Tetrahedron Letters No. 29, pp. 2709-2712, 1971. Pergamon Press. Printed in Great Britain.

PHOTOLYSIS OF POLYHALOMETHANES IN THE PRESENCE OF NITROSOALKANES
FORMATION OF ACYL ALKYL NITROXIDES

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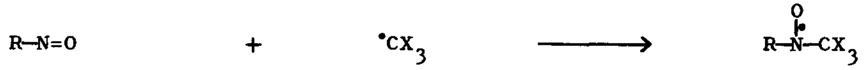
(Received in UK 9 June 1971; accepted in UK for publication 16 June 1971)

Polyhalomethyl radicals have been proposed as short-lived intermediates in numerous reactions[1]. Only recently the ESR Spin Trapping technique[2] has been used to convert these types of radicals into species sufficiently stable for ESR investigation. In a previous communication[3] we have reported the scavenging of trifluoromethyl and trichloromethyl radicals by monomeric nitrosoalkanes I to produce nitroxides II.



$$R{-}N{=}O \quad + \quad {}^{\bullet}CX_3 \quad \longrightarrow \quad R{-}\overset{\overset{O}{|\bullet}}{N}{-}CX_3$$

I, e.g. R = t-Bu   X = F,Cl   IIa, X = F
b, X = Cl

Our results concerning IIa have been confirmed by other investigators[4,5]. However the assignment of structure IIb to the observed ESR spectrum has been questioned[6]. In subsequent studies the ESR spectrum of IIb, showing resolved hyperfine splitting (hfs) of three chlorine atoms, has been described[6-8]. Because the ESR spectrum that we have reported[3] showed a_N = 6.5 G and g = 2.0070, it was suggested that an acyl alkyl nitroxide might be involved[6].

We now wish to report that the formation of acyl alkyl nitroxides is indeed observed when tri-, di- and monohalomethyl radicals are generated photochemically in the presence of I. The a_N and g values given in Table I are those expected for acyl alkyl nitroxides[9].

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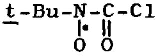
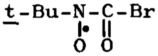
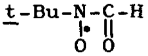
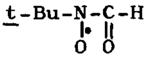
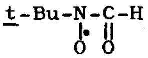
TABLE I. Scavenging of polyhalomethyl radicals by 2-nitroso-2-methylpropane I.

Radical source	Radical precursor	Nitroxide found[a]		ESR spectral data measured at 20°C.[b]
CCl_4[c]	$^{\bullet}CCl_3$	 $t\text{-Bu-}\underset{O^{\bullet}}{\underset{\mid}{N}}\text{-}\underset{O}{\underset{\parallel}{C}}\text{-Cl}$	(VIIa)	a_N = 6.5 G; a_{Cl} *not resolved;* g = 2.0070.
CBr_4[c]	$^{\bullet}CBr_3$	 $t\text{-Bu-}\underset{O^{\bullet}}{\underset{\mid}{N}}\text{-}\underset{O}{\underset{\parallel}{C}}\text{-Br}$	(VIIb)	a_N = 6.7 G; a_{Br} = 2.0 G; g = 2.0071.
$CHBr_3$[d]	$^{\bullet}CHBr_2$	 $t\text{-Bu-}\underset{O^{\bullet}}{\underset{\mid}{N}}\text{-}\underset{O}{\underset{\parallel}{C}}\text{-H}$	(VIIc)	a_N = 7.0 G; a_H = 1.4 G; g = 2.0071.
CHI_3[d]	$^{\bullet}CHI_2$	 $t\text{-Bu-}\underset{O^{\bullet}}{\underset{\mid}{N}}\text{-}\underset{O}{\underset{\parallel}{C}}\text{-H}$	(VIIc)	a_N = 6.9 G; a_H = 1.4 G; g = 2.0072.
CH_2I_2[d]	$^{\bullet}CH_2I$	 $t\text{-Bu-}\underset{O^{\bullet}}{\underset{\mid}{N}}\text{-}\underset{O}{\underset{\parallel}{C}}\text{-H}$	(VIIc)	a_N = 6.9 G; a_H = 1.4 G; g = 2.0072.

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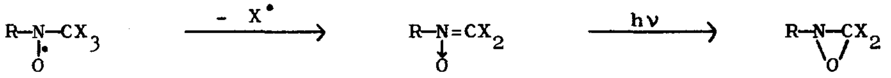
[a] The acyl alkyl nitroxides VII are stable for days at 20°C, as judged from the slow disappearance of the ESR signals.

[b] Liquid polyhalomethanes were used without cosolvent; (solid) CBr_4 and CHI_3 were dissolved in benzene.

[c] UV irradiation in the presence of benzoyl peroxide and I (± 5 mg/ml).

[d] UV or 680 nm irradiation in the presence of I′ (± 5 mg/ml)[10].

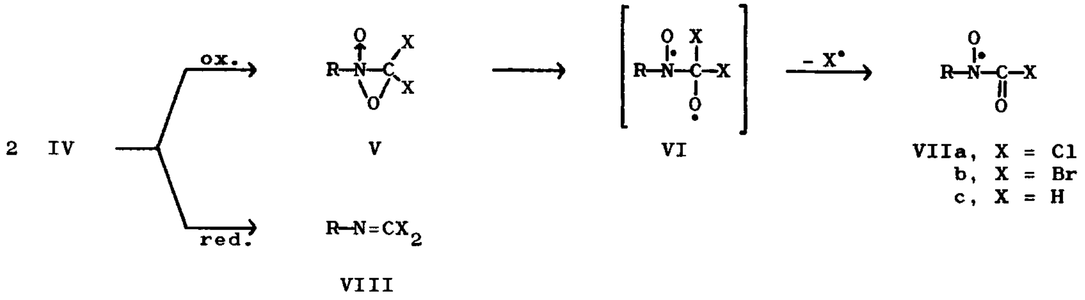
We propose initial formation of (poly)halomethyl alkyl nitroxides. Since elimination of a β-halogen atom is generally very easy in free radicals[11] our nitroxides produce halonitrones III.



II, X = Cl,Br III IV

The trifluoromethyl alkyl nitroxide IIa forms an exception and is very stable since C-F bond homolysis is difficult.

There may be several possibilities for the formation of acyl alkyl nitroxides from III. Light-induced isomerization[12] of the nitrone III might give the oxaziridine IV. Oxaziridines, being active-oxygen compounds, oxidize tertiary amines smoothly to N-oxides[13]. On the other hand they can also be oxidized (e.g. by peracetic acid) to ketones and nitrosoalkanes, presumably via N-oxides[14]. Therefore we assume that oxaziridine IV may undergo a bimolecular oxidation-reduction reaction in solution, parallel to other decomposition reactions[12,13,15].



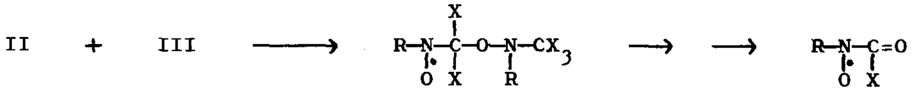
The unstable intermediate V does not decompose into phosgene (X = chlorine) and I, since it was not possible to generate VII by photolysis of a toluene solution of phosgene and I (neither in the presence of initiators such as benzoyl peroxide). It seems more likely that V undergoes (possibly concerted) ring-opening and elimination of a halogen atom to yield VII. Bromine hfs is present in the spectrum of VIIb; however, no chlorine hfs is resolved in VIIa. This is explained by the smaller nuclear magnetic moment and by the fact that chlorine is less bulky than bromine, which renders through-space interaction with the π-electron system less important.

When dihalomethyl radicals are trapped by I, similar reactions take place, ultimately leading to VIIc. (*cf*. Table I).

Nitroxide VIIc is also formed even when *mono*halomethyl radicals are generated in the presence of I. The initially formed monohalomethyl *t*-butyl nitroxide loses halogen to give the halogen-free nitroxide VI (X = H). Abstraction of hydrogen (*e.g.* by oxaziridine[16]) leads to VIIc. The structure of VIIc was supported by a preparation *via* an alternative route, *i.e.* hydrogen abstraction from formaldehyde (by *t*-butoxy radicals, generated thermally from di-*t*-butyl peroxyoxalate[17]) and addition of the formyl radical to I. This route may also be involved if V decomposes into formaldehyde and I.

Bluhm and Weinstein[16] have shown that various stable nitrones (*e.g.* α-phenyl-*N*-*t*-butyl nitrone) yield acyl alkyl nitroxides upon irradiation. These results can be explained by either of the above mechanisms.

Besides the routes indicated the possibility cannot be excluded that certain nitroxides form addition products with nitrones, which decompose into acyl alkyl nitroxides as reported by Holman and Perkins[18]:



$$\mathrm{II} + \mathrm{III} \longrightarrow \mathrm{R{-}\underset{O^{\bullet}}{N}{-}\overset{X}{\underset{X}{C}}{-}O{-}\underset{R}{N}{-}CX_3} \longrightarrow \longrightarrow \mathrm{R{-}\underset{O^{\bullet}}{N}{-}\underset{X}{C}{=}O}$$

(VII)

The decomposition of the intermediate is somewhat similar to the one proposed in the bimolecular reactions of *t*-butyl *p*-halophenyl nitroxides[19].

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