Photoaddition of Thionitrites to CC Double Bonds

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Summary The photolysis of thionitrites in the presence of compounds containing CC double bonds produces *C*-nitroso-compounds and nitroxides; the reaction can be adapted to the synthesis of *C*-nitroso-compounds.

THIONITRITES are thermally[1] and photochemically[1–3] unstable and are presumed to be sources of thiyl radicals. It is known that thiyl radicals will add to olefins[4,5] and to dienes.[6] The photolytic sources of these radicals have usually been thiols and disulphides. In recent years it has been shown that nitrosoamines can undergo efficient photoaddition to olefins in acid solution and this is attributed to initial attack of an aminium radical to the π bond followed by reaction of the resultant radical ion with nitric oxide.[7] It seemed possible to us to combine the known photochemical instability of thionitrites and the ease of thiyl radical addition to π bonds to give a synthetic route to sulphur-containing *C*-nitroso-compounds by a free radical mechanism using non-polar media. Attention has recently been drawn[8] to other aspects of the synthetic potentialities of thionitrites.

Trityl (**1**) and t-butyl thionitrites (**2**) were prepared by nitrosating the corresponding thiols.[1,9] They were photolysed using a medium pressure mercury lamp within the cavity of an e.s.r. spectrometer under the following conditions: solvent benzene, toluene, diethyl ether, or isopentane; thionitrite concentration *ca.* 3·0 × 10^{-2} M; alkene concentration *ca.* 10^{-1} M, temperature range 20 ± 2 °C, photolysis time 10 min. For four of the alkenes employed, e.s.r. spectra resulted and the results for two of these are presented in the Table. The Table shows that spectra characteristic of nitroxides[10] are obtained, and we suggest the sequence of reactions (1)—(4). The structures of

$$R^1SNO \xrightarrow{h\nu} R^1S\cdot + NO \qquad (1)$$

$$R^1S\cdot + R^2R^3C{=}CH_2 \rightarrow R^2R^3\underset{\bullet}{C}{-}CH_2SR^1 \qquad (2)$$

$$R^2R^3\underset{\bullet}{C}{-}CH_2SR^1 + NO \rightarrow \underset{\textbf{(3)}}{R^2R^3C(NO){-}CH_2SR^1} \qquad (3)$$

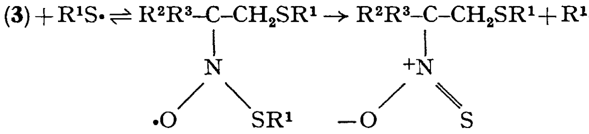
$$\textbf{(3)} + R^2R^3\underset{\bullet}{C}{-}CH_2SR^1 \rightarrow \underset{\textbf{(4)}}{(R^2R^3CCH_2SR^1)_2\dot{N}O} \qquad (4)$$

TABLE. E.s.r. parameters of radicals observed on photochemical addition of thionitrites Ph_3CSNO (**1**) and Bu^tSNO (**2**) to alkenes[a] using benzene as solvent

		Radical			
Thionitrite	Alkene	(A)	(B)	(C)	(D)
(**1**)	$PhCHCH_2$	$a_N = 15{\cdot}26^b$ $g = 2{\cdot}0062$	$a_N = 15{\cdot}06^b$ $g = 2{\cdot}0062$	$a_{H_p} = 2{\cdot}92$ $g = 2{\cdot}0025$	$a_N = 15{\cdot}46$—$15{\cdot}8$ $g = 2{\cdot}00695$
(**1**)	$PhCMeCH_2$	(A) = (B)	$a_N = 15{\cdot}36$ $g = 2{\cdot}0061$	+	—
(**2**)	$PhCHCH_2$	$a_N = 15{\cdot}46$ $a_{H\beta} = 9{\cdot}26$	$a_N = 15{\cdot}46$ $a_{H\beta} = 5{\cdot}66$	—	—

[a] + Radical present, — radical not detected. [b] Additional hyperfine splitting due to two equivalent β protons present.

nitroxides (A) and (B) are assigned as diastereoisomers of (**4**) on the basis of the close spectral similarity to the nitroxides obtained by Jonkman *et al.*[11] by addition of nitrogen oxides to styrene. The formation of the triphenylmethyl radical (C) is probably due to a minor side reaction (5) involving thermal C–S homolysis of a thioalkylnitroxide. The e.s.r. data of the fourth radical (D) are consistent with a structure of the type[12] $R\dot{N}(O)SR$ possibly arising *via* route (6).



$$(\mathbf{3}) + R^1S\cdot \rightleftharpoons R^2R^3\text{–}\underset{\underset{\cdot O\quad SR^1}{N}}{C}\text{–}CH_2SR^1 \rightarrow R^2R^3\text{–}\underset{\underset{-O\quad S}{{}^{+}N}}{C}\text{–}CH_2SR^1 + R^1\cdot \qquad (5)$$

$(R^1 = Ph_3C\cdot)$

$$Ph_3C\cdot + NO \rightleftharpoons Ph_3C\text{–}NO \xrightarrow{R^1S\cdot} Ph_3C\text{–}\dot{N}(O)\text{–}SR^1 \qquad (6)$$

This identification assumes that a_N for a triphenylmethylthiyl nitroxide is lower than for a t-butylthiyl nitroxide.

Reaction (2) follows the known[4] anti-Markownikoff pattern. The observation of nitroxide formation implied the possibility of other reactions typical[13] of the *C*-nitroso-compound (**3**), of which dimerisation [equation (7)] and isomerisation to the oxime (R^3 = H) [equation (8)] will be of major importance.

$$2\,(\mathbf{3}) \rightarrow cis\text{- or } trans\text{-}[R^2R^3C(NO)\text{–}CH_2SR^1]_2 \qquad (7)$$

(5)

$$R^2HC(NO)\text{–}CH_2SR^1 \rightarrow R^2C(NOH)CH_2SR^1 \qquad (8)$$

(6)

The known[1,8] thermal instability of thionitrites allows the reaction sequence leading to (**5**) to be carried out in the dark as well as using a light source. The reaction has synthetic potential and (**5**) can be obtained in 60% yield from (**1**) (R^2 = Ph, R^3 = H) and in 40% yield from (**2**) (R^2 = Ph, R^3 = H). The white crystalline adducts (**5**) are mixtures of diastereoisomeric *trans*-dimers; *trans*-dimeric 1-nitroso-1-phenyl-2-triphenylmethylthiylethane, m.p. 133—134 °C (decomp.); i.r. (KBr) 1235 cm^{-1} (*trans*-dimer); u.v. ($CHCl_3$) λ_{max} 301·5 nm, ϵ 5000 l mol^{-1} cm^{-1}; *trans*-dimeric 1-nitroso-1-phenyl-2-t-butylthiylethane, m.p. 131—132 °C (decomp.), i.r. (KBr) 1565 and 1200 cm^{-1}; u.v. ($CHCl_3$) λ_{max} 297·0 nm, ϵ 13400 l mol^{-1} cm^{-1}. In both cases microanalyses and n.m.r. spectra were in agreement with these structures.

H.C. thanks the Leverhulme Trust for the award of a Commonwealth Visiting Fellowship.

(*Received*, 17*th November* 1978; *Com.* 1232.)

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[1] H. van Zwet and E. C. Kooyman, *Rec. Trav. chim.*, 1968, **87**, 45.

[2] G. Kresze and U. Uhlich, *Chem. Ber.*, 1959, **92**, 1048.

[3] J. Mason, *J. Chem. Soc.* (*A*), 1969, 1587.

[4] C. Sivertz, *J. Phys. Chem.*, 1959, **63**, 34; D. M. Graham, R. L. Mieville, and C. Sivertz, *Canad. J. Chem.*, 1964, **42**, 2239; D. M. Graham, R. L. Mieville, R. H. Pallen, and C. Sivertz, *ibid.*, p. 2250.

[5] O. Ito and M. Matsuda, *Bull. Chem. Soc. Japan*, 1978, **51**, 427.

[6] M. E. Keuhne and R. E. Damon, *J. Org. Chem.*, 1977, **42**, 1825.

[7] Y. L. Chow, *Accounts Chem. Res.*, 1973, **6**, 354; H. H. Quon and Y. L. Chow, *Tetrahedron*, 1975, **31**, 2349; Y. L. Chow, S. K. Pillay, and H. H. Quon, *J.C.S. Perkin II*, 1977, 1255.

[8] L. Field, R. V. Dilts, R. Ravichandran, P. G. Lenhert, and G. E. Carnahan, *J.C.S. Chem. Comm.*, 1978, 249; S. Oae, Y. H. Kim, D. Fukushima, and K. Shinhama, *J.C.S. Perkin I*, 1978, 913.

[9] H. Rheinboldt, M. Dewald, and O. Diepenbruck, *J. prakt. Chem.*, 1931, **130**, 133.

[10] A. R. Forrester, J. M. Hay, and R. H. Thomson, 'Organic Chemistry of Stable Free Radicals,' Academic Press, London, 1968, Ch. 5.

[11] L. Jonkman, H. Muller, and J. Kommandeur, *J. Amer. Chem. Soc.*, 1971, **93**, 5833.

[12] I. H. Leaver and G. C. Ramsey, *Tetrahedron*, 1969, **25**, 5669.

[13] B. G. Gowenlock and W. Lüttke, *Quart. Rev.*, 1958, **12**, 321.