Photochemical Reactions of *N*-(Diphenylmethylene)methylthiomethylamine *N*-Oxide. The Diphenylmethylene(methylene)amine *N*-Oxyl Radical †

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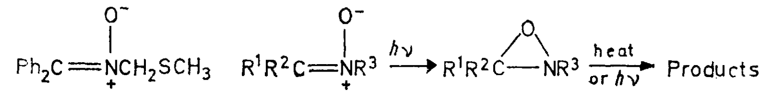
U.v. irradiation of the title compound in carbon tetrachloride and deuteriochloroform solutions cleanly gave benzophenone and eventually, but less cleanly, dimethyl disulphide. Initial homolysis gave the diphenylmethylene(methylene)amine *N*-oxyl radical which was detected and identified by e.s.r. spectroscopy. A second radical, possibly the methylthiyl radical, was observed. Subsequent reactions gave benzophenone and *N*-methylthiomethyleneamine, which in turn, photochemically and thermally, gave dimethyl disulphide and polymeric materials that in part involved chlorine abstraction from the solvent. The well-resolved e.s.r. spectra of the nitroxide radical have been analysed, and splitting constants have been assigned, by comparison with the spectra of partially and fully deuteriated nitroxides.

DIPHENYL *N*-(METHYLTHIOMETHYL)NITRONE ‡ (1) behaves rather differently from many other nitrones towards alkali,[1] acids,[2] and thermally.[3] We have already briefly reported that when heated, this nitrone generated radicals that were detected by e.s.r. spectroscopy, that the same radicals were also formed photochemically, and structures were given for them.[3] We now report our initial study of the photochemical formation and subsequent reactions of these radicals, and our analysis of their e.s.r. spectra.

The usual photochemical reaction of a nitrone is formation of an oxaziridine (2), which may be isolable, or which may react further thermally,[4] or photochemically forming a nitrene,[5] although one case of photochemical deoxygenation has recently been reported,[6] as has photochemical oxidation.[7] Radical addition to nitrones is also well known.[8]

RESULTS AND DISCUSSION

Solutions of the methylthiomethylnitrone (1) (0·125—0·475M) in carbon tetrachloride or deuteriochloroform were irradiated at room temperature with unfiltered light (λ > 300 nm) from a medium pressure mercury lamp. Thin-walled Pyrex glass tubes (n.m.r. tubes), thick-walled Pyrex tubes, and silica tubes were all used, with no variation in the overall reaction, only in the rate of loss of nitrone. In some samples the solvent was carbon tetrachloride vacuum-distilled from phosphorus pentoxide and degassed, while other solutions were degassed but not especially dried. Water and oxygen were deliberately added to other samples. From these experiments, neither oxygen nor water had any effect on the course of the reaction, the progress of which was followed by n.m.r. spectroscopy.



(1) (2)

On irradiation, the SCH_3 and CH_2 n.m.r. signals of the nitrone decreased in intensity, while a new SCH_3 signal appeared. The CH_2 signal of the nitrone was not at first replaced by any signal in the region τ 3—7. The aromatic proton region showed an increasing presence of benzophenone, whilst integration revealed the missing CH_2 intensity to be in the region τ 2·4—2·7. By using their low-field absorptions, the ratio of nitrone (2H at τ 2·0) to benzophenone (4H at τ 2·1—2·3) could be determined. As irradiation proceeded, the intermediate SCH_3 signal decreased in intensity to be replaced mainly by the signal due to dimethyl disulphide (5) (n.m.r. and g.l.c.), and one or two minor unidentified signals. A new CH_2 signal appeared, but not of sufficient intensity to balance the dimethyl disulphide, and a light buff, flocculent precipitate formed at this time. The Experimental section records typical results.

Our interpretation of these changes is outlined in the Scheme, and supporting evidence for each step is then discussed.

Step (1).—Loss of nitrone was followed for dilute solutions (*ca.* 10^{-4}M) by monitoring the u.v. absorption [$\lambda_{max.}$ ($CHCl_3$) 310 (ε 12,000); $\lambda_{max.}$ (CCl_4) 314 nm (14,400)], and was first order for >75% of reaction, showing that the product benzophenone had no effect (quenching or sensitising) on this reaction rate at these concentrations. This was confirmed when no difference

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† Preliminary results were reported at the Chemical Society Autumn Meeting, York, 1971, paper A32.

‡ The title uses the I.U.P.A.C. name for this compound and for the nitroxide $[Ph_2CN(O)CH_2]$. The nitrone and nitroxide nomenclatures are more commonly used.

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

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

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

[4] M. Lamchen, ' Mechanisms of Molecular Migrations,' ed. B. Thyagarajan, Interscience-Wiley, New York, 1968, vol. I, p. 1; K. Koyano, Y. Mori, H. Suzuki, and I. Tanaka, *Bull. Chem. Soc. Japan*, 1970, **43**, 3582.

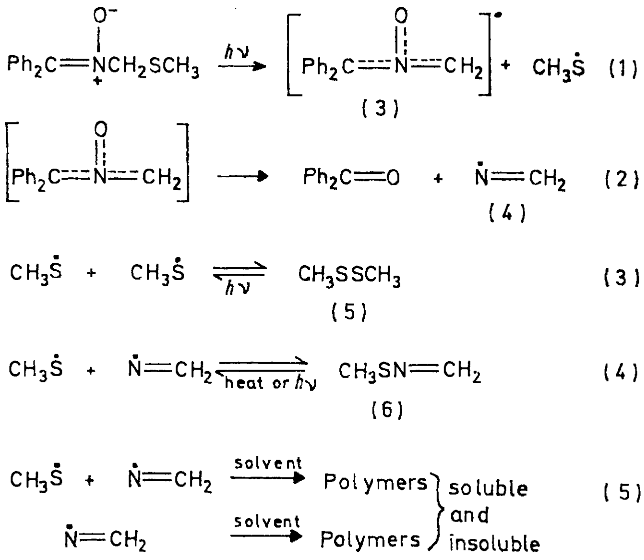
[5] M. Calvin and J. S. Splitter, *Tetrahedron Letters*, 1968, 1445.

[6] M. Calvin and J. S. Splitter, *Tetrahedron Letters*, 1970, 3995.

[7] A. L. Bluhm and J. Weinstein, *J. Amer. Chem. Soc.*, 1970, **95**, 1445.

[8] E. G. Janzen, *Accounts Chem. Res.*, 1971, **4**, 31.

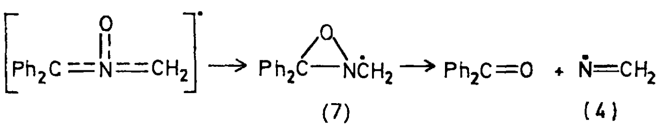
was observed between the rates using a solution of nitrone alone and a solution of nitrone with benzophenone added in an initially equimolar amount. A solvent effect was noted (rate ratio for $CCl_4 : CHCl_3$ was 1·3 : 1). Representative results are given in the Experimental section. When solutions were degassed, the absorption band of the nitrone was broadened and the rate of reaction was increased such that the act of taking the u.v. spectrum gave a measurable reaction. Investigations into the nature of the photoreactive species are in progress.



SCHEME

For the more concentrated solutions, studied by n.m.r., the initial rate of loss of nitrone was determined by the absorbed light intensity. Two radical species were detected by e.s.r. spectroscopy during the first 10% of reaction, and their identification is discussed in a separate section, below.

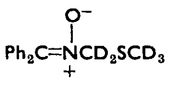
Step (2).—Loss of nitrone was accompanied by quantitative formation of benzophenone (n.m.r., i.r., t.l.c., 2,4-dinitrophenylhydrazone formation), and since the ketone was formed in dry degassed solutions, the oxygen atom of the ketone must have been that from the nitrone. This step might more explicitly involve the slow formation and rapid decay of a methyleneoxaziridine (7).



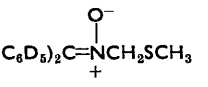
Step (3).—In the early stages of the reaction, the radical (3) was detected by e.s.r. spectroscopy a short time (<2 min) before the second signal built up to observable intensity, but dimethyl disulphide could not be detected by n.m.r. spectroscopy until late in the reaction, when the intermediate SCH_3 signal had begun to decay. These observations point to a rapid but reversible dimerisation of CH_3S to the disulphide (5), and slower reaction between the thiyl radical and the inferred imine radical[9] (4) when the latter became available from the decomposition of the nitroxide (3). It has been shown that dimethyl disulphide (5) is cleaved photolytically.[10]

Step (4).—The n.m.r. spectrum of the intermediate product had one SCH_3 signal, and the CH_2 signal was in the aryl region. Irradiation of the decadeuterionitrone (9) allowed the observation of this signal at τ 2·56 (2H, m, $W_{\frac{1}{2}}$ 5 Hz) increasing and decreasing in concert with the SCH_3 signal at τ 7·4. The *N*-methylthioimine structure (6) accommodates this evidence. An attempt to chromatograph a solution of this material in carbon tetrachloride on silica gel gave only dimethyl disulphide (5). Continued irradiation at room temperature gave the disulphide (5), whereas solutions containing the imine were unchanged during 24 h at room temperature without irradiation. A solution containing only benzophenone and the imine, when heated at 90° for 15 min showed considerable loss of imine and formation of the disulphide (5), together with the CH_2 signal assigned to soluble polymer, and some precipitate formed also.

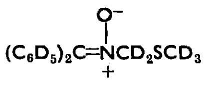
Step (5).—As reaction proceeded photochemically or thermally, a new CH_2 signal appeared in the n.m.r. spectrum, and a precipitate formed, which was analysed to contain (from a reaction open to the air) the elements C, H, N, Cl, S, and presumably O, in the approximate ratios 1 : 2·4 : 0·5 : 0·2 : 0·2 : 0·2. Thus some abstraction of chlorine from the solvent had taken place. On keeping at room temperature, the precipitate (presumably polymeric) smelt of methanethiol. Upon treatment with 2,4-dinitrophenylhydrazine in ethanol–hydrochloric acid, the precipitate gave the formaldehyde hydrazone (t.l.c., m.p. and mixed m.p.). A solution containing benzophenone and the imine (with 5% nitrone and 5% dimethyl disulphide) in carbon tetrachloride was taken to dryness at room temperature. The residual gum showed, in addition to the benzophenone, a series of slow-moving trailing spots on t.l.c., a CH_2 signal (τ 5·32) in its n.m.r. spectrum, and $\nu_{max.}$ 2960, 2920, and 2870 cm^{-1} attributable to saturated CH_2. This gum afforded a separable mixture of approximately equal amounts of the 2,4-dinitrophenylhydrazones of benzophenone and formaldehyde. The polymeric material that stayed in solution during the photochemical reaction probably contained $ClCH_2N^-$ and $^-OCH_2N^-$ units, with some SCH_3 groups incorporated in the precipitated material. There was finally insufficient disulphide (5) formed to balance the nitrone lost.


$Ph_2C{=}\overset{+}{N}(O^-)CD_2SCD_3$

(8)


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

(9)


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

(10)

Characterisation of the Radicals by E.s.r.—When a carbon tetrachloride solution of the nitrone (1) (*ca.* 5 × 10^{-3}M) was heated[3] to 180° or irradiated between −30 and 20° with u.v. light in the cavity of the e.s.r.

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[9] M. C. R. Symons, *Tetrahedron*, 1973, **29**, 615.

[10] J. J. Windle, A. K. Wiersema, and A. L. Tappel, *J. Chem. Phys.*, 1964, **41**, 1996.

spectrometer for a few minutes, a signal appeared which increased in intensity to a maximum in *ca.* 5 min (Figure 1). There were clearly two predominant radical species present giving rise to two signals, one *ca.* 5 G in width with g 2·001 (species I), and the other approximately 50 G in width with g 2·0062 (species II). On further irradiation, the wide absorption signal decreased in intensity to zero over a period of a few minutes, while the narrow signal, which had initially appeared after the wide one, remained virtually unchanged. If the u.v. lamp was turned off when the combined absorption was at a maximum, the same effect was observed but the absorption then decayed much more slowly.

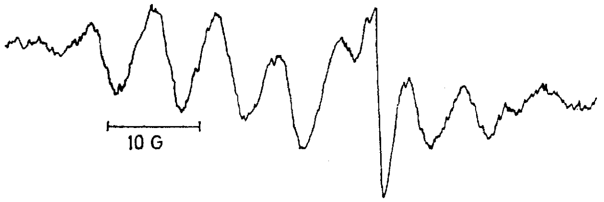


FIGURE 1 E.s.r. spectrum of the nitroxide and methylthiyl(?) radicals derived from the nitrone (1) at 20° in carbon tetrachloride

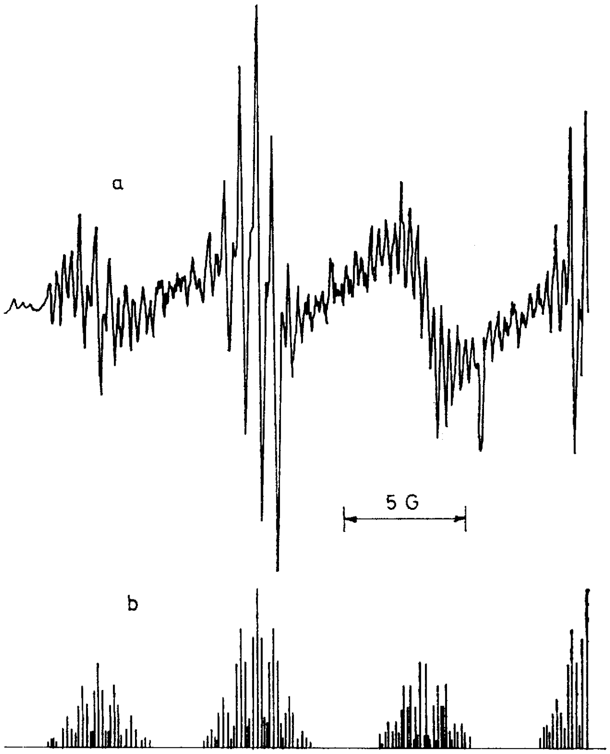


FIGURE 2 a, E.s.r. half-spectrum of the nitroxide radical (3) at 20° in carbon tetrachloride; b, computor simulated stick half-spectrum of radical (3), with splitting constants in Table 1. No allowance has been made for decay of radical during scan, for a possible anisotropy effect, or for a temperature effect possibly due to rotation about a C–N bond

Species I.—This signal, showing no hyperfine splitting, was observed on irradiating all the nitrones (1) and (8)—(10), and had the same g value in each case. Dimethyl disulphide was a major product of reaction, and a plausible explanation is that species I was the methylthiyl radical. However, the e.s.r. spectra cannot provide conclusive evidence for this. The appearance of this radical after the appearance of species II, and its continued presence after the disappearance of species II can be accounted for by the known reversible dimerisation of the radical [Scheme, step (3)]. Failure to detect the disulphide by n.m.r. in the early stages of photolysis is not inconsistent with the relative sensitivities of the e.s.r. and n.m.r. methods.

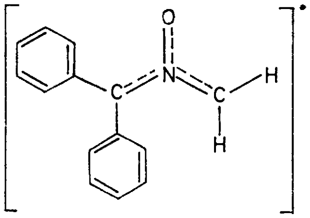
Species II.—Well-resolved spectra were obtained (Figure 2a), although the signal of the supposed methythiyl radical in the high-field half made the analysis more difficult, but it could be performed either by subtracting the spectrum of the methylthiyl radical, or by using the low-field half-spectrum and assuming the high-field half to be its mirror image. Both techniques were used.

The complex spectrum of species II (Figure 2a) arose from triplet splitting by ^{14}N, triplet splitting by two equivalent ^{1}H, septet splitting by six equivalent ^{1}H, and further small splitting presumably by four equivalent ^{1}H. Table 1 records these splitting constants, which are consistent with species II having the diphenylmethylene(methylene)amine *N*-oxyl structure (3). Figure 2b is a simulated half-spectrum using the parameters of Table 1. The chemical results discussed above can readily be accommodated by postulating this unusual nitroxide structure, and deuterium substitution experiments have made possible assignments of particular nuclei to particular splittings.

TABLE 1

Splitting constants for radical (3)

Atoms	Splitting constant (G)	Assignment
N	13·5	
2H	6·6	Methylene CH_2
6H	0·78	*ortho* and *para*
4H	0·18	*meta*



(3)

The three deuteriated nitrones (8)—(10) were prepared [11] and treated in exactly the same way as the parent nitrone (1). In each case, two radical species were observed, one possibly the SCX_3 radical ($X = H$ or D) and the other, species II, giving much wider e.s.r. spectra with the characteristic three groups of lines due to splitting by ^{14}N. Analysis of these spectra [Figures 3—5 from nitrones (8)—(10)] led to the assignments given in Table 2, supporting the nitroxide structure and

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[11] W. M. Leyshon and D. A. Wilson, *Org. Mass Spectrometry*, 1973, **7**, 251.

leading to the corresponding assignments for nitroxide (3), as noted in Table 1.

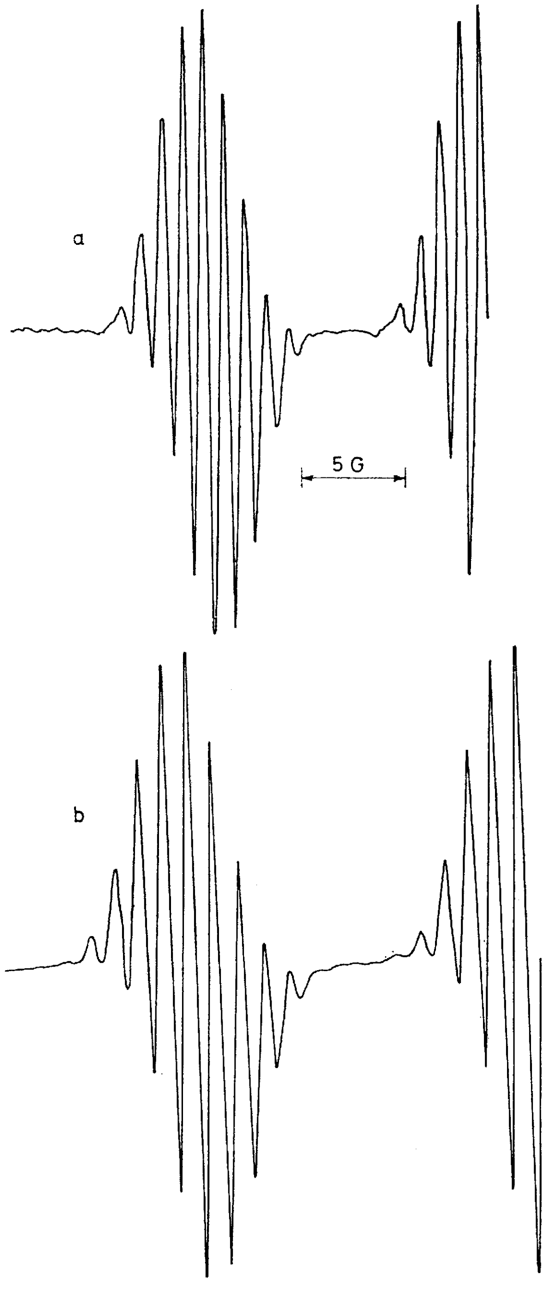

FIGURE 3 a, E.s.r. half-spectrum of the dideuterionitroxide radical derived from the nitrone (8) at 20° in carbon tetrachloride; computor simulated half-spectrum of the radical derived from nitrone (8), with line width 300 mG, and splitting constants in Table 2

TABLE 2

Splitting constants for radicals derived from nitrones (8)—(10)

	From (8) g 2·0063	From (9) g 2·0070	From (10) g 2·0071
^{14}N	13·4 G (3 lines)	13·6 G (3 lines)	13·8 G (3 lines)
Methylene	1·00 G (5 lines) [a]	6·6 G (3 lines)	0·99 G (5 lines) [a]
ortho and *para*	0·99 G (7 lines)	Not resolved	Not resolved
meta	0·2 G (2 lines) [b]	Not resolved	Not resolved

[a] Intensity ratio 1 : 2 : 3 : 2 : 1. [b] Not fully resolved; estimated from simulated spectrum (Figure 3b).

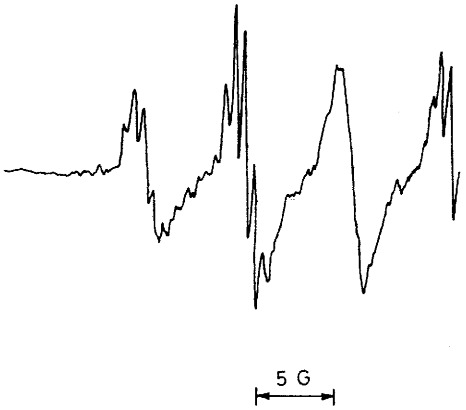

FIGURE 4 E.s.r. half-spectrum of the decadeuterionitroxide radical derived from the nitrone (9) at 20° in carbon tetrachloride

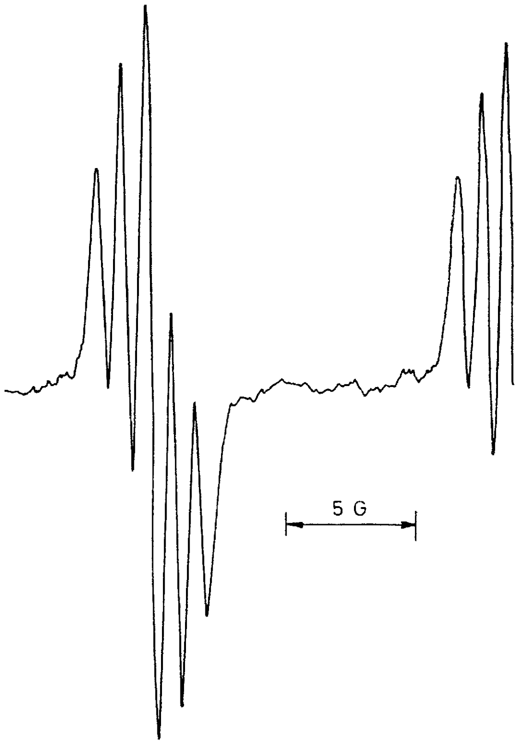

FIGURE 5 E.s.r. half-spectrum of the dodecadeuterionitroxide radical derived from the nitrone (10) at 20° in carbon tetrachloride

From a thermal reaction of diphenyl N-benzylhydrylnitrone, Vincent and Grubb[12] observed e.s.r. spectra attributable to the diphenyliminoxyl radical and a nitroxide radical arising from addition of a benzhydryl radical to the α-carbon atom of the nitrone. These possible structural types, as well as an oxaziridine structure, may be discounted for the radical species II reported herein.

The spectra shown in Figures 2—5 have nitrogen hyper-

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[12] J. S. Vincent and E. J. Grubb, *J. Amer. Chem. Soc.*, 1969, **91**, 2022.

fine interactions of *ca.* 13·5 G, and this is similar to values for radicals such as dibenzyl nitroxide (14·9 G)[13] and diphenyl nitroxide (10·9 G),[14] whereas iminoxyl radicals RR′C=NO•, prepared by numerous workers in recent years,[15] have nitrogen splitting of *ca.* 30 G. The possibilities that species II may have an oxaziridine structure [*cf.* (7)], or be a nitroxide derived from addition to the α-carbon atom to give a structure of type (11) can be dismissed, since in neither case would one expect to observe hyperfine splitting due to the hydrogens of the phenyl rings. For similar reasons, species II cannot be a radical formed by a dimerisation. No products of dimerisation or addition have been detected. Whereas in the iminoxyl radical (a_N *ca.* 30 G) the odd electron is contained in an orbital which is derived from a *p* orbital on oxygen and a non-bonding sp^2 orbital on nitrogen, giving a σ radical with *ca.* 45% of the unpaired spin associated with the nitrogen nucleus,[16] the radical (3) (a_N 13·5 G) would involve more extensive delocalisation and, one would expect, less σ character.

TABLE 3

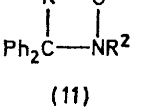
Composition of irradiated solutions, determined by n.m.r.

Time (min)	Nitrone(1) [a,b]	$Ph_2C=O$ [a]	Imine (6) [b]	$(CH_3S)_2$ [b]	Soluble polymer [c]	Other CH_3S [b]
(i) Nitrone (1) (0·16 M) in $CDCl_3$ in sealed n.m.r. tube (Pyrex; 4 mm i.d., 5 mm o.d.)						
0	100	0	0	0	0	0
15	78	22	22	0	0	0
45	37	63	59	0	0	4
75	18	82	76	Trace	Trace	5
135	0	*ca.* 100	50	25	10	10
195 *	0	*ca.* 100	33	53	23	6
(ii) Nitrone (1) (0·475M) in $CDCl_3$ in sealed n.m.r. tube						
0	100	0	0	0	0	0
15	92	8	8	0	0	0
45	75	25	25	0	0	0
75	67	33	34	0	0	0
135	40	60	53	Trace	0	5
195	18	82	73	5	6	4
(iii) Nitrone (1) (0·20M) in $CDCl_3$ in open silica tube (3 mm i.d., 4 mm o.d.)						
0	100	0	0	0	0	0
15	74	26	26	0	0	0
45	39	60	58	0	0	3
75	10	90	67	10	8	10
105 *	*ca.* 5	*ca.* 95	45	30	15	20
135 *	0	*ca.* 100	8	48	30	20

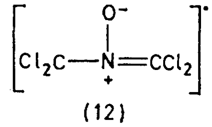
* Precipitate began to form by this time.

[a] % Derived from low-field aryl proton signals, ±4%. [b] % Derived from SCH_3 signals, ±2%. [c] % Derived from CH_2 signal compared to total integral, ±5%.

Subsequent to our initial report[3] of this nitroxide radical (3), Astley and Sutcliffe[17] briefly reported that chlorine atoms react with dichloro-*N*-trichloromethylnitrone by chlorine abstraction to give the bisdichloromethylene nitroxide (12), rather than by the expected chlorine addition to give bistrichloromethyl nitroxide. The nitrogen hyperfine splitting reported for radical (12) was 7·4 G.



(11)



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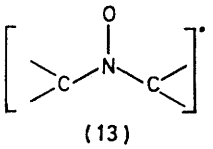

(13)

In the parent bismethylene nitroxide system (13), the two carbons, the nitrogen, and the oxygen, in addition to forming σ-bonds, each have available a *p* orbital, and linear combination of these will result in four molecular orbitals to accommodate five electrons. Thus in radical (3) the unpaired electron is delocalised over these four atoms and the two phenyl rings in a π-type molecular orbital resulting, overall, in a 17 π-electron system. Astley and Sutcliffe,[17] however, regard their radical (12) as an allyl system that did not involve the oxygen atom. A Hückel and McLachlan theoretical investigation is proceeding for radical (3) and others related to it in an attempt to resolve this difference.

EXPERIMENTAL

N.m.r. spectra were measured on a Perkin-Elmer R14 100 MHz instrument. G.l.c. experiments used a Perkin-Elmer 452 instrument with helium as carrier gas, and columns packed with polypropylene glycol (15%) on Chromosorb W, and silicone grease (20%) on Chromosorb P. Irradiations studied by n.m.r. and u.v. spectroscopy employed an Osram M.E.D. medium pressure mercury lamp, whilst irradiations studied by e.s.r. spectroscopy employed the same source or a Varian u.v. 100 lamp system. The e.s.r. spectra were recorded on a Varian E3 instrument fitted with a V 4540 temperature control. Hyperfine

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[13] J. Q. Adams, S. W. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, 1966, **45**, 654; J. R. Thomas, *J. Amer. Chem. Soc.*, 1960, **82**, 5955.

[14] J. C. Baird and J. R. Thomas, *J. Chem. Phys.*, 1961, **35**, 1507.

[15] B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1966, 86; 722; J. W. Lown, *ibid.*, pp. 441, 644; B. C. Gilbert and W. M. Gulick, jun., *J. Phys. Chem.*, 1969, **73**, 2448; B. C. Gilbert, V. Malatesta, and R. O. C. Norman, *J. Amer. Chem. Soc.*, 1971, **93**, 3290.

[16] M. C. R. Symons, *J. Chem. Soc.*, 1963, 1189; 1965, 2276; W. M. Fox and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1966, 1503.

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

splitting constants were measured with the Varian Fieldial attachment and by comparison with Fremy's salt (a_N 13·0 G). g Factors were measured in the normal way by comparison with diphenylpicrylhydrazyl. The temperature controller was calibrated by means of a prestandardised copper–constantan thermocouple. Solutions for e.s.r. study were degassed by bubbling nitrogen through them and subsequent repeated freezing and thawing under high vacuum.

TABLE 4

Chemical shifts of nitrone (1) and its products

	Chemical shift (τ)	
Group	$CDCl_3$	CCl_4
Nitrone CH_3	7·50 ± 0·02	7·50 ± 0·01
Nitrone CH_2	5·23 ± 0·03	5·40 ± 0·01
Imine CH_3	7·39 ± 0·02	7·41 ± 0·02
Imine CH_2	2·56	
CH_3SSCH_3	7·60 ± 0·01	7·63 ± 0·01
Soluble polymer	5·31 ± 0·03	5·38 ± 0·01

Typical Runs followed by N.m.r.—The samples were cooled by compressed air and typical data are shown in Tables 3 and 4. The chemical shifts of the nitrone and the products were slightly solvent dependent, notably the nitrone CH_2. They were not concentration dependent within the range used, nor did they depend on the other solutes present.

Insoluble Polymer.—A solution of the nitrone (1) (0·30M) in CCl_4 was irradiated at room temperature in an open tube until no more precipitate formed (*ca.* 6 h). The buff precipitate was filtered off, washed, and dried, m.p. 130—140° (Found: C, 32·3; H, 6·2; Cl, 18·3; N, 18·3; S, 16·5).

Typical Runs followed by U.v.—Freshly prepared solutions in 1 cm silica cells were used giving the typical data in Table 5.

TABLE 5

Reaction of nitrones followed by u.v. (O.D. at $\lambda_{max.}$)

Time (s)	(a)	(b)	(c)	(d)
0	1·19	1·19	1·37	1·50
10	1·03	1·04	1·12	1·24
20	0·89	0·91	0·92	1·03
30	0·75	0·78	0·73	0·83
40	0·63	0·67	0·59	0·67
50	0·54	0·57	0·47	0·54
60	0·45	0·48	0·38	0·43
Slope * ($\times 10^3$)	−7·1	−6·6	−9·3	−9·5

[a] Nitrone (1) in $CHCl_3$. [b] Nitrone (8) in $CHCl_3$. [c] Nitrone (1) in CCl_4. [d] Nitrone (8) in CCl_4.
* Plot of log O.D. against time.

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