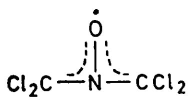
Revised Assignment of the Electron Spin Resonance Spectrum obtained during Photolysis of *N*-(Diphenylmethylene)methylthiomethylamine *N*-Oxide. The Bis(methylthiomethyl) Nitroxide Radical

By **George Brunton** and **Keith U. Ingold,*** Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A OR9

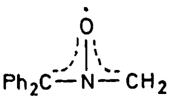
Photolysis of *N*-(diphenylmethylene)methylthiomethylamine *N*-oxide, $Ph_2C{=}N(\rightarrow O)CH_2SCH_3$, yields bis(methylthiomethyl) nitroxide, $(CH_3SCH_2)_2N\dot{O}$, rather than, as previously reported, the diphenylmethylene(methylene)amine *N*-oxyl radical, $[Ph_2C\overset{\cdots}{—}N(\overset{\cdots}{—}O)\overset{\cdots}{—}CH_2]^{\bullet}$. The e.s.r. spectrum of $(CH_3SCH_2)_2N\dot{O}$ shows an alternating line width effect at ambient and lower temperatures.

NITROXIDE radicals have been studied assiduously during the past few years.[1] They have an inherently stable electronic arrangement around the nitrogen and oxygen atoms [1] which makes dimerization *via* the NO portions of two radicals a rather unfavoured process.[2] Indeed, it has been pointed out [1] that certain organic systems which increase the delocalization of the unpaired electron (*e.g.*, phenyl) have a potentially 'destabilizing' effect because they increase the number of reactive positions in the radical.

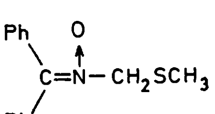
In previous work from this laboratory [3] we have studied the kinetics and mechanism by which a variety of organic nitroxides decay and have investigated various factors which influence the persistence of these radicals. It was with considerable interest, therefore, that we read reports on the detection of the delocalized radicals (1) [4] and (2).[5] Radical (1) was reported to be formed during the reaction of chlorine or phenyl radicals with the nitrone, $Cl_3CN(O){=}CCl_2$. However, it has been suggested [6] that the e.s.r. spectrum assigned to (1) is actually due to the acyl nitroxide, $ClC({=}O)N(\dot{O})CCl_3$, since such species are known to be formed from halogen-containing nitroxides.[7,8]



(1)



(2)



(3)

Structure (2) was assigned by Wilson and his co-workers [5] to a radical detected during the thermal or photolytic decomposition of *N*-(diphenylmethylene)-methylthiomethylamine *N*-oxide (3). As a continuation of our studies on novel types of persistent radicals [9] we decided to reinvestigate this decomposition.

RESULTS

A sample of compound (3) in carbon tetrachloride was found to exhibit a weak e.s.r. spectrum prior to photolysis. On photolysis in the cavity of the spectrometer with the unfiltered light from a 500 W high pressure mercury lamp the intensity of this signal at first increased quite considerably, but after *ca.* 10 min of continuous photolysis the signal had disappeared. The e.s.r. spectrum obtained at 20° in carbon tetrachloride is shown in Figure 1. It consists of *nine* major groups of lines rather than the *seven* previously

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

[2] G. D. Mendenhall and K. U. Ingold, *J. Amer. Chem. Soc.*, 1973, **95**, 6390.

[3] (*a*) K. Adamic, D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1971, **93**, 902; (*b*) D. F. Bowman, J. L. Brokenshire, T. Gillan, and K. U. Ingold, *ibid.*, p. 6551; (*c*) D. F. Bowman, T. Gillan, and K. U. Ingold, *ibid.*, p. 6555; (*d*) G. D. Mendenhall, and K. U. Ingold, *ibid.*, 1973, **95**, 6395.

[4] V. Astley and H. Sutcliffe, *Chem. Comm.*, 1971, 1303.

[5] J. C. Evans, E. D. Owen, and D. A. Wilson, *J.C.S. Perkin II*, 1974, 557.

[6] B. C. Gilbert, in 'Electron Spin Resonance,' Chem. Soc. Specialist Periodical Reports, 1973, vol. 1, ch. 9.

[7] R. J. Holman and M. J. Perkins, *Chem. Comm.*, 1971, 244.

[8] J. W. Hartgerink, J. B. F. N. Engberts, and Th. J. de Boer, *Tetrahedron Letters*, 1971, 2709.

[9] (*a*) G. D. Mendenhall, D. Griller, and K. U. Ingold, *Chem. in Brit.*, 1974, **10**, 248; (*b*) D. Griller and K. U. Ingold, *Accounts Chem. Res.*, 1976, **9**, 13.

reported (but see Figure 1 of ref. 5, which does, in fact, show evidence of two more lines outside the seven reported). An identical spectrum could be produced by photolysis of (3) in a variety of solvents (*e.g.*, benzene, cyclopropane, Freon 12, *etc.*) which rules out any possibility that the radical is derived from a reaction with a photolabile solvent. The resolution of the e.s.r. spectra depends on the temperature (see below). Under no conditions was the previously reported [5] single line at g 2.001 detected.

The e.s.r. spectral parameters for our radical and those reported by Wilson and his co-workers [5] are given in the Table. Comparison of these parameters and comparison of the spectra leaves no doubt that the radicals are identical and that the earlier assignment [5] resulted from failure to observe the two outermost multiplets. That is, the previous workers interpreted their spectra in terms of *two* methylene protons (a^H 0.66 mT) rather than *four*. Their septet (a^H 0.078 mT) was assigned to six equivalent ring protons (4 *ortho* + 2 *para*) and they also reported an additional splitting (4 *meta*) of 0.018 mT which we were unable to observe under any conditions.

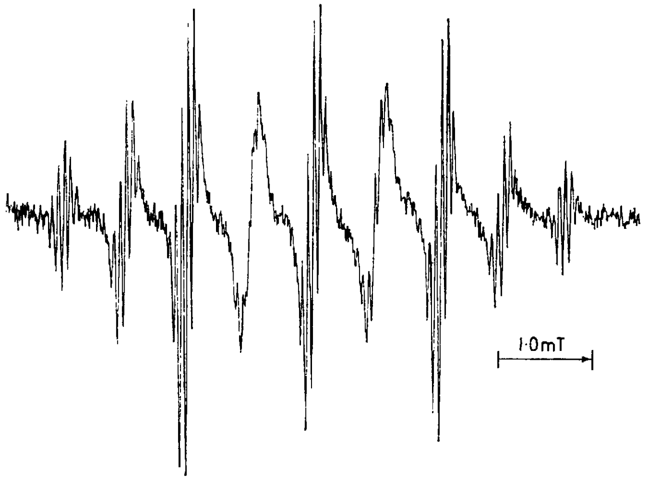
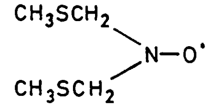


FIGURE 1 E.s.r. spectrum obtained by photolysis of (3) in CCl_4 at 20°

E.s.r. parameters for the radical derived by photolysis of (3) in CCl_4 at 20° (h.f.s. in mT)

This work		Ref. 5	
g	2.006 26	g	2.006 2
a^N	1.350	a^N	1.35
$a^H(4H)$	0.660	$a^H(2H)$	0.66
$a^H(6H)$	0.065	$a^H(6H)$	0.078
		$a^H(4H)$	0.018
Assigned to (4)		Assigned to (2)	

Our e.s.r. spectrum is completely inconsistent with radical (2). However, it is consistent with the spectrum expected for bis(methylthiomethyl) nitroxide (4). This radical has


(4)

not previously been characterized and we were not able to synthesize two potential precursors, $(CH_3SCH_2)_2NH$ or $(CH_3SCH_2)_2NOH$. However, photolysis of a mixture of dimethyl sulphide and n-butyl nitrite (5 : 1 v/v) at −20° gave a spectrum in which the highest and lowest field multiplets due to (4) were unmistakable. The seven more central multiplets of (4) were, unfortunately, masked by signals due to other radicals. This experiment provides unequivocal proof that the 0.065 mT septet is not due to six aromatic protons. The formation of (4) in this system can be understood in terms of an initial photolysis of the nitrite [10] and subsequent reactions of the n-butoxyl radical and nitric oxide (Scheme 1).

$$Bu^nONO \xrightarrow{h\nu} Bu^nO^{\bullet} + NO$$

$$Bu^nO^{\bullet} + CH_3SCH_3 \longrightarrow Bu^nOH + CH_3S\dot{C}H_2$$

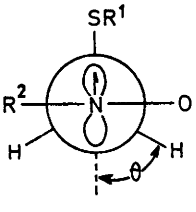
$$CH_3S\dot{C}H_2 + NO \longrightarrow CH_3SCH_2NO$$

$$CH_3S\dot{C}H_2 + CH_3SCH_2NO \longrightarrow (CH_3SCH_2)_2N\dot{O}$$

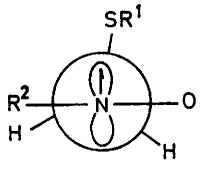
SCHEME 1

DISCUSSION

There are a number of interesting features in the e.s.r. spectrum shown in Figure 1 which aid its characterization and favour its assignment to radical (4) rather than to (2). The magnitude of the hyperfine splittings (h.f.s.) by the four equivalent protons (0.660 mT) is characteristic of a nitroxide of the type $R^1SCH_2N(\dot{O})R^2$.[11] This characteristic h.f.s. arises because the alkylthiomethyl group favours a conformation in which the SR^1 group is eclipsed or nearly eclipsed, by the N $2p_z$ orbital, *i.e.*, (5) or (6) if we assume planarity at nitrogen. As a consequence, the dihedral angle, θ, between the β-protons and the N $2p_z$ orbital is *ca.* 60° and so the β-proton h.f.s. are about half as large as those of related nitroxides in which free rotation can occur [12] [*e.g.*, 1.23 mT in $(CH_3)_2N\dot{O}$ [13] in which the average value of θ is 45°].



(5)



(6)

The multiplet having a^H 0.065 mT (or 0.078) [5] was previously assigned to six of the ring protons of (2), while we assign it to the six methyl protons of (4). As Wilson has pointed out,[5] this splitting cannot be due to the ring protons of a nitroxide formed by radical addition to the nitrone, *i.e.*, $XPh_2CN(\dot{O})CH_2SCH_3$ since the preferred conformation of such a nitroxide would prevent appreciable interaction between the unpaired electron and the ring protons.[14] In fact, we have shown that at ambient and lower temperatures this nitrone does not act as a spin trap towards thermally or photochemically generated $(CH_3)_3CO^{\bullet}$ and $(EtO)_2\dot{P}{=}O$ radicals. In these

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[10] P. A. S. Smith, 'The Chemistry of Open-chain Organic Nitrogen Compounds,' Benjamin, New York, 1966, vol. 2, p. 466.

[11] G. Brunton, B. C. Gilbert, and R. J. Mawby, *J.C.S. Perkin II*, 1976, 650.

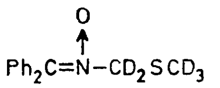
[12] See *e.g.*, H. Fischer in 'Free Radicals,' ed. J. K. Kochi, Wiley, New York, 1973, vol. 2, ch. 19.

[13] J. Q. Adams, S. N. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, 1966, **45**, 654.

[14] See *e.g.*, E. G. Janzen, *Topics Stereochem.*, 1971, **6**, 177.

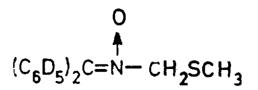
experiments only the spectrum due to (4) could be observed.

Wilson and his co-workers supported the assignment of their e.s.r. spectrum to (2) by a series of experiments with three deuteriated analogues of (3), compounds (7)—(9).[5] We propose an alternative interpretation of their spectra which is consistent with our assignment of structure (4).



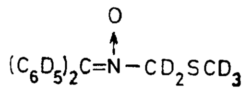
$Ph_2C{=}\overset{\overset{O}{\uparrow}}{N}{-}CD_2SCD_3$

(7)



$(C_6D_5)_2C{=}\overset{\overset{O}{\uparrow}}{N}{-}CH_2SCH_3$

(8)



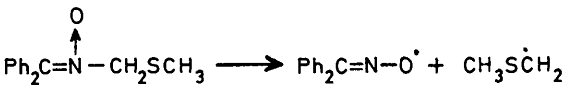
$(C_6D_5)_2C{=}\overset{\overset{O}{\uparrow}}{N}{-}CD_2SCD_3$

(9)

Photolysis of (7) and (9) would, in our view, yield the perdeuteriated nitroxide, $(CD_3SCD_2)_2N\dot{O}$. This radical should have an e.s.r. spectrum showing a nitrogen triplet (a^N 1.35 mT) with further splitting into nine-line multiplets with relative intensities of 1 : 4 : 10 : 16 : 19 : 16 : 10 : 4 : 1 due to the four equivalent deuteriums (^2H has a nuclear spin of 1). Since the H/D magnetogyric ratio is 6.5[15] the h.f.s. due to the deuterium will be *ca.* 0.1 mT and splitting by the six equivalent deuteriums will be too small to detect. These parameters provide a perfectly reasonable interpretation of the spectra obtained from (7) and (9) (see Figures 3 and 5 in ref. 5). Thus, in the case of (7) all 27 lines appear to be nicely resolved, but the reported h.f.s. were ^{14}N 1.34 (3 lines), methylene 0.100 (5 lines), *ortho* and *para* 0.099 (7 lines), (0.100 − 0.099 = 0.001, which is somewhat surprising resolution for a line width of 0.03), *meta* 0.02 (2 lines! but this splitting is not visible in the published spectrum). In the case of (9) the spectrum is less well resolved showing only 5 lines (0.099) rather than 9 in each triplet (1.38). In the case of (8), the spectrum (Figure 4 of ref. 5) appears to be due to the same radical as that derived from (3) though it is less well resolved. The e.s.r. parameters are given as ^{14}N 1.36 (3 lines), methylene 0.66 (3 lines) and it is stated that *ortho*- and *para*-deuteriums are not resolved. However, the published spectrum shows the 0.065 (or 0.078) splitting quite clearly that was attributed to the *ortho*- and *para*-hydrogens in the radical derived from (3).

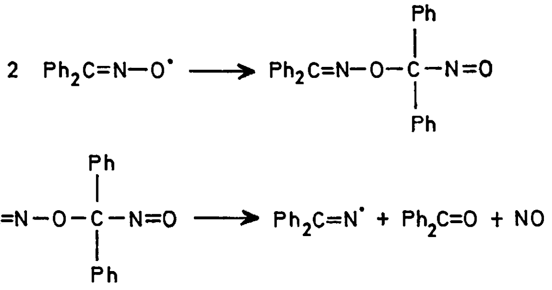
On the basis of the foregoing results and discussion we believe that we have established unequivocally that the e.s.r. spectrum observed during the decomposition of (3) is due to the nitroxide (4) and not to the delocalized nitroxide (2).

The mechanism by which (4) is produced is uncertain. Since the e.s.r. spectrum due to (4) disappears fairly rapidly during continuous photolysis there is a distinct possibility that (4) is produced by a minor side reaction. If this is indeed the case, product studies after extensive photolysis[5,16] (or thermolysis)[17] are unlikely to reveal the mechanism by which (4) is formed. Two possible routes to (4) have suggested themselves to us. In the first place, it has been reported[18] that (3) can be hydrolysed by acid to give among other products, the hydroxylamine $(CH_3SCH_2)_2NOH$, which is an obvious precursor for the nitroxide. Secondly, (4) might be formed from the nitrone by initial cleavage of the N–CH_2 bond (Scheme 2).[19] The diphenyliminoxyl radical is known to decay to give benzophenone as one of the major products.[20] By analogy with other dialkyliminoxyl radicals[20,21] it seems likely that benzophenone is formed, at least in part, *via* an initial head-to-tail coupling of the radicals, followed by decomposition of this dimer as in Scheme 3. The nitric oxide and $CH_3S\dot{C}H_2$ radical would lead to (4) in the manner indicated earlier.



$$Ph_2C{=}\overset{\overset{O}{\uparrow}}{N}{-}CH_2SCH_3 \longrightarrow Ph_2C{=}N{-}O^{\bullet} + CH_3S\dot{C}H_2$$

SCHEME 2



$$2\ Ph_2C{=}N{-}O^{\bullet} \longrightarrow Ph_2C{=}N{-}O{-}\underset{Ph}{\overset{Ph}{C}}{-}N{=}O$$

$$Ph_2C{=}N{-}O{-}\underset{Ph}{\overset{Ph}{C}}{-}N{=}O \longrightarrow Ph_2C{=}N^{\bullet} + Ph_2C{=}O + NO$$

SCHEME 3

Finally, we note that the formation of a nitroxide by the decomposition of a nitrone is not unique. For example,[22] the thermolysis or photolysis of $C_6H_5CH{=}N(\rightarrow O)CMe_3$ yields $(Me_3C)_2NO^{\bullet}$.

Wilson also reported[5] that a single line spectrum (*g* 2.001) was observed during photolytic studies. We could not reproduce this observation. The single line was tentatively assigned to $CH_3S^{\bullet}$, but this cannot be correct since it is now accepted that alkylthiyl radicals cannot be detected by e.s.r. spectroscopy in solution because of extreme line broadening arising from a

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[15] J. E. Wertz and J. R. Bolton, 'Electron Spin Resonance,' McGraw-Hill, New York, 1972.

[16] W. M. Leyshon and D. A. Wilson, *J.C.S. Perkin II*, 1975, 1925.

[17] I. W. Jones, D. A. Kerr, and D. A. Wilson, *J. Chem. Soc.* (*C*), 1971, 2595.

[18] I. W. Jones, D. A. Kerr, and D. A. Wilson, *J. Chem. Soc.* (*C*), 1971, 2591.

[19] J. S. Vincent and E. J. Grubbs, *J. Amer. Chem. Soc.*, 1969, **91**, 2022; J. A. Villarreal and E. J. Grubbs, *ibid.*, 1974, **96**, 7594.

[20] J. L. Brokenshire, J. R. Roberts, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1972, **94**, 7040.

[21] G. D. Mendenhall and K. U. Ingold, *J. Amer. Chem. Soc.*, 1973, **95**, 2963.

[22] K. Sommermeyer, W. Seiffert, and W. Wilker, *Tetrahedron Letters*, 1974, 1821.

marked anisotropy of the *g* factor.[23] Previous assignments of spectra to this class of radical have been questioned recently.[23]

Variable Temperature Studies.—The e.s.r. spectrum of (4) shows an alternating line width effect (see Figure 2). At 40° all the lines are well resolved, but as the temperature is lowered the $m_I = \pm\frac{1}{2}$ lines due to the methylene protons broaden and become virtually undetectable at temperatures in the range —60 to —80°. At still lower temperatures new lines appear, which indicates that the four methylene protons are no longer equivalent.

There are two different effects, either or both of which could contribute to the temperature dependence of the spectrum. In the first place, radical (4) can exist in two energetically equivalent conformations in which the four methylene hydrogens divide into two pairs (an α and a β pair) with the methylene hydrogens of each methylthiomethyl group being non-equivalent, *i.e.*, (10) and (11) if we assume a planar nitrogen and a fully eclipsed SCH_3 group. At temperatures above ambient rapid rotation about the N–C bond will make the α- and β-protons equivalent. As the temperature is lowered, rotation slows down, and these two protons become non-equivalent. This kind of phenomenon has been used to explain alternating line width effects in a number of nitroxides.[24,25] Alternatively, in a nitroxide such as (4) the four methylene protons may divide into two pairs (the α- and β-protons) as a consequence of restricted

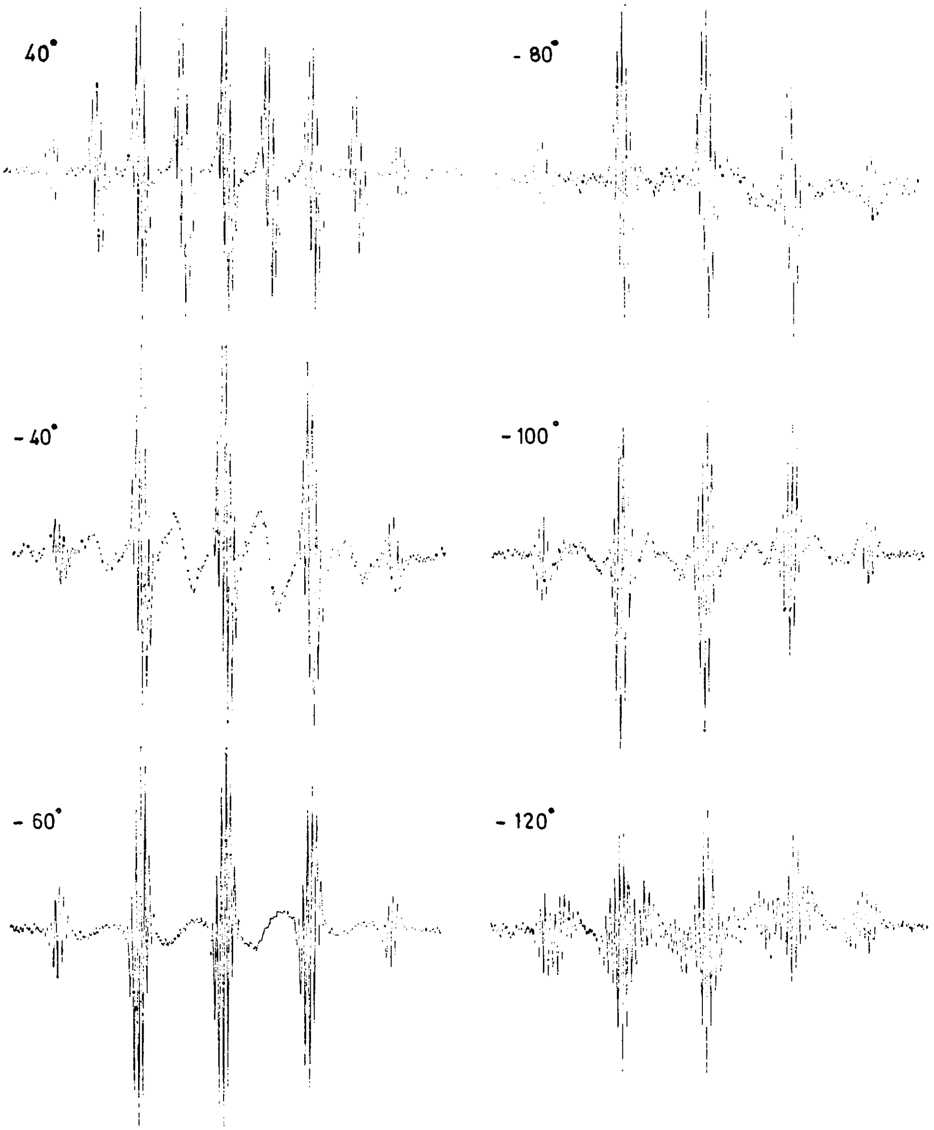

FIGURE 2 E.s.r. spectra obtained by photolysis of (3). The +40° spectrum was measured in benzene. All other spectra were measured in cyclopropane

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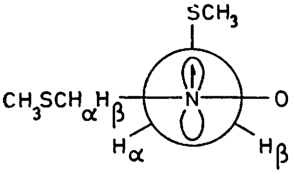
[23] See M. C. R. Symons, *J. Amer. Chem. Soc.*, 1969, **91**, 5924; *J.C.S. Perkin II*, 1974, 1618; B. C. Gilbert, H. A. H. Laue, R. O. C. Norman, and R. C. Sealy, *ibid.*, 1975, 892.

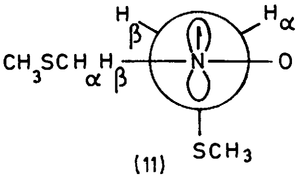
[24] G. Chapelet-Letourneux, H. Lemaire, R. Lenk, M. A. Marechal, and A. Rassat, *Bull. Soc. chim. France*, 1968, 3963.

[25] O. W. Maender and E. G. Janzen, *J. Org. Chem.*, 1969, **34**, 4072.

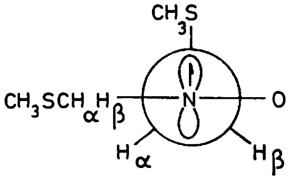
rotation about the $CH_3S{-}CH_2$ bonds, *i.e.* (10) and (12). In this case, the two conformers will probably not be of exactly equal energy. This kind of phenomenon has been used to explain line width effects in $CF_3SCH_2\dot{C}H_2$ [26] and in $CF_3SCH_2\dot{C}(CMe_3)_2$.[27]



(10)



(11)



(12)

Fortunately, the rate constant k for the process which makes the methylene protons magnetically equivalent can be calculated without knowing the mechanism. The temperature of maximum line broadening is *ca.* −70° and at this temperature $k = 6.22 \times 10^7 \Delta a$ s^{-1},[28] where Δa (in mT) is the difference in the hyperfine splittings of H_α and H_β. From the spectrum at −120°, Δa is *ca.* 1.0 mT, and therefore $k = 6 \times 10^7$ s^{-1} at −70°.

EXPERIMENTAL

Our e.s.r. procedures have been adequately described elsewhere.[29] The *N*-(diphenylmethylene)methylthiomethylamine *N*-oxide (3), was prepared from benzophenone oxime [30] by Miss J. F. Taylor using the method previously described,[31] except that a reaction time of 12 h was found to give the nitrone in higher yield. All other compounds were commercial materials that were used without purification.

Repeated attempts to synthesize $(CH_3SCH_2)_2NH$ or $(CH_3SCH_2)_2NOH$ from which the nitroxide (4) could be unequivocally generated by oxidation were unsuccessful. Thus, although chloromethyl methyl sulphide reacted directly with liquid ammonia [32] no free amine could be isolated on subsequent basification with sodium hydroxide. Similarly, when chloromethyl methyl sulphide was reacted with potassium phthalimide to form *N*-methylthiomethyl phthalimide, m.p. 112—113°, δ ($CDCl_3$) 2.22 (CH_3) and 4.70 (CH_2) no free amine could be isolated following hydrolytic decomposition of the phthalimide with hydrazine hydrate.[33] Attempts to synthesize $(CH_3SCH_2)_2NOH$ by reaction of chloromethyl methyl sulphide with hydroxylamine were also unsuccessful.

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[5/2303 *Received, 25th November,* 1975]

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[26] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1971, **93**, 846.

[27] D. Griller and K. U. Ingold, *J. Amer. Chem. Soc.*, 1974, **96**, 6715.

[28] G. A. Russell, G. R. Underwood, and D. C. Lini, *J. Amer. Chem. Soc.*, 1967, **89**, 6636.

[29] See ref. 3*a* and subsequent papers in this series.

[30] A. Lachman, in ' Organic Syntheses,' ed. by A. H. Blatt, Wiley and Sons, New York, 1948, Coll. Vol. II, p. 70.

[31] D. A. Kerr and D. A. Wilson, *J. Chem. Soc.* (*C*), 1970, 1718.

[32] See *e.g.*, L. Jirousek and J. V. Kostir, *Chem. Listy*, 1949, **43**, 183.

[33] J. C. Sheehan and W. A. Bolhofer, *J. Amer. Chem. Soc.*, 1950, **72** 2786.