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ELECTRON SPIN RESONANCE SPECTRUM OF A 5-MEMBERED CYCLIC ALKOXY NITROXYL RADICAL

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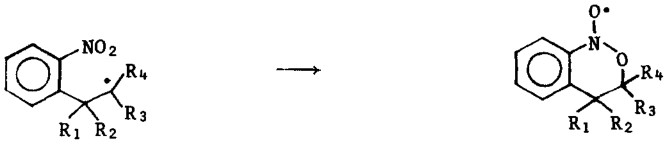
ABSTRACT: The esr spectrum of a 5-membered cyclic alkoxy nitroxyl radical is reported.

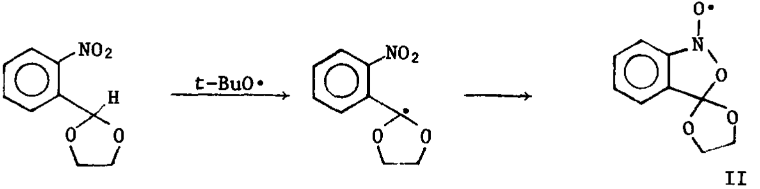
Intramolecular trapping of a β-substituted carbon-centered radical by an ortho-substituted nitro group to form 6-membered ring alkoxy nitroxyl radicals has been demonstrated (1).



I

e.g. for $R_1 = R_2 = R_3 = H$; $R_4 = OAc$; $a_N = 15.45$; $a^H_{o,p} = 3.5$; $a^H_m = 1.15$ G

Since alkoxyalkyl radicals readily add to nitro functions (2,3) the possibility that 5-membered ring alkoxy nitroxyl radicals could be formed from intramolecular trapping of α-alkoxyalkyl radicals by an ortho-nitro group was investigated. Thus o-nitrobenzaldehyde ethylene acetal (4) was reacted with tert-butoxy radicals obtained from a thermal source (di-tert-butylperoxalate, DBPO) at room temperature in benzene. The first esr spectrum obtained is shown in Figure 1(a). The simple splitting pattern is typical of aryl nitroxyls with approximately equivalent sets of ortho/para and meta hydrogens. The g-value is 2.0046 ±0.0002. The spectrum is assigned to the cyclic alkoxy aryl nitroxyl (II):



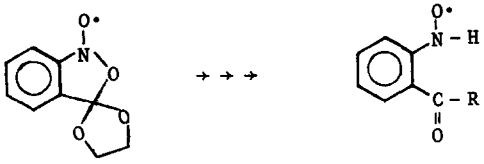
II

$a_N = 15.80$; $a^H_{o,p} = 3.09$; $a^H_m = 1.09$ G

The intermediate benzyl radical could not be trapped with 2-methyl-2-nitrosopropane. The ethylene acetals of m- and p-nitrobenzaldehyde gave more complex spectra probably due to the adducts of intermolecular trapping of the alkoxybenzyl radicals.

The spectrum due to II is replaced within hours by another spectrum with the following coupling constants (Figure 1(b)): $a_N = 7.93$; $a^H_{NH} = 11.67$; $a^H_{o,p} = 2.96$; $a^H_m = 0.96$ G.

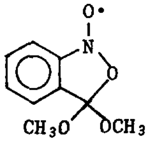
This spectrum is assigned to an aryl hydronitroxyl radical (III) with an electron withdrawing substitutent in the ortho position (5):



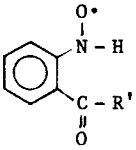
III

Photolysis of solutions of o-nitrobenzaldehyde ethylene acetal in benzene gave spectra due to II (major) and III (minor). Heating in benzene at refluxing temperatures produced spectra due to III even in the absence of a radical source.

o-Nitrobenzaldehyde dimethyl acetal (6) gave a strong signal due to V. Treatment with tert-butoxy radicals produced a mixture spectrum of three components. Spectra similar to Figure 1(a) and (b) are assigned to IV and V but the third component cannot be assigned at this time.



IV



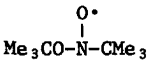
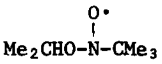
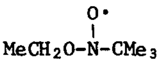
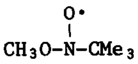
V

$a_N = 15.55$; $a^H_{o,p} = 3.16$; $a^H_m = 1.03$ G

$a_N = 7.84$; $a^H_{NH} = 11.59$; $a^H_{o,p} = 2.91$; $a^H_m = 0.96$ G

o-Nitrobenzyl alcohol and o-nitrobenzyl methyl ether also gave nitroxyl type spectra with tert-butoxy radicals but the patterns are complex and clearly due to mixtures of radicals. These reactions and the scope of intramolecular spin trapping by the ortho-nitro function are being investigated further.

It is of interest to compare the nitrogen hyperfine splitting constants (N-hfsc) of the cyclic and open chain aryl nitroxyls with those of alkoxy alkyl nitroxyls. The latter have characteristically larger N-hfsc's than dialkyl nitroxyls; compare a_N for di-tert-butyl nitroxyl (7) a_N = 15.1 (hexane), 17.2 (water) G with the following:

	 $Me_3CO\text{-}\overset{O\bullet}{N}\text{-}CMe_3$	 $Me_2CHO\text{-}\overset{O\bullet}{N}\text{-}CMe_3$	 $MeCH_2O\text{-}\overset{O\bullet}{N}\text{-}CMe_3$	 $CH_3O\text{-}\overset{O\bullet}{N}\text{-}CMe_3$
a_N =	27.0 G	29 G	29.1 G	29.6 G
a_H =	–	–	1.1	1.4
solvent:	tert-butanol	2-propanol	ethanol	methanol
reference:	8	9	10	10,11

This difference is not nearly as large when alkoxy aryl nitroxyls are compared with alkyl aryl nitroxyls. With certain substitutents the range of the N-hfsc's overlaps for these two kinds of radicals:

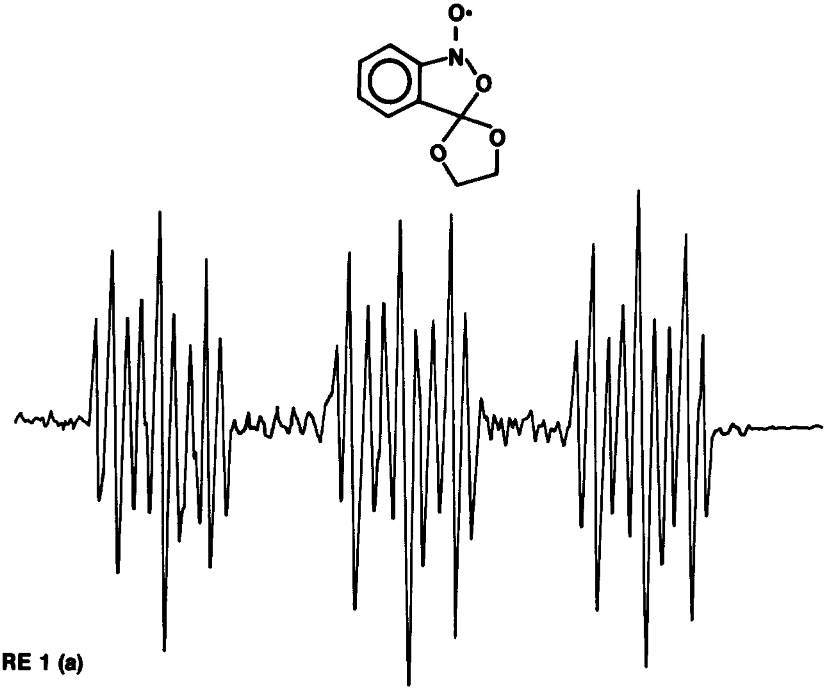


FIGURE 1 (a)

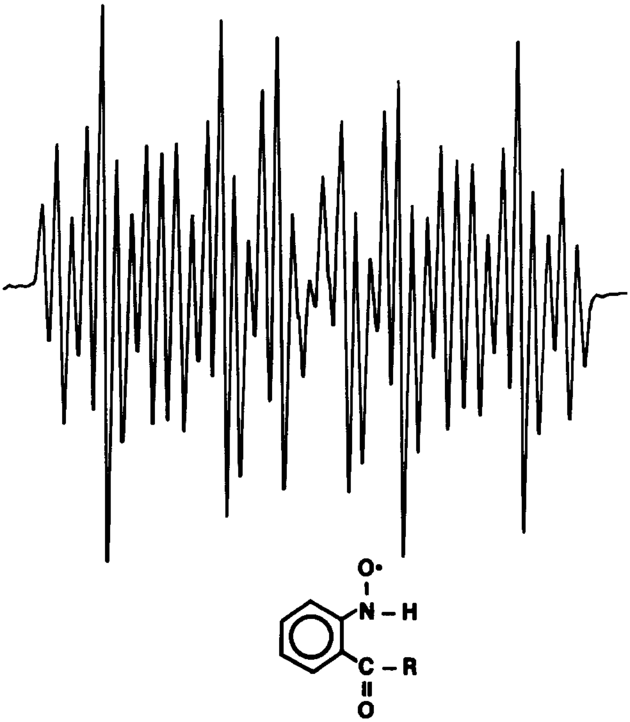
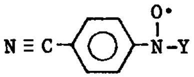
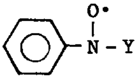
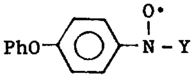
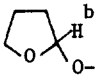
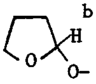
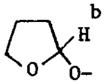


FIGURE 1 (b)







Y =	Me$_3$C–[a]	[b]	Me$_3$C–[a]	[b]	Me$_3$C–[a]	[b]
a_N =	11.3	12.95	13.4	15.06	13.5	15.75
a_o^H =	2.32	3.03	1.9	2.98	1.80	2.99
a_m^H =	0.92	1.04	0.8	1.13	0.77	1.00
a_α^H =	—	—	—	0.32	—	0.35
a_p =	0.35(N)	1.04(N)	1.9	2.98	—	—

(a) in ethylene glycol (12)
(b) in tetrahydrofuran (13)

The N-hfsc for I and II fall within the range of substituted alkoxy aryl nitroxyls studied as do the H-hfsc's for the aryl hydrogens. Thus if the nitroxyl function in the 5-membered ring is assumed to be planar (as has been found to be the case in alicyclic 5-membered ring nitroxyls (14)) a comparison of the esr parameters indicates that the nitroxyl function in the non-cyclic alkoxy aryl nitroxyls is probably also planar. Whether the relatively large N-hfsc in alkoxy alkyl nitroxyls is due to non-planarity about nitrogen or increased spin density on nitrogen cannot be answered at this time. This question will be investigated further.

Acknowledgement

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References

1. A.L.J. Beckwith and M.D. Lawton, J. Chem. Soc., Perkin II, 2134 (1973).
2. W.E. Griffiths, G.F. Longster, J. Myatt and P.F. Todd, J. Chem. Soc. (B), 1130 (1966); 533 (1967); M. McMillan and R.O.C. Norman, J. Chem. Soc. (B), 590 (1968).
3. D.J. Cowley and L.H. Sutcliff, Chem. Commun., 201 (1968); J. Chem. Soc. (B), 590 (1970); E.G. Janzen and J.L. Gerlock, J. Am. Chem. Soc., 91, 3108 (1969); see R.L. Ward, J. Chem. Phys., 38, 2588 (1963) for first publication of this type of spectrum.
4. H.E. Baumgarten, D.L. Pedersen and M.W. Hunt, J. Am. Chem. Soc., 80, 1977 (1958).
5. Th. A.J.W. Wajer, M. Mackor, T.J. de Boer and J.D.W. van Voorst, Tetrahedron Lett., 1941 (1967).
6. D.J.W. Goon, N.G. Murray, J-P Schoch and N.J. Bunce, Can. J. Chem., 51, 3827 (1973).
7. B.R. Knauer and J.J. Napier, J. Am. Chem. Soc., 98, 4395 (1976).
8. F.P. Sargent and E.M. Gardy, Can. J. Chem., 52, 3645 (1974); A. Mackor, Th. A.J.W. Wajer, Th. J. de Boer and J.D.W. van Voorst, Tetrahedran Lett., 385 (1967).
9. F.P. Sargent and E.M. Gardy, J. Phys. Chem., 81, 1215 (1977).
10. F.P. Sargent and E.M. Gardy, J. Phys. Chem., 80, 854 (1976).
11. C. Lagercrantz, J. Phys. Chem., 75, 3466 (1971).
12. A.R. Forrester, J.M. Hay and R.H. Thomson, "Organic Chemistry of Stable Free Radicals", Academic Press, New York, N.Y. 1968, p. 202.
13. J.L. Gerlock, "ESR Study of Mono-, Di- and Trinitrobenzene Photolysis in Tetrahydrofuran", Ph.D. Dissertation, University of Georgia, Athens, Georgis, 1970.
14. J. Lajzerowics-Bonneteau in "Theory and Application", L.J. Berliner, editor, Academic Press, New York, N.Y., 1976, Ch. 6, pp. 239-249.

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