collected in Table 4.

TABLE 4

Photolysis of compound (I) in presence of a five-fold molar excess of radical scavenger S in CCl_4

S	NOCl	NO₂	Cl₂[a]	Br₂[b]	NO[c]
$10^{-2}c_0$/M	4·27	3·76	4·88	5·16	2·82
A	9	5	4		56
B	12	18		4	34
C	56	2	28		0·4
D	Trace		1·3		0·1
E	11	71		1	12·4
F	10 (2)		60 (9)	2 (3)	

* Product yields in mole per mole of (I), c_0 and product designations as in Table 3. [a] Additional product: 98% NOCl, unknowns: two main components, seven minor components. [b] Main product: 94% 1-bromo-1-chlorocyclohexane. [c] Reaction in the dark, additional products NO₂ and N₂ not determined.

Reaction of Nitric Oxide with Compound (I).—Nitric oxide reacted rapidly with (I) in methanol without any gas evolution to yield the product distribution summarised in the

* Yields of 0·47 mole of methyl nitrite per mole of trichloronitrosomethane upon photolysis in methanol have been reported elsewhere.[13]

[11] A. H. M. Kayen, L. R. Subramanian, and Th. J. de Boer, *Rec. Trav. chim.*, 1971, **90**, 866.

last row of Table 1. In aprotic solvents the reaction proceeded sluggishly with formation of N_2 and NO_2,1-chloro-cyclohexene, cyclohexanone, and 1-chloro-1-nitrocyclo-hexane (Table 4, column 6). 1,1-Dichlorocyclohexane, the main product of photolysis in almost all aprotic solvents, is not formed in this dark reaction.

Photolysis of Other Chloronitrosoalkanes in Alcohols.—A recent [11] study of the photolysis of 2-chloro-2-nitrosoadamantane has been reported. We found that for each mole of nitroso-compound *ca.* 0·5 mole of 2,2-dimethoxyadamantane, adamantanone oxime, and methyl nitrite were formed together with small amounts of adamantanone. Only adamantanone and its oxime had been reported previously [11] as the photolysis products. The photolysis of 3-chloro-3-nitrosopentane in isopropyl alcohol similarly gave high yields of isopropyl nitrite (42 mole per 100 mole of nitroso-compound for a 4·8 × 10⁻³M solution) and photolysis in methanol produced methyl nitrite and 3,3-dimethoxypentane. In a detailed recent investigation [12] none of these products were reported.

A preliminary investigation of the photolysis of tri-chloronitrosomethane in ethanol showed that the products consist mainly of ethyl nitrite,* dichloroformoxime, and diethyl carbonate. Photolysis in aprotic solvents is extremely slow and leads to formation of nitrosyl chloride. Further work on this compound is in progress.

DISCUSSION

Comparison of our results for the photolysis of compound (I) in methanol (Table 1) with those obtained in aprotic solvents (Table 3) shows that the type and distribution of products changes fundamentally by the use of a protic, nucleophilic solvent like methanol. A similar solvent effect upon the photolysis of 2-chloro-2-nitrosobutane was observed by Creagh and Trachtenberg.[14] Recent results for the photolysis of 3-chloro-3-nitrosopentane [12] and 2-chloro-2-nitrosoadamantane [11] indicate the same difference. The solvent influence was explained by postulating C–NO cleavage in benzene and $CHCl_3$, and C–Cl cleavage in alcohols and ethers.[14] Subsequently it was concluded that in hydrogen-donating solvents the photoexcited nitroso-group would react with the solvent.[11,12]

Mechanism of Photolysis in Alcohols.—Evidence presented here and elsewhere [10,13,15] shows that in alcohols as solvents all monomeric tertiary nitroso-compounds give rise to the formation of alkyl nitrites derived from the solvent. With α-chloro-nitroso-compounds in particular the yields of nitrites approach 0·5 mole per mole of nitroso-compound. This result is not in agreement with a mechanism based on abstraction of hydrogen from the solvent by an excited state of the nitroso-compound. The formation of a solvent-derived nitrite rather requires that the original C–NO bond be split. As in both nitrogen-containing products (oxime and
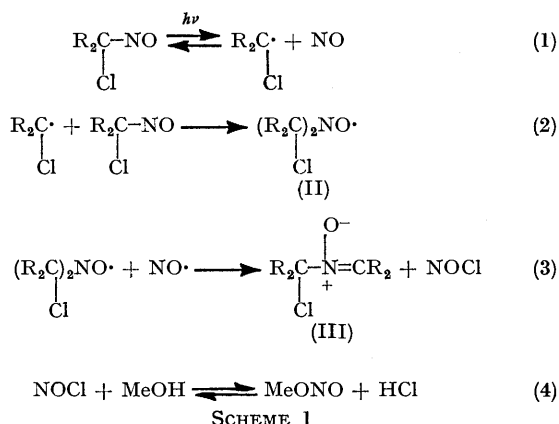
[12] E. F. J. Duynstee and M. E. A. H. Mevis, *Rec. Trav. chim.*, 1971, **90**, 932.

[13] B. G. Gowenlock, G. Kresze, and J. Pfab, *Tetrahedron Letters*, 1972, 593.

[14] L. Creagh and I. Trachtenberg, *J. Org. Chem.*, 1969, **34**, 1307.

[15] B. G. Gowenlock, G. Kresze, and J. Pfab, *Tetrahedron*, 1973, **29**, 3587.

nitrite) the oxidation state of the nitrogen atom is identical with that in the starting material, reduction or hydrogen abstraction must therefore be absent. In the case of geminal nitro-nitroso-compounds we demonstrated that the solvolysis of an α-nitro-substituted nitrone formed *via* a nitroxide is responsible for the observed product distribution. We suggest a similar scheme for the mechanism of the photodecomposition of α-chloronitrosoalkanes R_2CClNO which is based on initial rupture of the C–NO bond (Scheme 1). *O*-Nitrosohydr-

$$R_2C\overset{hv}{\underset{Cl}{\text{—NO}}} \rightleftharpoons R_2\overset{\cdot}{\underset{Cl}{C}} + NO \qquad (1)$$

$$R_2\overset{\cdot}{\underset{Cl}{C}} + R_2\overset{}{\underset{Cl}{C}}\text{—NO} \longrightarrow (R_2\underset{Cl}{C})_2NO\cdot \qquad (2)$$
$$(II)$$

$$(R_2\underset{Cl}{C})_2NO\cdot + NO\cdot \longrightarrow R_2\overset{O^-}{\underset{Cl}{\underset{+}{C}}\text{—N}}=CR_2 + NOCl \qquad (3)$$
$$(III)$$

$$NOCl + MeOH \rightleftharpoons MeONO + HCl \qquad (4)$$

SCHEME 1

oxylamine formation followed by nitrite ester exchange with the alcohol [13,15] and subsequent loss of chloride ion as summarised by equation (5) cannot be excluded as an alternative.

$$(R_2\underset{Cl}{C})_2NONO + MeOH \longrightarrow$$

$$R_2\overset{OH}{\underset{+}{C}\text{—N}}=CR_2 + Cl^- + MeONO \qquad (5)$$
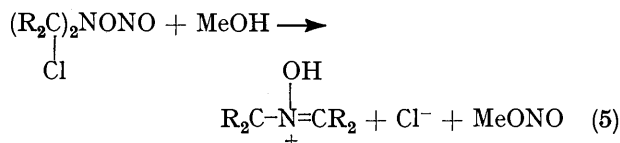
β-Chloronitroxides of similar type to (II) have been characterised by e.s.r. spectroscopy [10,16-21] and are known to eliminate chlorine atoms with formation of nitrones.[22] The formation of *N*-dichloromethylenetrichloromethylamine *N*-oxide [23] has been explained similarly.[18] We [10] and others [12,16] have not been able however to detect nitroxides of type (II) during irradiation of several geminal chloronitrosoalkanes in spite of the fact that radicals generated from an independent source are trapped most readily,[10] yielding the predicted β-chloro- or β,β'-polychloro-nitroxides. This surprising negative evidence indicates that reaction (3) is very efficient in preventing the build-up of a detectable stationary concentration of (II).

The observed products apart from methyl nitrite

[equations (4) and (5)] are formed by the fast acid catalysed or slow non-catalysed (in the presence of a slight excess of amine) alcoholysis of nitrone (III) [equations (6) and (7)]. The observed product yields agree well

$$R_2\overset{O^-}{\underset{Cl}{\underset{+}{C}\text{—N}}}=CR_2 + 2MeOH \xrightarrow{\text{(HCl)}}$$
$$R_2\overset{}{\underset{Cl}{C}\text{—NHOH}} + R_2C(OMe)_2 \qquad (6)$$

$$R_2\overset{}{\underset{Cl}{C}\text{—NHOH}} \longrightarrow R_2C=NOH + HCl \qquad (7)$$

with the stoicheiometry predicted by Scheme 1 and equations (6) and (7) (Table 2), if the formation of free HCl is suppressed by added amine. The solvolysis of nitrone (III) is much faster in the presence of free HCl, but as the secondary dark reactions are also more rapid the product distribution deviates from theory and changes with initial concentration (Table 1). Thus 6-hydroxy-imino-1-methoxycyclohexene is likely to be formed *via* an acid catalysed α-oximation of cyclohexanone by methyl nitrite [equation (8)]. It can certainly not be regarded as a direct photolysis product. The failure of other authors to identify methyl nitrite as an essential product of the photolysis of geminal chloro-nitroso-compounds in methanol and their subsequent misinterpretations of α-hydroxyimino-ketone formation [12,14,24,25] is thus readily explicable.

$$(8)$$
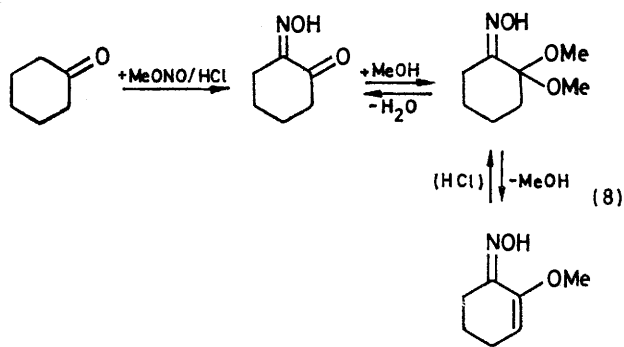
Our results regarding the addition of nitric oxide to the nitroso-compound appear to indicate that this reaction may be involved. The high methyl nitrite yield indicates however that reactions (9) and (10) can only be of minor importance in the absence of added NO.

Similar reactions are well documented.[26-29] As the

[16] A. H. M. Kayen and Th. J. de Boer, personal communication.
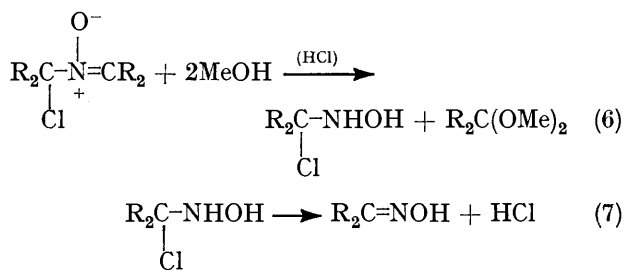[17] K. Torsell, *Tetrahedron*, 1970, **26**, 2759.
[18] C. N. Camaggi, R. J. Holman and M. J. Perkins, *J.C.S. Perkin II*, 1972, 501.
[19] E. G. Janzen, B. R. Knauer, L. T. Williams, and W. B. Harrison, *J. Chem. Phys.*, 1970, **74**, 3025.
[20] J. H. Lever, G. C. Ramsey, and E. Suzuki, *Austral. J. Chem.*, 1969, **22**, 1891.
[21] H. Sutcliffe and H. W. Wardale, *J. Amer. Chem. Soc.*, 1967, **89**, 5487.

[22] J. W. Hartgerink, J. B. F. N. Engberts, and Th. J. de Boer, *Tetrahedron Letters*, 1971, 2709.
[23] V. Astley and H. Sutcliffe, *Tetrahedron Letters*, 1971, 2707.
[24] S. Mitchell and J. Cameron, *J. Chem. Soc.*, 1938, 1964.
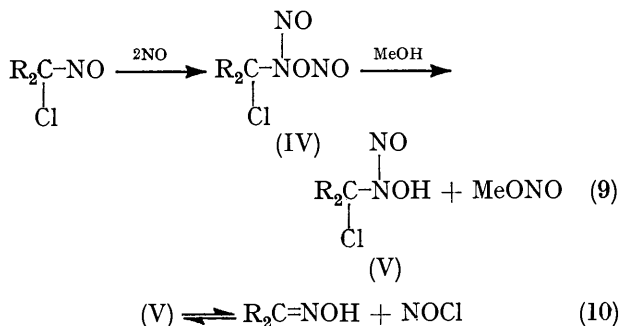[25] J. E. Baldwin and N. H. Rogers, *Chem. Comm.*, 1965, 524.
[26] E. Müller and U. Heuschkel, *Chem. Ber.*, 1959, **92**, 78.
[27] V. A. Ginsburg, L. L. Martynova, and M. M. Vasil'eva, *Zhur. Obshchei Khim.*, 1967, **37**, 1083 (*Chem. Abs.*, 1968, **68**, 12,368t).
[28] E. Müller and U. Heuschkel, *Z. Naturforsch.*, 1964, **19b**, 1021.
[29] R. Sartorius, Dissertation, Universität Giessen, 1939.

oxime is a main product a rearrangement of (V) similar to that observed with other N-nitrosohydroxylamines [28,30,31] appears to be bypassed in methanol by equation (10)

$$R_2C-NO \xrightarrow{2NO} R_2C-\overset{\overset{\displaystyle NO}{|}}{N}ONO \xrightarrow{MeOH}$$
$$\overset{|}{Cl} \qquad \overset{|}{Cl}$$
$$(IV) \qquad$$

$$R_2C-\overset{\overset{\displaystyle NO}{|}}{N}OH + MeONO \quad (9)$$
$$\overset{|}{Cl}$$
$$(V)$$

$$(V) \rightleftharpoons R_2C{=}NOH + NOCl \qquad (10)$$

followed by (4). In aprotic solvents equation (10) is known to proceed in the opposite direction.[32]

It is apparent from the preceding discussion that the photolysis of geminal chloro-nitroso-compounds in alcohols can be adequately understood on the basis of C–NO bond cleavage in the primary step without postulating C–Cl bond cleavage,[14] hydrogen abstraction by an excited state,[11,12] or elimination of HNO[4] or HCl.[24] This interpretation is confirmed by our results of a reinvestigation of the photolysis of 2-chloro-2-nitroso-adamantane and 3-chloro-3-nitrosopentane in methanol, which clearly showed that previous investigators[11,12] had overlooked both methyl nitrite as well as the dimethyl acetal of the parent ketone and is also supported by our results of the photolysis of trichloronitrosomethane in methanol.
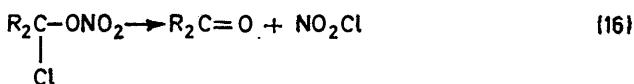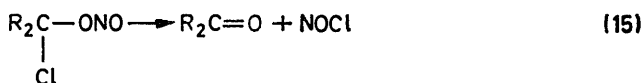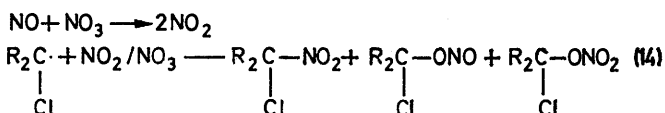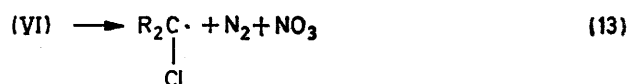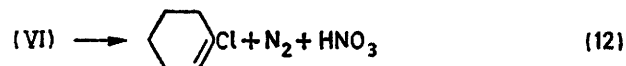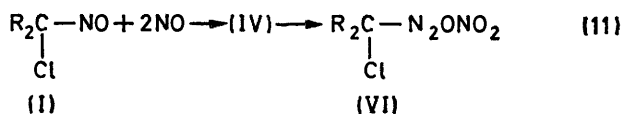
Mechanism of Photolysis in Aprotic Solvents.—In contrast to the photolysis in alcohol solutions, where our experimental results and our interpretation differ considerably from previous work,[11,12,14] we find closer agreement in the case of aprotic solutions. The formation of nitrogen[12,14] suggests the participation of a diazonium nitrate *via* reaction (11). The homolytic or heterolytic decomposition of the latter explains three of the observed products,[33] namely 1-chlorocyclohexene, cyclohexanone, and 1-chloro-1-nitrocyclohexane (Scheme 2). That the main photolysis product, 2,2-dichlorocyclohexane, can, however, not be formed *via* this sequence is apparent from its absence among the products obtained from the direct dark reaction of nitric oxide with (I). Unlike other authors[11,12] we conclude therefore, that reaction (1) and Scheme 2 alone are not sufficient to explain the course of photolysis. Scheme 2 will only take place if a sufficiently high stationary concentration of nitric oxide can build up.* Therefore we

* One of the referees found the negative e.s.r. evidence for nitroxide (II) surprising. A build-up of nitric oxide in conjunction with reaction (3) may account for the absence of a detectable concentration of (II). E.s.r. experiments showing that β-chloronitroxides decay rapidly in the presence of NO are described elsewhere.[10]

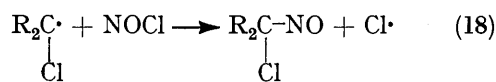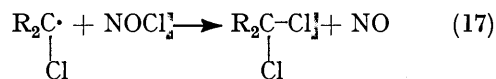[30] P. R. Hills and R. A. Johnson, *Internat. J. Appl. Radiation Isotopes*, 1961, **12**, 80.

[31] T. Koenig, M. Deinzer, and J. A. Hoobler, *J. Amer. Chem. Soc.*, 1971, **93**, 938.

conclude that reactions (1)—(3) are followed by (17) explaining both the formation of the main product, 1,1-dichlorocyclohexane, as well as the accumulation of NO necessary for Scheme 2 to occur. We were unable to obtain direct evidence for the intermediacy of NOCl in the case of compound (I) owing to its subsequent reactions [(4), (17), and (20)]. With other substrates

$$R_2C-NO + 2NO \rightarrow (IV) \rightarrow R_2C-N_2ONO_2 \qquad (11)$$
$$\overset{|}{Cl} \qquad\qquad\qquad \overset{|}{Cl}$$
$$(I) \qquad\qquad\qquad\qquad (VI)$$

$$(VI) \rightarrow \langle\!\!\!\rangle Cl + N_2 + HNO_3 \qquad (12)$$

$$(VI) \rightarrow R_2C{\cdot} + N_2 + NO_3 \qquad (13)$$
$$\overset{|}{Cl}$$

$$NO + NO_3 \rightarrow 2NO_2$$
$$R_2C{\cdot} + NO_2/NO_3 \longrightarrow R_2C-NO_2 + R_2C-ONO + R_2C-ONO_2 \quad (14)$$
$$\overset{|}{Cl} \qquad\qquad\qquad \overset{|}{Cl} \qquad \overset{|}{Cl} \qquad\quad \overset{|}{Cl}$$

$$R_2C-ONO \rightarrow R_2C{=}O + NOCl \qquad (15)$$
$$\overset{|}{Cl}$$

$$R_2C-ONO_2 \rightarrow R_2C{=}O + NO_2Cl \qquad (16)$$
$$\overset{|}{Cl}$$

SCHEME 2
R_2C = cyclohexyl

R^1R^2CXNO however, NOX could be identified unambiguously (NOCl, where X, R^1, and R^2 = Cl; NOBr, where X = Br, R^1 = Me, and R^2 = Bu^t; N_2O_3, where X = NO$_2$, R^1 and R^2 = Me[15]).

$$R_2C{\cdot} + NOCl_2^1 \rightarrow R_2C-Cl_2^1 + NO \qquad (17)$$
$$\overset{|}{Cl} \qquad\qquad\quad \overset{|}{Cl}$$

$$R_2C{\cdot} + NOCl \rightarrow R_2C-NO + Cl{\cdot} \qquad (18)$$
$$\overset{|}{Cl} \qquad\qquad\quad \overset{|}{Cl}$$

Indeed the product distribution changes very little if the photolysis of (I) is conducted in the presence of added NOCl under conditions where the photolysis of NOCl was estimated to be negligible.[34-36] These results cannot rule out reaction (18), but a thermochemical estimation as well as related experiments[30] suggest that reaction (17) is more favourable than (18).

The invariance of product distribution with the nature of the aprotic solvent shows clearly that hydrogen

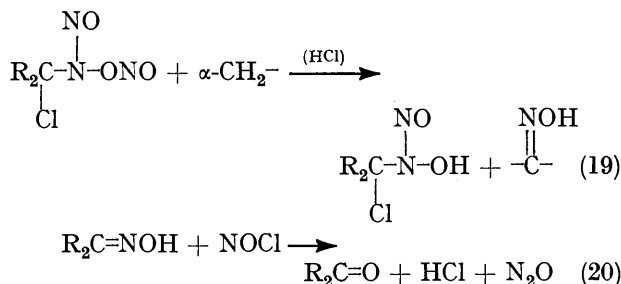[32] H. Rheinboldt and M. Dewald, *Annalen*, 1927, **455**, 300.

[33] K. A. Ogloblin, V. A. Nikitin, T. L. Yufa, and A. A. Potekhin, *Zhur. Org. Khim.*, 1969, **5**, 1364; *J. Org. Chem. U.S.S.R.*, 1969, 1333.

[34] K. Atwood and G. K. Rollesfson, *J. Chem. Phys.*, 1941, **9**, 506.

[35] C. F. Goodeve and S. Katz, *Proc. Roy. Soc.*, 1939, *A*,**172**, 432.

[36] See ref. 2, pp. 584—586 and references therein.

abstraction from the solvent by an excited state is absent. Furthermore the almost complete absence of chlorocyclohexane (traces were found with the solvents cyclohexane and p-di-isopropylbenzene) suggests that the rate of hydrogen abstraction by an α-chlorocyclohexyl radical generated in the primary step is much smaller than the sum of the rates for reactions (2) and (17). Even in the case of diethyl ether, where reaction (17) is less efficient as judged from the small yield of geminal dichloro-compound, it appears doubtful whether the increased yield of cyclohexanone oxime hydrochloride can be assigned to hydrogen abstraction by an excited nitroso-group. Our results cannot at present rule out an ionic dark reaction of the type (19), which *via* reaction (10), may lead to oxime formation. The increase of the yield of the latter and the apparent change of the course of the photolysis observed when high concentrations of compound (I) were photolysed are in agreement with this interpretation. The formation of N_2O observed under these conditions then is a consequence of the well known nitrosative deoximation [37] (20).

$$R_2C\overset{\overset{\displaystyle NO}{|}}{\underset{\underset{\displaystyle Cl}{|}}{N}}\text{-ONO} + \alpha\text{-CH}_2\text{-} \xrightarrow{\text{(HCl)}}$$

$$R_2C\overset{\overset{\displaystyle NO}{|}}{\underset{\underset{\displaystyle Cl}{|}}{N}}\text{-OH} + \overset{\overset{\displaystyle NOH}{\|}}{\text{-C-}} \quad (19)$$

$$R_2C\text{=NOH} + \text{NOCl} \longrightarrow$$
$$R_2C\text{=O} + \text{HCl} + N_2O \quad (20)$$

The results obtained by studying the influence of several radical scavengers indicate that here, too, photolytic C–NO cleavage takes place. Thus 1-chloro-1-nitrocyclohexane is the main product formed in the presence of NO_2 and 1-chloro-1-bromocyclohexane is the almost exclusive product (94% yield) in the presence of added bromine. In each case the main product retained the original C–Cl bond. Thus our results support conclusions by others [11,12] that chlorine is not split off in the primary step.

EXPERIMENTAL

Instruments and Apparatus.—G.l.c. separations were performed using a Perkin-Elmer F20 and F and M 720 gas chromatograph. Relative peak areas and retention times were determined with an Autolab 6300 digital integrator. Irradiations were carried out with vacuum degassed solutions under N_2 as described [15] unless stated otherwise.

Solvents.—Great care was exercised in the purification of solvents [15] particularly with the removal of hydroxylic contaminants in aprotic solvents. All solvents were stored and handled under N_2 or vacuum.

Starting Material and Reference Compounds.—All geminal chloro-nitroso-compounds were prepared using known methods.[8,11,38] 1,1-Dimethoxycyclohexane [39] and 3,3-dimethoxypentane [40] were obtained as described.

2,2-*Dimethoxyadamantane* (*dimethyl acetal of adamantanone*). A mixture of adamantanone (1·4 g, 9·3 mmol), acetyl chloride (0·5 ml), trimethyl orthoformate (10 ml), and methanol (30 ml) was heated under reflux for 5 min. Work-up after neutralisation of HCl by triethylamine afforded the *product* (1·62 g, 90%), an oil which crystallised on standing, b.p. 108—109° at 12 mmHg, m.p. 27—28° (Found: C, 73·2; H, 10·0. $C_{12}H_{20}O_2$ requires C, 73·45; H, 10·05%), $\nu_{max.}$ (CCl$_4$) 2810, 1118, 1098, 1072, 1055, and 918 cm^{-1}, δ (CCl$_4$) 1·42, 1·58, 1·78, 2·00 (14H, m), and 3·10 (6H, s).

1,1-Dichlorocyclohexane was obtained in 15% yield as a side-product of the preparation of 1-chlorocyclohexene [41] after distillation with a spinning-band column: 1-chlorocyclohexene, b.p. 91° at 150 mmHg; 1,1-dichlorocyclohexane, b.p. 103° at 120 mmHg. α-Chlorocyclohexanone,[42] 1-chloro-1-nitrocyclohexane, and 3-chloro-3-nitropentane [43] were obtained by standard methods. 1-Methoxycyclohexene was prepared by refluxing a mixture of cyclohexanone, trimethyl orthoformate, and methanol in the presence of toluene-p-sulphonic acid followed by fractional distillation of the resulting mixture.

Reaction of Cyclohexanone with Methanol in the Presence of HCl.—A 0·1M solution of HCl and cyclohexanone was prepared by adding the required amount of acetyl chloride to a solution of cyclohexanone in methanol. G.l.c. showed that after 5 min 95% of the ketone had disappeared with formation of 1,1-dimethoxycyclohexane and a small amount of 1-methoxycyclohexene.

Reaction of Cyclohexanone Oxime Hydrochloride with Methyl Nitrite in Methanol.—The reaction was started by adding isopropyl nitrite (17 mmol) to a solution of the oxime hydrochloride (10 mmol) in methanol, the total volume being 100 ml. Aliquot portions were withdrawn at 5 min intervals and quenched by addition to a methanolic solution of triethylamine. The methyl nitrite content was followed by spectrophotometry, that of the products cyclohexanone, cyclohexanone dimethyl acetal, and 1-methoxycyclohexene by g.l.c. Plots of product yields *versus* time showed maxima for cyclohexanone and its acetal at 20 min and a maximum for 1-methoxycyclohexane at 27—32 min. The rate of methyl nitrite disappearance was highest at 18—20 min.

Reaction of Nitric Oxide with 1-*Chloro*-1-*nitrosocyclohexane* (I).—The reaction was conducted with a 2·82 × 10^{-2}M solution of (I) in carbon tetrachloride at a nitric oxide pressure of *ca.* 950 mmHg and resulted in formation of a colourless gas (presumably nitrogen) and nitrogen dioxide. Experimental details and work-up were as described previously [15] for 2-nitro-2-nitrosopropane. For results see Table 4. A 5 × 10^{-2}M solution of (I) in methanol absorbed the gas more rapidly and gave a colourless solution. The results (Table 1) were obtained after removal of excess of nitric oxide. Upon standing, the product yields changed in secondary reactions. Isopropyl alcohol solutions of (I) treated similarly gave yields of isopropyl nitrite close to 2 moles per mole of (I).

Photolysis of (I) *in Concentrated Methanol Solutions.*—1—3M Solutions of (I) in methanol were photolysed by

[37] J. M. Kliegmann and R. K. Barnes, *J. Org. Chem.*, 1972, **37**, 4224.

[38] M. Kosinsky, *Lodz. Towarz. Nauk., Acta Chim.*, 1964, **9**, 93.

[39] W. J. Hickinbottom, 'Reactions, of Organic Compounds,' Longmans, London, 1948, p. 239.

[40] H. Meerwein in Houben-Weyl, ' Methoden der Organischen Chemie,' Georg Thieme Verlag, Stuttgart, 1971, vol. 6/3, p. 227.

[41] E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 1950, 2017.

[42] M. S. Newman, M. D. Farbman and H. Hipsher, *Org. Synth.*, 1945, **25**, 23.

[43] See ref. 40, p. 123.

external irradiation with tungsten lamps. After irradiation for 5—8 h (I) had disappeared. Dark brown, strongly acidic solutions were obtained. Filtration afforded a small amount (*ca.* 1 weight %) of an insoluble, yellow, undetermined product (elemental composition *ca.* $C_6H_8N_2O_2$ and strong i.r.-absorptions at 3200 and 1530 cm^{-1}). The filtrate afforded a small amount of colourless liquid, which was shown to consist of a mixture of 1,1-dimethoxycyclohexane and cyclohexanone by i.r., n.m.r., and g.l.c. The black oily distillation residue afforded a hygroscopic hydrochloride, m.p. 98° (decomp.). Neutralisation and recrystallisation from benzene–hexane afforded white crystals of m.p. 148° in 5% yield, shown to consist of 6-*hydroxyimino*-1-*methoxycyclohexene* (Found: *m/e* 141. $C_7H_{11}NO_2$ requires M^+, 141·17) (Found: C, 59·8; H, 8·1; N, 10·1. $C_7H_{11}NO_2$ requires C, 59·55; H, 7·85; N, 9·95%), $\nu_{max.}$ (KBr) 3180, 2918, 2819, 1620, 1200, 1157, 1003, and 968 cm^{-1}, δ (CDCl$_3$) 5·30 (1H, t, *J* 4 Hz, =CH), 3·61 (3H, s, OMe), 2·70 (2H, t, *J* 7 Hz), 2·22 (2H, q, *J* 5 Hz), and 1·78 (2H, m, *J* 6 Hz). The filtrate of the hydrochloride afforded cyclohexanone oxime in 25% yield after steam distillation along with further cyclohexanone.

Quantitative analyses were carried out with the following varying results: HCl 92—97%, cyclohexanone oxime 40—45%, cyclohexanone 10—19%, 1,1-dimethoxycyclohexane 4—10%.

Photolysis of Concentrated Solutions of (I) *in Cyclohexane and Benzene.*—Exposure to white light produced a tarry brown resin that prevented any further transmission of light. Evolution of gaseous products was negligible. I.r. spectra of the black deposits exhibited a very broad and strong absorption in the region 3200—2300 cm^{-1} and a strong absorption at 1400 cm^{-1} suggesting the presence of a protonated hydroxyimino-group. With methanol, black-brown solutions containing free HCl were obtained. After neutralisation with methanolic sodium methoxide solution cyclohexanone oxime and 1,1-dimethoxycyclohexane were identified by g.l.c. Photolysed cyclohexane solutions of (I) gave cyclohexanone oxime hydrochloride directly apart from black-brown resin. From the latter both cyclohexanone as well as its oxime were obtained by steam distillation.

Quantitative analyses gave the following results: 53% overall * yield of cyclohexanone oxime (hydrochloride) and 20% cyclohexanone in benzene as solvent; 51% overall * yield of the oxime (hydrochloride) and 16% cyclohexanone in cyclohexane as solvent.

N_2O *Formation during Photolysis of* (I) *in Benzene.*—Solutions of (I) in benzene (initial concentration c_0 10^{-2}M) were sealed with a rubber septum. After completed photolysis with light of wavelength >540 nm, liquid samples (50 µl) were withdrawn and directly analysed for dissolved N_2O by gas–solid chromatography with the results: c_0 1·84mM, N_2O present, but too small for quantitative determination; c_0 15·3mM, N_2O 0·7 mole per 100 mole (I); c_0 80·7mM, N_2O 1·2 mole per 100 mole (I).

Photolysis of Dilute Solutions of (I) *in Various Solvents.*—Photodecomposition was achieved by exposing the solutions to the bichromate-filtered light of a sodium high pressure lamp as described earlier.[15] The analytical results obtained for methanol solutions of varying initial concentration are collected in Table 1. Results of the photolysis of a 9·5 × 10^{-2}M methanolic solution in the presence of a slight excess of triethylamine are collected in Table 2. Photolysis was sufficiently rapid (20 min) to avoid interference caused by the instability of solutions of (I) in the presence of the amine. The slow change of product distribution after completed photolysis was followed by g.l.c.

Photolysis of (I) in aprotic solvents proceeded with formation of gas and of small amounts of brownish, insoluble precipitate which was usually absent in the presence of air or oxygen. Results of the product analyses are given in Table 3.

Photolysis of (I) *in the Presence of Various Radical Scavengers.*—Amounts of stock solutions of NOCl, NO_2–N_2O_4, Cl$_2$, and Br$_2$ in absolute CCl$_4$ corresponding to a five-fold molar excess were added to a solution of (I) in the same solvent under nitrogen. Photolysis was completed after 10—15 min. The excess of scavenger was removed by extraction with an aqueous hydrogen carbonate solution, followed by drying the organic layer (CaCl$_2$), evaporation of the bulk of solvent, and g.l.c. analysis (Table 4). When Cl$_2$ was the scavenger, the product (NOCl; 98%) was determined as methyl nitrite by u.v. spectroscopy.

Preparation of 1-*Bromo*-1-*chlorocyclohexane by Photolysis of* (I) *in the Presence of Bromine.*—Compound (I) (15·4 g) containing 15% 1,1-dichlorocyclohexane as impurity and bromine (26 ml) dissolved in CCl$_4$ (600 ml) was photolysed with filtered light from a sodium lamp. After the nitroso-compound had disappeared (2 h) the excess of bromine was removed with aqueous hydrogen sulphite solution–ice. Work-up afforded 1-bromo-1-chlorocyclohexane (13 g, 74%) of 99·8% purity, b.p. 66·5—67° at 13 mmHg (lit.,[44] 77·5° at 17 mmHg) (Found: C, 36·4; H, 5·15. Calc. for $C_6H_{10}BrCl$: C, 36·4; H, 5·1%).

Photolysis of 2-*Chloro*-2-*nitrosoadamantane in Methanol.*—A degassed solution (initial concentration 5·54 × 10^{-2}M) photolysed to completion with light of wavelength >540 nm afforded the following products (in mole per 100 mole nitroso-compound): methyl nitrite (44), 2,2-dimethoxyadamantane (52), adamantanone (5), adamantanone oxime (hydrochloride) (52), and hydrogen chloride.

Photolysis of 3-*Chloro*-3-*nitrosopentane in Methanol.*—A 0·2M solution photolysed to completion within 35 min in the presence of air and a slight excess of triethylamine afforded 30% methyl nitrite and 10% 3,3-dimethoxypentane immediately after completed photolysis and 31% of the latter, when analysed after 3 days at ambient temperature. Photolysis of a 4·8 × 10^{-3}M solution in isopropyl alcohol in the absence of triethylamine afforded 47% isopropyl nitrite.

Quantitative Analyses and Identification of Products.—Methyl nitrite was determined and identified as described.[15] Isopropyl nitrite in propan-2-ol was analysed by u.v. [$\lambda_{max.}$ 358 nm (ε 62·8)], 1-methoxycyclohexene, 1,1-dimethoxycyclohexane, and cyclohexanone by g.l.c. (6 ft × ¼ in column of 10% Carbowax 20M on Chromosorb W; AW; DMCS; 80—100 mesh; 90°; 40 ml He min^{-1}) and i.r. 2,2-Dimethoxyadamantane and adamantanone were determined on the same column and identified by m.p., i.r., mass spectra, and comparison with reference samples. 3,3-Dimethoxypentane was identified by g.l.c. and analysed with toluene as standard. 1-Chlorocyclohexene, 1,1-dichlorocyclohexane, 1-chloro-1-bromocyclohexane, cyclohexanone, α-chlorocyclohexanone, and 1-chloro-1-nitrocyclohexane were isolated by g.l.c. and identified by i.r. Quantitative analyses of these products were carried out at 75°

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* Analysis included soluble as well as insoluble product.

[44] H. L. Goering and L. L. Sims, *J. Amer. Chem. Soc.*, 1957, **79**, 6272.

with a 2 m × 1·8 in column (0·5% Apiezon L and 0·5% Carbowax 20M on 80—100 mesh Chromosorb G; AW; DMCS) using bromobenzene as internal standard. Oximes were identified by m.p. and i.r. and analysed spectrophoto-metrically after conversion into chloro-nitroso-compounds.

HCl was determined by titration with silver nitrate solution employing dichlorofluorescein as adsorption indicator. A gravimetric control determination gave identical results.