Tetrahedron Vol 23, pp 4021 to 4026 Pergamon Press Ltd 1967 Printed in Great Britain

C-NITROSO COMPOUNDS—II

ON THE PHOTOCHEMICAL AND THERMAL FORMATION OF NITROXIDES FROM NITROSO COMPOUNDS, AS STUDIED BY E.S.R.

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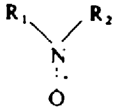
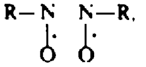
(*Received* 29 *December* 1966; *accepted for publication* 3 *February* 1967)

Abstract—It is demonstrated that nitroxides can be generated by photochemical or thermal decomposition of C-nitroso compounds. The nitroxide-formation takes place in both cases via the nitroso monomer. The influence of the wavelength on the photochemical reaction is discussed.

IN PART I of this series,[1] we demonstrated by ESR the formation of dialkylnitroxides,



from monomeric nitroso-alkanes by irradiation with red light; no dark reaction was found at room temperature. These results are in marked contrast with those of other authors. In a recent paper Theilacker *et al.*[2] reported the thermal formation of radicals from dimeric nitroso compounds, to which they ascribed the structure



$$\underset{\dot{O}}{R-N}\quad\underset{\dot{O}}{N-R},$$

but subsequently it was stated by Strom and Bluhm,[3] that the radicals obtained from nitroso-alkanes were in fact the dialkylnitroxides. The latter authors succeeded in obtaining the same ESR signals by irradiation of nitroso-alkanes with the unfiltered light of a high pressure mercury lamp.[4] Finally, Maruyama *et al.*[5] produced diphenylnitroxides from substituted nitrosobenzenes by irradiation with UV light.

With respect to the mechanism of the formation of the nitroxides both Strom and Bluhm, and Theilacker have pointed out, that the presence of the dimeric form of the nitroso compounds is necessary for this formation, and that completely monomeric nitroso compounds like *p*-nitrosodimethylaniline do not give radical signals after heating[2] or UV irradiation.[3] From this it was concluded that the dimer is involved

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[1] A. Mackor, Th. A. J. W. Wajer, Th. J. de Boer and J. D. W. van Voorst, *Tetrahedron Letters*, 2115 (1966).

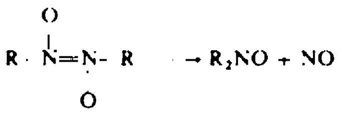
[2] W. Theilacker, A. Knop and H. Uffmann, *Angew. Chem.* **77**, 717 (1965).

[3] E. Th. Strom and A. L. Bluhm, *Chem. Comm.* 115 (1966).

[4] E. Th. Strom, private communication.

[5] K. Maruyama, R. Tanikaga and R. Goto, *Bull. Chem. Soc. Japan*, **37**, 1893 (1964).

in both the thermal[2] and photochemical[3] formation of nitroxides; the reaction was described by Strom and Bluhm as follows:



$$R-\overset{O}{\overset{|}{N}}=\underset{O}{N}-R \rightarrow R_2NO + NO$$

The present paper deals with:

(a) Structural factors that favour thermal nitroxide-formation from nitroso-alkanes.
(b) The role of monomeric and/or dimeric nitroso compounds in thermal and photochemical nitroxide-formation.
(c) The influence of the wavelength on the photochemical reaction.

Thermal reaction. It is found that a nitroxide, which can be formed photochemically, generally can also be obtained by a thermal reaction from the same nitroso compound. In contrast with the photochemical formation there are differences in reactivity, depending on the nature of the alkyl substituent.

Secondary nitroso compounds are thermally less reactive than tertiary, while the presence of a phenyl group at the α-carbon-atom greatly enhances the tendency to form nitroxides. Thus tertiary nitroso-alkanes form nitroxides at about 80° in 0·1 molar solutions, while secondary compounds require higher temperatures (100–120°).

The activating influence of phenyl substituents in the α-position is demonstrated by the increasing ease of nitroxide-formation from phenylnitrosomethane, 1-phenylnitrosoethane, and diphenylnitrosomethane (at about 80°, 60° and 20° respectively). More striking is the difference in photochemical and thermal behaviour of nitrosobenzene and 1-acetoxy-1-nitrosocyclohexane. Nitrosobenzene remains unchanged with red light, UV light being necessary for the formation of the diphenylnitroxide, while thermal nitroxide-formation proceeds even slightly above room temperature.

On the other hand 1-acetoxy-1-nitrosocyclohexane does form the di-(1-acetoxycyclohexyl)nitroxide with red light, while thermally no nitroxide can be generated at temperatures up to 120°. In this respect, Lown[6] obtained a radical by reaction of the 1-acetoxy-1-nitrosocyclohexane with base (triethylamine). We have proved that this radical is the same as formed by irradiation with red light, and that it is the di-(acetoxycyclohexyl)nitroxide, because of the close agreement in g-values ($g = 2{\cdot}0061$) and hyperfine coupling constants ($a_N = 13{\cdot}2$ gauss; $a_{H_1} = 0{\cdot}65$ gauss (4H) and $a_{H_2} = 0{\cdot}32$ gauss (4H)). A radical-anion of the nitroso compound as suggested by Lown should have essentially different h.f.s.-constants and must therefore be excluded.

Mechanism of the photochemical nitroxide-formation. t-Butylphenylnitroxide is formed as the only product by photolysis of t-nitrosobutane in the presence of excess nitrosobenzene, which by itself is stable with red light. From this fact it can be concluded that a relatively long-living intermediate, arising from the monomer must be present. The product formation from the intermediate is determined by the probability of meeting another molecule of nitroso compound. These results exclude

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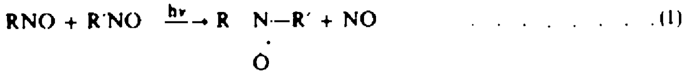
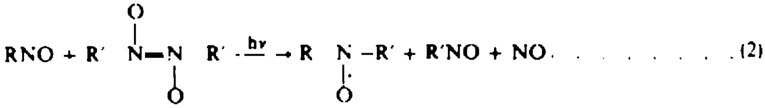
[6] J. W. Lown, *J. Chem. Soc.* B 441 (1966).

the intramolecular dimer reaction in this case. There are two possibilities for the intermolecular reaction:



$$\mathrm{RNO + R'NO \xrightarrow{h\nu} R\underset{\dot{O}}{N}{-}R' + NO} \qquad \ldots\ldots\ (1)$$



$$\mathrm{RNO + R'\overset{O}{\overset{|}{N}}{=}\underset{\underset{O}{|}}{N}R' \xrightarrow{h\nu} R\underset{\underset{O}{|\cdot}}{N}{-}R' + R'NO + NO} \qquad \ldots\ldots\ (2)$$

In order to decide between (1) and (2), experiments were carried out with mixtures of two nitroso-alkanes—the tertiary 1-acetoxy-2-methyl-2-nitrosopropane, which is largely present as monomer, and an excess of the secondary 2-nitrosopropane, which is known to exist almost entirely in the dimeric form at or below room temperature.[7] By irradiation with red light at −25° only the di-t-alkylnitroxide is formed, but at +40° the dimeric secondary 2-nitrosopropane dissociates partly and the mixed nitroxide appears (Fig. 1). This indicates again, that the ratio of the monomeric nitroso compounds determines the product ratio. This is only compatible with an

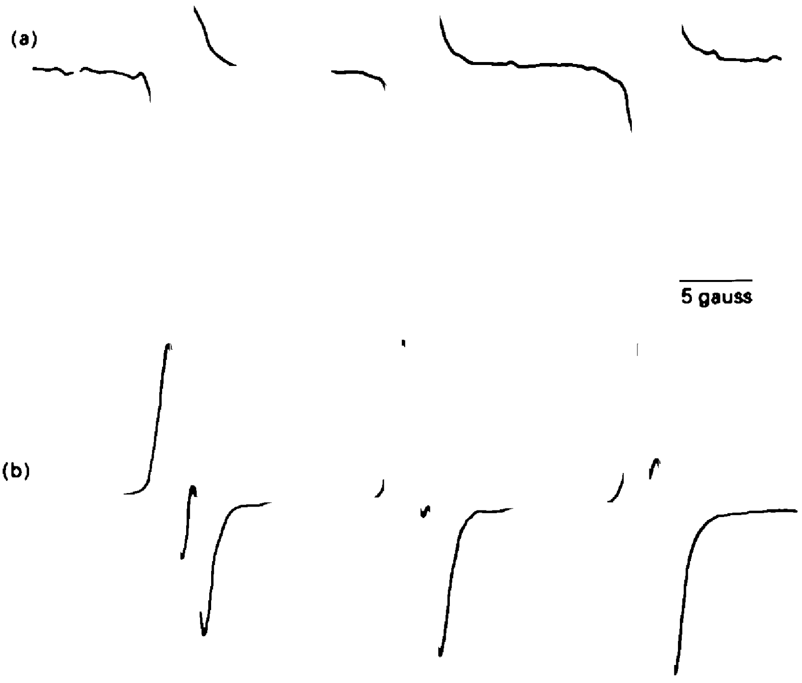


FIG. 1. ESR spectra of nitroxides generated by photolysis (680 nm) of 2-methyl-2-nitrosopropane and 2-nitrosopropane at (a) −25° and (b) +40°.

B. G. Gowenlock and W. Lüttke, *Quart. Rev.* 12, 321 (1958).

intermolecular reaction between two monomer molecules, thus proving the correctness of (1), excluding the intramolecular dimer-mechanism as suggested by Strom and Bluhm[3] for the photochemical reaction. Further evidence for this conclusion comes from the formation of the nitroxide by photolysis of 1-acetoxy-1-nitrosocyclohexane, which is completely monomerized.[8]

The reason why *p*-nitrosodimethylaniline does not give a nitroxide itself thermally or photochemically, is the strong mesomeric interaction between the dimethylamino group and the nitroso group, thus conferring partly double bond character on the C NO bond.[9] However, this compound can participate in the formation of a mixed nitroxide both photochemically and thermally (120°), by adding it in excess to a reactive tertiary nitroso-alkane. The assignment of the h.f.s. due to the aromatic protons is supported by comparison of the ESR spectrum with that of the *ortho*-dideuterated compound.

Mechanism of thermal nitroxide-formation. Possible pathways leading to the thermal formation of nitroxides are: (a) intramolecular reaction of a dimer and (b) intermolecular reaction between a reactive monomer or dimer with a "non-reactive" monomer or dimer. All possibilities but the monomer-monomer mechanism can be excluded on the basis of the following experiments:

Formation of the mixed nitroxide from completely monomeric *p*-nitrosodimethylaniline and a monomeric tertiary nitrosoalkane proves that a dimer is not essential. The same conclusion can be drawn from experiments with solutions of diphenylnitrosomethane. At room temperature the di-(diphenylmethyl)nitroxide is formed. By addition of an excess of the less reactive 1-acetoxy-2-methyl-2-nitrosopropane only the ESR spectrum of the mixed diphenylmethyl-t-alkyl nitroxide is found (Fig. 2).

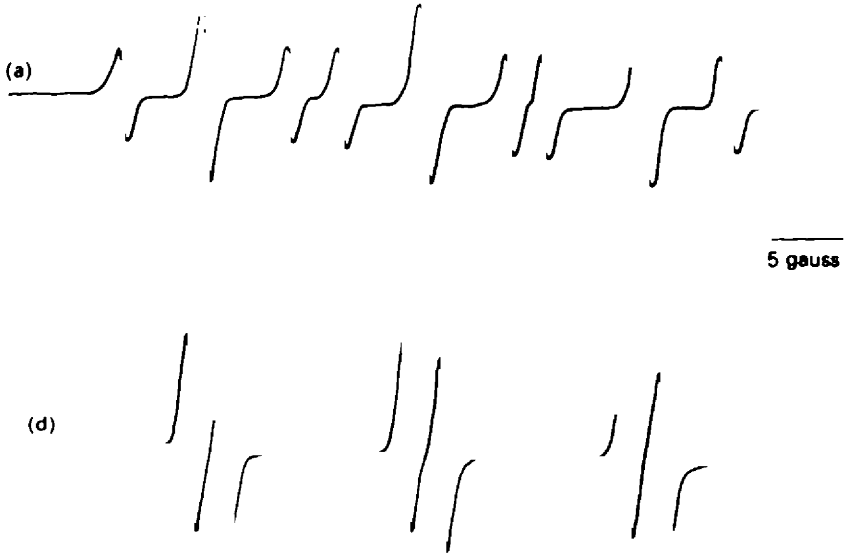


FIG. 2. ESR spectra of nitroxides, generated thermally from: (a) Diphenylnitrosomethane at 20°; (b) Diphenylnitrosomethane with an excess of 1-acetoxy-2-methyl-2-nitrosopropane at 40°.

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[8] H. Kropf, *Angew. Chem.* 77, 1030 (1965).

[9] P. K. Korver, thesis, Amsterdam (1966).

The spontaneous formation if diphenylnitroxide from monomeric nitrosobenzene and the general observation of the non-reactivity of dimeric nitroso-alkanes suggest that some monomeric diphenylnitrosomethane must have been present and initiated the reaction. This is in accordance with the observation that isomerization of diphenylnitrosomethane to benzophenone oxime, which proceeds via the monomeric form, takes place at temperatures, where nitroxide-formation is also important. Final support for these conclusions is obtained by the reaction between mixtures of (monomeric) t-nitrosobutane and (dimeric) 2-nitrosopropane. When a 1:3 mixture of the t-nitrosobutane and 2-nitrosopropane is heated to 120° only the di-t-butylnitroxide is formed. With a 1:250 mixture the signal of the t-butyl-isopropylnitroxide is obtained. In the former case there is an excess of the monomeric t-nitrosobutane, while in the latter case monomers are present in comparable concentrations. On the basis of the foregoing results the possibility of the thermal nitroxide-formation via an (intramolecular) dimer-reaction as supposed by Theilacker *et al.*[2] and Strom and Bluhm[3] can be excluded.

The influence of the wavelength on photochemical nitroxide-formation. For monomeric nitroso compounds both UV and visible absorption bands have been described, while for dimeric nitroso compounds only a UV absorption band is known.[7] We have already mentioned the action of red light (ca. 680 nm) upon monomeric nitrosoalkanes and of UV-light (320 360 nm) upon nitrosobenzene.[1]

TABLE 1. ESR-SPECTRA OF NITROXIDES R_1R_2NO (IN *o*-XYLENE)

R_1	R_2	Splittings (in gauss)					
		a_N	$a_{H-\alpha}$	$a_{H-\beta}$	$a_{o,p}$	a_m	Ref.
ϕ	ϕ	9·7			1·9	0·8	14
—$C(Me)_3$	—$C(Me)_3$	15·7					15
—$C(Me)_2CH_2Cl$	—$C(Me)_2CH_2Cl$	14·7					
$C(Me)_2CH_2OH$	$C(Me)_2CH_2OH$	14·9					
—$C(Me)_2CH_2OCHO$	—$C(Me)_2CH_2OCHO$	15·2					
$C(Me)_2CH_2OAc$	$C(Me)_2CH_2OAc$	15·2					
—$C(Me)_2CH(Me)_2$	—$C(Me)_2CH(Me)_2$	14·8					
—$C(Me)_2\phi$	—$C(Me)_2\phi$	15·3					
$CH(Me)\phi$	—$CH(Me)\phi$	15·1	9·4				
—$CH\phi_2$	—$CH\phi_2$	14·7	5·7				
—$CH_2\phi$	—$CH_2\phi$	15·1	8·7				16
—$CH(Me)_2$	—$CH(Me)_2$	15·0	4·2	0·22			17
—cyclohexyl	—cyclohexyl	14·6	4·4	0·85			3
—cyclopentyl	—cyclopentyl	14·9	4·4				
1-acetoxycyclohexyl-	—1-acetoxycyclohexyl-	13·5					
—$C(Me)_2NO_2$	—$C(Me)_2NO_2$	11·5*					
n-$BuCH(CH_2)_3OH$	n-$BuCH(CH_2)_3OH$	14·6	4·6				
—$CH\phi_2$	—$C(Me)_2CH_2OAc$	14·2	2·4				
—$CH(Me)_2$	—$C(Me)_3$	15·4	1·4	0·34			17
—$CH(Me)_2$	—$C(Me)_2CH_2OAc$	14·7	1·7				
ϕ	—$C(Me)_3$	12·4			2·0	0·9	18
$(Me)_2NC_6H_4$—	$C(Me)_2CH_2OAc$	12·5			2·0	1·0	
$(Me)_2NC_6D_2H_2$	—$C(Me)_2CH_2OAc$	12·5			2·0		

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* $a_{N\,(NO_2)} = 5·3$

In the following typical cases we have demonstrated the formation of symmetrical nitroxides by irradiation with UV light (313 nm) from nitrosobenzene, 1-acetoxy-1-nitrosocyclohexane, t-nitrosobutane and nitrosocyclohexane. In a systematic study of the effective wavelength it has been found that the two spectral regions, mentioned above, are capable of producing nitroxides from nitroso-alkanes.[10] These coincide with the absorption bands of the monomer; the spectral interval between those bands is not active. Nitrosocyclohexane does not give nitroxide signals at 20° after irradiation with red light, indicating that no monomer is present. However, the nitroxide is formed with UV light at 313 nm. Since we have directly demonstrated, that dimeric nitroso-alkanes are dissociated into two monomers by irradiation with UV light at low temperatures,[11] this can also be explained in terms of a monomer mechanism. This evidence makes it probable that after cleaving the dimer, the resulting monomer can be converted into a nitroxide, although the possibility of a more direct pathway from the excited dimer cannot be entirely excluded in UV light induced reactions.

EXPERIMENTAL

The compounds 2,3-dimethyl-2-nitrosobutane, phenylnitrosomethane, 1-phenylnitrosoethane, diphenylnitrosomethane and nitrosocumene were prepared by photochemical nitrosation of the corresponding hydrocarbons.[12] All other compounds were synthesized according to known methods.[13] The ESR-spectra were measured using a Varian V 4502 ESR spectrometer with 100 kc/s modulation along with a V 4531 multipurpose cavity and a variable temp. accessory, financed by the Stichting voor Scheikundig Onderzoek in Nederland.

Acknowledgement We thank Mr. R. Sitters for his assistance in part of the experimental work. One of us (Th. A. J. W. W.) is indebted to the Stichting voor Organisch Chemisch Onderzoek for financial support.

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[11] A. Mackor, Th. A. J. W. Wajer and Th. J. de Boer, to be published.

[12] Part of the forthcoming thesis of A. Mackor.
A. Mackor, J. U. Veenland and Th. J. de Boer, to be published.

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