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AN ELECTRON SPIN RESONANCE STUDY OF THE RING-OPENING OF SILYL-SUBSTITUTED CYCLOPROPYLMETHYL RADICALS

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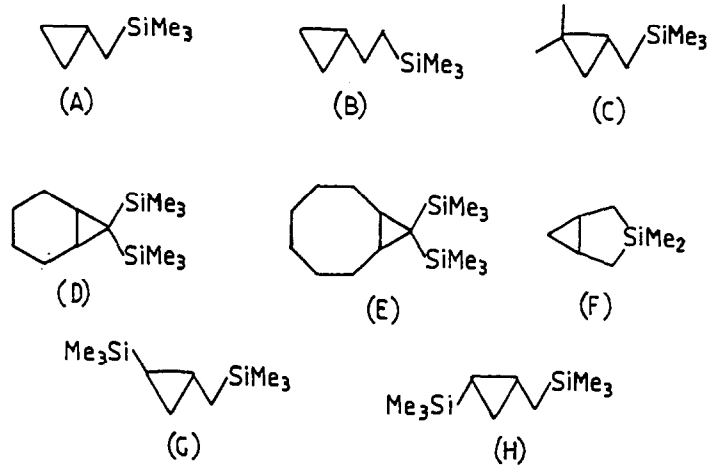
Summary

ESR spectroscopy has been used to monitor the radicals formed when the silylated cyclopropanes (A–H) react with t-butoxyl radicals from photolysis of di-t-butyl peroxide.



Hydrogen atoms are abstracted from methylene groups activated by cyclopropyl or trimethylsilyl substituents, the former being the more effective. The cyclopropylmethyl radicals which are formed undergo ring-opening to give homoallylic radicals.

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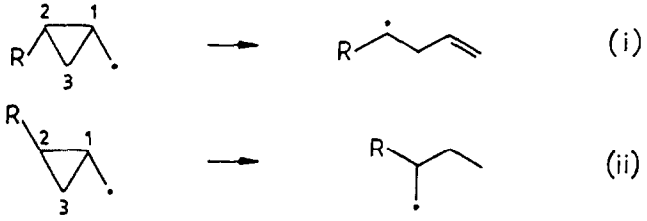
Compound C gives the tertiary radical, and compounds D–F give the corresponding cycloalkenylmethyl radicals, but G and H behave differently from each other; whereas the *trans* isomer G gives what is tentatively identified as the 1,4-bis-silylbut-3-en-1-yl radical, the *cis* isomer H appears anomalously to give the 1,4-bis-silylbut-2-en-1-yl radical.

The various factors which control the regioselectivities and the ESR parameters are discussed.

Introduction

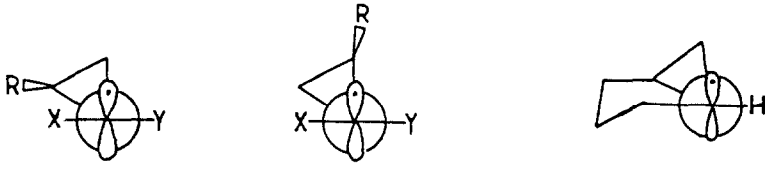
Much work has been carried out in recent years on the regioselectivity of the ring-opening of ring-substituted cyclopropylmethyl radicals [1]. If a *cis*-2-alkyl substituent is present, the secondary alkyl radical is formed (eq. i), but a *trans*-2-alkyl substituent leads to the formation of the thermodynamically less stable primary alkyl radical (eq. ii).



Four principal factors have been considered to contribute to the regioselectivity.

(1) The thermodynamic stability of the radical which is formed would favour the sequence tertiary > secondary > primary alkyl. This effect is probably less important than usual because angle strain in the cyclopropyl ring causes the reaction to be strongly exothermic so that the transition state resembles the reactants more than the products.

(2) Steric interaction between a *cis*-2-alkyl substituent and the α-substituents X and Y in the transition state 1 which would give the primary alkyl radical is minimised in the transition state 2 which would give the secondary alkyl radical. In monocyclic compounds, this effects seems to be of over-riding importance.



(1) (2) (3)

(3) In norcarane derivatives, the regioselectivity is probably dominated by the geometrical condition that, in the transition state leading to ring-opening, the *p* orbital containing the unpaired electron must eclipse the σ or σ^* orbital of the bond which is to break. This leads to the formation of the exocyclic radical as shown in **3**.

(4) Electronic interaction by a substituent on the 2-position of the ring would break the degeneracy between the molecular orbitals of the C(1)–C(2) and C(1)–C(3)

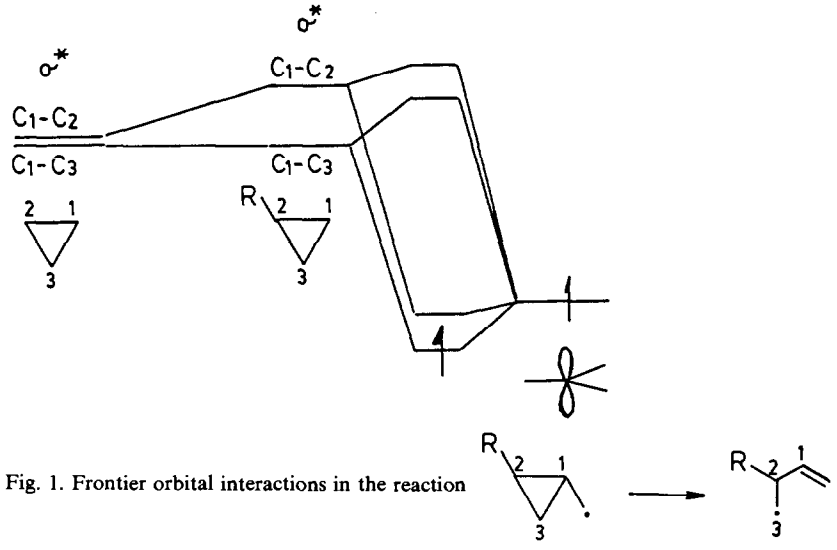


Fig. 1. Frontier orbital interactions in the reaction

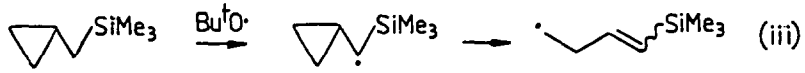
bonds and control their interaction with the singly-occupied *p* orbital in the approach to the early transition state. This control of the SOMO–LUMO interaction has been suggested to account for the regioselectivity of the reaction of *trans*-2-alkyl-cyclopropylmethyl radicals (eq. ii), and is illustrated in Fig. 1 [1,2].

We describe here a study by ESR spectroscopy of the ring-opening of a series of cyclopropylmethyl radicals carrying methylsilyl groups, and discuss the regioselectivities which are observed, in terms of these four factors.

Results and discussion

The silylated cyclopropanes which were studied are shown in formulae **4**–**11** in Table 1. Mixtures of the silanes and of di-t-butyl peroxide in cyclopropane solution were irradiated with ultraviolet light in an ESR cavity; details of the spectra which were observed are given in Table 1.

t-Butoxyl radicals arising from the photolysis of the peroxide abstracted hydrogen from the methylene group in the side chain of compound **4** and the only radical which could be observed from −120 to −10°C was the homoallylic radical (**13**) resulting from ring-opening (eq. iii).



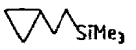
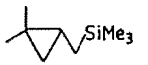
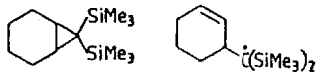
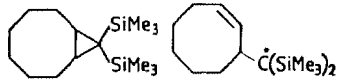
(4) (13)

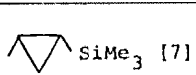
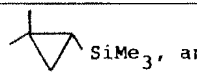
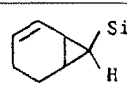
The spectrum obtained from the homologue **5** was similar but weaker. These spectra are like those of other homoallylic radicals which have been prepared previously (e.g. $^{\cdot}CH_2CH_2CH{=}CHOH$, $a(2H_\alpha)$ 22.2 G, $a(2H_\beta)$ 30.0 G, $a(H_\gamma)$ 0.8 G) [8] and require no further comment.

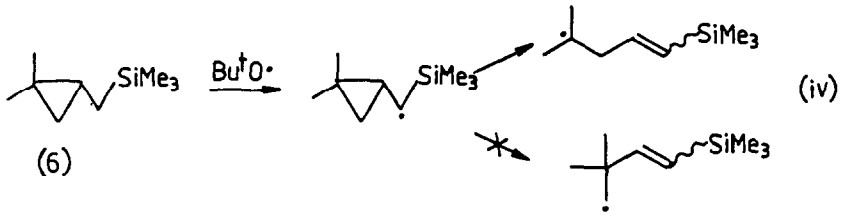
The question of regioselectivity in ring opening arises first with the *gem*-dimethyl compound **6** (eq. iv).

TABLE 1

ESR SPECTRA OF SILYLATED HOMOALLYLIC RADICALS

	Reactant [a]	Radical	a (G)			T (°C)	g	Ref.
(4)		$^{\cdot}CH_2CH_2CH{=}CHSiMe_3$	22.5 ($2H_\alpha$)	27.5 ($2H_\beta$)	0.7 (H_γ)	−70 to −100	2.0027	3
(5)		$^{\cdot}CH_2CH_2CH{=}CHCH_2SiMe_3$	22.0 ($2H_\alpha$) 22.0 ($2H_\alpha$)	29.0 ($2H_\beta$) 28.0 ($2H_\beta$)	0.7 (H_γ) 0.7 (H_γ)	−115 −20	2.0027	
(6)		$(CH_3)_2\dot{C}CH_2CH{=}CHSiMe_3$	23.0 ($6H_\alpha$)	16.0 (H_β)	0.7 (H_γ)	−30 to −100	2.0028	
(7)			6.1 (H_β)	ca. 0.35 (18H)	[b]	−30 to −128	2.0025	4
(8)			21.8 ($2H_\alpha$) 21.8 ($2H_\alpha$)	26.5 (H_β) 25.5 (H_β)	0.7 (H_γ) 0.7 (H_γ)	−116 −66	2.0027	5
(9)			4.5 (H_α)	0.35 (18H)	[b]	−66 to −125	2.0025	4
(10)		$Me_3SiCHCH{=}CHSiMe_3$	20.3 (H_α)	24.0 ($2H_\beta$)	0.35 (9H) [b]	−125	2.0027	6
(11)		$Me_3SiC^{a}H_2C^{b}H{=}C^{c}HC^{d}HSiMe_3$ [c]	7.36 ($2H_a$)	14.25 and 18.22 (H_b and H_d) 3.25 (H_c)		−122	2.0027	

[a] Reactions were also carried out with the compounds  [7],  , and  but the spectra which were obtained were too weak to be interpreted. [b] Hyperfine coupling to the γ(olefinic) proton of ca. 0.7 G may also be present, but it could not be distinguished from coupling to the protons of the methyl groups. [c] Tentative interpretation; see text.



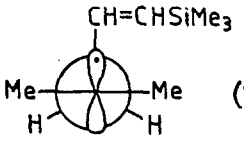
(6) (iv)

The ESR spectrum shows the exclusive formation of the tertiary rather than the primary homoallylic radical, and this is consistent with Chen, Edge, and Kochi's study of the ring-opening of the 1,2,2-trimethylcyclopropylmethyl radical to the radical **14** (eq. v) [9].

(14) (v)

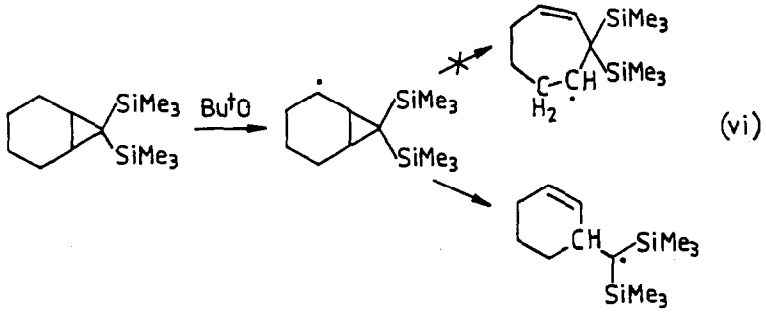
This regioselectivity would be consistent with the operation of factors (1) and (2) discussed above: no example is yet known of a monocyclic cyclopropylmethyl radical carrying a *cis*-2-alkyl substituent (as **6** does) giving principally the less alkylated radical, although the (2,2-difluorocyclopropyl)methyl radical is reported to give the 2,2-difluorobut-3-enyl radical [10].

The low value of $a(H_\beta)$ of 16.0 G in the radical obtained from **6** implies that steric repulsion by the α-methyl groups forces the C_β–C_γ bond to eclipse the singly-occupied p orbital, placing the β protons at ca. 30° to the nodal plane (formulae **15**); a similar effect is observed in the radical **14**, which shows $a(6H_\beta)$ 23.0 G, $a(2H_\beta)$ 17.5 G, at −54°C [9].



(15)

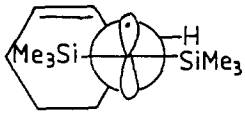
The reaction of the silylated bicycloheptane (**7**) illustrates the pseudoallylic character of the cyclopropylalkyl system in the reactivity of its α-methylene group. Hydrogen is abstracted from the methylene groups of the cyclohexane ring adjacent to the bridgeheads, and opening of the three-membered ring in principle could lead to either a cycloheptenyl radical or to a cyclohexenylmethyl radical (eq. vi).



(vi)

The ESR spectrum shows unambiguously the formation of the latter radical. The

hyperfine coupling of 0.35 G by the many protons of the methyl groups is characteristic of an α-silylalkyl radical (e.g. $Me_3SiCH_2\cdot$, $a(2H_\alpha)$ 20.88 G, a(9H, Me_3) 0.41 G, g 2.0025) [11]. The very low coupling (6.1 G) by the unique β proton implies that the βC–H bond lies in the nodal plane of the singly-occupied p orbital, so as to minimise steric repulsion between the trimethylsilyl groups and the cyclohexene ring (formulae **16**).



(16)

The related norcarane radical (**17**) undergoes ring-opening with a similar regioselectivity (eq. vii) but the radical (**18**) which is formed shows a much higher value of $a(H_\beta)$ of 25.7 G at $-87°C$, because this steric constraint is now absent [12].

(17) (18) (vii)

The regioselectivity is probably dominated, irrespective of other factors, by the need for the singly-occupied p orbital to eclipse the bond which is to break (our factor 3), as illustrated in **3**.

The spectrum of the radical derived from the silabicyclohexyl derivative **8** is shown in Fig. 2. Again, clearly the exocyclic radical has been formed, presumably because of the same geometrical condition for orbital interaction. Without the trimethylsilyl substituents at the radical centre, rotation about the C_α–C_β bond is

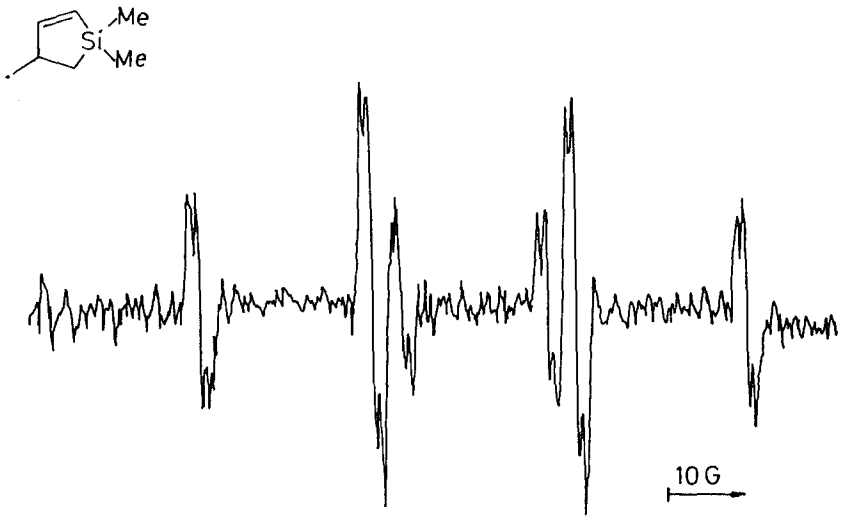
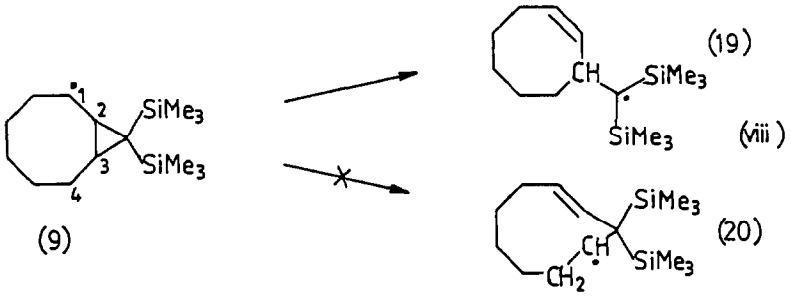


Fig. 2. ESR spectrum of the radical obtained by photolysis of di-t-butyl peroxide in the presence of the silabicyclohexyl compound **8** in cyclopropane at $-116°C$.

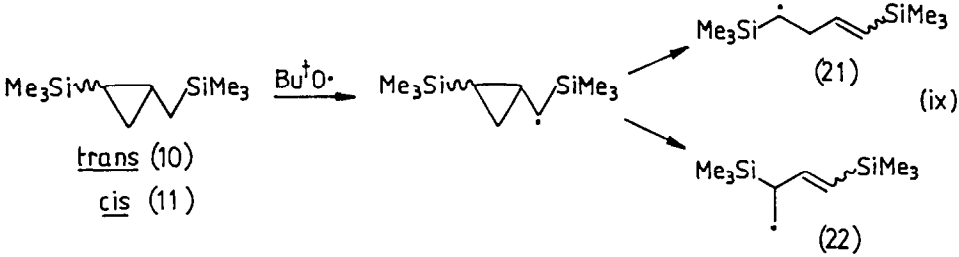
relatively free and the value of $a(H_\beta)$ is "normal" at 26.5 G (at $-128°C$).

The ESR spectrum of the radical obtained from the bicyclononane **9** showed a small hyperfine coupling to one unique proton, and partially resolved coupling to the methyl protons, showing that the exocyclic radical **19** is being formed to the exclusion of the endocyclic radical **20**. Again, the low value of $a(H_\beta)$ can be ascribed to a conformation similar to that of compound **16**.



Inspection of Dreiding molecular models suggests that the geometrical condition for orbital interaction is most severe in the [3,1,0]-bicyclopentyl radicals, and should relax with increasing ring size so that it may not be significant with the [6,1,0]-bicyclononyl system. However, factor (2) (and perhaps also factor (1)) outlined above should still operate to favour the formation of the exocyclic radical: steric hindrance by the two bulky trimethylsilyl groups would outweigh that by the methylene group at position 4, and lead to formation of the most sterically conjested radical.

We expected that the reaction of the *cis* and *trans* isomers **10** and **11** would provide information on the directive effect of the trimethylsilyl substituent on the ring-opening of a cyclopropylcarbinyl radical (eq. ix), although the spectra of both **21** and **22** would consist of a doublet of triplets.



The spectra which were observed are shown in Figs. 3 and 4, respectively, and it is immediately apparent that quite different radicals are being formed from the two reactants.

The principal hyperfine coupling constants and the *g*-factors for the radical derived from the *trans*-isomer **10** (Fig. 3) would be reasonable for either the radical **21** or **22**, but the magnitude of the coupling to the methyl protons (0.35 G) which is apparent in the expansion of the spectrum (inset Fig. 3) appears to favour the α-silylalkyl radical **21**. A similar hyperfine coupling to the Me_3Si groups of 0.35 G was observed in the α-silylalkyl radicals derived from the reactants **7** and **9**, and the radical $Me_3SiCH_2\cdot$ shows a(9H) 0.41 G [12], whereas the largest hyperfine coupling to a trimethylsilyl substituent in the β position that appears to have been reported is 0.10 G in the radical $Me_3SiCH_2CH_2\cdot$ [13], and here the Me_3Si group eclipses the singly occupied orbital.

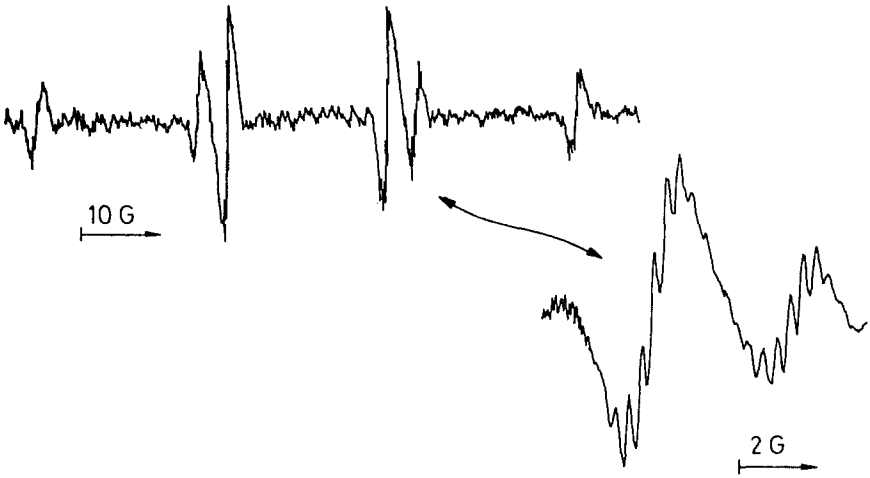


Fig. 3. ESR spectrum of the radical **21** obtained by photolysis of di-t-butyl peroxide in the presence of *trans*-(2-trimethylsilyl)cyclopropylmethyltrimethylsilane (**10**) in cyclopropane at −125°C. The inset expansion illustrates the hyperfine coupling by the protons of the Me_3Si group.

The spectrum obtained from the *cis*-isomer **11** (Fig. 4) clearly cannot be ascribed to either the radical **21** or **22**, and with an overall spectral width of only 50 G, and a hyperfine coupling to one unique proton of 3.25 G, there seems no reasonable alternative to an allylic structure for the radical. The same spectrum was obtained from two separate preparations of **11**, which were purified by GLC, and it seems unlikely that an impurity could be responsible for the spectrum. The best simulation

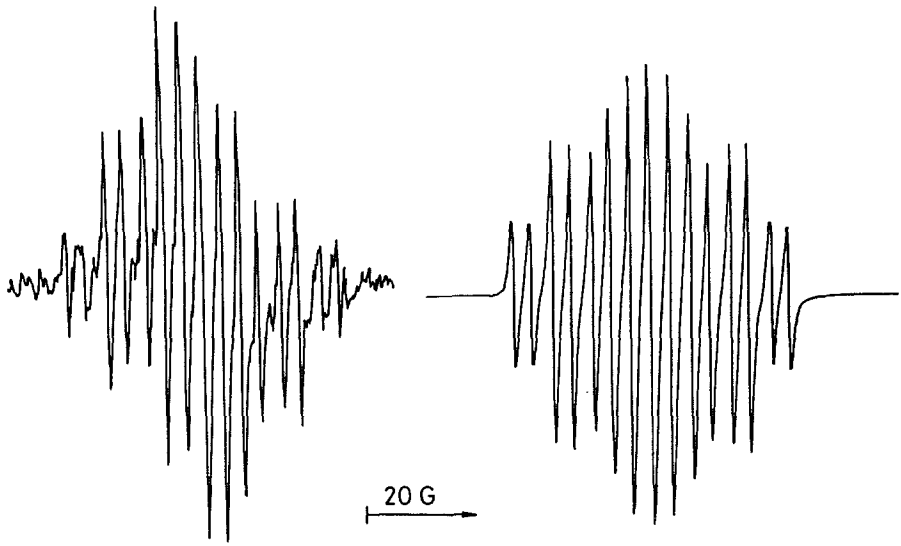
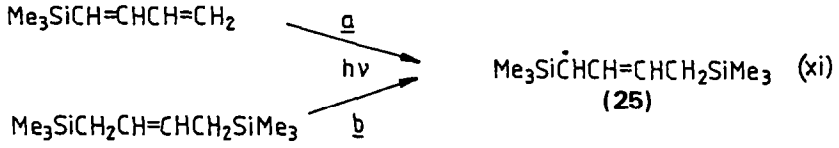


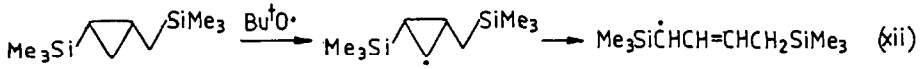
Fig. 4. ESR spectrum, and simulation, of the allylic radical **25** which is formed by photolysis of di-t-butyl peroxide in the presence of *cis*-(2-trimethylsilyl)cyclopropylmethyltrimethylsilane (ii) in cyclopropane at −122°C. The relative intensities of the lines vary with temperature, probably because a mixture of isomers is formed.

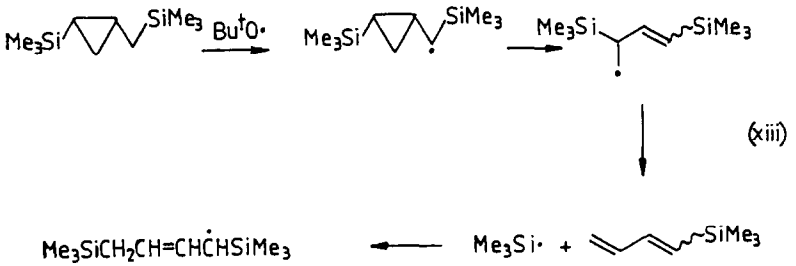
(see Fig. 4) was obtained using the hyperfine coupling constants given in Table 1, with ΔH_{pp} 0.85 G, and we believe that the radical has the allylic structure $Me_3SiCH{-}CH{=}CHCH_2SiMe_3$, for which there are four possible isomers. Similar spectra were obtained by treating a *cis/trans* mixture of 1-trimethylsilylbuta-1,3-diene with trimethylsilyl radicals, and by treating an impure sample of a *cis/trans* mixture of 1,4-bis(trimethylsilyl)but-2-ene with t-butoxyl radicals (eq. xi); the overall spectral width of about 50 G and the small coupling constant of 3.25 G were unchanged, and differences in the relative intensities of some of the signals might be caused by the presence of a different ratio of geometric isomers.



Reagents: a Me_3SiH, $Bu^t_2O_2$. b $Bu^t_2O_2$.

Two routes by which the allylic radical might be formed from **11** are shown in eqs. xii and xiii, though objections can be raised to both.





The first (eq. xii) assumes that attack will be at the cyclopropyl ring rather than at the exocyclic CH_2 group, and it is not apparent why a change from *trans* to *cis* stereochemistry should induce this, and further it assumes that the cyclopropyl radical undergoes rapid opening under mild conditions. The second (eq. xiii) assumes that, even though a *cis*-substituent is present, ring opening of the cyclopropylmethyl radical can lead to the formation of a primary alkyl radical, and then it assumes a novel 1,2-rearrangement.

In an attempt to trap an intermediate Me_3Si radical, a mixture of the *cis*-isomer **11**, di-t-butyl peroxide, and 1,1-di-t-butylethene was photolysed. A strong spectrum of an adduct $Bu^t_2\dot{C}CH_2X$ was observed, $a(2H_\beta)$ 11.4, $a(18H_\gamma)$ 0.49 G, g 2.0025, with a half-life of a few minutes at $-110°C$, whereas the radical $Bu^t_2\dot{C}CH_2SiMe_3$ shows $a(2H_\beta)$ 15.76, $a(18H_\beta)$ 0.36 G, g 2.0025 [14]. The trapped radical X· therefore cannot be Me_3Si·, and it is probably a carbon-centred radical: as a model, the radical $Bu^t_2\dot{C}CH_2Me$ shows $a(2H_\beta)$ 11.1, $a(18H_\gamma)$ 0.48 G, g 2.0025 [15].

For compounds **4–9**, the regioselectivity of the attack of $Bu^tO^\cdot$ radicals, the regioselectivity of the ring opening, and the ESR spectra of the radicals which are formed, are all in accord with established principles. On the other hand, the behaviour of the isomers **10** and **11** appears to contravene some of these principles. We hope now to devise, synthesise, and examine the behaviour of some new types of cyclopropylmethyl compounds in order to resolve this problem which the present work has identified.

Experimental

The silylated cyclopropanes **4–10** were prepared by Rawson and Harrison's modification of the Simmons and Smith methylenation [16] of the corresponding alkenes; some of the details have been published, and references are given in Table 1. Compound **11** was prepared by dichloromethylenation of allyltrimethylsilane; the dichlorocyclopropane was reduced with tributyltin hydride to the monochlorocyclopropane, which was then silylated with trimethylchlorosilane and lithium [17].

We were unable to obtain a pure sample of 1-trimethylsilylbutadiene by Petrov's method [18], as much trimethylsilanol was eliminated during the final dehydration with $KHSO_4$. However, the crude material which was used showed the appropriate NMR spectrum. 1,4-Bis(trimethylsilyl)but-2-ene was prepared by method described in ref. 19.

Mixtures of the silanes and of di-t-butyl peroxide in cyclopropane solution in Suprasil silica tubes were irradiated with light from a high pressure mercury arc, in the cavity of a Varian E4 or E109 ESR spectrometer.

Acknowledgement

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