Electron Spin Resonance Studies of Radical Addition to Methylenecycloalkanes

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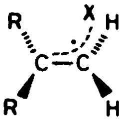
E.s.r. spectroscopy has been used to investigate homolytic addition to methylenecyclo-propane, -butane, and -pentane and to the acyclic 2-methylpropene. Regiospecific addition of $Me_3SiO^{\bullet}$, $Bu^t\dot{O}H^+$, and $Me_3Si^{\bullet}$ to the unsubstituted (tail) end of the double bond takes place with 2-methylpropene and methylenecyclo-butane and -pentane. However, although $Me_3Si^{\bullet}$ adds to the tail carbon of methylenecyclopropane, substituted but-3-enyl radicals result from the reactions of this alkene with $Me_3SiO^{\bullet}$, $Bu^tO^{\bullet}$, or $Bu^t\dot{O}H^+$. Ring opening thus accompanies or follows initial addition of the electrophilic radicals to the head carbon atom of methylenecyclopropane. This unusual regioselectivity is attributed to the dominance of polar effects in determining the activation energies for addition.

Homolytic addition to carbon–carbon double bonds is one of the more important free radical reactions and the orientation of addition to unsymmetrically substituted double bonds has been studied extensively. Addition to an acyclic 1,1-dialkylated ethylene invariably takes place with high selectivity at the unsubstituted carbon atom (the 'tail' end of the double bond) to give the tertiary radical (**1**) rather than the primary radical (**2**)

$$X^{\bullet} + R_2C{=}CH_2 \longrightarrow \underset{(\mathbf{1})}{R_2\dot{C}{-}CH_2X} + \underset{(\mathbf{2})}{XR_2C{-}\dot{C}H_2} \qquad (1)$$

('head' addition).[1–3] This regioselectivity is the result of steric and electronic effects which act to render the transition state (**3**) more stable than (**4**). Of the ultimate products, the tertiary radical (**1**) is more stable than the primary radical (**2**), because increased unpaired electron delocalisation by hyperconjugation is possible in the former and because less steric congestion is present if the relatively bulky alkyl groups are attached to the three-co-ordinate carbon atom. For exothermic radical addition to simple alkenes an early transition state, in which hyperconjugative delocalisation of the unpaired electron is of relatively little importance, is thought to be involved, and steric effects are believed to be dominant in determining activation energies.[1–3]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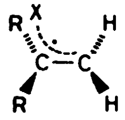
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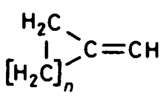
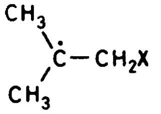

(**5**)

Qualitative consideration of the relative stabilities of the adduct radicals involved led us to conclude that head addition to the methylenecycloalkanes (**5**) should become less disfavoured thermodynamically as compared with tail addition as the size of the ring decreases. Lunazzi, Placucci, and Grossi[4–6] have previously investigated the reactions of trialkylsilyl and methylthiyl radicals with the methylenecycloalkanes (**5**; *n* = 1—4) using e.s.r. spectroscopy, and reported only tail addition in each case (no adduct was identified in the reaction of $MeS^{\bullet}$ with methylenecyclopropane). In the present paper we extend this study to other radical addenda and report evidence for predominant head addition of trimethylsiloxyl and protonated t-butoxyl radicals to methylenecyclopropane.

Results

E.s.r. spectra were recorded during continuous u.v. irradiation of liquid samples directly in the microwave cavity of the spectrometer.[7] The photochemically generated addenda investigated were (source shown in parentheses): trimethylsiloxyl[8] ($Me_3SiOOSiMe_3$), protonated t-butoxyl[9] (Bu^tOOBu^t + CF_3CO_2H), and trialkylsilyl[10,11] radicals (Me_3SiH or Et_3SiH + Bu^tOOBu^t). The reactions of these radicals with methylenecyclo-propane, -butane, and -pentane and, for comparison, with 2-methylpropene were studied generally in cyclopropane solution in the temperature range *ca.* 150—220 K. The relative concentrations of the transient carbon-centred radicals detected by e.s.r. spectroscopy may be taken to reflect the relative rates of their formation,[12] and it can safely be assumed that no interconversion of adduct radicals takes place within their lifetimes under the conditions employed.

In agreement with previous work,[5,13] when trimethylsilyl radicals were generated in the presence of each alkene (*ca.* 15% v/v), the e.s.r. spectrum of the corresponding tertiary alkyl radical (**6**—**9**; X = Me_3Si), resulting from tail addition to the double bond, was observed and no evidence for head addition was found. The e.s.r. parameters for all the adducts detected in this work are collected in Table 1. Similarly, photolysis of bis(trimethylsilyl) peroxide in the presence of 2-methylpropene afforded a spectrum of the adduct (**6**; X = Me_3SiO), the e.s.r. parameters of which agree well with those reported previously for this radical derived from another source.[14] No spectra of radicals resulting from head addition or from allylic hydrogen abstraction could be detected. Similarly, tail addition was the only mode of reaction of $Me_3SiO^{\bullet}$ with methylenecyclo-pentane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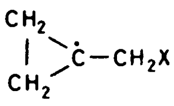
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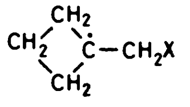
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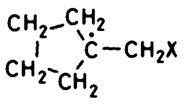

(**9**)

Table 1. E.s.r. parameters for the adduct radicals (**6**)—(**9**) in cyclopropane

Adduct radical	X	T/K	g-Factor	Hyperfine splittings (G)			$da(2H_\beta)/dT$[c] mG K^{-1}	Ref.[d]
				$a(2H_\beta)$	$a(nH_\beta)$[a]	Others[b]		
(**6**)	Me_3Si	185	2.0027	15.1	22.2		+4	
	Et_3Si	182	2.0027	15.3	22.2		+6	*e*
	Me_3SiO	183	2.0027	20.6	23.1		*ca.* 0	*f*
	Bu^tOH^+	188	2.0027	13.7	23.5		+20	
(**7**)	Me_3Si	151	2.0027	15.4	21.8		+30	*g*
	Et_3Si	153	2.0027	16.1	21.9			*g*
(**8**)	Me_3Si	175	2.0027	16.8	34.8	1.0 ($2H_\gamma$)	+18	
	Et_3Si	176	2.0027	16.9	34.5	1.1 ($2H_\gamma$)	+16	*g*
	Me_3SiO	167	2.0027	18.4	35.0	1.2 ($2H_\gamma$)		
	Bu^tOH^+	165	2.0027	13.3	35.9	1.1 ($2H_\gamma$)	+16	
	MeS	223		13.2	33.6	1.1 ($2H_\gamma$), 0.5 (CH_3S)	+10	*h*
(**9**)	Me_3Si	200	2.0027	15.4	32.6		+9	
	Et_3Si	189	2.0027	15.8	32.8		+12	*g*
	Me_3SiO	176	2.0027	18.8	33.7		*ca.* 0	
	Bu^tOH^+	174	2.0027	12.8	34.1		+20	
	MeS	223		12.6	32.0	0.45 ($4H_\gamma$), 0.45 (CH_3S)	+10	*h*

[a] For (**6**), $n = 6$; for (**7**)—(**9**), $n = 4$. [b] Nuclei indicated in parentheses. [c] Approximate (± 3 mG K^{-1}) temperature dependence in the region of the quoted temperature. [d] This work, unless otherwise stated. [e] First reported in ref. 13. [f] First reported in ref. 14. [g] First reported in ref. 5. [h] Data from ref. 6.

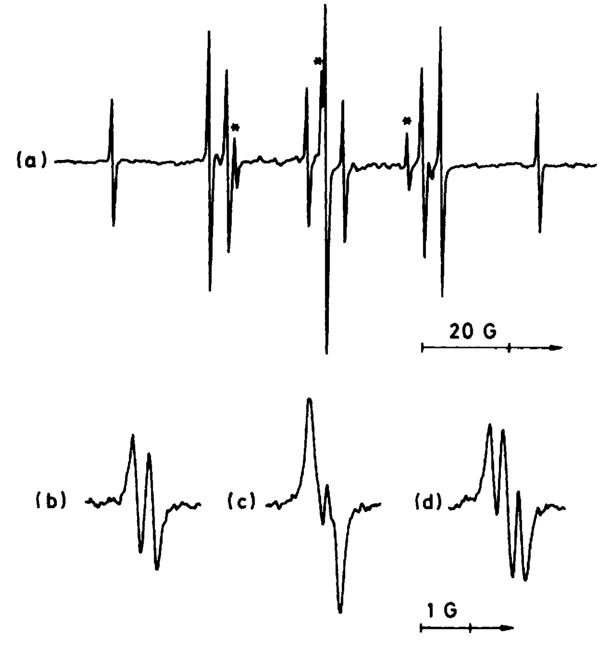
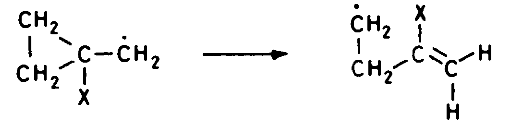


Figure. (a) E.s.r. spectrum of the 3-trimethylsiloxybut-3-enyl radical (**11**; X = Me_3SiO) at 145 K in cyclopropane, produced during photolysis of $Me_3SiOOSiMe_3$ in the presence of methylenecyclopropane. At such low temperatures the $M_I(H_\beta) = 0$ lines are broadened relative to the other lines in the spectrum and this lineshape effect is characteristic of out-of-phase modulation of the splittings from instantaneously non-equivalent β-protons. The unsubstituted but-3-enyl radical shows a different type of selective line broadening (see refs. 17 and 27). The lines marked with asterisks arise from $Me_3SiOSiMe_2O\dot{C}H_2$ (see text). (b), (c), (d) Expansions of lines 1, 2, and 3, respectively, from the spectrum of (**11**; X = Me_3SiO) at 172 K in cyclopropane, showing second-order effects on lines 2 and 3

or -butane (see Table 1).[4,8] However, photolysis of $Me_3SiOOSiMe_3$ in the presence of methylenecyclopropane gave rise to the spectrum shown in the Figure and which we assign to the substituted but-3-enyl radical (**11**; X = Me_3SiO), probably formed by ring-opening rearrangement of the intermediate cyclopropylmethyl radical (**10**) or possibly in a concerted



(**10**) (**11**) (2)

process. Even at the lowest accessible temperature (129 K in propane solvent), the spectrum of (**10**; X = Me_3SiO) was not detected, and hence ring opening would have to be extremely rapid, as it is known to be for the parent cyclopropylmethyl radical[15] (**10**; X = H) and for the 1-methyl analogue[16] (**10**; X = Me). The e.s.r. parameters for (**11**; X = Me_3SiO) are given in Table 2 and are in accord with expectation based on those reported previously for (**11**; X = H or Me).[16,17] The spectrum of (**11**; X = H) shows two small doublet splittings, the larger (0.62 G) of which is assigned to H_γ (≡X) and the smaller (0.35 G) to one of the non-equivalent δ-protons.[17] In the spectrum of (**11**; X = Me_3SiO) only the smaller doublet splitting is detectable (see Figure), although second-order splittings are also evident for 'lines' of greater than unit intensity. The value of $a(2H_\beta)$ for (**11**; X = Me_3SiO) is smaller than that for (**11**; X = H) and similar to that for (**11**; X = Me), indicating that the bulk of the γ-substituent exerts an effect on the conformation of these species about the C_α–C_β bond.

An e.s.r. spectrum[8] [a(2H) 19.4 G, g 2.0033 at 181 K], very probably due to $Me_3SiOSiMe_2O\dot{C}H_2$, which could originate indirectly from the $Me_3SiOOSiMe_3$ after its rearrangement to $Me_3SiOSiMe_2OMe$, is also evident in the Figure. The same spectrum was present in the absence of alkene, but when methylenecyclopropane was replaced by similar concentrations of methylenecyclo-butane or -pentane or 2-methylpropene, only the appropriate tail adduct spectrum was detected. Since $Me_3SiOSiMe_2O\dot{C}H_2$ is presumably formed by hydrogen transfer to $Me_3SiO^\bullet$ in competition with addition of the latter to the C=C moiety, this result implies that methylenecyclopropane undergoes homolytic addition less readily than the other alkenes. Also just visible in the Figure is a very weak third spectrum which, although it could not be analysed conclusively, appears unlikely to arise from the tail adduct (**7**; X = Me_3SiO).

It has been shown previously[9] that the protonated t-butoxyl radical (the t-butyl alcohol radical cation), like $Me_3SiO^\bullet$,[8]

Table 2. E.s.r. parameters for the 3-substituted but-3-enyl radicals (**11**) in cyclopropane

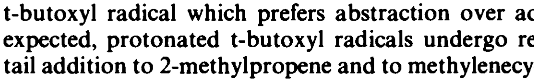
X	T/K	g-Factor	Hyperfine splittings (G)				Ref.
			$a(2H_\alpha)$	$a(2H_\beta)$	$a(1H_\gamma)$	$a(1H_\delta)$	
Me_3SiO	171	2.0027	22.3	26.3		0.34	*a*
Bu^tOH^+	163	2.0026	22.2	27.1		0.43	*a*
Bu^tO	158	2.0026	22.3	27.0		0.43	*a*
H	160	2.0028	22.25	29.42	0.62	0.35	*b*
Me	203		22.18	26.86			*c*

[a] This work. [b] Ref. 17. [c] Ref. 16.

prefers to *add* to carbon–carbon double bonds rather than to *abstract* allylic hydrogen atoms, in contrast to the neutral t-butoxyl radical which prefers abstraction over addition. As expected, protonated t-butoxyl radicals undergo regiospecific tail addition to 2-methylpropene and to methylenecyclo-butane and -pentane to afford (**6**), (**8**), and (**9**) ($X = Bu^tOH^+$), respectively. No evidence for head addition or allylic hydrogen abstraction was found.

However, with methylenecyclopropane a strong e.s.r. spectrum assigned to (**11**; $X = Bu^tOH^+$), the product of ring-opening, was observed. A second, much weaker, spectrum was also present and this was similar to that derived from the reaction of $Me_3SiO^\bullet$ with methylenecyclopropane (see before) and likewise probably does not arise from the tail adduct (**7**; $X = Bu^tOH^+$). After extended irradiation of cyclopropane solutions containing methylenecyclopropane, Bu^tOOBu^t, and CF_3CO_2H (15, 15, and 8% v/v, respectively), an unidentified spectrum became evident and the intensity of this was greater if the sample had not been kept at 77 K prior to irradiation, which was the usual practice in order to avoid the possibility[18] of thermal reactions of the alkenes. Replacement of the CF_3CO_2H with CF_3CO_2D had no noticeable effect on the e.s.r. spectra obtained.

Lunazzi *et al.*[4] have reported that unprotonated t-butoxyl radicals react with methylenecycloalkanes to afford the allylic radicals (**12**; n = 1—4). When n = 2—4 only (**12**) was detected,



(**3**)

(**12**)

but with methylenecyclopropane the spectrum of a second radical, analysed in terms of a(2H) 21.8, a(2H) 26.8, a(1H) 0.55, and a(1H) 0.26 G, was observed along with that attributed to (**12**; n = 1) and this second radical was thought to be but-3-enyl (**11**; X = H). However, the reported splitting constants for the second radical differ rather markedly from those (Table 2) of (**11**; X = H); in particular, $a(2H_\beta)$ is closer to the corresponding values for (**11**; $X = Me_3SiO$ or Bu^tOH^+). Furthermore, it is not easy to see how the but-3-enyl radical ($C_4H_7^\bullet$) could arise from methylenecyclopropane (C_4H_6) under the experimental conditions. We were thus prompted to repeat the experiment.

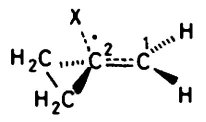
In our hands, irradiation of cyclopropane solutions containing di-t-butyl peroxide and methylenecyclopropane afforded overlapping e.s.r. spectra of at least two radicals. The most readily identified and easily analysed spectrum appeared as a triplet of triplets under low resolution [a(2H) 22.3, a(2H) 27.0 G, g 2.0026 at 158 K], as reported by Lunazzi *et al.*[4] for their second radical, but under higher resolution the wing lines were clearly seen to be 1:1 doublets [a(1H) 0.43 G, ΔB_{p-p} 0.15 G at 158 K] rather than 1:1:1:1 quartets. Further towards the centre of the spectrum, this fine structure was obscured by lines from (an)other radical(s) and, of course, second-order splittings also contributed to the appearance of 'lines' of greater than unit intensity. We are therefore forced to conclude that the radical (**11**; $X = Bu^tO$) is being formed in this system rather than the but-3-enyl radical, as suggested previously.[4] It is not surprising that neutral t-butoxyl radicals should undergo *relatively* rapid addition to methylenecyclopropane, since the allylic C–H bonds in this alkene would be expected to be much stronger than those in the larger-ring methylenecycloalkanes or in 2-methylpropene.

The e.s.r. parameters of (**11**; $X = Bu^tO$) are experimentally indistinguishable from those attributed to the *O*-protonated analogue and therefore we cannot exclude the possibility that, although Bu^tOH^+ adds to methylenecyclopropane, the ultimate product radical is not in fact protonated to a significant extent at oxygen, perhaps because the basicity of this atom is reduced by attachment to the unsaturated system.

Discussion

The tertiary adduct radical (**1**) resulting from homolytic addition to an acyclic alkene $R_2C=CH_2$ is more stable than the primary radical (**2**) and the activation energy for tail addition to the alkene is lower than that for head addition.[1–3] However, although tail addition to methylenecyclopropane produces a tertiary adduct radical, this will be appreciably *destabilised* by virtue of also being a cyclopropyl radical [DH°(cyclo-C_3H_5–H) = 445 kJ mol^{-1} *cf.* DH°(Me_2CH–H) = 398 kJ mol^{-1}].[19] Moreover, although head addition to methylenecyclopropane produces a primary adduct radical, this will be *stabilised* to some extent relative to (**2**) by virtue of being a cyclopropylmethyl radical.[20] Thus, the enthalpy changes involved in head or tail addition to methylenecyclopropane are likely to be fairly similar and head addition could even be the more exothermic reaction. Although polar factors are probably also responsible in part, these thermodynamic effects are reflected in the *kinetics* of hydrogen abstraction from methylcyclopropane and from 2-methylpropane (Me_3CH) by t-butoxyl radicals: the former hydrocarbon gives cyclopropylmethyl rather than the tertiary 1-methylcyclopropyl radical,[17a] whilst the latter gives mainly t-butyl.

On the basis of the foregoing discussion, methylenecyclopropane might well undergo homolytic addition more slowly than the larger-ring methylenecycloalkanes and 2-methylpropene, and some qualitative evidence for this has been found (see Results section). As a consequence, the transition states (**13**) and (**14**) for addition to methylenecyclopropane are likely to occur further along the reaction co-ordinate than the early transition states usually assumed[1–3] for addition to acyclic alkenes.



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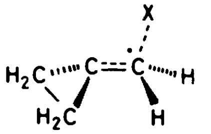


(**14**)

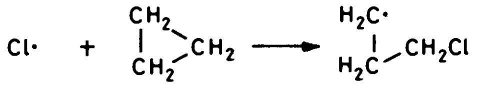
If the geometry of the transition state for head addition is as shown in (**13**), then the axis of the developing C(1)–2p SȮMO will be close to perpendicular to the plane of the ring, an orientation unfavourable for cyclopropylmethyl stabilisation.[20] It is generally accepted[21] that the optimum transition state geometry for ring opening of cyclopropylmethyl radicals such as

(**10**) requires effective overlap of the C_α–$2p$ SOMO with the orbitals of the C–C σ-bond which is to undergo cleavage. In the transition state (**13**) the SOMO will overlap only poorly with the ring C–C σ orbitals and hence, if it proceeds through (**13**), head addition to methylenecyclopropane is unlikely to be concerted with ring-opening to give (**11**) and a discrete intermediate (**10**), in which rotation about C_α–C_β is relatively unhindered, is probably involved.

We propose that the orientation of homolytic addition to methylenecyclopropane is controlled by a delicate balance between steric and polar effects which governs the relative energies of the transition states (**13**) and (**14**). Steric effects will favour tail addition, particularly for more bulky addenda, but could be less decisive than for addition to acyclic alkenes.

If $X^\bullet$ is an electrophilic radical such as $Me_3SiO^\bullet$, $Bu^tO^\bullet$, or $Bu^t\dot{O}H^+$ there will be a build-up of negative charge on X in the transition state for addition and a consequent build-up of positive charge on the tail carbon of (**13**) and on the head carbon of (**14**). The geometry at the head carbon in (**14**) would be expected to be non-planar, since the cyclopropyl radical product will be pyramidal at C_α, whilst planarity should be maintained at the tail carbon in (**13**). Since cyclopropylmethyl cations are relatively stable* whilst cyclopropyl cations are destabilised,[22] such charge separation in the transition states will favour head addition of electrophilic radicals to methylenecyclopropane. Conversely, for addition of a nucleophilic radical such as $R_3Si^\bullet$ there will be a build-up of negative charge at the tail carbon of (**13**) and the head carbon of (**14**). Since cyclopropyl anions are relatively stable,[22] nucleophilic radicals should show a much greater tendency to add to the tail carbon than do the electrophilic radicals.

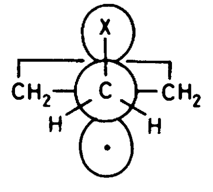
Consideration of the frontier molecular orbital[23] (FMO) interactions involved in the addition of an electrophilic radical to methylenecyclopropane suggests an alternative explanation for the ease of head attack leading to ring-opening. The dominant FMO interaction should be between the SOMO of the addendum and the HOMO of the alkene. For simple alkenes the HOMO is the C–C π orbital, but for methylenecyclopropane a filled ($4B_2$) orbital, which is mainly ring C–C σ bonding in character, is close in energy.[24] This orbital has a large contribution from the head C–$2p_\sigma$ orbital perpendicular to the exocyclic σ bond, and attack of an electrophilic addendum on the head carbon might thus be favoured when the radical approaches in the plane of the ring and perpendicular to the exocyclic bond. Bonding to the addendum might then be concerted with exothermic ring-opening, the C–C π bond would not be disrupted, and a discrete intermediate cyclopropylmethyl radical would not be involved. Viewed in this way, the reaction of methylenecyclopropane with electrophilic radicals is analogous to the homolytic (S_H2) ring-opening of cyclopropane by, for example, chlorine atoms [equation (4)].[25]



(4)

In a very recent report, which appeared while our paper was in preparation, Fields *et al.*[26] have described the reactions of Br_2, Cl_2, and CF_3I with substituted perhalogenated derivatives of methylenecyclopropane. In order to explain the products from these radical chain reactions, Fields *et al.*[26] also propose the occurrence of homolytic head addition accompanied or followed by rapid ring-opening.

Conformations of Adduct Radicals.—The magnitudes and temperature dependences of the β-proton coupling constants can be used to deduce the preferred conformations of the adduct radicals described in Table 1.[27] The eclipsed form (**15**) is evidently preferred for all the tail adducts to the methylenecycloalkanes, and similar conclusions have been reached previously by Lunazzi *et al.* for the methylthiyl and trialkylsilyl radical adducts.[5,6]



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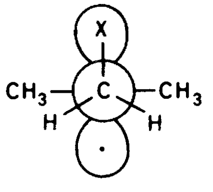

(**16**)

This preference for the eclipsed conformation (**15**) is particularly marked[27] for (**8**) and (**9**) ($X = Bu^tOH^+$) which, as when X = MeS,[6] exhibit a low value of $a(2H_\beta)$ in the region of 13 G which increases with increasing temperature. Torsional motion about C_α–C_β is less restricted when $X = Me_3SiO$, as evidenced by the larger values of $a(2H_\beta)$. This difference is likely to be partly steric in origin, the Bu^tOH^+ group, with the $CF_3CO_2^-$ counteranion probably in close attendance, being more bulky than Me_3SiO, but electronic effects could also be important. The Bu^tOH^+ group is presumably more electronegative than Me_3SiO and e.s.r. evidence indicates that a β-CF_3O substituent has a greater tendency to 'bridge' than the less electronegative CH_3O group in radicals of the type $ROCH_2\dot{C}HMe$ and $ROCH_2\dot{C}Me_2$.[28] Furthermore, it has been suggested[29] on the basis of molecular orbital calculations that protonation of the oxygen atom in $HOCH_2\dot{C}H_2$ significantly reduces the activation energy for 1,2-shift of the oxy substituent *via* a bridged transition state. Fairly rigid locking in the eclipsed conformation (**16**) is indicated by the magnitude of $a(2H_\beta)$ for the acyclic adduct (**6**; $X = Bu^tOH^+$). Torsional motion about C_α–C_β is less restricted for (**6**; $X = R_3Si$), although (**16**) is still preferred,[27] but evidently (**6**; $X = Me_3SiO$) has little conformational preference.

Experimental

E.s.r. Spectroscopy.—Spectra were recorded using a Varian E-4 or E-109 instrument operating at *ca.* 9.2 GHz. The techniques used for sample preparation and for the detection of transient free radicals generated photochemically in the spectrometer cavity have been described previously.[7]

g-Factors and hyperfine splitting constants were computed from the measured microwave frequency and line positions, the latter determined using an n.m.r. gaussmeter and corrected for the field difference between the sample and the n.m.r. probe using the pyrene radical anion (*g* 2.00271) as a standard.[30] Best-fit spectroscopic parameters were generally obtained using Preston's program ESRLSQ which employs an exact solution of the isotropic Hamiltonian and an iterative least-squares fitting procedure.[31]

Materials.—2-Methylpropene, propane, and cyclopropane (Matheson), methylenecyclopropane (Fluka), methylenecyclobutane and -pentane, triethylsilane, and trifluoroacetic acid (Aldrich), and trimethylsilane (Fluorochem) were used as received. Di-t-butyl peroxide (Fluka) was purified before use and bis(trimethylsilyl) peroxide was prepared as described previously.[32]

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* Such stability will not be substantially developed in (**13**) because of the unfavourable orientation of the three-membered ring.[22]

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