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C-NITROSO COMPOUNDS.

PART III. ALKOXY-ALKYL-NITROXIDES AS INTERMEDIATES IN THE REACTION OF ALKOXY-RADICALS WITH NITROSO COMPOUNDS*).

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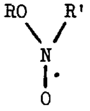
Nitrosoalkanes possess free-radical scavenging properties. The reaction with alkylradicals has been shown to proceed via dialkylnitroxides, stable free radicals with characteristic e.s.r.-spectra (1,2).

In this paper we wish to describe the formation of alkoxy-alkyl-nitroxides



obtained by addition of alkoxy-radicals to nitroso compounds.

During photolysis of various alkylnitrites with UV-light in (cyclo-) alkanes or in alkylbenzenes signals of at least two radicals appear (table 1). One of the radicals is identified as the dialkylnitroxide with known nitrogen-($a_N \sim 15$ gauss) and hydrogen-h.f.s. constants. Its formation can be explained by the following sequence of reactions:

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*) Part of the forthcoming thesis of A. Mackor.

Part II. Th.A.J.W. Wajer, A. Mackor, Th.J. de Boer and J.D.W. van Voorst, to be published.

$$RONO \xrightarrow{h\nu} RO^{\bullet} + NO^{\bullet}$$

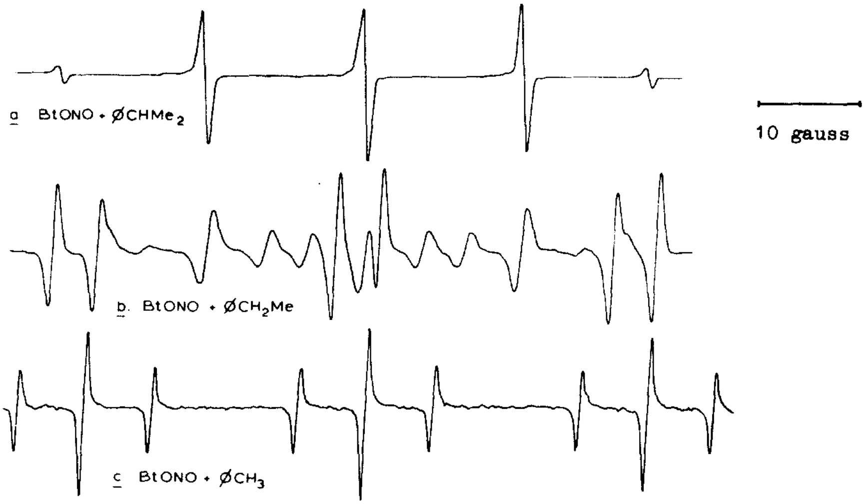
$$RO^{\bullet} + R'H \longrightarrow ROH + R'^{\bullet}$$

$$R'^{\bullet} + NO^{\bullet} \longrightarrow R'NO$$

$$R'^{\bullet} + R'NO \longrightarrow R'_2NO^{\bullet}$$

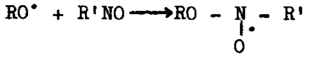
The presence of nitrosoalkanes during these photolyses has been demonstrated (3). The second radical has a high spin density on a nitrogen atom ($a_N \sim 25\text{-}30$ gauss) and a g-value, slightly different from that of ordinary dialkylnitroxides. Its e.s.r.-signal is predominant over that of the dialkylnitroxide at temperatures below -40°C, but it disappears rapidly upon interruption of the irradiation. Information concerning the structure of this radical was obtained by photolysis in the presence of various hydrocarbons of tertiary butylnitrite (BtONO). With cumene, ethylbenzene and toluene, these radical signals show interaction with an increasing number of hydrogen atoms at the α-carbon-atom i.e. none, one and two respectively (fig. 1).

FIG. 1



These results are in accordance with a structure $X - \underset{\underset{O}{|\,\cdot}}{N} - R'$, in which $R' = Ø\text{-}\underset{|}{C}Me_2$, $Ø\text{-}\underset{|}{C}HMe$ or $Ø\text{-}\underset{|}{C}H_2$.

Photolyses of cumene with tertiary and with secondary butyl nitrite lead to formation of dicumylnitroxide as judged from the e.s.r.-spectra. The nitrogen coupling constants of the other radical obtained with these two nitrites are different, supporting the presence of alkoxy-alkyl-nitroxides with a tertiary butoxy-group (fig. 2a)and a secondary butoxy-group (fig. 2b) arising through



$$RO^{\bullet} + R'NO \longrightarrow RO - \underset{O}{\overset{}{\underset{|\bullet}{N}}} - R'$$

FIG. 2

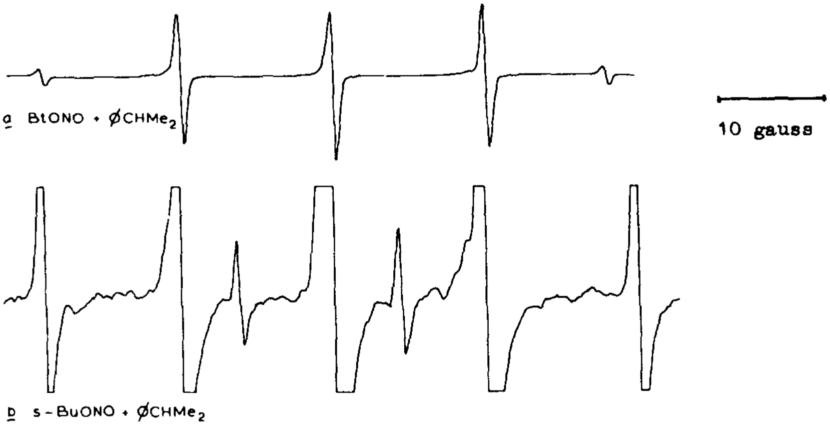


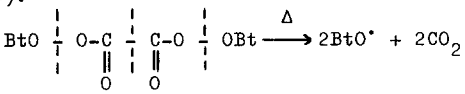
TABLE 1

Radicals formed during photolysis of alkylnitrites in hydrocarbon solvents.

Alkylnitrite	Solvent	Dialkylnitroxide		Alkoxy-alkyl-nitroxide	
tertiary	tertiary H *)	a_N	a_H (gauss)	a_N	a_H (gauss)
BtONO	cumene	15.3		28.0	
BtONO	isobutane	15.7		28.3	
BtONO	2,3-dimethylbutane	14.9		27.6	
	secondary H *)				
BtONO	ethylbenzene	15.1	9.4 (2H)	26.9	4.2 (1H)
BtONO	cyclohexane	14.3	4.4 (2H)	26.9	4.4 (1H)
	primary H *)				
BtONO	toluene	not observed		27.0	6.5 (2H)
secondary	tertiary H *)				
s-BuONO	cumene	15.2		29.6	
primary					
n-BuONO	cumene	15.1		not observed	

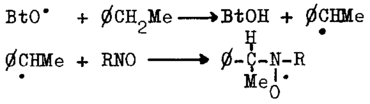
*) Abstraction of the indicated type of hydrogen is observed exclusively.

This was proved independently by mixing tertiary nitroso compounds with tertiary butyl-peroxy-oxalate (TBPO) in inert solvents like $CFCl_3$ or benzene. TBPO decomposes at roomtemperature exclusively according to the following equation as was found by Bartlett (4):



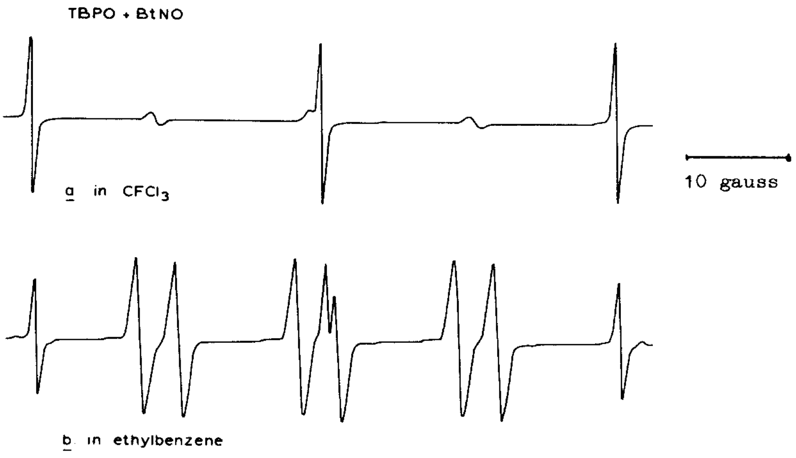
$$\mathrm{BtO} \mid \mathrm{O{-}\underset{\underset{\displaystyle O}{\|}}{C}} \mid \mathrm{\underset{\underset{\displaystyle O}{\|}}{C}{-}O} \mid \mathrm{OBt} \xrightarrow{\Delta} 2\mathrm{BtO}^{\bullet} + 2\mathrm{CO_2}$$

The tertiary butoxy-radicals are thus produced in a very "clean" way. At the start only the alkoxy-alkyl-radical signal is present, while a signal of the dialkylnitroxide is slowly built up during the reaction, probably by decomposition of the unstable alkoxy-alkyl-nitroxide (fig. 3a). If the reaction of BtO-radicals (from TBPO) with the tertiary nitroso compound is carried out in ethylbenzene, a competition between addition of $BtO^{\bullet}$ to the nitroso compound and abstraction by $BtO^{\bullet}$ of benzylic hydrogen from the solvent takes place. This gives rise to the α-phenylethyl radical, which adds to the nitroso-alkane with formation of the tertiary alkyl-α-phenylethyl-nitroxide (fig. 3b)



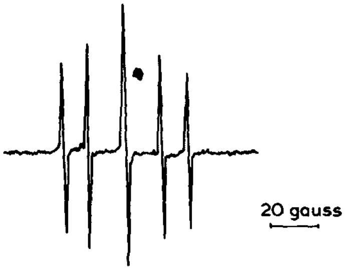
$$\mathrm{BtO}^{\bullet} + \emptyset\mathrm{CH_2Me} \longrightarrow \mathrm{BtOH} + \emptyset\underset{\bullet}{\mathrm{C}}\mathrm{HMe}$$
$$\emptyset\underset{\bullet}{\mathrm{C}}\mathrm{HMe} + \mathrm{RNO} \longrightarrow \emptyset{-}\overset{\mathrm{H}}{\underset{\mathrm{Me}}{\mathrm{C}}}{-}\underset{\mathrm{O}^{\bullet}}{\mathrm{N}}{-}\mathrm{R}$$

FIG. 3

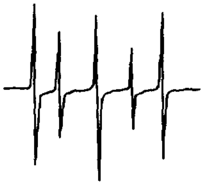


The structural relationship between alkoxy-alkyl-nitroxides and nitroalkane radicalanions is illustrated in their e.s.r.-spectra. In the aliphatic series Hoffmann et al. (5) have obtained a mixture of the tertiary nitrobutane radicalanion and di-tertiary butylnitroxide signals during electrochemical reduction of tertiary nitrobutane, comparable with the signals obtained by photolysis of tertiary butylnitrite in isobutane (fig. 4).

FIG. 4



t-NITROBUTANE RADICALANION
+ DI-t-BUTYLNITROXIDE in glyme



t-BUTOXY-t-BUTYLNITROXIDE
+ DI-t-BUTYLNITROXIDE in isobutane

In the aromatic series: the nitrobenzene radical anion $\emptyset NO_2^{\dot{-}}$ (6) has splitting constants, which have been listed in table 3, together with those of t-butoxy-phenyl-nitroxide $\emptyset NO_2Bt$. A very strong signal of the latter radical was obtained by us in the reaction of TBPO with nitrosobenzene. It has the same splitting constants as found by Ward for the $\emptyset NO_2H$- radical (7), apart from a small additional splitting by the hydroxyl proton. The results with TBPO are collected in table 2.

References for the preparation of nitrosoalkanes are given in (1) and for alkylnitrites in (8).

We thank the Koninklijke/Shell Laboratory, Amsterdam for a generous gift of isobutane of high purity.

TABLE 2

Radicals formed during reaction of t-butyl-peroxy-oxalate with nitroso compounds.

Nitroso compound	Solvent	Temp. (°C)	Dialkylnitroxide a_N	a_H (gauss)	Alkoxy-alkyl-nitroxides a_N	a_H (gauss)
Me_3CNO	$CFCl_3$	20	15.4		28.1	
Me_3CNO	ethylbenzene	20	15.3	3.8 (1H)	28.1	
$(AcO)Me_2CNO$	$CFCl_3$	20	15.1		28.0	
$(AcO)Me_2CNO$	benzene	20	15.2		27.8	
Ø$CH(NO)Me$	benzene and $CFCl_3$	30	15.4	10.0 (2H)	27.1	4.3 (1H)
nitrosocyclohexane	benzene	40	14.7	(mixture)	26.9	4.4 (1H)
nitrosobenzene	$CFCl_3$	+20 to -70	not observed		14.9	3.1 (o,p) 1.0 (m)

TABLE 3

Comparison of nitrogen- and hydrogen- h.f.s. constants in nitrobenzene radicalanion, hydroxy-phenyl-nitroxide and t-butoxy-phenyl-nitroxide.

Radical	a_N	a_H^o	a_H^p	a_H^m	a_H^{OH} (gauss)	Solvent	Ref.
Ø$NO_2^{\ominus}$	10.3	3.3	3.5	1.1		MeCN	(6)
ØNO_2H	15.0	3.1	3.1	1.1	0.38	THF	(7)
ØNO_2Bt	14.9	3.1	3.1	1.0		$CFCl_3$	this paper

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