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THE PHOTOLYSIS OF SOME α-IODO-NITROALKANES IN SOLUTION

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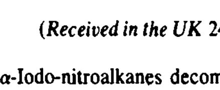
Abstract—α-Iodo-nitroalkanes decompose photochemically into α-nitroalkyl radicals and iodine. The α-nitroalkyl radical is detected by trapping with 2-methyl-2-nitrosopropane and identified by the hfs-constants of the resulting β-nitronitroxide observed with ESR. In the absence of nitroso compounds the α-nitroalkyl radicals can lose hydrogen to give nitro-olefins (70–80%). Minor products are nitroalkane (<5%) and ketone (10%), the latter via rearrangement of the α-nitroalkyl radical and loss of ˙NO. When the HI elimination is blocked, as is the case with 2-iodo-2-nitroadamantane, the yield of ketone increases to 80%. Upon stabilization of the α-nitroalkyl radical by a phenyl group, dimerization becomes important. In the case of 1-cyclopropyl-1-iodo-1-nitroethane a considerable amount of ring opened product is isolated.

INTRODUCTION

In a previous paper[1] we reported on the photolysis of 2-iodo-2-nitroadamantane in hydrogen-donating solvents at room temperature. The present paper deals with the behaviour of various α-nitroalkyl radicals in "inert" solvents.

Spin trapping of the α-nitroalkyl radical. Most α-iodo-nitroalkanes give relatively stable β-nitronitroxides 1



$$R^1{-}\overset{\overset{NO_2}{|}}{\underset{\underset{R^2}{|}}{C}}{-}\underset{\underset{O^{\cdot}}{|}}{N}{-}C(CH_3)_3$$

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(a_N(nitroxide) = 12–14 Gauss) upon irradiation at −40° (λ = 292–303 nm) in the cavity of the ESR apparatus in the presence of 2-methyl-2-nitrosopropane as spin trap. Suitable solvents are toluene, cumene, methanol, isopropyl alcohol and carbon tetrachloride, in the temperature range of −50° to 0°. Above and below this range no signal could be observed. Irradiation at about 300 nm causes excitation via an $n \rightarrow \sigma^*$ transition on iodine.[2] Due to the antibonding character of the σ* orbital an iodine atom is ejected. The quantum yield of this reaction is sometimes close to one.[2]

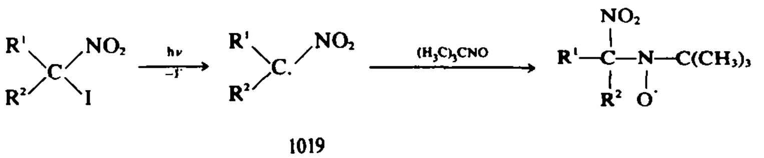
Depending on the ratio of the hfs-constants, the spectrum gives 9 lines (a triplet, each line consisting of three lines) with equal intensity or a septet with relative intensities 1:1:2:1:2:1:1, the latter arising when the a_N(nitroxide) happens to be twice the a_N(nitro). The hfs-constants are almost solvent-independent. 1-Iodo-1-nitrocyclohexane 3 gives two β-nitro-nitroxides with a slight difference in g-value and with the same hfs-constants. This may be explained by assuming the existence of two nitroxides with the nitro group axial and equatorial respectively. No signal is observed from the nitroxide derived from the α-nitroalkyl radical trapped via its oxygen atom. This is either due to the low spin density on oxygen or the inherent instability of the resulting nitroxide. The expected hfs-constant should be in the range of other alkoxy-alkylnitroxides (viz 25 Gauss[3]).

From 1-iodo-1-nitro-1-phenylethane 5 no signal is observable. It is remarkable that upon photolysis of 1-cyclopropyl-1-iodo-1-nitroethane 6 always the ring closed α-nitroalkyl radical is trapped, though a substantial amount of ring opening is found in large scale experiments (*vide infra*). The measured hfs-constants are summarized in Table 1 and are consistent with the values of β,β′-dinitronitroxides[4] previously observed.

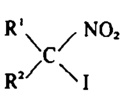
Table 1. Hfs-constants of β-nitronitroxides

R^1	R^2	a_N(nitroxide)	a_N(nitro)[a)]
adamantylidene		14.02	7.01 [b)]
$-(CH_2)_5-$		12.42	6.21 [b)]
H_3C-	H_3C-	12.60	4.42 [c)]
	H_3C-	13.11	3.95 [c)]
C_6H_5-	H_3C-	no signal observable	

a) a_N-values in Gauss.
b) Septet with rel. int. 1:1:2:1:2:1:1.
c) Three (1:1:1) triplets, nine lines with same intensity

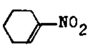
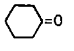
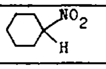


Photolysis of 2-iodo-2-nitropropane **2**, *1-iodo-1-nitrocyclohexane* **3** *in inert solvents*. Photolysis of the α-iodo-nitroalkanes **2** and **3** in inert solvents (Scheme 1) in the absence of oxygen (He atmosphere) results mainly in 2-nitropropene (70%) and 1-nitrocyclohexene (up to 88%) respectively. Minor products are ketones (up to 16%) and nitroalkanes (<5%). In all cases molecular iodine is produced almost quantitatively. A solution of HI in several inert solvents appeared to be unstable under photolytic conditions and gives rise to a quantitative production of iodine.[2] Hardly any change in product distribution was found by a 10-fold variation in the concentration of the substrate from 0·012M to 0·118M (in general 0·06M). Almost all α-iodo-nitroalkanes were thermally stable in refluxing benzene. The results of photolysis of **3** are summarized in Table 2.



2: $R^1 = R^2 = Me$
3: $R^1,R^2 = (CH_2)_5$ (cyclohexylidene)
4: R^1,R^2 = adamantylidene
5: $R^1 = C_6H_5$, $R^2 = Me$
6: R^1 = cyclopropyl, $R^2 = Me$

Table 2. Product yields from photolysis of 1-iodo-1-nitrocyclohexane **3** in various solvents (yields in % of **3**)

solvent (conc.)			
benzene (0.012M)	81	9	-
benzene (0.118M)	72	16	trace (< 5%)
methylenechloride (0.062M)	83	12	-
cyclohexane (0.059M)	88	7	trace
carbontetrachloride (0.047M)	75	16	trace [a)]

a) No 1-chloro-1-nitrocyclohexane could be detected.

The photolysis of **2** in chlorobenzene is followed in the time in the presence of scavengers (Fig. 1). In the presence of one equivalent of iodine the rate of photolysis is seriously reduced but the product distribution remains unchanged. The trapping of radicals by molecular iodine has usually an activation energy below 1 kcal/mole,[5] thus regeneration of starting material should be an important process, slowing down the overall rate of reaction. Additional evidence for the rapid scavenging of α-nitroalkyl radicals by molecular iodine is obtained from an experiment in which 2-nitro-2-nitrosopropane is converted almost completely into 2-iodo-2-nitropropane upon photolysis with 500–700 nm light in the presence of one equivalent of I_2 (λ_{max} of 2-nitro-2-nitrosopropane = 650 nm[4]). When oxygen is bubbled through a 0·155M solution of **2** during photolysis, the overall decomposition rate is increased and the yield of acetone increases at the expense of 2-nitropropene. Obviously, oxygen is a more efficient radical scavenger than iodine, because of its bi-radical character in the ground state (cf. C in Fig. 1).

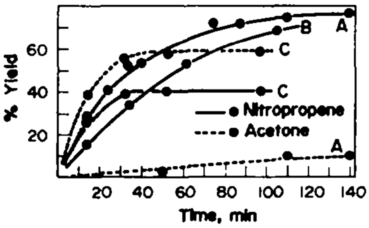
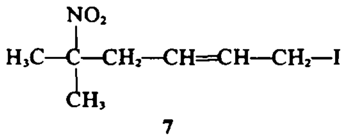


Fig. 1. Product formation from photolysis of 2-iodo-2-nitropropane **2** in chlorobenzene. (A) Photolysis of a 0·155M solution in He atmosphere. (B) As sub A, but in the presence of an equimolar amount of iodine. (C) Photolysis of a 0·155M solution in the presence of oxygen.

With an excess of oxygen and very low concentrations of **2** (by dropwise addition), HI elimination is seriously suppressed and the yield of 2-nitropropene is reduced to about 20%. Presumably this means that elimination of HI *within* the solvent cage occurs to the same extent.

Upon addition of 1,3-butadiene, a typical triplet quencher ($E_T \sim 60$ kcal/mole[6]), no C_3-products can be detected anymore, because the quencher traps the α-nitroalkyl radical and leads ultimately to (Z)-6-iodo-5-methyl-5-nitro-2-hexene **7**.

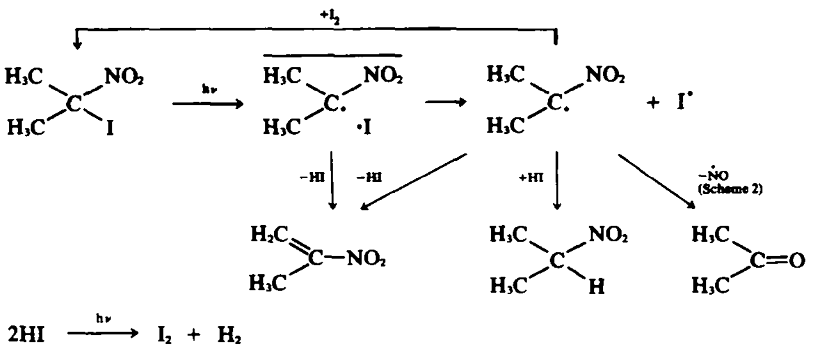


$$H_3C-\overset{NO_2}{\underset{CH_3}{C}}-CH_2-CH{=}CH-CH_2-I$$

7

As far as we know no other triplet quenchers that do not absorb at 300 nm are known in the same energy-region.

The formation of nitroalkane cannot exclusively be explained by disproportionation of two α-nitroalkyl radicals. Accumulation of the efficient radical scavengers I_2 and HI makes a bimolecular radical disproportionation more and more improbable. Because HI is an excellent hydrogen donor it can react with the α-nitroalkyl radical to give the nitroalkane, especially in the later stages of the reaction. In a sense this formation of nitroalkane and 1-nitroalkene from α-nitroalkyl radicals can be considered as an indirect disproportionation, catalyzed by iodine atoms as hydrogen carriers. This hydrogen donation may be partly responsible for ketone formation (see our previous paper[1]). These data are best explained by the mechanism outlined in Scheme 1.



Scheme 1. Typical mechanism of photolysis of a β-hydrogen containing α-iodo-nitrocompound in an inert solvent.

Rearrangement of the α-nitroalkyl radical; photolysis of 2-iodo-2-nitroadamantane **4** *in inert solvents.* The question arises, what course the reaction takes if the α-iodo-nitroalkane contains no β-hydrogen and consequently no HI and no alkene can be formed. This has been investigated for 2-iodo-2-nitroadamantane **4**. The only processes now left for the α-nitroalkyl radical are recombination with iodine and rearrangement, with ultimate ketone formation. The latter is precisely what we find upon photolysis of **4** in benzene; adamantanone is produced in a yield of 80%. As expected the rate of photolysis is considerably slowed down. From the rate of iodine production it can be shown that the retardation amounts at least to a factor two. As shown in Scheme 2, ketone formation is accompanied by loss of NO; in the gases escaping from the reaction mixture this was qualitatively detected. Because substrate concentration has no influence on product composition (Table 2), we conclude that ketone formation is a mono-molecular process. The formation of ketone can be rationalized by rearrangement of the α-nitroalkyl radical **8** to an oxaziridine-N-oxyl **9** followed by homolytic β-cleavage to ketone and NO.

The loss of NO is formulated via two routes, **a** and **b**. It is hard to say which of these prevails.

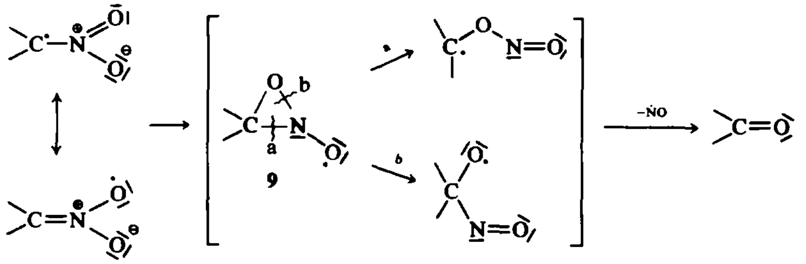
Strong support for the rearrangement is found in an experiment in which cyclohexanone-isoxime **10**[7] is treated with the specific N-oxidizing agents PbO_2 and Ag_2O.[8] In both cases cyclohexanone is formed quantitatively.

In this connection we should like to point out that ketones have also been found among the oxidation products from α-nitrocarbanions by Todd *et al.*[9] These authors formulated a mechanism with an initial ring closure of the anion and subsequent oxidation to **9**. We now believe that it is more probable that it is not the anion that cyclizes but the radical formed by initial oxidation.

The previous paper in this series[1] points out that the spin density in the α-nitroalkyl radical is almost completely located on carbon. As a consequence the ring closure may be considered as an attack of a carbon-centered radical on a nitro group, a process which is well documented.[10]

Photolysis of 1-iodo-1-nitro-1-phenylethane **5**. Photolysis of 1-iodo-1-nitro-1-phenylethane **5** in benzene gives an α-nitroalkyl radical stabilized by a phenyl group. Despite the presence of β-hydrogens there is found no elimination of HI (no α-nitrostyrene formation). Instead, the products are acetophenone (45%) and 2,3-dinitro-2,3-diphenylbutane (55%). The structure of the dimer was proved by a new independent—and unambiguous—synthesis, based on reaction of the α-iodo-nitroalkane with sodium thiosulfate, photochemically as well as thermally (Experimental).

Apparently increased stabilization of radicals tends to



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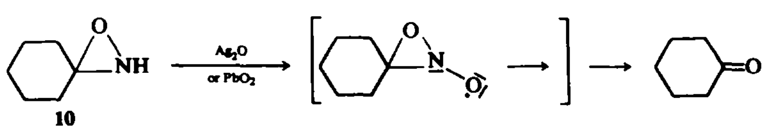

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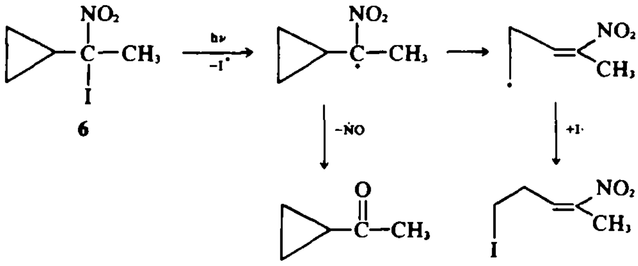
give more dimerization rather than disproportionation. Obviously, this radical is so stable that it does not even form a nitroxide in the presence of a nitroso-scavenger. It is in agreement with the calculated unpaired electron density on carbon[1] that the dimer formation occurs exclusively by C–C (not C–O or O–O) bond formation.

Upon prolonged refluxing of **5** (24 hr) in benzene most of the starting material remains unchanged; acetophenone is formed in 10% yield. This shows that **5** does not undergo appreciable thermal reaction under conditions of photolysis (3 hr at −10°).

Photolysis of 1-*cyclopropyl*-1-*iodo*-1-*nitroethane* **6**. A radical position adjacent to a cyclopropyl ring usually causes fast ring opening (10^8 sec^{-1} at 30°)[11] unless there are substituents (e.g. cyano) stabilizing the radical by delocalization of the unpaired electron.[12] No ring opened radical is trapped by 2-methyl-2-nitrosopropane, only ring closed β-nitronitroxide is detected. Apparently—like cyano—the nitro group is capable of spin delocalisation away from the cyclopropyl group, which is thus safeguarded against ring rupture. However, in general the (high) rate of ring opening is comparable to the rate of addition of radicals to the nitroso function.[13] Therefore, in the absence of fast spin trapping agents ring opening may still occur. This is in fact what we find when the photolysis of **6** is carried out in methylene chloride: 5-iodo-2-nitro-2-pentene **12** is isolated in 62% yield.* Minor amounts of the ring closed cyclopropylmethylketone **11** (20%) and iodine (21%) are formed as well (Scheme 3). This is a further indication of the moderate stabilizing capacity of the nitro group towards an α-radical position.



6 **11** **12**

Recently it has been mentioned[15] that bromoalkanes are photochemically stable under conditions where iodoalkanes decompose, despite the presence of a suitable absorption band in the bromo derivatives. We can confirm this for bromides with an α-nitro group. α-Bromonitrocyclohexane remains unchanged when irradiated for a fortnight.

EXPERIMENTAL

M.pts are uncorrected. NMR spectra were determined on a Varian A-60 instrument, using TMS as internal standard. IR spectra were recorded on a Perkin Elmer 257 or a Unicam SP200, UV spectra on a Zeiss PMQII and ESR spectra on a Varian E-3 instrument fitted with an optical transmission accessory. Concentrations of approx. 0·01M of α-iodo-nitroalkane and 0·005M of 2-methyl-2-nitrosopropane were used.

Table 3. Spectral characteristics of compounds $R^1R^2C(NO_2)I$

R^1	R^2	yield %	IR ($CHCl_3$) cm^{-1}	UV (CH_2Cl_2) λ_{max} nm (ϵ_{max})	NMR ($CDCl_3$) δ in ppm
H_3C	H_3C	80	1540, 1332	297 (430)	2.44 (s)
$-(CH_2)_5-$		75	1545, 1335	300 (550)	1.62 (m,6H) 2.45 (m,4H)
	H_3C	83	1540, 1330	310 (450)	0.80 (m,4H) 1.85 (m,1H) 2.25 (s,3H)
C_6H_5-	H_3C	80$^{a)}$	1546, 1328	275 (1080)	2.86 (s,3H) 7.4 (m,5H)
adamantylidene		70$^{b)}$	1538, 1340	308 (690)	1.85 (m,8H) 2.25 (m,4H) 2.88 (m,2H)

a) mp. = 41°.

b) mp. = 126°-127°.

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*The configuration around the double bond is not known, though E is expected.[14]

Starting materials. α-Iodo-nitroalkanes were prepared by the method of Kornblum.[16] Physical data are summarized in Table 3. All compounds were analytically pure.

2-Nitropropane and nitrocyclohexane were commercial products. α-Nitro-ethylbenzene, 1-cyclopropyl-1-nitroethane and 2-nitroadamantane were prepared by a literature procedure.[17]

Vicinal dinitroalkane synthesis was accomplished by reduction of α-iodo-nitroalkanes by sodium thiosulfate. A typical procedure is described.

2-Iodo-2-nitropropane (2 g) and sodium thiosulfate (2·5 g) dissolved in a mixture of acetonitrile (50 ml) and water (30 ml) are irradiated as described earlier[1] at 5° for 5 min. (At higher concentrations of sodium thiosulfate only acetone and 2-nitropropane could be isolated.) The ppt was isolated and drained with water. After drying a white crystalline product results; yield: 80%, IR ($CHCl_3$): 1540 and 1341 cm^{-1}; NMR ($CDCl_3$): $\delta = 1{\cdot}73$ ppm (s); m.p. = 151–152°. Correct microanalysis was found. Except for 2-iodo-2-nitroadamantane this new method gave in all cases high yields of symmetrical vicinal dinitroalkanes.

Photolyses. The photolysis procedure has been described previously.[1] A Zeiss high pressure Xenon lamp (450 W) fitted with a monochromator was used as light source (292–303 nm), in experiments where the iodine production was followed with the aid of a spectrophotometer as well as in ESR experiments. The quantitative data were determined by GLC on the same columns as described.[1] The structure of the products was confirmed by independent synthesis.

The dropwise addition of substrate (40 ml of a 0·01 M solution was added over 7 hr to 40 ml of solvent) was accomplished with a peristaltic pump. Dried oxygen was flushed through the solution as fast as possible.

NO was detected by oxidizing it with oxygen to NO_2. The latter reacted with alkali to inorganic nitrite which was determined spectrophotometrically with antipyrine in acidic medium.[18]

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