Trimethylsilyloxy-radicals from Peroxides: Electron Spin Resonance Study of Homolytic Substitution on Silicon

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The photolysis of trimethylsilyl t-butyl peroxide results in homolytic fission of the O–O bond. In the presence of alkenes the e.s.r. spectra of adducts of trimethylsilyloxy-radicals are observed, together with those of allylic radicals derived from hydrogen abstraction. In the absence of reactive substrates, trimethylsilyloxy-radicals are involved in an induced decomposition of the silyl peroxide by an S_H2 reaction at silicon, and the e.s.r. spectrum of the displaced t-butylperoxy-radical can be observed. The latter can also be trapped by 1,3-butadiene and the resultant allylic radical is involved in a further S_H2 reaction with the silyl peroxide. The e.s.r. spectrum observed in this case is due to *cis*-α-trimethylsilylallyl radical produced by the secondary photolysis of the butadiene adduct with loss of formaldehyde. The possibility of homolytic rearrangement of an allylic intermediate is ruled out.

TRIMETHYLSILYL t-BUTYL PEROXIDE $Me_3SiO{\cdot}OBu^t$ is the silicon analogue of the well-established di-t-butyl peroxide and represents a potential source of trimethylsilyloxy-radicals. It is readily prepared, thermally rather stable, and resembles its parent in its ability to initiate free-radical reactions.[1] In vinyl polymerizations it has certain advantages over di-t-butyl peroxide in that it decomposes more slowly and leads to a larger degree of branching in the polymer chain.[2] Its thermal decomposition proceeds with an activation energy of 41 kcal mol^{-1} and Hiatt identified acetone, t-butyl alcohol, and hexamethyldisiloxane in the pyrolysate.[3] However, for thermolyses at 180—200 °C the material balance among these products was poor and large amounts of tar were also formed.

Although no literature report on the photolytic decomposition of this peroxide has appeared, our initial interest was to employ it in e.s.r. studies as a precursor for trimethylsilyloxy-radicals, by analogy with earlier studies of t-butoxy-radicals from di-t-butyl peroxide.[4] During this investigation, we discovered a series of unusual reactions which are consistent with homolytic substitution on silicon. There are as yet few authenticated examples of homolytic displacements on silicon, although S_H2 reactions at other nuclei are known.[5] Recently, the cleavage of hexamethyldisilane by ethylene bromide has been presented as a radical-chain process in which one of the propagation steps involved [6] is (1).

$$Br^{\cdot} + Me_3Si{\cdot}SiMe_3 \longrightarrow BrSiMe_3 + {\cdot}SiMe_3 \text{ etc.} \qquad (1)$$

We now present an e.s.r. study of the photolytic decomposition of trimethylsilyl t-butyl peroxide. The detection and identification of various free-radical intermediates and adducts (in the presence of alkenes) during photolysis can be used to present a consistent formulation for the generation of trimethylsilyloxy-intermediates and S_H2 reactions on this peroxide.

RESULTS AND DISCUSSION

Photolysis of Trimethylsilyl t-Butyl Peroxide in an Inert Medium.—U.v. irradiation of the peroxide in cyclopropane solution at temperatures between −50 and −149 °C initially affords an intense singlet e.s.r. absorption. The *g*-factor of this species is 2·01502 ± 0·00004 and the peak-to-peak linewidth at low modulation is approximately 1·5 G, which agree with the e.s.r. parameters reported for the t-butylperoxy-radical in solution.[7]

The same spectrum is obtained when a dilute solution of t-butyl hydroperoxide in cyclopropane is irradiated under equivalent conditions, although it is many times more intense than that from trimethylsilyl t-butyl peroxide. The spectrum obtained from the silyl peroxide decays relatively rapidly when the light is shuttered in comparison with t-butylperoxy-radical generated from t-butyl hydroperoxide. It is unlikely that the e.s.r. spectrum is due to trimethylsilyloxy- or trimethylsilyltrioxy-radicals. Thus we were unable to observe ^{29}Si splittings, despite the high signal-to-noise levels of the spectrum. Further, the e.s.r. spectrum of the trimethylsilyloxy-radical, like that of the t-butoxy-radical, should be unobservable in solution owing to the orbitally degenerate ground state.[8] Finally, alkyltrioxy-radicals though less stable than the peroxy-analogues, have *g*-factors which are considerably lower (*ca.* 2·004) than those reported for alkylperoxy-radicals.[9]

We could find no evidence for the formation of trimethylsilyl radicals [10] during the photolysis of trimethylsilyl t-butyl peroxide. On continued photolysis, the strong singlet absorption disappears and is replaced by two other spectra, which are clearly associated with the

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[1] (*a*) W. Hahn and L. Metzinger, *Makromol. Chem.*, 1956, **21**, 113; (*b*) E. Buncel and A. G. Davies, *Chem. and Ind.*, 1956, 1052; (*c*) E. Buncel and A. G. Davies, *J. Chem. Soc.*, 1958, 1550.

[2] (*a*) A. F. Harris and G. A. Mortimer, Fr.P. 1,383,459, 1914; *Chem. Abs.*, 1965, **63**, 13,448d; (*b*) O. L. Mageli, R. E. Light, and G. J. Varnogy, U.S.P. 3,388,864; *Chem. Abs.*, 1967, **67**, 91,391a; (*c*) M. Nakano and Y. Minoura, *Koygo Kagaku Zasshi*, 1967, **70**, 1935; *Chem. Abs.*, 1968, **68**, 115,033; (*d*) G. A. Mortimer, U.S.P. 3,450,686, 1969; *Chem. Abs.*, 1969, **71**, 50,639b.

[3] R. Hiatt, *Canad. J. Chem.*, 1964, **42**, 985.

[4] J. K. Kochi and P. J. Krusic, *Chem. Soc. Special Publ.*, 1970, **24**, 147.

[5] (*a*) K. U. Ingold and B. P. Roberts, ' Free Radical Substitution Reactions,' Wiley-Interscience, New York, 1971, p. 90 *et seq.*; (*b*) A. G. Davies and B. P. Roberts, ' Free Radicals,' Wiley-Interscience, New York, 1973, chap. 10.

[6] A. Hosomi and H. Sakurai, *J. Amer. Chem. Soc.*, 1972, **94**, 1385.

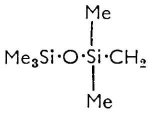
[7] (*a*) K. U. Ingold and J. R. Morton, *J. Amer. Chem. Soc.*, 1964, **86**, 3400; (*b*) P. D. Bartlett and G. Guaraldi, *ibid.*, 1967, **89**, 4799.

[8] M. C. R. Symons, *J. Amer. Chem. Soc.*, 1969, **91**, 5924.

[9] R. W. Fessenden, *J. Chem. Phys.*, 1968, **48**, 3725.

[10] (*a*) S. W. Bennett, C. Eaborn, A. Hudson, R. A. Jackson, and K. D. J. Root, *J. Chem. Soc.* (*A*), 1970, 348; (*b*) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1969, **91**, 3938.

cyclopropyl radical and the trimethylsilyloxy-dimethylsilylmethyl radical (I), which can be generated in-



$$Me_3Si{\cdot}O{\cdot}\underset{Me}{\overset{Me}{Si}}{\cdot}CH_2{\cdot}$$

(I)

$$A_{H\alpha} = 21{\cdot}10\ \text{G (triplet)}$$
$$A_{H\gamma} = 0{\cdot}74\ \text{G (septet)}$$
$$\langle g \rangle = 2{\cdot}00258 \pm 0{\cdot}00003$$

dependently from hexamethyldisiloxane and di-t-butyl

$$Me_3CO{\cdot} + Me_3Si{\cdot}O{\cdot}SiMe_3 \longrightarrow Bu^tOH + (I) \tag{2}$$

peroxide[11]* [reaction (2)]. These observations are consistent with the occurrence of processes (3) and (4) in the initial phases of the photolysis.

$$Me_3SiO{\cdot}OBu^t \xrightarrow{h\nu} Me_3SiO{\cdot} + Bu^tO{\cdot} \tag{3}$$
$$Me_3SiO{\cdot} + Me_3SiO{\cdot}OBu^t \longrightarrow Me_3Si{\cdot}O{\cdot}SiMe_3 + Bu^tOO{\cdot} \tag{4}$$

SCHEME 1

We attribute the disappearance of t-butylperoxy-radicals on continued photolysis to depletion of trimethylsilyl t-butyl peroxide by the second-order process (4), which is presumably replaced by a reaction involving attack on the solvent or hexamethyldisiloxane whose concentration is building up as the irradiation is prolonged. In agreement with this postulate, the singlet due to t-butylperoxy-radical is very weak at low concentrations of the silyl peroxide, and in some cases it is not observed at all. At high concentrations of trimethylsilyl t-butyl peroxide the singlet is observed for periods of up to 40 min before the secondary species predominates, although in these cases radical (I) can also be observed after *ca.* 10 min. Both t-butoxy- and trimethylsilyloxy-radicals are sufficiently reactive to be capable of abstracting the hydrogen from hexamethyldisiloxane and cyclopropane.† However, it appears that only the trimethylsilyloxy-radical can effect the substitution reaction (4), since Hiatt[3] has shown that our peroxide was not attacked by t-butoxy-radicals derived from the decomposition of di-t-butyl peroxalate at 45 °C.‡

The photolysis of trimethylsilyl t-butyl peroxide in dichlorodifluoromethane (Freon 12) also affords initially the spectrum of t-butylperoxy-radical, and that of radical (I) on further irradiation. There is no evidence for solvent-derived radicals. The latter confirms the absence of trimethylsilyl radicals from this system, since they react readily with dichlorodifluoromethane to afford chlorodifluoromethyl radicals[12] [reaction (5)].

$$Me_3Si{\cdot} + Cl_2CF_2 \longrightarrow Me_3SiCl + Cl\dot{C}F_2 \tag{5}$$

It is worthwhile commenting on alternative but less attractive explanations for these observations. For example, the formation of t-butylperoxy-radicals may be attributed to hydrogen abstraction from adventitious t-butyl hydroperoxide generated *via* the thermal reaction (6) from trimethylsilanol (derived secondarily from trimethylsiloxy-radicals). However, the e.s.r. spectrum of t-butylperoxy-radical appears immediately upon irradiation, and we do not expect this polar reaction to occur so readily at the low temperatures and in the non-polar medium used in this study. Further, g.l.c. analysis of the reaction mixture on partial photolysis showed no t-butyl hydroperoxide.

Radical-trapping studies described in the following section were employed to probe for the possible homolysis of the Si–O bond in the primary photochemical process, *e.g.*, (7).

$$Me_3SiOH + Me_3SiO{\cdot}OBu^t \rightleftharpoons Me_3Si{\cdot}O{\cdot}SiMe_3 + Bu^tO{\cdot}OH \tag{6}$$
$$Me_3SiO{\cdot}OBu^t \longrightarrow Me_3Si{\cdot} + Bu^tO{\cdot}O{\cdot} \tag{7}$$

Photolysis of Trimethylsilyl t-Butyl Peroxide in the Presence of Alkenes: Trimethylsilyloxy-adducts and Allylic Radicals.—Ethylene. Photolysis of the peroxide in the presence of ethylene produces an intense e.s.r. spectrum shown in Figure 1 consisting of a triplet of triplets. The spectrum is assigned to the adduct (II) of trimethylsilyloxy-radical to ethylene. Adduct (II) is formed readily when the photolysis is carried out in the presence of relatively large amounts of ethylene. When ethylene is diluted with cyclopropane, the first spectrum observed on the commencement of photolysis is the singlet due to t-butylperoxy-radical which is gradually replaced by the spectrum of (II) on further irradiation.

$$Me_3SiO{\cdot} + CH_2{=}CH_2 \longrightarrow \underset{(II)}{Me_3Si{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}} \tag{8}$$

The e.s.r. parameters of adduct (II) in Table 1 are consistent with those of other β-oxygen-substituted alkyl radicals[13] listed for comparison. The spectrum is not associated with a t-butoxy-precursor since the photolysis (9) of di-t-butyl peroxide under the same conditions gives no e.s.r. spectrum, and chemical studies also indicate that they do not readily add to ethylene.[14] Interestingly, the spectrum shown in Figure 1 undergoes no detectable linewidth alternation with changes in temperature. The hyperfine splitting of the α-protons is

$$Bu^tO{\cdot} + CH_2{=}CH_2 \nrightarrow Bu^tO{\cdot}CH_2{\cdot}CH_2{\cdot} \tag{9}$$

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* The peroxy-analogue of (I) derived by attack on trimethylsilyl t-butyl peroxide cannot be rigorously ruled out, although it is unlikely.

† However, photolysis of di-t-butyl peroxide under the same conditions affords only a weak spectrum of cyclopropyl radicals.

‡ Deduced by the absence[3] of a significant induced pathway for the thermolysis of trimethylsilyl t-butyl peroxide. Reaction (4) could lead to induced decomposition with a limited kinetic chain length.

[11] (*a*) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147; (*b*) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1969, **91**, 6161.

[12] (*a*) Unpublished results; (*b*) *Cf.* A. J. Bowles, A. Hudson, and R. A. Jackson, *Chem. Phys., Letters* 1970, **5**, 552.

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

[14] C. Walling and W. Thaler, *J. Amer. Chem. Soc.*, 1961, **83**, 3877.

temperature-independent, but the hyperfine splitting of the β-methylene protons varies with temperature (Figure 2) in a manner similar to that exhibited by other alkyl radicals.[4,13] There is no detectable splitting from the δ-methyl groups although linewidths (0·20 G) are somewhat greater than those for other alkyl radicals.

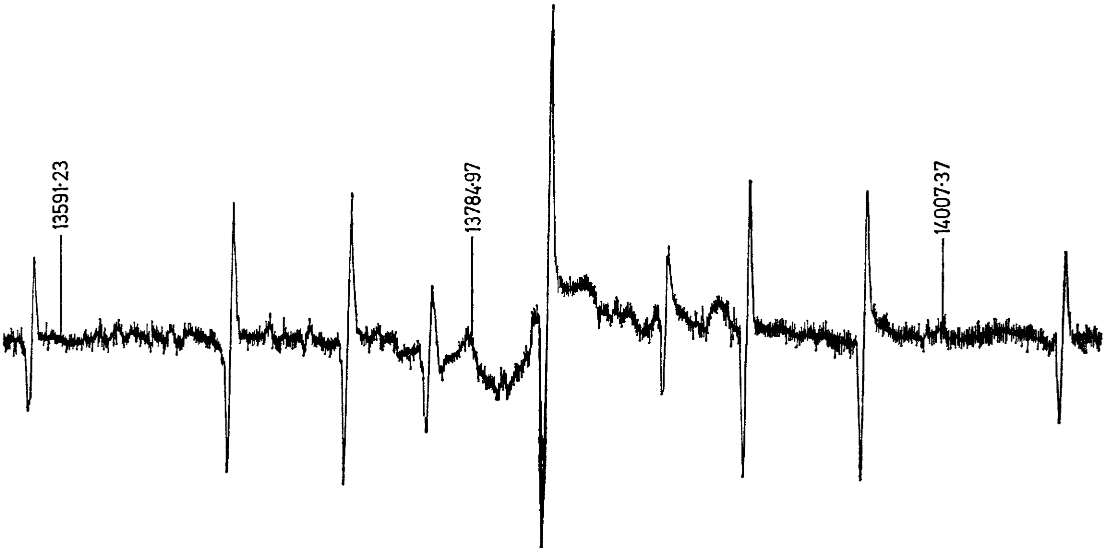


FIGURE 1 The e.s.r. spectrum of the adduct of trimethylsilyloxy-radical to ethylene, $Me_3Si{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}$, at −128 °C in cyclopropane solutions. The ^1H n.m.r. field markers are in kHz

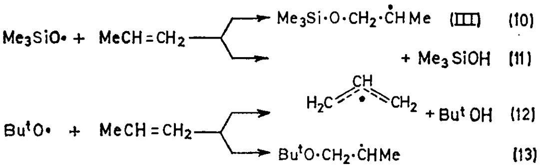
TABLE 1

E.s.r. parameters for the trimethylsilyloxy-adducts to alkenes in solution

Adduct	⟨*g*⟩	*T*/°C	*A*(αH)	*A*(βH) gauss	*A*(βCH₃)	Ref.
$Me_3Si{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}$	2·00259	−113	22·10	34·36		This
$Me_3Si{\cdot}O{\cdot}CH_2{\cdot}\dot{C}H_2Me$	2·00268	−116	21·92	27·12	24·73	This
$Me_3Si{\cdot}O{\cdot}CH_2{\cdot}\dot{C}Me_2$	2·00260	−116		20·12	22·96	This
$EtO{\cdot}CH_2{\cdot}CH_2{\cdot}$	2·00257	−111	22·15	33·76		This
$HO{\cdot}CH_2{\cdot}CH_2{\cdot}$	2·00247	−71	22·00	31·67		*b*
$CF_3O{\cdot}CH_2{\cdot}CH_2{\cdot}$	2·00253	−92	22·76	29·35	1·94 [d]	This [a]
$HO{\cdot}CH_2{\cdot}\dot{C}HMe$		−80	21·8 ± 0·1	24·7	24·7 ± 0·1	*c*

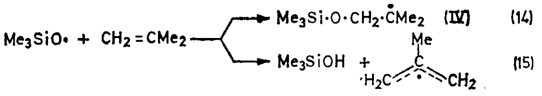
[a] Ref. 13. [b] R. Livingston and H. Zeldes, *J. Chem. Phys.*, 1966, **44**, 1245. [c] H. J. Hefter, T. A. Hecht, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1972, **94**, 2793. [d] Fluorine quartet splitting.

Propene. The spectrum obtained on irradiation of a solution of trimethylsilyl t-butyl peroxide in propene consists of two overlapping spectra. The first is obviously associated with the allyl radical, which is also formed when di-t-butyl peroxide is used in place of the silyl peroxide.[4] The other spectrum consists of a doublet of quartets split further into temperature-dependent triplets and is clearly an adduct to propene

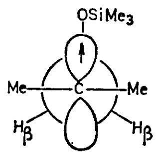


(Table 1). Since no analogous adduct of the t-butoxy-radical can be observed during the photolysis of di-t-butyl peroxide or t-butyl peracetate in the presence of propene, the spectrum must be due to the trimethylsilyloxy-adduct (III). Chemical studies at −78 °C also show that addition (13) of t-butoxy-radicals to propene cannot compete with hydrogen abstraction (12).[14]

Isobutene. The superposition of two spectra is observed when a solution of the silyl peroxide in isobutene is photolysed. The same β-methylallyl radical formed from the reaction of isobutene and t-butoxy-radical[4] is clearly discernible, in addition to a second spectrum consisting of a triplet of septets due to the



isobutene adduct (IV). The invariance of the triplet β-proton splitting with temperature shown in Figure 2 is no doubt due to the symmetric conformation (V), which is similar to that of the t-pentyl radical discussed earlier.[13]



(V)

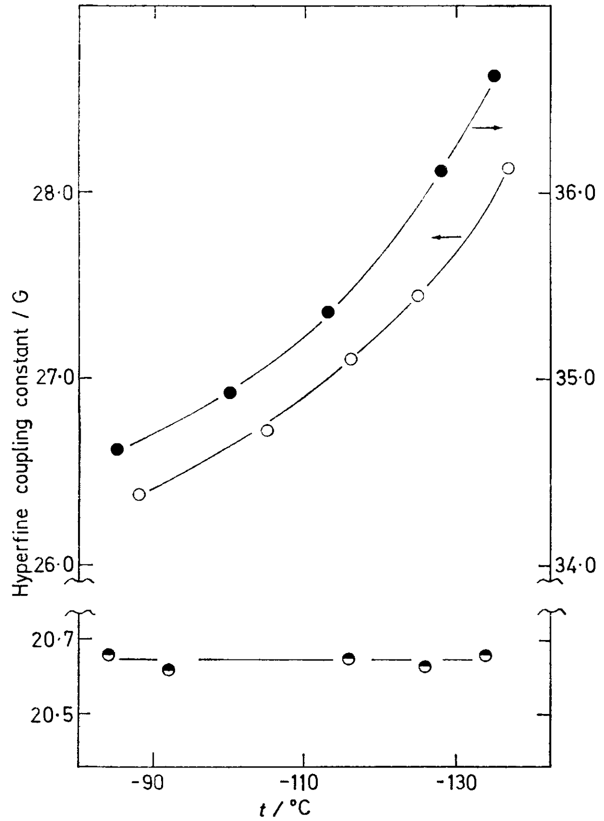


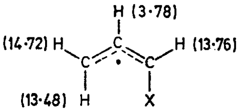
FIGURE 2 Temperature-dependence of the β-proton (methylene) hyperfine coupling constant of the adducts of trimethylsilyloxy-radicals to ●, ethylene; ○, propene; and ◓, isobutene

Trimethylsilyloxy-radicals.—The identity of the alkene adducts (II)—(IV) obtained during the photolysis of trimethylsilyl t-butyl peroxide clearly points to the homolysis of the *peroxidic* bond [equation (3)]. Trimethylsilyl radicals also readily add to alkenes,[13] but the absence of these adducts during photolysis of the silyl peroxide indicates that Si–O homolysis in it is not significant under these conditions.

$$\mathrm{Me_3Si\cdot} + \rangle\mathrm{C{=}C}\langle \longrightarrow \mathrm{Me_3Si{\cdot}\overset{|}{\underset{|}{C}}{\cdot}\overset{|}{\underset{|}{C}}\cdot} \qquad (16)$$

Our experiments do not allow us to determine quantitatively the relative rates of addition to [equations (10) and (14)] and hydrogen abstraction from [equations (11) and (15)] alkenes. It is clear, however, that trimethylsilyloxy-radicals are much more prone than t-butoxy-radicals to add to C=C bonds. The same is true of hydroxy- and even benzoyloxy-radicals.[15] Thus, among oxygen-centred species, t-butoxy-radicals are rather unique in their propensity for abstraction. Quantitative product studies are needed to delineate these differences further.

*Photolysis of Trimethylsilyl t-Butyl Peroxide in the Presence of Buta-*1,3-*diene.*—The photolysis in either buta-1,3-diene as solvent or diluted with cyclopropane (to allow lower temperatures to be attained) affords a spectrum shown in Figure 3 due to a free radical * with $g = 2{\cdot}00265 \pm 0{\cdot}00002$. The spectrum at −124 °C consists of four doublets with a rather characteristic set of hyperfine splittings of 3·78, 13·48, 13·76, and 14·72 G, indicative of an α-substituted allyl radical (VI). The proton hyperfine splittings of *cis*- and *trans*-α-methylallyl radicals are given in (VII) and (VIII), respectively, for comparison.[4] Of the two possible geometric isomers, the hyperfine splittings of structure (VI) corresponds more closely to a *cis* rather than a *trans*-allylic skeleton. After a number of attempts (see Table 2), we identified



(VI)

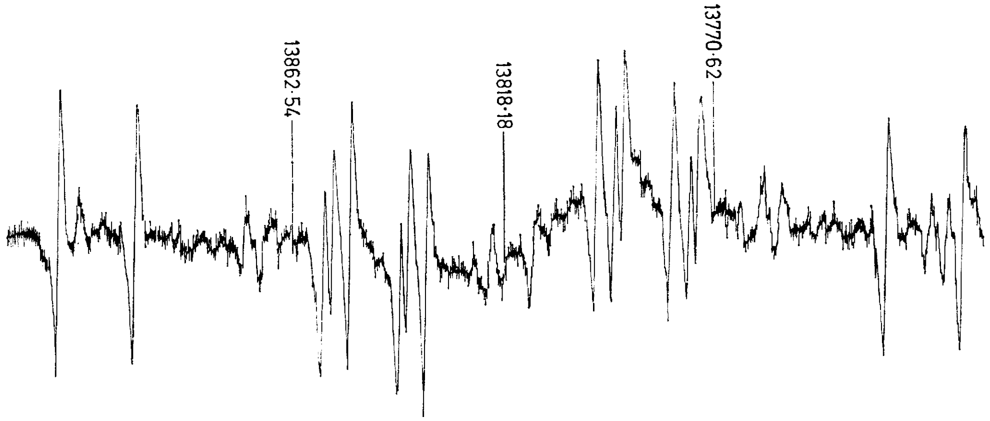


FIGURE 3 The e.s.r. spectrum of *cis*-α-trimethylsilylallyl radical obtained during photolysis of trimethylsilyl t-butyl peroxide in 1,3-butadiene at −117 °C. (The weaker lines are due to part of the spectrum of the adduct of t-butoxy-radicals to butadiene.) The same spectrum is obtained from the reaction of *cis*-propenyltrimethylsilane and t-butoxy-radical.

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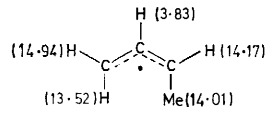
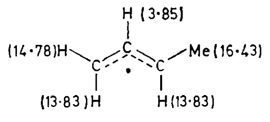
* The weaker lines in Figure 3 are due to part of the spectrum of the adduct of t-butoxy-radicals to butadiene. It is also possible that these weaker lines are due to trimethylsilyloxy-adducts since the e.s.r. parameters of both species are similar.

[15] (*a*) *Cf.* also H. J. Hefter, T. A. Hecht, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1972, **94**, 2793; (*b*) J. K. Kochi, *ibid.*, 1962, **84**, 1572; (*c*) D. J. Edge and J. K. Kochi, to be published.

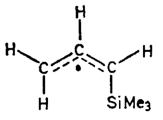


(VII)



(VIII)

(VI) as the *cis*-α-trimethylsilylallyl radical (IX) in the following manner.

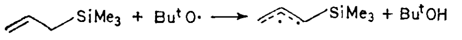


(IX)

t-Butoxy-radicals from the photolysis of di-t-butyl peroxide selectively remove the allylic hydrogens from a variety of alk-1-enes to generate *trans*-α-substituted allylic radicals (X).[16] Treatment of allyltrimethylsilane in this manner produces *trans*-α-trimethylsilylallyl radical (XI) shown in Figure 4 and the e.s.r. parameters of which are listed in Table 2. On the other hand, the photolysis of *cis*-propenyltrimethylsilane and di-t-butyl peroxide affords an e.s.r. spectrum which is identical in all respects with that of (IX). In both cases no isomerization occurred, since the spectrum of compound (XI) was uncontaminated by that of (IX) and *vice versa*. The latter is consistent with the rather high (13 kcal mol^{-1}) activation energy for *cis–trans*-isomerization of allyl radicals.[17] The e.s.r. spectra of radicals (XI) and (IX) are readily distinguishable owing to the presence of a decet splitting (0·27 G) by the methyl protons in (XI) which are unresolved (<0·05 G) in the *cis*-isomer (IX).

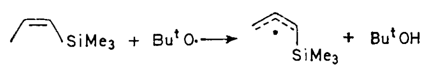
(17)

(X)



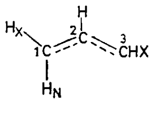
(18)

(XI)



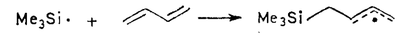
(19)

(IX)



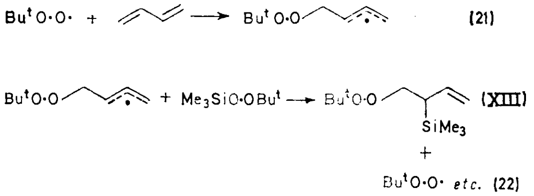
(XII)

It is noteworthy that trimethylsilyl radicals (independently generated from trimethylsilane) readily add to buta-1,3-diene under these conditions to afford only *trans*-α-trimethylsilylmethylallyl radicals.[13] The addition (20) of trimethylsilyl radical to the *s-trans*-conformation of butadiene is consistent, thus, with the addition of other radicals under similar conditions.[4] Moreover, the absence of this adduct provides further evidence that trimethylsilyl radicals are not important intermediates in the photolytic reactions of trimethylsilyl t-butyl peroxide.



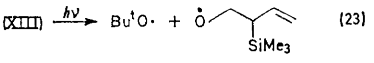
(20)

The observation of only the spectrum of (IX) during the photolysis of a solution of the silyl peroxide in butadiene is highly unusual and unexpected. It could be shown, however, that structure (IX) *results from a secondary reaction.* Thus, a mixture of the peroxide and butadiene was irradiated in the cavity of the spectrometer for 30 min and the e.s.r. spectrum of (IX) monitored continuously. G.l.c. of the mixture showed that 30% of the original peroxide had been consumed, and t.l.c. indicated the presence of another component (which was absent when no butadiene was present). The sample was concentrated on a molecular still until *no* butadiene (by g.l.c.) remained in the concentrate, the n.m.r. spectrum of which showed weak low-field resonances due to allylic (δ 3·6—4·0 p.p.m.) and olefinic (δ 4·8—6·2 p.p.m.) protons in addition to intense absorptions due to t-butyl (δ 1·05 p.p.m.) and trimethylsilyloxy- (δ 0·25 p.p.m.) groups. The concentrate was dissolved in cyclopropane and the solution re-photolysed, whereupon the spectrum of (IX) *reappeared.* These experiments demonstrate the formation of a relatively stable species (XIII) during the photolysis of a mixture of trimethylsilyl t-butyl peroxide and butadiene. We suggest that (XIII) is the adduct of trimethylsilyl t-butyl peroxide to butadiene formed as in Scheme 2.



Scheme 2

The photolysis of the adduct (XIII) is expected to afford (IX) on photolysis as in reactions (23) and (24). The photolysis (23) of the peroxidic bond is followed by the well known β-scission (24)[18] of the oxy-radical to



(23)

(24)

(IX)

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[16] J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 1968, **90**, 7157.

[17] D. M. Golden, N. A. Gac, and S. W. Benson, *J. Amer. Chem. Soc.*, 1969, **91**, 2137.

[18] P. Gray, R. Shaw, and J. C. J. Thynne, *Progr. Reaction Kinetics*, 1967, **4**, 65.

generate the resonance-stabilised (IX) and formaldehyde. The latter could be detected qualitatively by the chromotropic acid and carbazole colour tests.[19]

There are several features of this mechanistic scheme which merit elaboration. t-Butylperoxy-radicals required in equation (21) may be formed by S_H2 processes described earlier and are expected to add readily to butadiene.[20] The formation of (XIII) together with the 1,4-adduct as represented by equation (22) is an S_H2 process which lends chain character to the photolysis.* Indeed, the photolysis of trimethylsilyl t-butyl peroxide in butadiene leads to 43% decomposition under the same conditions in which the same peroxide in cyclopropane is only 20% decomposed. Thus, the kinetic chain length for Scheme 2 is greater than unity, but not very long. Although steric factors may be important, it is not completely clear why the photolysis of (XIII) in equations (23) and (24) affords only the e.s.r. spectrum of the *cis*-trimethylsilylallyl isomer (IX).

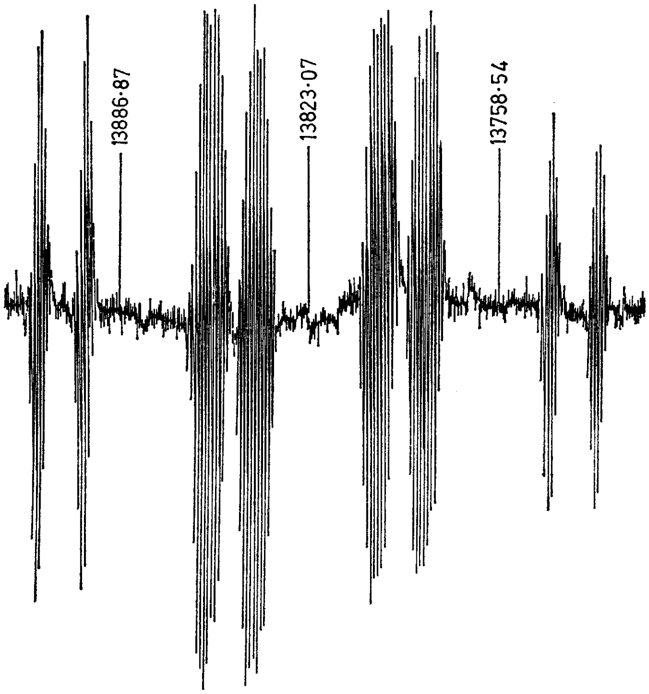

FIGURE 4 The e.s.r. spectrum of *trans*-α-trimethylsilylallyl radical in cyclopropane solution obtained from allyltrimethylsilane by hydrogen abstraction with photochemically generated t-butoxy-radical at −113 °C. ^1H n.m.r. field markers are in kHz

TABLE 2

E.s.r. parameters of α-substituted allyl radicals (XII) in solution

				Hyperfine coupling constant (G)				
	X	T/°C	$\langle g \rangle$	$A(H_{1N})$	$A(H_{1X})$	$A(H_2)$	$A(H_3)$	$A(X)$
trans	Me_3Si	−124	2·00265	12·49	14·20	3·69	12·49	0·27 [a]
cis	Me_3Si	−123	2·00265	13·47	14·73	3·78	13·76	<0·05 [a]
trans	HO [c]	−95	2·00296	13·15	14·23	3·66	13·15	
cis	HO [c]	−95	2·00287	13·33	13·86	3·16	13·86	
trans	Bu^tO	−102	2·00295	13·07	13·65	2·91	13·07	0·18 [a]
cis	Bu^t	−121	2·00264	13·45	14·89	3·91	14·19	<0·05 [a]
trans	$Bu^tO\cdot CH_2$ [d]	−137		13·74	14·83	3·88	13·74	16·97 [b]
cis	$Me_3SiO\cdot CH_2$	−110	2·00260	13·49	14·62	3·81	14·01	14·18 [b]
trans	$Me_3SiO\cdot CH_2$	−116	2·00261	13·79	14·72	3·79	13·79	16·59 [b]
trans	$Me_3SiO\cdot OC$	−111	2·00315	12·73	13·57	3·68	12·51	

[a] Decet splitting due to three methyl groups. [b] Triplet splitting due to methylene group. [c] *Cf.* ref. *b*, Table 1. [d] From ref. 16.

We have also attempted to show qualitatively the participation of S_H2 processes in the reaction of trimethylsilyl t-butyl peroxide with other free radicals. Photolysis of a mixture of the peroxide and t-butyl peracetate in cyclopropane solutions affords the spectrum of methyl radical superimposed on that of the t-butylperoxy-radical. G.l.c. shows that tetramethylsilane is

$$\cdot CH_3 + Me_3SiO\cdot OBu^t \longrightarrow Me_4Si + Bu^tO\cdot O\cdot \qquad (25)$$

formed, although in low yields [reaction (25)]. Similarly, analysis of the photolysate of the silyl peroxide in

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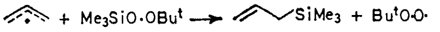
* The formation of (XIII) under these conditions must be rapid since the e.s.r. spectrum of (IX) appears immediately after the start of irradiation. Isolation, characterization, and synthesis of adducts such as (XIII) are under investigation.

[19] F. Feigl, 'Spot Tests,' vol. II, Elsevier, Amsterdam, 1952, pp. 240—241.

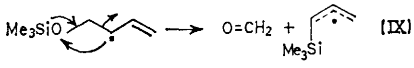
[20] F. R. Mayo, *J. Amer. Chem. Soc.*, 1958, **80**, 2465, 2497.

propene (described earlier) indicates the presence of allyltrimethylsilane [reaction (26)].

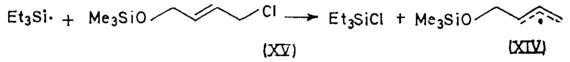

(26)

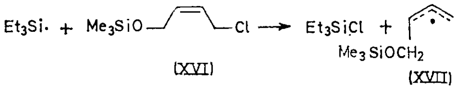
We also expect trimethylsilyloxy-radicals formed in the primary photochemical step (3) to add to butadiene. The adduct (XIV) offers the interesting possibility of direct rearrangement to (IX) by an intramolecular


(27)

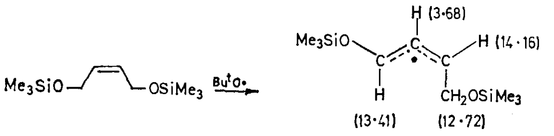

(28)

S_H2 process (28). However, both the *cis*- and *trans*-isomers of (XIV) generated independently from the chlorobutenyl ethers, (XV) and (XVI) and triethylsilyl radicals afforded only the spectra of the unrearranged radicals (XIV) and (XVII), respectively, listed in Table 2.


(29)


(30)

Similarly, the treatment of the bistrimethylsilyl ether of *cis*-butene-1,4-diol with t-butoxy-radicals afforded only the spectrum of the unrearranged allylic radical (XVIII) with $\langle g \rangle = 2{\cdot}00301$ at -60 °C.


(31)

(XVIII)

It should be emphasized that the e.s.r. spectra obtained under these conditions are related only to the (quasi-)steady-state concentrations of radicals, which are not necessarily in direct proportion to their importance as reactive intermediates. For example, if chain processes such as those in Scheme 2 are involved, the radicals may not be present in sufficiently high concentrations to be observed by e.s.r. The comparative e.s.r. spectra of t-butylperoxy- and trimethylsiloxy-radicals and their adducts to butadiene and simple alkenes may be such a case since radicals add to simple alkenes more slowly than they add to butadiene.

Conclusions.—The observation of the spectrum of t-butylperoxy-radical and the formation of hexamethyldisiloxane during the decomposition of trimethylsilyl t-butyl peroxide is accommodated by an S_H2 reaction (4) at the silicon centre. The absence of trimethylsilyl radicals suggests that photolysis of the peroxide does not take place at the Si–O bond. The radical-chain addition of the peroxide to buta-1,3-diene is also consistent with an S_H2 process at silicon. The lack of long kinetic chains either in the decomposition of the peroxide or its addition to butadiene, however, indicate that homolytic displacements of t-butylperoxy-radicals from trimethylsilyl t-butyl peroxide are not highly favoured.

EXPERIMENTAL

Materials.—Di-t-butyl peroxide was obtained from the Shell Chemical Co., washed, and redistilled at reduced pressure before use. Trimethylsilyl t-butyl peroxide was a gift from Dr. O. L. Mageli (Lucidol). The n.m.r. spectrum showed two equal resonances, 0·25 and 1·05 p.p.m. downfield from a tetramethylsilane standard. G.l.c. analysis on a 9 ft × $\frac{1}{8}$ in SF96 20% on firebrick column at 55 °C gave only one peak, and by comparison with a known sample showed the absence of any t-butyl hydroperoxide.

Ethylene, propene, isobutene, buta-1,3-diene, cyclopropane, and Freon 12 were from Matheson Co. Allyltrimethylsilane and hexamethyldisilazane were from Pierce Chemical Co., and trimethylchlorosilane from Sigma Chemical Co. 2-Bromoethyl ethyl ether and triethylsilane were from Columbia Organic Chemicals Co., bistrifluoromethyl peroxide from Pennisular Chemical Co., and *cis*-4,4-dimethylpent-2-ene from Chemical Samples. Allyl alcohol was from the Shell Chemical Co. and allyl t-butyl ether was prepared [22] by reaction between allyl alcohol and t-butyl alcohol.

cis-Propenyltrimethylsilane was prepared from 1-bromopropene (Chemical Samples) *via* the Grignard reagent, which was treated with trimethylchlorosilane.[23] The n.m.r. spectrum of the redistilled product, b.p. 86—87 °C (lit.,[23] 85—88 °C), showed by comparison with the published spectra [23] that it contained at least 90% of the *cis*-isomer.

The trimethylsilyl ether of but-3-en-1-ol [22] was prepared from the alcohol by a modification of the method of Fessenden and Crowe,[24] from hexamethyldisilazane. The distilled product (b.p. 120—121 °C), had δ 0·1 (9H, s), 2·45 (2H, dt), 3·65 (2H, t), 5·10—5·30 (2H, m), and 5·70—6·40 p.p.m. (1H, m). The mass spectrum had a base peak at *m/e* 73, characteristic of trimethylsilyl ethers,[25] together with an intense peak at *m/e* 103, characteristic of silyl ethers of the type $RCH_2{\cdot}OSiMe_3$,[25] and another at *m/e* 129, corresponding to the loss of a methyl group ($M - 15$), another characteristic fragmentation pattern.[25]

The trimethylsilyl ether of 2-methylpent-3-en-2-ol (prepared from allyl Grignard reagent and acetone) was prepared in the following manner. A 1·5M-solution of methyl-lithium (70 ml) in ether (Foote Mineral Company) was added dropwise to a stirred solution of the alcohol (10 g) in ether (50 ml) at below 5 °C. The mixture was stirred for 30 min at 0 °C and then trimethylchlorosilane (11 g) in ether (30 ml) was added dropwise, again below 5 °C. After the addition was complete, the mixture was allowed to warm to room temperature and stirred for an additional 2 h. The ether was partially removed by distillation, the solution filtered to remove lithium chloride, and the remainder of the ether distilled off. The residue was then distilled *in vacuo* and the ether collected at 40—41 °C (20 mmHg); δ 0·10 (9H, s), 1·05 (6H, s), 2·00 (2H, d), 4·9—5·1 (2H, m), and 5·5—6·3 p.p.m. (1H, m). The mass spectrum showed

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[21] *Cf.* A. Hudson and R. A. Jackson, *Chem. Comm.*, 1969, 1323.

[22] R. A. Sheldon and J. K. Kochi, *J. Amer. Chem. Soc.*, 1970, **92**, 5175.

[23] D. Seyferth and L. G. Vaughan, *J. Organometallic Chem.*, 1963, **1**, 138.

[24] R. J. Fessenden and D. F. Crowe, *J. Org. Chem.*, 1961, **26**, 4638.

[25] A. E. Pierce, 'Silylation of Organic Compounds,' Pierce, Rockford, 1968, pp. 33—39.

a parent peak at *m/e* 73, a strong peak at *m/e* 147 characteristic of trimethylsilyl ethers of the type $RCMe_2{\cdot}O{\cdot}SiMe_3$ [25] and another at *m/e* 157, corresponding to the ($M - 15$) peak.

Trimethylsilyl α-bromoisobutyrate (Columbia) was prepared by the method of Birkofer *et al.*[26] It had b.p. 64—66 °C/14 mmHg (lit.,[26] 60 °C/11 mmHg).[26] Trimethylsilyl crotonate (Matheson, Coleman and Bell) was prepared by the same method, and it had b.p. 54—56 °C/12 mmHg (lit.,[27] 47 °C/9 mmHg).[27] The bistrimethylsilyl ether of *cis*-but-2-ene-1,4-diol (General Aniline) was prepared by a modification of the method of Sprung and Nelson.[28] It had b.p. 90—92 °C/17 mmHg); δ 0·1 (9H, s), 4·1 (2H, d), and 5·4 p.p.m. (1H, t). *cis*-4-Chlorobut-2-en-1-ol was prepared from the corresponding glycol by treatment with thionyl chloride,[29] and had b.p. 78—80 °C/11 mmHg (lit.,[29] 79—81 °C/11 mmHg). The trimethylsilyl ether of this chlorohydrin was then prepared by a modification of Speier's method,[30] with triethylamine as the acid acceptor; b.p. 79—81 °C/21 mmHg; δ 0·1 (9H, s), 4·0 (2H, d), 4·2 (2H, d), and 5·3—5·6 p.p.m. (2H, m). The mass spectrum showed a parent peak at *m/e* 73, a large peak at 163 ($M -$ 15), and another at 143 ($M - 35$) from loss of chlorine.

trans-But-2-ene-1,4-diol was prepared from the corresponding dichloride (Petrotex Chem. Corp.) by initially forming the diacetate,[31] followed by hydrolysis with ethanol containing 4% sodium ethoxide,[32] and had b.p. 100—101 °C/2·5 mmHg (lit.,[32] 102—104 °C/2·5 mmHg). The diol was converted into the corresponding chlorohydrin with thionyl chloride by the same procedure as that for the *cis*-isomer [29] and had b.p. 76—77 °C/10·5 mmHg (lit.,[31] 75—78 °C/10 mmHg). The trimethylsilyl ether, prepared by the procedure described for the *cis*-isomer,[32] had b.p. 62—64 °C/15 mmHg; δ 0·1 (9H, s), 4·0—4·3 (4H, m), and 5·4—5·9 p.p.m. (2H, m). The mass spectrum was very similar to that obtained for the *cis*-isomer and had the same major peaks.

Analytical Procedures.—To determine the amount of conversion of trimethylsilyl t-butyl peroxide during photolysis with and without butadiene, two samples made up in the same way and as identical as possible were irradiated for equal lengths of time (20 min) in the e.s.r. cavity. One of the tubes contained the silyl peroxide, butadiene, and cyclopropane, the other contained only peroxide and cyclopropane. After irradiation the sample tubes were opened and the gas carefully removed; n-heptane was added as an internal standard and the amount of the peroxide remaining determined by g.l.c. on a 9 ft × $\frac{1}{8}$ in SF96 20% on firebrick column at 55 °C.

To determine the presence of tetramethylsilane in the product mixture obtained by photolysis of trimethylsilyl t-butyl peroxide and t-butyl peracetate, the tube was quickly opened and the contents transferred at low temperature to a container which was sealed with a rubber septum cap. This vial was stored at 0 °C, and the gas sampled after warming to room temperature and analysed on a 15 ft × $\frac{1}{4}$ in 30% Dowtherm column at room temperature and compared with a standard sample of tetramethylsilane. To determine the presence of allyltrimethylsilane in the product mixture obtained by photolysis of the silyl peroxide and propene, the tube was opened and the gases removed. The liquid phase was sampled and analysed on two columns, one a 9 ft × $\frac{1}{8}$ in SF96 20% on firebrick at 55 °C and the other an 8 ft × $\frac{1}{8}$ in Carbowax 20M–5% KOH on Chromosorb W 60—80 at 45 °C. On both columns, there was a peak having an identical retention time to that of an authentic sample of allyltrimethylsilane under the same conditions.

Spectrometry.—E.s.r. spectra were taken with a modified Varian *X*-band spectrometer with 100 kHz modulation. The microwave bridge was designed around a three-port ferrite circulator. A backward diode (Philco L4154B) was employed as detector in conjunction with a low-noise, wide-band preamplifier (Philco P301). The latter was provided with an impedance-matching input circuit and a simple d.c. circuit to monitor the crystal current by means of a sensitive galvanometer. The input transformer was wound in a ferrite pot core (Ferroxcube) and was carefully shielded with many layers of high magnetic permeability foil. An attenuator was placed before the tunable detector mount and was used during tuning to avoid excessive microwave power on the detector. The field of a Varian V3600 12 in magnet was swept very linearly by a Varian V3508 magnet flux stabilizer and slow-sweep unit. The spectral scans were accurately calibrated by means of a field marker operating in conjunction with a Harvey–Wells G502 n.m.r. gaussmeter and a Hewlett–Packard frequency counter. The field marker causes the superposition of markers at accurately known field values directly on the spectral record. The microwave frequency was determined directly on a Hewlett–Packard 5255A frequency converter and a Hewlett–Packard X281A microwave adapter in conjunction with a Hewlett–Packard 5248L frequency counter. The *g*-factors were determined with the perylene cation-radical ($g = 2{\cdot}00258$) [33] as a daily standard in the configuration employed. A correction, usually 5×10^{-5}, was made to the measured values. The accuracy of such measurements is thought to be ±0·00003, and *g*-factors made under these conditions were in agreement with those obtained by Fessenden and Schuler.[11a] In most cases hyperfine splittings were determined by positioning each line precisely, applying second-order corrections,[34] and then recomputing the distance between each line.

The light source, variable-temperature equipment, and the sample tubes were as described.[13] The temperature in the tube was calibrated with a thermocouple and accurate to ±5 °C. The photolyses were carried out in typical cases as follows: For photolysis using trimethylsilyl t-butyl peroxide, a mixture of the peroxide, the compound under investigation, and cyclopropane were used in the ratio of 1 : 1 : 10, this ratio being varied at times as noted in the text. For photolysis involving di-t-butyl peroxide similar mixtures were employed, with a slightly smaller amount of the peroxide. All samples were thoroughly degassed by use of a freeze–pump–thaw cycle. When spectra were weak or not observed the amounts of the various components were varied to obtain optimum concentrations.

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[26] L. Birkofer, A. Ritter, and J. Schramm, *Chem. Ber.*, 1962, **95**, 426.

[27] K. Rühlmann, *J. prakt. Chem.*, 1962, **16**, 172.

[28] M. M. Sprung and L. S. Nelson, *J. Org. Chem.*, 1955, **20**, 1750.

[29] J. Colonge and G. Poilane, *Bull. Soc. chim. France*, 1955, 953.

[30] J. L. Speier, *J. Amer. Chem. Soc.*, 1952, **74**, 1003.

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[32] C. S. Marvel and C. H. Young, *J. Amer. Chem. Soc.*, 1951, **73**, 1066.

[33] B. G. Segal, M. Kaplan, and G. K. Fraenkel, *J. Chem. Phys.*, 1965, **43**, 4191.

[34] R. W. Fessenden, *J. Chem. Phys.*, 1962, **37**, 747.

N.m.r. spectra were obtained on a Varian A60 instrument with tetramethylsilane as a standard and mass spectra were obtained on a Varian CH7 instrument, operating at an ionizing voltage of 70 eV.

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