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C-NITROSO COMPOUNDS—XXIV

PHOTOLYSIS OF SOME GEMINAL NITRO-NITROSOALKANES ("PSEUDONITROLES")

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Abstract—Photolysis of the "pseudonitrole" 1-nitro-1-nitrosocyclohexane with red light in the absence of oxygen occurs by homolytic C-NO fission, and generates a radical pair: NO and the α-nitro-cyclohexyl radical. If one radical of this pair adds to the NO-group of unchanged starting material, there results a paramagnetic nitroxide, that can combine with the other radical of the pair to a diamagnetic intermediate, forming two isomeric intermediate adducts to the NO double bond. The ratio in which these isomers are formed depends on solvent. In methanol, solvolysis leads to equimolar amounts of cyclohexanone and cyclohexanone-oxime, together with methyl nitrite. In benzene, the major product is cyclohexanone. Small amounts are formed of 1,1-dinitrocyclohexane, 1-nitrocyclohexene and nitrocyclohexane; arising directly from the α-nitrocyclohexyl radical. The nitroxide derived from this radical and the starting material can be detected by ESR.

The photolytic behaviour of 1-nitro-1-nitroso-1-cyclopropylethane illustrates the strong interaction between a nitrogroup and an adjacent C-radical centre: only *ring-closed* products are formed, showing considerable spin delocalisation away from the cyclopropyl ring.

INTRODUCTION

As part of our studies on the photolysis of aliphatic nitroso-compounds, we have investigated some readily accessible gem-nitro-nitrosoalkanes, "pseudonitroles".[1] In the literature the photochemical instability of these compounds has been noted,[2] but the only recorded photochemical investigations involve irradiation with red light *in the presence of oxygen.*[3,4] This leads to gem-dinitro-derivatives, and under optimal conditions this route has some preparative value.[2-4] As a convenient model for the study of the photolysis in the absence of oxygen we have chosen 1-nitro-1-nitrosocyclohexane (**2**).

A recent publication[5] on the somewhat related photolysis of gem-chloro-nitroso compounds has been very helpful in understanding the mechanism of photolysis, especially in methanol as a solvent, and has prompted us to report our results not only with this solvent but also with benzene.

Nitroxide detection by ESR.

Upon irradiation with red light (in the cavity of the ESR apparatus), 1-nitro-1-nitrosocyclohexane gives at −40°C both in toluene, carbon tetrachloride and methanol, a complicated strong signal, presumably consisting of a superposition of nitroxide signals, as suggested by the change in relative intensities at the periphery of the spectrum, when the temperature is varied.

A less complicated spectrum can be obtained from the simplest pseudonitrole 2-nitro-2-nitrosopropane: after brief irradiation nine lines develop, persisting for at least half an hour at −40°C. These lines have relative intensities 1:2:4:4:5:4:4:2:1 (Fig 1). These can be explained by the presence of nitroxide **1**. Normally such nitroxides would be expected to give a spectrum with 15 lines, but in our case this number is reduced by fortuitous overlap: the hfs constant of the central nitrogen (10·4 G) happens to be twice that of the two equivalent nitrogens in β-position (5·2 G).[6]

We have not been able to identify a nitroxide signal, arising from the addition of NO to a pseudonitrole,* although product formation (*cf* next section) suggests that such an addition must take place especially in a solvent like benzene. It seems that such radicals are prone to enter rapidly into radical combination reactions, especially in the aliphatic series. Thus diamagnetic species are formed, the key intermediates to more stable reaction products.

Photolysis of 1-*nitro*-1-*nitrosocyclohexane in benzene.*

When 1-nitro-1-nitrosocyclohexane **2** in benzene is photolysed with red light with exclusion of air, the main product is cyclohexanone **7** (50%). Smaller amounts are formed of gem-dinitro-cyclohexane **4** (14%), nitrocyclohexane (3%) and 1-nitrocyclohexene **3** (12%).

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*The radical, resulting from addition of NO$^\cdot$ to an *aromatic* nitroso compound is known. A.T. Balaban, N. Negoită and I. Pascaru, *Rev. Roumaine Chim.* **16**, 721 (1971).

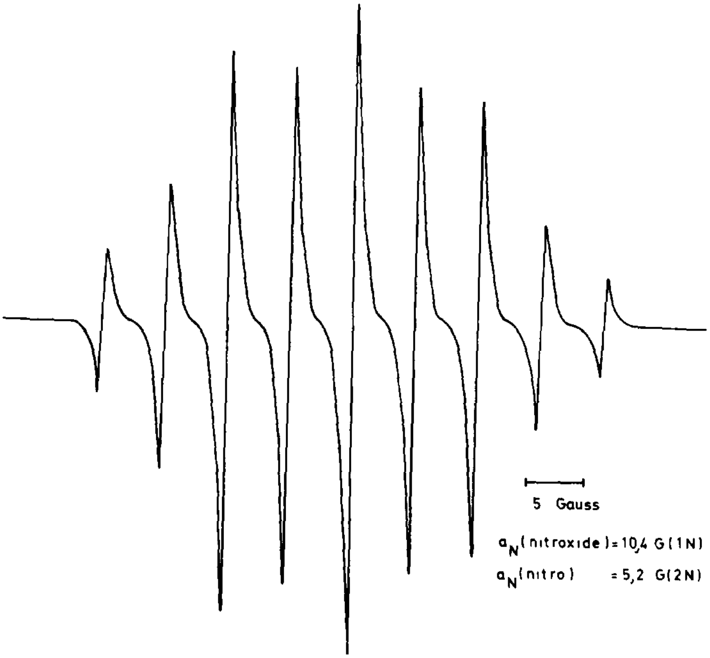
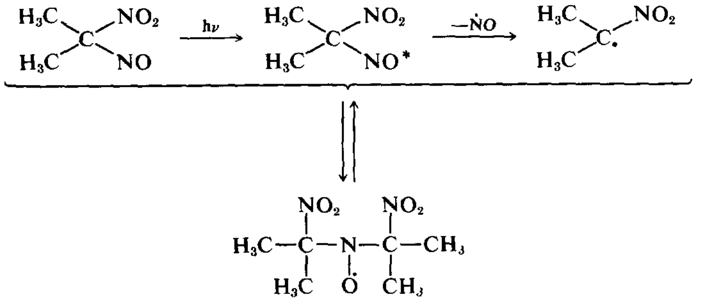


Fig 1. ESR spectrum of nitroxide 1 after irradiation of 2-nitro-2-nitrosopropane in toluene at − 40°.



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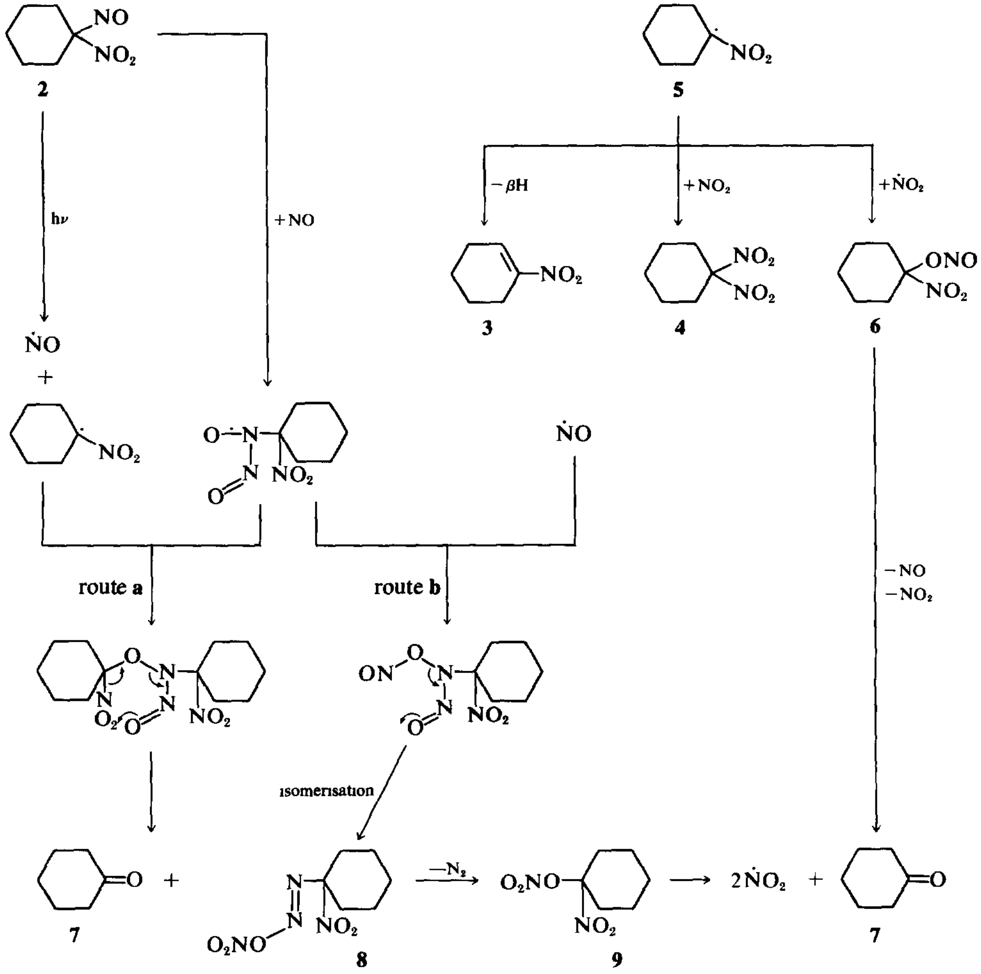
A similar product distribution results from thermal decomposition at 30°C (although the rate is several powers of ten lower), supporting the view that reaction starts with C-NO fission, which is known to be a facile process for all monomeric aliphatic nitroso compounds.[7] Because pseudonitroles do not dimerise in solution, conditions for nitroxide formation are optimal. The NO generated can add to unchanged starting material, a reaction well documented in the literature.[8,9] The resulting nitroxide is highly unstable and can react further with other radicals, i.e. with the α-nitroalkyl radical or with NO.

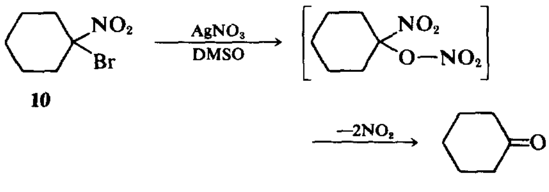
Which of these scavenging reactions (route **a** or **b**) is most important is hard to say, because either route yields ultimately the same ketone and nitrogen-oxides. Route **b** is known as the Donaruma-Carmody reaction[8] and involves a diazonium nitrate (**8**) as the key intermediate. The reaction is particularly favoured when NO is passed into a solution of an aliphatic nitroso compound (provided it is at least partly present in the monomeric form). In a separate dark experiment with gem-nitro-nitrosocyclohexane and excess NO, the same products are formed as under photolytic conditions (*cf.* Experimental).

In our case the concentration of NO is low, especially in the early stages of the reaction. We therefore postulate an alternative route **a** to the diazonium nitrate, producing simultaneously a ketone (*in casu* cyclohexanone). The diazonium nitrate (formed via either route) can lose nitrogen to give a gem-nitro-nitrate (**9**). Such compounds are unknown in the literature as far as we know, presumably because of their inherent instability: elimination of $2NO_2(N_2O_4)$ leaves a ketone, which is naturally the same as already formed earlier via route **a**. Similar results (ketone formation) are ob-



SCHEME 1. Photolysis of **2** in benzene.

tained when the gem-nitro-nitrate **9** is generated as an unstable intermediate in the reaction of 1-bromo-1-nitrocyclohexane **10** with silver nitrate:



It should be noted that catalytic amounts of water may also hydrolyse the nitrate and form an α-nitro-alcohol, which decomposes into ketone and nitrous acid. In the apolar solvent the latter decomposes into nitrogen-oxides and water, which can re-enter into solvolytic processes.

The NO_2 formed ultimately by decomposition of the diazonium nitrate, does not escape from the solution, but is scavenged by the α-nitroalkyl (α-nitrocyclohexyl) radical **5** to give the stable by-product 1,1-dinitrocyclohexane **4** or the unstable gem-nitro-nitrite **6**, which decomposes, like the gem-nitro-nitrate, into ketone and nitrogen-oxides. It should be noted that a nitrosoalkane can in principle be oxidised by NO_2 to a nitroalkane, as shown by Gowenlock.[10] Thus part of the 1,1-dinitrocyclohexane is probably formed from starting material and NO_2, as supported by a blank experiment (this route has not been formulated separately in Scheme 1).

The α-nitrocyclohexyl radical **5** can also lose a β-hydrogen which combines with some other radical or an identical radical (disproportionation), thus forming the by-product 1-nitrocyclohexene.*

If the photolysis is carried out in solvents with increasing hydrogen donating capacity, e.g. toluene, ethylbenzene and cumene, there is found no influence on the product distribution. This shows that

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*The yields under various conditions are tabulated in the Experimental section (*cf.* Table 2).

the photochemically generated α-nitro(cyclo)alkyl radicals do not abstract hydrogen from these hydrocarbons, either because other competitive radical processes prevail, or because of the inherent low reactivity (stability) of α-nitroalkyl radicals. Strong support for the stabilizing interaction between a nitro group and a neighbouring radical centre comes from a study of the photolysis and thermolysis of 1-nitro-1-nitroso-1-cyclo-propylethane **11**. In an inert solvent and also in methanol (cf next section), this leads essentially to ring-closed products only (cf Table 1). In the literature it is recorded that ring opening due to a neighbouring radical possition is very rapid (10^8 sec^{-1} at 30°C),[11] unless there are groups (e.g. cyano) that stabilize the radical.[12] Obviously the nitro-group is effective in spin delocalisation away from the cyclo-propyl group, which is thus safeguarded against ring rupture.

Photolysis of 1-nitroso-1-nitrocyclohexane in methanol

When the photolysis of 1-nitroso-1-nitrocyclohexane **2** is carried out in the presence of methanol (co-solvent acetonitrile), the most conspicuous change in product distribution is the formation of cyclohexanone-oxime **12** (45%), cyclohexanone (37%) and large amounts of methyl nitrite ("120%", i.e. a molar amount of 1.2 times that of the original pseudonitrole). This latter "yield" shows that both the NO and the NO_2 group in the original pseudonitrole can end up in the methyl nitrite. It is known[13] that nitrites can react with oximes, especially in the presence of mineral acids, yielding ketone and N_2O. In one experiment (cf Experimental Section) we found 10% of N_2O, and we therefore suggest that at least part of the ketone arises from the interaction of oxime and methyl nitrite (or HNO_2). It should be noted that the high yield of methyl nitrite is thus found despite this scavenging reaction.

When methanol is replaced by water, the oxime is again absent (as in benzene) and the yield of ketone goes up to 85%. In this case, instead of methyl nitrite, nitrous acid is generated and this converts all the oxime to ketone. This view is supported by the effect of urea, which scavenges the nitrous acid, thus protecting the oxime against decomposition.

These results are best explained by the mechanism outlined in Scheme 2. Part of this scheme, i.e. the solvolysis of the intermediary nitrone, was first suggested by Gowenlock, Kresze and Pfab* and was based on their earlier elucidation of the mechanism of the photolysis of gem-chloro-nitrosoalkanes in methanol. According to these authors the nitroxide **13** combines with NO to a "nitrite", and this undergoes ester exchange with methanol (Scheme 3). The nitrone is formed by loss of HNO_2.

We consider it equally probable that the nitroxide **13** loses NO_2, which combines with NO (possibly in a concerted way) to give N_2O_3 (cf Scheme 2). This

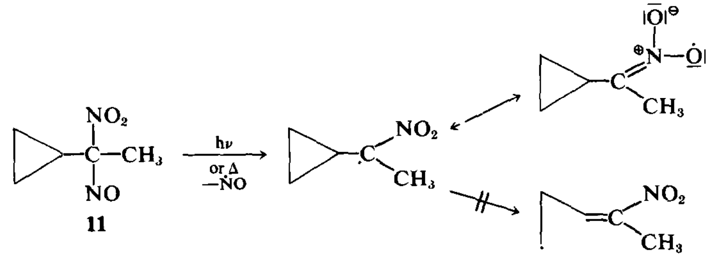

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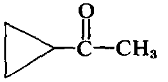
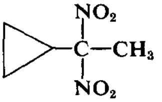
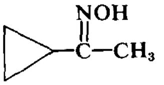
Table 1. Product yields from photolysis and thermolysis of **11**

Conditions-solvent[a]	yields in percentage of **11**. 			
Photolysis				
CH_2Cl_2-$CFCl_3$ (1:6)	39	47	—	[b]
MeOH-$CFCl_3$ (1:4)	21	trace	35	70% MeONO
Thermolysis				
CH_2Cl_2-$CFCl_3$ (1:6)	28	34	—	
MeOH-$CFCl_3$ (1:4)	40	8	30	113% MeONO

[a] Detailed conditions, see Experimental.
[b] Trace of 1-nitro-1-cyclopropylethene.

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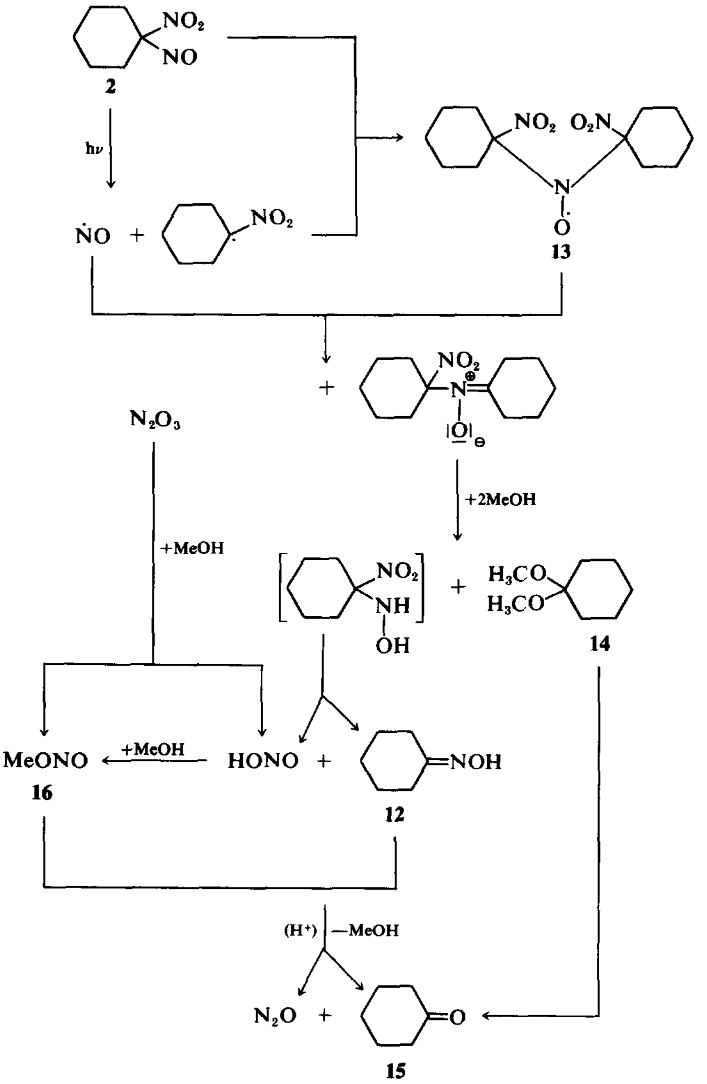
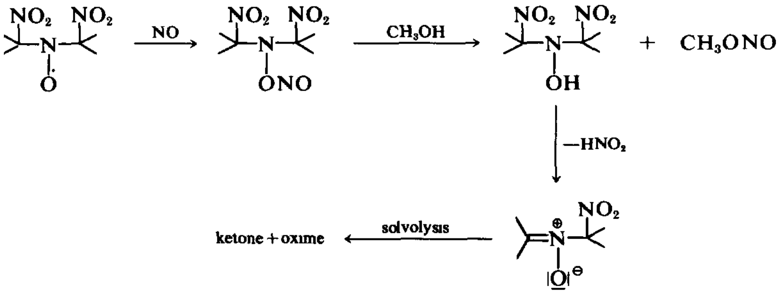
*Private Communication.



SCHEME 2. Photolysis of gem-nitro-nitrosocyclohexane(2) in methanol.



SCHEME 3

reacts with methanol, thus logically explaining the high yield of methyl nitrite **16**. It should be noted that GLC analysis of reaction mixtures leads to decomposition of the acetal **14** into the ketone **15**, which is detected as such. The essential difference with the earlier mechanism is that we suggest an alternative nitrone formation by homolytic loss of NO_2 from the nitroxide **13** (β-fission)[14 15]* instead of the heterolytic ester-exchange reaction.

EXPERIMENTAL

All m.ps are uncorrected. NMR spectra were determined on a Varian A-60, using tetramethylsilane (TMS) as internal standard. IR spectra were obtained on a Unicam SP 200, UV spectra on a Zeiss PMQ II and ESR spectra on a Varian E-3 instrument, fitted with an optical transmission accessory at concentrations of approximately 0·02 M.

Gem-nitro-nitrosoalkanes were prepared by nitrosation[1] of the aci-form of aliphatic nitro compounds with sodium nitrite in sulphuric acid at 0°C. 2-Nitropropane and nitrocyclohexane were commercial products. 1-Nitro-1-cyclopropylethane was prepared by trifluoroperacetic acid oxidation of the corresponding oxime.[16] *2-nitro-2-nitrosopropane*, yield 60%; IR ($CHCl_3$): 1585, 1545 and 1340 cm^{-1}; UV ($CHCl_3$): $\lambda_{max} = 650$ nm, $\epsilon_{max} = 18$; NMR ($CDCl_3$): $\delta = 1·7$ ppm (singlet); mp 74°–76·5°. *1-nitro-1-nitrosocyclohexane*, yield 72%; IR ($CHCl_3$): 1570, 1550 and 1345 cm^{-1}; UV ($CHCl_3$): $\lambda_{max} = 649$ nm, $\epsilon_{max} = 19$; NMR ($CDCl_3$): $\delta = 1·65$ ppm (multiplet, 6H); $\delta = 2·35$ ppm (multiplet, 4H); mp 73°–74°. *1-nitro-1-nitroso-1-cyclopropylethane*, yield 89%; (*Warning*: This unstable nitroso compound may explode) IR ($CHCl_3$): 1582, 1552 and 1348 cm^{-1}; UV (CH_2Cl_2): $\lambda_{max} = 652$ nm, $\epsilon_{max} = 14$; NMR ($CDCl_3$): $\delta = 0·82$ ppm (multiplet, 4H), $\delta = 1·82$ ppm (singlet, 3H), $\delta = 1·85$ ppm (multiplet, 1H), mp 56°–57°; Found C 41·45, H 5·56, N 19·26; $C_5H_8N_2O_3$ requires C 41·66, H 5·59, N 19·44%.

Photolyses

The photolyses were carried out in a glass vessel fitted with a cooling jacket. A Philips high pressure sodium lamp HPI SON of type HNF 003 (400W) ($\lambda_{max} = 565$, 580 and 590 nm) was used in all experiments. Dry N_2 was passed through the solution during the photolysis. The temperature was 7° in the case of gem-nitro-nitrosocyclohexane and −20° with 1-nitro-1-nitroso-1-cyclopropylethane, to prevent thermal decomposition. All irradiations were continued until the blue colour had disappeared; this took (for a 0·08M solution) about 15 min. The structures of the products were confirmed by independent syntheses. The quantitative data were determined by GLC (except for the oxime) on a 2·7m silicone oil SE 30 (∅ = 4 mm) on 80/100 chromosorb AW column and toluene as internal standard. The yield of oxime was measured by UV absorption of the corresponding gem-chloro-nitroso derivative by passing chlorine through a chloroform solution of the residue. Methyl nitrite and starting material were determined by their characteristic UV absorptions. Gaseous products were identified on a Porapack Q column (2·5 m) (∅ = 4 mm) The thermolyses were carried out in the dark at 30°. In the case of 1-nitro-1-nitrosocyclohexane this lasted for a fortnight and in the case of 1-nitro-1-nitroso-1-cyclopropylethane this took just one hour. A survey of the data of the photolysis and thermolysis of gem-nitro-nitrosocyclohexane is given in Table 2

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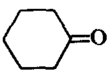
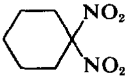
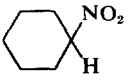
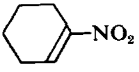
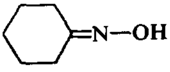
Table 2. Product yields in photolysis and thermolysis of gem-nitro-nitrosocyclohexane **2**.

Conditions-solvent	Yields in percentage of **2** 				
Photolysis					
benzene	50	14	3	12	—
chloroform	61	13	trace	9	—
1-hexane	45	4	—	4	—
Methanol-acetonitrile (1:4)	37	6	trace	—	45[a]
Water-acetonitrile (1:4)	85	5	—	—	—[b]
Thermolysis					
benzene	20	25	—	9	—

[a] 10% N_2O

[b] 25% inorganic nitrite

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*In these papers[14 15] other groups than NO_2 in β-position (H, Cl, Br) are shown to be eliminated with extreme ease.

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