

C-NITROSO COMPOUNDS—VI

ACYL-ALKYL-NITROXIDES FROM ACYL RADICALS AND NITROSO COMPOUNDS AS STUDIED BY ESR¹

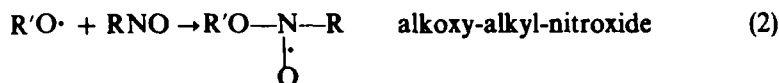
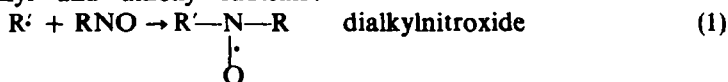
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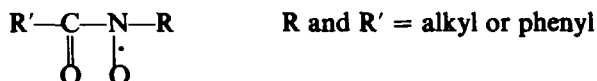
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Abstract—Acyl radicals combine with nitroso compounds to give acyl-alkyl-nitroxides, which are identified by their ESR spectra. The acyl radicals are generated by oxidation of aldehydes with suitable hydrogen-acceptors such as *t*-butoxy radicals or by intermediates obtained in the photochemical and thermal decomposition of nitroso compounds. During photolysis of alkyl nitrites in hydrocarbon solvents the acyl-alkyl-nitroxides appear also and this is explained on the basis of known reactions of alkyl nitrites and their decomposition products.

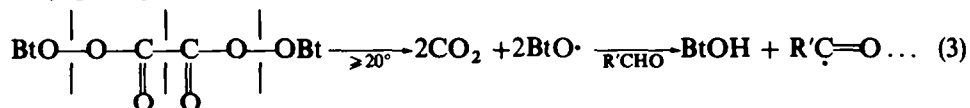
IN PREVIOUS parts^{2,3} we have demonstrated the scavenging properties of nitroso compounds for alkyl and alkoxy radicals:



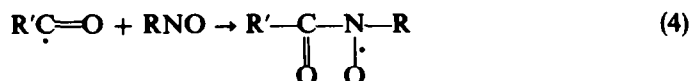
This paper describes three methods (I, II and III) for the formation of *acyl-alkyl-* and *acyl-phenyl-nitroxides*, as intermediates in the reaction of acyl radicals with nitroso compounds, sufficiently stable for detection by ESR.



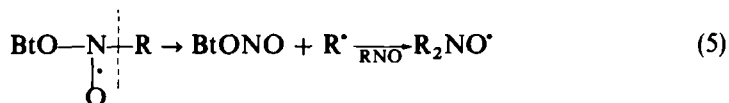
Method I. The acyl radicals can be generated by oxidation of an aldehyde with *tertiary* butoxy radicals,⁴ formed during the thermal decomposition of *tertiary* butyl peroxyoxalate (TBPO).⁵



In the presence of a small amount of nitroso compound the acyl radicals add to the nitroso group:



In the absence of aldehyde TBPO and RNO form the t-butoxy-alkyl-nitroxide³ and from this the dialkyl nitroxide by reaction 5:



With a large excess of aldehyde however, the t-butoxy radicals predominantly abstract the aldehydic hydrogen atom and the ESR-spectrum of the acyl-alkyl-nitroxide is observed, while that of the t-butoxy-alkyl-nitroxide is weak or absent.

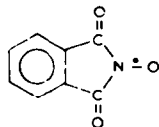
Only two acyl-phenyl-nitroxides have been previously described in the literature, viz. acetyl-phenyl- and benzoyl-phenyl-nitroxide, obtained by oxidation of the corresponding N-phenylhydroxamic acids.⁶ This direct method leaves no doubt as to the structure of the radicals. There is a close agreement between the hyperfine splitting (hfs) constants of these radicals and the values listed in Table 1 for some radicals obtained via method I. The typical ESR spectrum of benzoyl-phenyl-nitroxide is given in Fig. 1.

TABLE I. ACYL-ALKYL- AND ACYL-PHENYL-NITROXIDES BY REACTION OF TBPO WITH ALDEHYDES AND NITROSO COMPOUNDS (IN BENZENE AT 20°)

Nitroxide	a_N	a_H^{α}	a_H^{β}	a_H^{CH} (Gauss)	g-Values	Ref.
$\phi-\overset{\cdot}{\text{C}}(\text{O})-\text{N}-\phi$	7.7	1.6	0.7		2.0065	
	lit.: 7.55	1.54	0.64			6
$\text{Me}-\overset{\cdot}{\text{C}}(\text{O})-\text{N}-\phi$	7.3	1.5	0.6	0.3		
	lit.: 7.18	1.47	0.62	0.23		6
$\phi-\overset{\cdot}{\text{C}}(\text{O})-\text{N}-\text{CMe}_2(\text{CH}_2\text{OAc})$	8.1				2.0068	
$\triangle-\overset{\cdot}{\text{C}}(\text{O})-\text{N}-\text{CMe}_2(\text{CH}_2\text{OAc})$	8.3				2.0069	
$\text{Me}-\text{CH}=\text{CH}-\overset{\cdot}{\text{C}}(\text{O})-\text{N}-\text{CMe}_2(\text{CH}_2\text{OAc})$	8.0				2.0067	
$\text{Me}-\overset{\cdot}{\text{C}}(\text{O})-\text{N}-\text{CMe}_3$	8.0				2.0068	

The ESR spectra of these nitroxides are characterized by a relatively small nitrogen hfs constant ($a_N \sim 7-8$ gauss), indicating a lower spin density on the N atom than is found for the dialkyl nitroxide, derived from the same nitroso compound. The acyl-alkyl-nitroxides have g-values, which are somewhat larger than those of the

dialkylnitroxides in the same apolar solvents (2·0065–69 and 2·0058–62 resp.) and smaller linewidths. Therefore in acyl-alkyl-nitroxides the free electron must be localised on the carbonyl group to a considerable extent.* This is further supported by the ESR spectrum of the nitroxide, derived from N-hydroxyphtalimide, in which



the NO[•]-group is flanked by two carbonyl groups. As expected the a_N -value decreases further to 4·23 gauss, while the g -value increases to 2·0073.⁷ While the α -C—H groups from the alkyl substituent attached to N give observable hf splittings, no such fine structure is found for the acyl substituent, despite the considerable spin density on the carbonyl group.† Ramsbottom and Waters⁸ demonstrated *cis-trans* isomerism in the related acyl-nitroxide radicals R'CO(H)NO[•], due to (partly) double bond character of the C—N bond. In the present study this isomerism is not observed for acyl-alkyl- and acyl-phenyl-nitroxides.

Method II for the formation of the acyl-alkyl-nitroxides is the photochemical and thermal decomposition of nitrosoalkanes in the presence of an excess of aldehyde (Table 2). Without aldehyde the dialkylnitroxide is formed.⁹ Primary and secondary nitrosoalkanes exist almost entirely in the dimeric form at room temperature, while tertiary nitrosoalkanes are monomeric in solution to a considerable extent.¹⁰ Accordingly the acyl-alkyl-nitroxides are formed photochemically at room temperature from tertiary nitrosoalkanes and aldehydes by irradiation with red light ($\lambda \sim 680$ nm) or thermally above 40°. From primary and secondary nitroso dimers monomer is generated by heating to about 60°. At that temperature the thermal reaction of the monomer is accompanied by the photochemical reaction with red light. At the time it is not clear whether acyl radicals are formed from aldehydes through hydrogen abstraction directly by the excited nitroso compound or by its decomposition products (e.g. alkyl radicals). This is under investigation.

Method III. In an earlier paper³ we demonstrated the formation of dialkyl-nitroxides and alkoxy-alkyl-nitroxides during photolysis of various alkyl nitrites in (cyclo)alkanes or in alkylbenzenes. Some systems showed an additional radical signal with low N hfs constant ($\sim 7\cdot5$ –8 gauss), which could not be identified hitherto. In photolyses of *primary* nitrites this dominated in the ESR-spectrum and in those cases the signal of the alkoxy-alkyl-nitroxide was weak or absent. The N hfs constant and the g -value of the unknown radical are in agreement with those of acyl-alkyl-nitroxides. The formation of these radicals takes place via addition of intermediately formed acyl radicals to nitroso compounds, which are products of the photolysis of

* This conclusion is in contrast to that of D. F. Minor, W. A. Waters and J. V. Ramsbottom [*J. Chem. Soc. B*, 180 (1967)], who compared some acyl-methyl-nitroxides with acyl-nitroxides (R = H; $a_N \sim 6$ gauss). From the higher a_N in the former case and the absence of *cis-trans*-isomerism they inferred no transfer of spin density to the carbonyl group.

† The methyl-H-atoms in acetyl-phenyl-nitroxide form an exception to this rule since they give a very small hyperfine splitting.

TABLE 2. ACYL-ALKYL-NITROXIDES BY PHOTOCHEMICAL (hv) AND THERMAL (Δ) REACTION OF NITROALKANES WITH ALDEHYDES (MEASURED AT 20°).

Nitroso compound	Aldehyde	Nitroxide	Solvent	Reaction temp (°C)	a_N a_H (gauss)	g -Value
t-Nitrosobutane	MeCHO	$\begin{array}{c} \text{Me}-\text{C}-\text{N}-\text{Bt} \\ \quad \\ \text{O} \quad \text{O} \end{array}$	MeCHO	0 (hv)	8.0 —	2.0068
t-Nitrosobutane	MeCHO	$\begin{array}{c} \text{Me}-\text{C}-\text{N}-\text{Bt} \\ \quad \\ \text{O} \quad \text{O} \end{array}$	CFCI ₃	0 (hv)	7.9 —	not det.
t-Nitrosobutane	MeCHO	$\begin{array}{c} \text{Me}-\text{C}-\text{N}-\text{Bt} \\ \quad \\ \text{O} \quad \text{O} \end{array}$	benzene	0 (hv)	8.0 —	2.0068
t-Nitrosobutane	EtCHO	$\begin{array}{c} \text{Et}-\text{C}-\text{N}-\text{Bt} \\ \quad \\ \text{O} \quad \text{O} \end{array}$	benzene	60 (Δ)	8.0 —	not det.
ON—CMe ₂ (CH ₂ OAc)	MeCHO	$\begin{array}{c} \text{Me}-\text{C}-\text{N}-\text{CMe}_2(\text{CH}_2\text{OAc}) \\ \quad \\ \text{O} \quad \text{O} \end{array}$	benzene	50 (Δ)	8.2 —	not det.
ON—CMe ₂ (CH ₂ OAc)	ϕ CHO	$\begin{array}{c} \phi-\text{C}-\text{N}-\text{CMe}_2(\text{CH}_2\text{OAc}) \\ \quad \\ \text{O} \quad \text{O} \end{array}$	benzene	60 (Δ)	8.2 —	not det.
Nitrosocyclohexane	MeCHO	$\begin{array}{c} \text{Me}-\text{C}-\text{N}-\text{C}_6\text{H}_{11} \\ \quad \\ \text{O} \quad \text{O} \end{array}$	benzene	60 (hv, Δ)	7.5 2.6 ³ (1H)	2.0068
ϕ CH ₂ NO	MeCHO	$\begin{array}{c} \text{Me}-\text{C}-\text{N}-\text{CH}_2\phi \\ \quad \\ \text{O} \quad \text{O} \end{array}$	benzene	60 (hv, Δ)	7.5 5.0 (2H)	2.0065

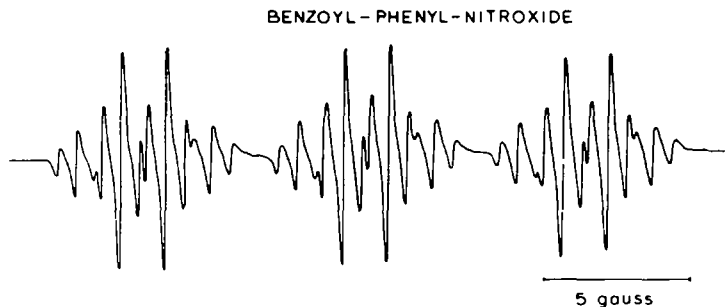
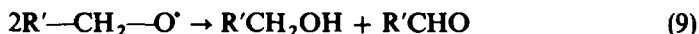


FIG. 1 ESR-spectrum of benzoyl-phenyl-nitroxide in benzene at 20°.

alkyl nitrites in hydrocarbons¹¹ and are formed in the following sequence of reactions:

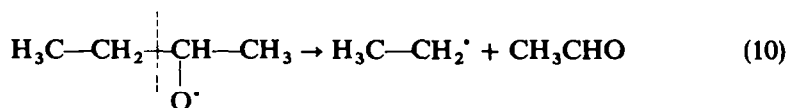


The addition of an alkyl radical to the nitrosoalkane would lead to the formation of a dialkylnitroxide (reaction 1). This radical is also regularly observed in these nitrite ester photolyses, especially when the hydrocarbon contains tertiary hydrogen. *Hydrogen-abstraction* (reaction 7) is not the only reaction that is open to alkoxy radicals, alternative pathways being *disproportionation* and *decomposition*.¹² The course of the reaction is determined by the nature of these radicals. *Primary* nitrite esters give *primary* alkoxy-radicals after photodissociation and from these aldehydes are formed by disproportionation.



The photolysis of *n*-butyl nitrite gives butanal in 22% yield.¹³

Acyl radicals may arise through H-abstraction from the aldehyde by alkoxy radicals as in reaction 3. In the photolysis of *n*-butyl nitrite in cumene a strong signal of butyryl-*t*-cumyl-nitroxide is observed together with di-*t*-cumylnitroxide, and similar radicals are found with other primary nitrites. In these cases the alkoxy-alkyl-nitroxide is absent or hardly detectable (Fig. 2c). This shows that both disproportionation and hydrogen abstraction from cumene and from the intermediary aldehyde are important reactions of *primary* alkoxy radicals. Disproportionation of *secondary* alkoxy radicals will yield ketones. However, these radicals can also *decompose via a β-C—C cleavage*, the most stable alkyl radical being split off, leaving an aldehyde;¹³⁻¹⁵ e.g. from 2-butyl nitrite a 10% yield of acetaldehyde is obtained.



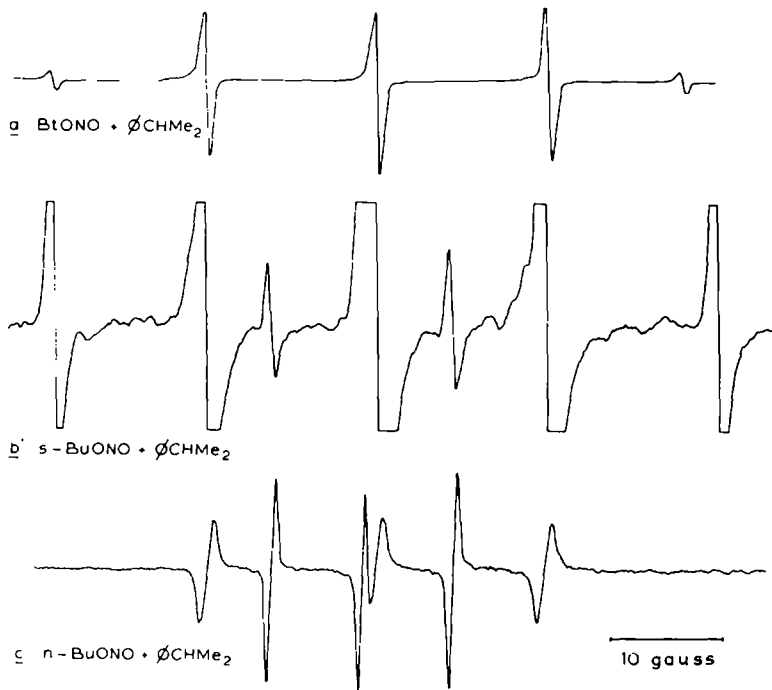


FIG. 2 ESR-spectra obtained with cumene and *primary*, *secondary* and *tertiary* butyl nitrite.

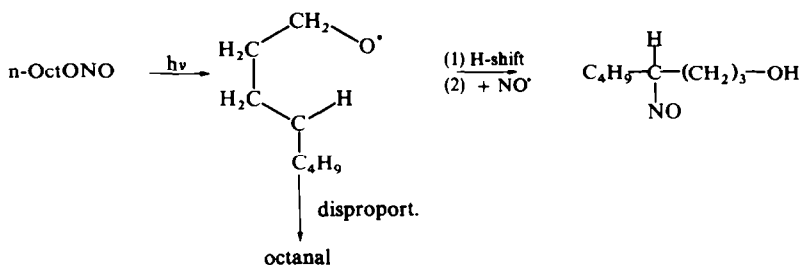
Decomposition of a secondary alkoxy radical requires a higher energy of activation than H-abstraction or disproportionation and consequently aldehydes are formed with difficulty. Therefore a weak ESR-signal of acetyl-t-cumyl-nitroxide is observed in the photolysis of *sec*-butyl nitrite in cumene (Fig. 2b). The main reaction of the *secondary* radical is intermolecular hydrogen abstraction from cumene. In this system strong signals of di-*t*-cumyl- and *sec*-butoxy-*t*-cumyl-nitroxide are produced. At higher temperatures decomposition competes more strongly with hydrogen abstraction and accordingly the signal due to the acetyl-cumyl-nitroxide increases.

None of the known reactions for *tertiary* alkoxy radicals gives rise to the formation of aldehydes. In accordance with this no ESR-spectra of acyl-alkyl-nitroxides are observed during photolysis of *t*-butyl nitrite (BtONO) in secondary and tertiary hydrocarbons like cumene (Fig. 2a). Only the di-(*ar*)alkylnitroxide ($a_N \sim 15$ gauss) and the alkoxy-(*ar*)alkyl-nitroxide ($a_N \sim 28$ gauss) are present. The assignment of the acyl-alkyl-nitroxides is further supported by carrying out the photolysis of *n*-butyl nitrite in the presence of various hydrocarbons. With cumene, ethylbenzene and toluene these radical-signals show hyperfine structure by an increasing number of H atoms at the α -carbon atom, i.e. none, one and two respectively (Fig. 3). These results are in accordance with the structure $n\text{-Pr}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\cdot}{\text{N}}-\text{R}$, in which

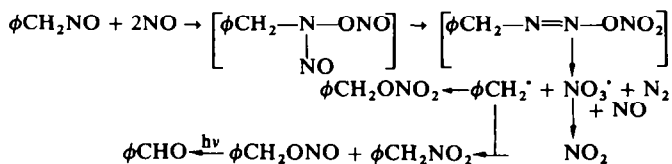


$\text{R} = \phi\text{CMe}_2$, ϕCHMe - and ϕCH_2 -. If the alkoxy radical contains a straight chain of at least four carbon atoms, then the possibility of an *intramolecular hydrogen*-

abstraction (the Barton reaction) exists via a six-membered transition state: photolysis of *n*-octyl nitrite in an inert solvent¹⁶ has been shown to lead to the formation of 45% of dimeric 4-nitroso-octanol-1 and 15% of octanal via:



When irradiated as a pure liquid *n*-octyl nitrite forms the expected acyl-alkyl-nitroxide from the disproportionation product octanal and the Barton reaction product 4-nitroso-octanol-1. The above-mentioned and previous results³ suggest that photolysis of *t*-butyl nitrite in toluene would lead to *t*-butoxy-benzyl-nitroxide and dibenzylnitroxide. At -40° alkoxy-alkyl-nitroxide is formed exclusively. Unexpectedly at higher temperatures an ESR-signal of an acyl-alkyl-nitroxide appears and this is the only radical present at room temperature. It is very probable that this radical is the benzoyl-benzyl-nitroxide. The hfs constants and *g*-value are in agreement with the values of the same radical, formed by photolysis of benzyl nitrite in toluene. This can be explained on the basis of known reactions between the nitroso monomer, arisen via reactions (6)–(8), and NO, resulting in this case in the formation of some benzaldehyde as judged from IR-spectra.



The results obtained in nitrite ester photolyses are collected in Table 3. Abstraction of the type of hydrogen atoms, indicated in the sub-headings is observed only.

EXPERIMENTAL

Nitrosoalkanes and alkyl nitrites were prepared by known methods.^{2,3} The ESR-spectra were measured as before.² *g*-Values were determined, using solid diphenyl-dipicryl-hydrazyl (*g* = 2.0036) as a standard, with an accuracy of 0.0002.

TABLE 3. ACYL-ALKYL-NITROXIDES BY PHOTOLYSIS OF ALKYL NITRITES IN HYDROCARBON SOLVENTS (AT 20°).

Alkyl nitrite	Hydrocarbon with abstractable	Nitroxide	a_N	a_H	g-value
<i>primary H</i> EtONO	<i>primary H</i> toluene	acetyl-benzyl-	7.7	4.9 (2H)	2.0068
<i>n-BuONO</i>	toluene	butyryl-benzyl-	7.6	5.0 (2H)	2.0067
$\phi\text{CH}_2\text{ONO}$	toluene	benzoyl-benzyl-	7.5	4.9 (2H)	2.0069
<i>secondary H</i> EtONO	<i>secondary H</i> ethylbenzene	acetyl- α -phenethyl-	7.7	2.9 (1H)	2.0068
<i>n-BuONO</i>	ethylbenzene	butyryl- α -phenethyl-	7.7	2.9 (1H)	2.0068
$\phi\text{CH}_2\text{ONO}$	ethylbenzene	benzoyl- α -phenethyl-	7.6	3.1 (1H)	2.0068
<i>n-BuONO</i>	cyclohexane	butyryl-cyclohexyl-	7.5	2.6 (1H)	2.0068
<i>tertiary H</i> EtONO	<i>tertiary H</i> cumene	acetyl-t-cumyl-	8.2	—	2.0067
<i>n-BuONO</i>	cumene	butyryl-t-cumyl-	8.1	—	2.0068
<i>n-BuONO</i>	2,3-dimethylbutane	butyryl-2,3-dimethyl-2-butyl-	7.4	—	2.0068
$\phi\text{CH}_2\text{ONO}$	cumene	benzoyl-t-cumyl-	8.3	—	2.0067
<i>n-OctONO</i>	no solvent	octanoyl-(1-hydroxy-oct-4-yl)-	7.6	1.3 (1H)	2.0068
<i>secondary H</i> s-BuONO	<i>primary H</i> toluene	acetyl-benzyl-	7.4	4.9 (2H)	2.0068
<i>secondary H</i> s-BuONO	<i>secondary H</i> ethylbenzene	acetyl- α -phenethyl-	7.7	2.8 (1H)	2.0068
<i>tertiary H</i> s-BuONO	<i>tertiary H</i> cumene	acetyl-t-cumyl-	8.1	—	2.0067
<i>tertiary H</i> EtONO	<i>primary H</i> toluene	benzoyl-benzyl-	7.5	4.9 (2H)	2.0068
<i>secondary H</i> EtONO	<i>secondary H</i> ethylbenzene	no acyl-alkyl-nitroxide	—	—	—
<i>tertiary H</i> EtONO	<i>tertiary H</i> cumene	no acyl-alkyl-nitroxide	—	—	—

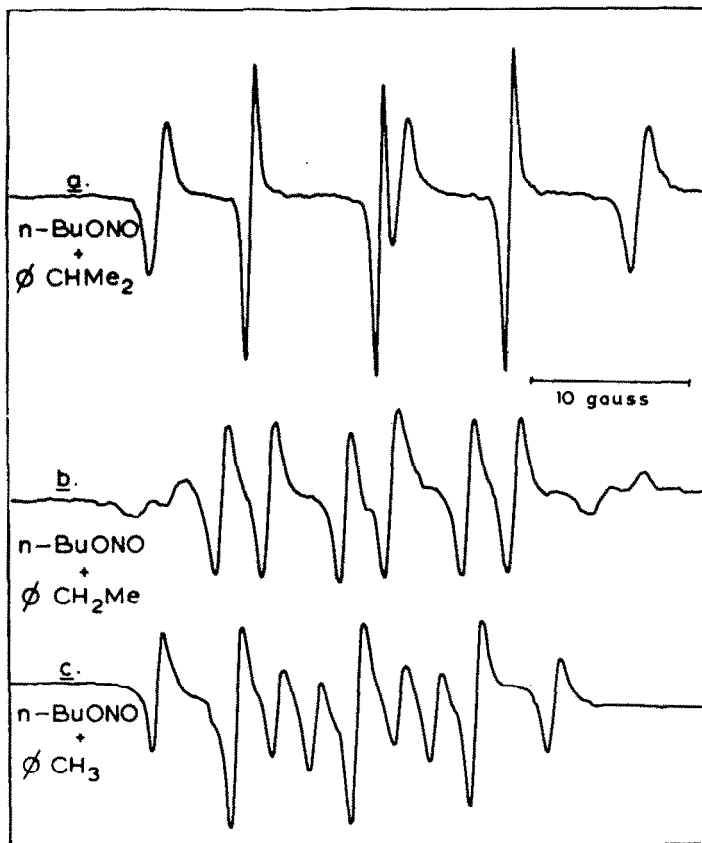


FIG. 3 ESR-spectra obtained with n-butyl nitrite and cumene, ethylbenzene and toluene.

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