

when $E_s < E_\pi$, the π polarization dominates. When $E_s > E_\pi$, the s polarization dominates. Reference to 23 and 24 translates this into case B for $E_s > E_\pi$ and case A for $E_s < E_\pi$. These are indeed both cases which result in polarization away from s , as in 21, and this completes the demonstration.

Finally we inquire about the energy dependence of the magnitude of the polarization. For the acceptor case the polarization is given by $c_{\pi^*,\pi''}$ from (48), which is larger the closer s lies to π , *i.e.*, the lower s lies for realistic acceptors. For the donor case the polar-

ization is proportional to

$$c_{\pi^*,\pi''} + c_{s,\pi'} c_{s,\pi^*}' = \frac{H_{\pi,s} H_{s,\pi^*}'}{E_\pi - E_s} \times \left(\frac{1}{E_\pi - E_{\pi^*}} - \frac{1}{E_s - E_{\pi^*}} \right) = \frac{K'}{(E_\pi - E_{\pi^*})(E_s - E_{\pi^*})} \quad (55)$$

This is larger in magnitude the closer s lies to π^* , *i.e.*, the higher s lies. Thus the "better" the donors or acceptors are, respectively, the more effective they should be at polarizing the π system.

Substituent Effects in the Bridging by Oxygen in Alkyl Radicals by Electron Spin Resonance

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Abstract: Trifluoromethoxy radicals generated photochemically from bistrifluoromethyl peroxide add to ethylene, propylene, and isobutylene, and the esr spectra of the adducts can be observed over a range of temperatures. Analysis of the β -proton hyperfine splitting and its temperature dependence indicates that the propylene adduct exists in a stable conformation in which the β oxygen eclipses the p orbital at the radical center. The adducts of PhCO_2 and PrOCO_2 radicals show similar conformational preferences, which are unusual since the β - CH_3O , n -BuO, HO, and $(\text{CH}_3)_3\text{SiO}$ analogs prefer stable conformations in which the β oxygen is staggered relative to the half-filled p orbital similar to the conformation of the *sec*-butyl radical. Homoconjugative and hyperconjugative interactions of the β - CF_3O , PhCO_2 , and PrOCO_2 groups to the radical center are discussed, but neither of them is sufficiently strong to force the ethylene adduct to a similar eclipsed conformation. Comparisons of the sulfur and other oxygen adducts indicate that bridging is much more important with sulfur. Bridging can be induced only when electronegative groups are present on the oxygen center and are noticeable when energy differences between conformations are relatively small as in the β -substituted isopropyl radicals. A β -fluorine substituent is similar to β - CF_3O in this regard.

Stabilization of alkyl radicals and stereoselectivity in free radical reactions due to bridging and anchimeric assistance are subjects which have been discussed at length and are of current chemical interest.^{1,2} The dominant chemical effects are exerted by heteroatom substituents at the β carbon relative to the radical center, and they are especially pronounced with the halogens, bromine and chlorine, and sulfur.

The electron spin resonance (esr) spectra is an effective tool for the study of the structure and conformations of free radicals. The technique has been greatly aided by the development of procedures for the production of specific alkyl radicals in sufficiently high concentrations in solution to examine over a range of temperatures.^{3,4} The conformations and structures of a variety of β -sulfur substituted radicals have been examined by esr,^{5,6} but there is no example heretofore of an oxygen substituent involved in bridging. In order to determine whether a first row element in the

periodic table such as oxygen can participate in radical bridging, we examined the esr spectra of a variety of β -oxygen substituted alkyl radicals in solution.

Results

Photolysis of Bistrifluoromethyl Peroxide. The photolysis of bistrifluoromethyl peroxide in dichlorodifluoromethane (Freon-12) solutions at temperatures between -50 and -130° gave rise to no detectable esr spectrum. In order to optimize conditions for the observation of transient paramagnetic species, the



microwave power as well as the modulation amplitude were varied widely. The presence of trifluoromethoxy radical was undetected probably due to line broadening in the spectrum by relaxation effects described previously in attempts to observe alkoxy radicals in solution.⁷

Photolysis of bistrifluoromethyl peroxide in eq 1 probably proceeds by the same process involved in the previously studied di-*tert*-butyl peroxide.⁶ Moreover, we could find no evidence for photolytic scission at the C-O bond, since the spectrum of neither trifluoromethyl

(1) P. S. Skell and K. J. Shea in "Free Radicals," Wiley-Interscience, New York, N. Y., 1973, Chapter 26.

(2) L. Kaplan, "Bridged Free Radicals," Marcel Dekker, New York, N. Y., 1972.

(3) H. Fischer in ref 1, Chapter 19.

(4) J. K. Kochi and P. J. Krusic, *Chem. Soc., Spec. Publ.*, No. 24, 147 (1970).

(5) T. Kawamura, M. Ushio, T. Fujimoto, and T. Yonezawa, *J. Amer. Chem. Soc.*, **93**, 908 (1971).

(6) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971).

(7) M. C. R. Symons, *J. Amer. Chem. Soc.*, **91**, 5924 (1969).

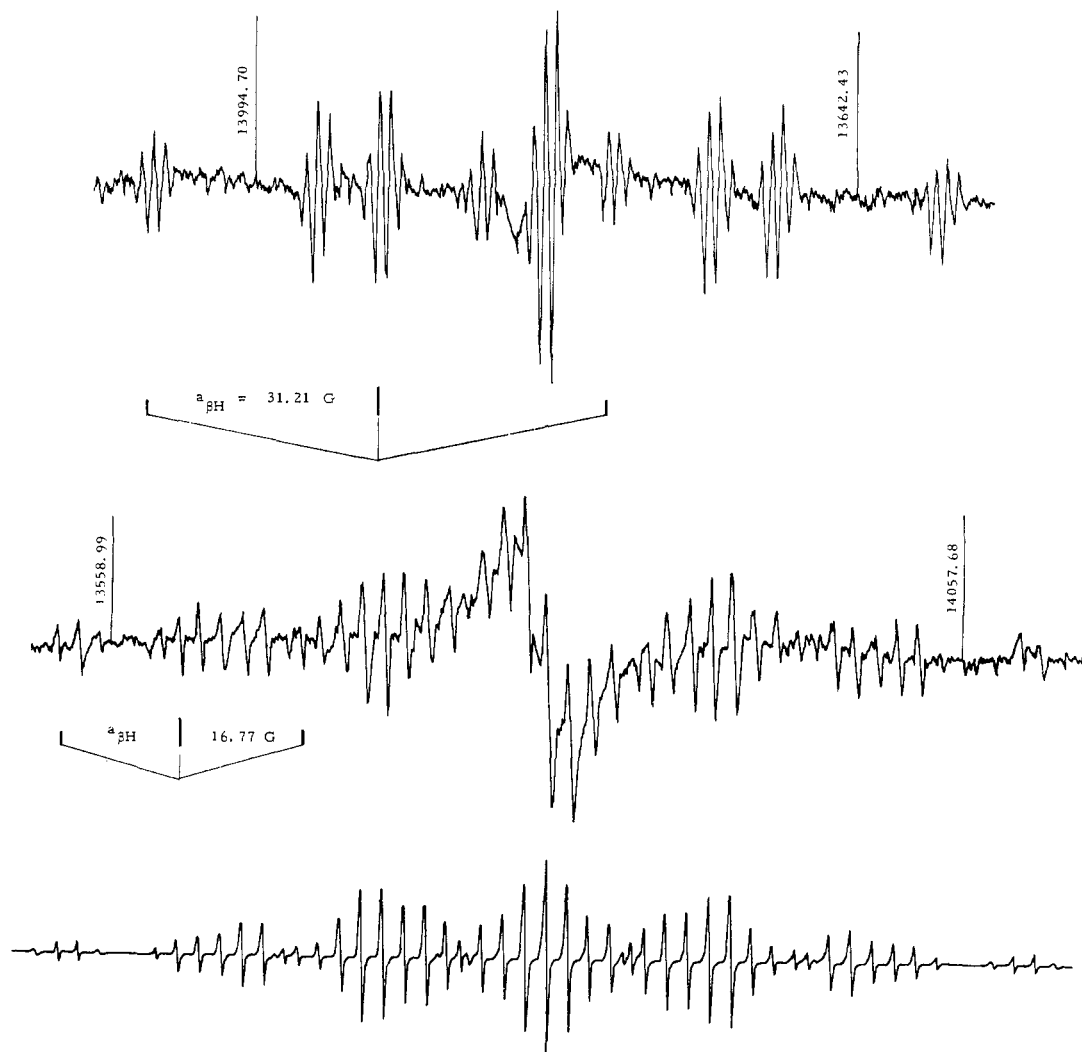
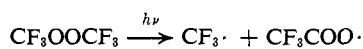
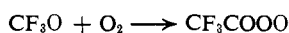


Figure 1. ESR spectra of (a, top) $\text{CF}_3\text{OCH}_2\dot{\text{C}}\text{H}_2$ and (b, bottom) $\text{CF}_3\text{OCH}_2\dot{\text{C}}\text{HCH}_3$ at -137 and -91° , respectively, in Freon-12 solutions. Proton nmr field markers are in kHz.



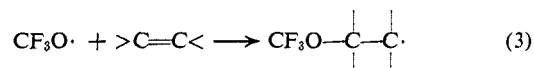
nor trifluoromethylperoxy radical is observed.⁸ An earlier study⁹ carried out at *ca.* -190° in $\text{CF}_4\text{-CClF}_3$ solutions afforded the same esr spectrum from both bis-trifluoromethyl peroxide and trifluoromethyl hypofluorite. The spectrum ($\langle g \rangle = 2.0041$) consisting of a doublet (6.72 G) of triplets (0.54 G) was assigned to a nonlinear $\text{CF}_3\text{O}\dot{\text{O}}$ showing inequivalent fluorines, but it was subsequently shown⁸ to be due to $\text{CF}_3\text{OO}\dot{\text{O}}$, presumably formed by reaction of $\text{CF}_3\dot{\text{O}}$ with adventitious oxygen.



The photolysis of bistrifluoromethyl peroxide carried out in cyclopropane solutions afforded a well-resolved esr spectrum of the cyclopropyl radical. The formation

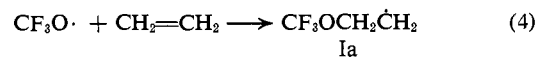


of trifluoromethoxy radicals in high yields by photolysis of bistrifluoromethyl peroxide is shown further by the intense esr spectra of the adducts formed in the presence of various alkenes (eq 3). The structure and conforma-

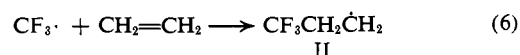
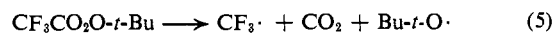


tion of the ethylene, propylene, and isobutylene adducts are presented in the following order, and compared to the sulfur analogs studied earlier.⁶

Trifluoromethoxy Adduct to Ethylene. The photolysis of bistrifluoromethyl peroxide in a Freon-12 solution of ethylene afforded the well-resolved esr spectrum shown in Figure 1a.¹⁰ The hyperfine splitting con-



sisting of a triplet of triplets of quartets with the correct binomial intensity ratio is consistent with the adduct Ia in eq 4. The spectrum of the adduct cannot be due to the addition of trifluoromethyl radical. The latter can be generated independently in eq 5 from the photolysis of *tert*-butylperoxy trifluoroacetate, and the adduct II to ethylene in eq 6 affords an entirely dif-



ferent esr spectrum.¹¹

(8) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **44**, 434 (1966); **43**, 2704 (1965); R. W. Fessenden, *ibid.*, **48**, 3725 (1968).

(9) B. Vanderkooi, Jr., and W. B. Fox, *J. Chem. Phys.*, **47**, 3634 (1967).

(10) Also reported in a previous study (see ref 6).

(11) Unpublished results.

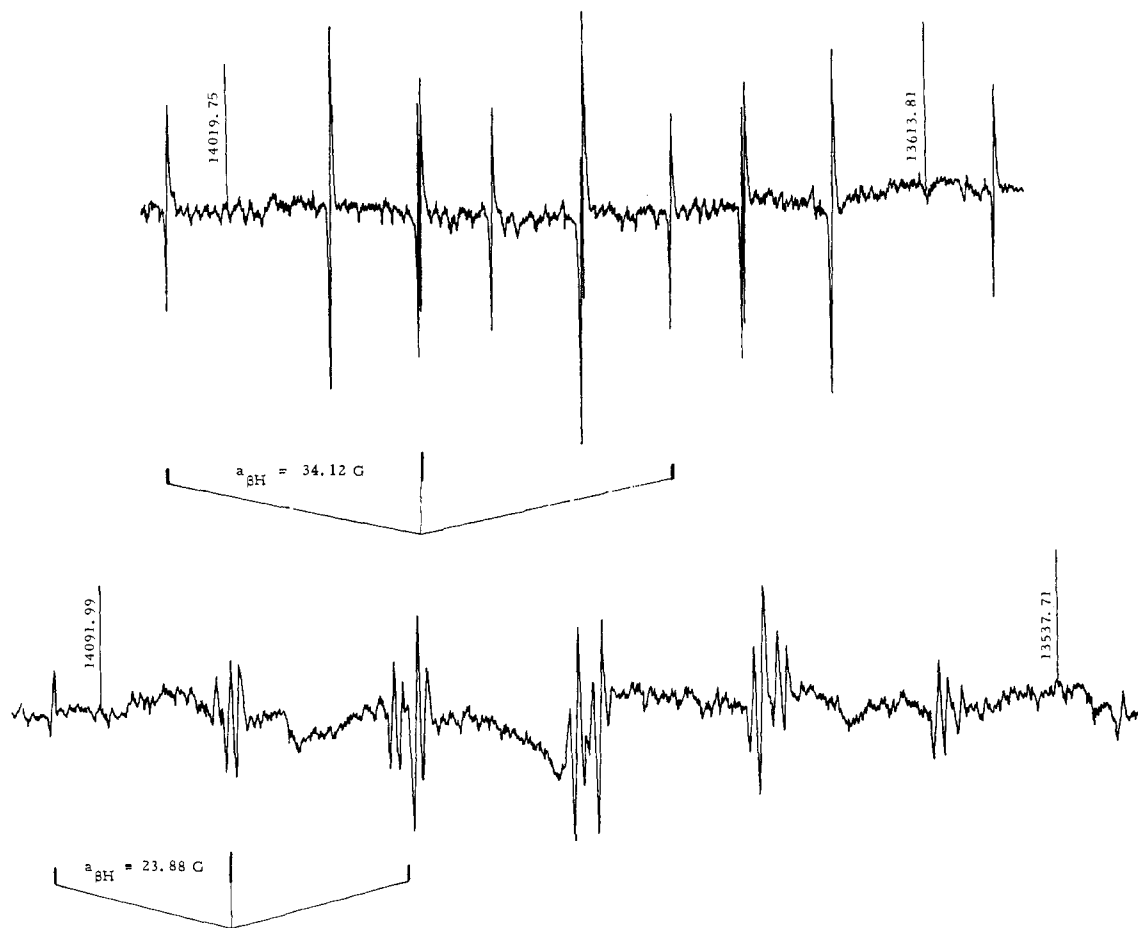
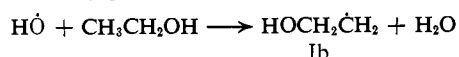
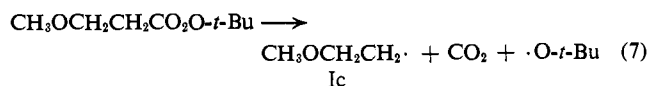


Figure 2. ESR spectra of (a, top) $\text{CH}_3\text{OCH}_2\dot{\text{C}}\text{H}_2$ and (b, bottom) $\text{CH}_3\text{OCH}_2\dot{\text{C}}\text{HCH}_3$ at -121 and -91° , respectively, in cyclopropane solutions. Proton NMR field markers are in kHz.

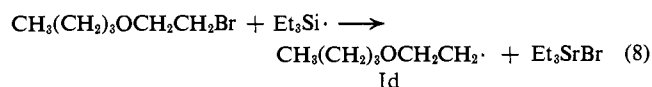
The ESR parameters for β -trifluoromethoxyethyl radical in Table I are the same as those of the hydroxy analog Ib generated by hydrogen abstraction from ethanol with photochemically generated hydroxy radicals.¹²



The ESR spectrum of Ia (Figure 1) is also similar to that of the methoxy analog Ic (Figure 2a), generated independently from the acyl peroxide in eq 7, as well



as that of the *n*-butoxy analog Id generated from the alkyl halide in eq 8.¹³ No significant selective line



broadening was observed in the spectra of Ia, Ic, and Id between -50 and -130° . The β -proton hfs in all the radicals showed the same negative temperature dependence shown in Figure 3 for the *n*-propyl radical, although the magnitudes of the hfs differed slightly. The ESR parameters of these β -oxyethyl radicals are all collected in Table I.

Trifluoromethoxy Adduct to Propylene. The ESR spectrum in Figure 1b obtained during the photolysis of

- (12) R. Livingston and H. Zeldes, *J. Chem. Phys.*, **44**, 1245 (1966).
 (13) D. J. Edge and J. K. Kochi, *J. Amer. Chem. Soc.*, **95**, 2635 (1973).

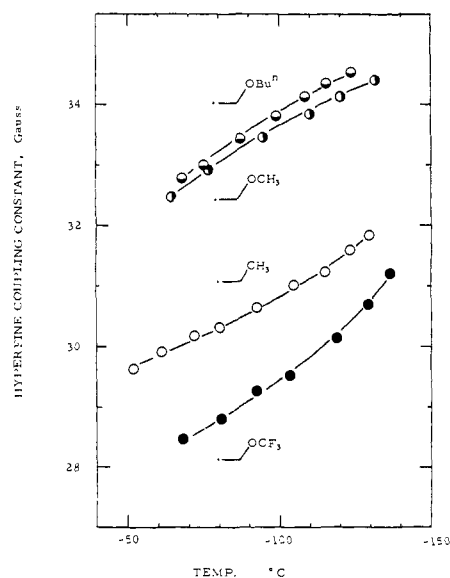


Figure 3. Temperature dependences of the β -proton hyperfine splittings in β -oxygen substituted ethyl radicals: (●) $\text{CF}_3\text{O}\cdot$; (○) $\text{CH}_3\cdot$; (◐) $\text{CH}_2\text{O}\cdot$; (◑) *n*-BuO \cdot .

bistrifluoromethyl peroxide and propylene in Freon-12 solution consisted of a single species. The coincidence with the computer simulation using the parameters in Table II indicates the species to be the propylene adduct IIIa in eq 9. Interestingly, there is clearly no evidence for the presence of the allyl radical in the spectrum.

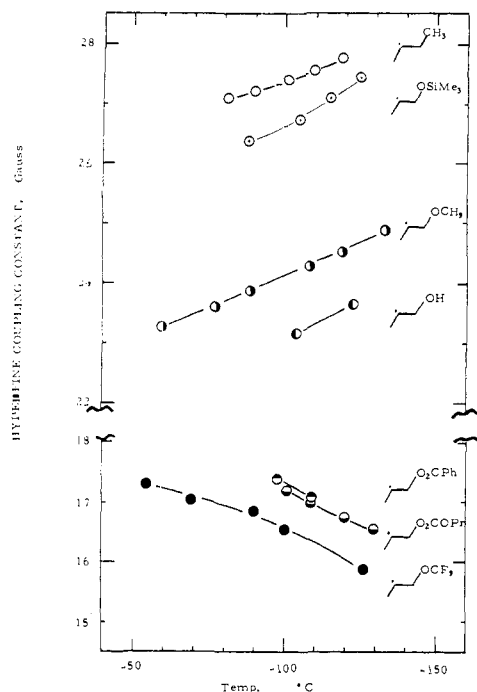


Figure 4. Temperature dependences of the β -proton hyperfine splittings for β -oxygen substituted isopropyl radicals: (●) CF_3O ; (⊙) $n\text{-PrOCO}_2$; (⊙) PhCO_2 ; (○) HO ; (○) CH_3O ; (○) CH_3 ; (○) $\text{OSi}(\text{CH}_3)_3$.

Table I. ESR Parameters of β -Oxygen Substituted Ethyl Radicals in Solution

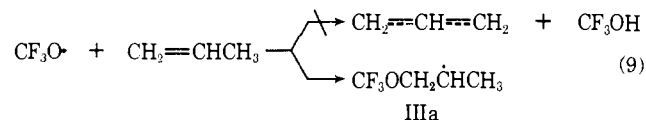
Radical	Temp, °C	$\langle g \rangle$	Hyperfine splitting, G			Solv. ^a
			$a_{\text{H}\alpha}$	$a_{\text{H}\beta}$	a_γ	
$\text{CF}_3\text{OCH}_2\text{CH}_2\cdot$	-136	2.00257	22.59	31.21	1.47	F
$\text{CH}_3\text{OCH}_2\text{CH}_2\cdot$	-136	2.00257	22.17	34.61	0.41	C ^b
$n\text{-BuOCH}_2\text{CH}_2\cdot$	-115	2.00258	21.96	34.35	NR	C ^b
$\text{HOCH}_2\text{CH}_2\cdot$	-71		22.00	31.67		
$\text{CH}_3\text{CH}_2\text{CH}_2\cdot$	-108	2.00287	22.13	31.17	0.27	E

^a Solvent: F = Freon 12, C = cyclopropane, E = diethyl ether.
^b From ref 13. ^c From ref 12. NR = not resolved.

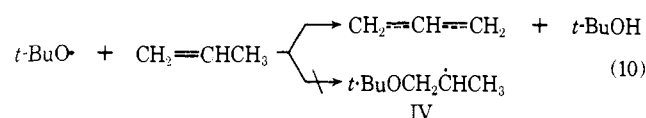
Table II. ESR Parameters for β -Oxygen Substituted Isopropyl Radicals

Radical	Temp, °C	$\langle g \rangle$	Hyperfine splitting, G				Solv. ^a
			$a_{\text{H}\alpha}$	$a_{\text{H}\beta}$	a_{CH_3}	a_δ	
$\text{CF}_3\text{OCH}_2\dot{\text{C}}\text{HCH}_3$	-100	2.00255	22.69	16.56	25.56	2.87	F
$\text{CH}_3\text{OCH}_2\dot{\text{C}}\text{HCH}_3$	-88	2.00259	21.92	23.88	25.14	<0.2	C
$\text{CH}_3\text{OCH}_2\dot{\text{C}}\text{HCH}_3$	-85	2.00259	21.98	23.60	25.17	<0.2	F
$\text{HOCH}_2\dot{\text{C}}\text{HCH}_3$	-122	2.00260	21.73	23.68	25.02		C
$\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HCH}_3$	-90	2.00275	21.90	27.20	24.63	0.39	C

^a Solvent: F = Freon 12, C = cyclopropane.

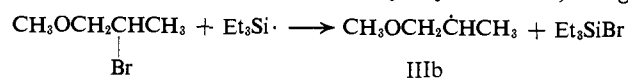


Under the same conditions, di-*tert*-butyl peroxide afforded only the spectrum of allyl radical (eq 10), and



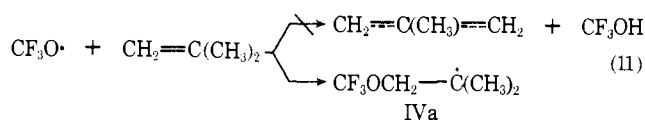
no significant spectrum of the adduct IV.⁶

The methoxy (Figure 2b) and hydroxy analogs IIIb and IIIc to the propylene adduct were generated from the corresponding oxy-substituted alkyl bromides with photochemically generated triethylsilyl radicals,¹⁴ e.g.



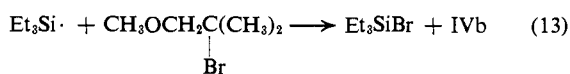
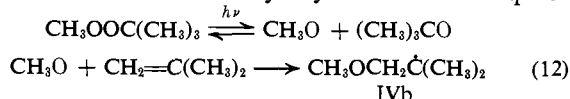
The esr parameters for IIIa, IIIb, and IIIc are all similar with one striking exception: namely, the hyperfine splitting of 17 G for the β protons in the trifluoromethoxy adduct is significantly smaller than the 23-G splitting observed for the hydroxy and methoxy analogs. Furthermore, as shown in Figure 4, the temperature dependence of the β -proton splitting is *positive*, whereas the temperature dependences of the β -proton splitting for the hydroxy and methoxy analogs are *negative* like that of the *sec*-butyl radical.

Trifluoromethoxy Adduct to Isobutylene. Trifluoromethoxy radicals generated from the photolysis of bis-trifluoromethyl peroxide in Freon-12 solution also only add to isobutylene. The esr spectrum shown in Figure 5 is derived from the adduct IVa in eq 11 and there is no



evidence for the presence of the β -methallyl radical. The esr parameters for IVa are listed in Table III.

The methoxy analog IVb was generated in eq 12 during photolysis of a solution of *tert*-butyl methyl peroxide and isobutylene in cyclopropane.¹⁵ The same species IVb was also generated by an independent procedure from the methoxyalkyl bromide in eq 13.



The hyperfine splitting of the α -methyl groups in IVa and IVb are the same. However, the splitting of 10 G in the trifluoromethoxy adduct is unusually small for β protons and it shows a *sharply positive* temperature dependence (Figure 6), in contrast to the smaller temperature dependences of the β -proton splittings in the methoxy analog IVb and in the hydrocarbon analog, the *tert*-amyl radical, also shown in Figure 6 for comparison.

Photolysis of Bistrifluoromethyl Disulfide. Adducts of Trifluoromethylthiyl Radicals to Alkenes. The

(14) Cf. A. Hudson and R. A. Jackson, *Chem. Commun.*, 1327 (1969).
 (15) I. H. Elson, unpublished results.

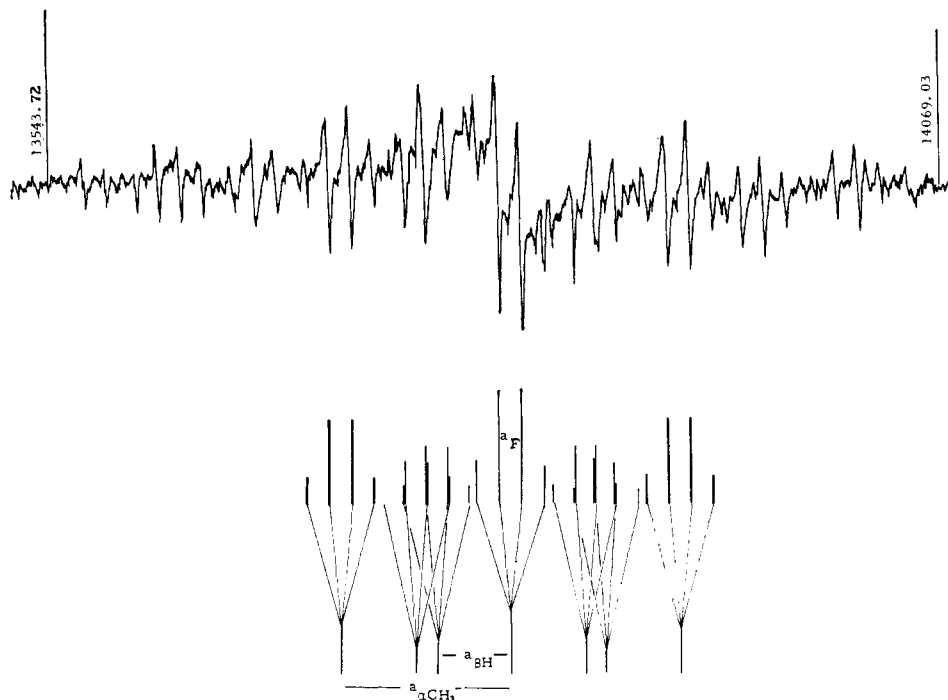


Figure 5. ESR spectrum of $\text{CF}_3\text{OCH}_2\dot{\text{C}}(\text{CH}_3)_2$ at -91° in Freon-12 solution. Stick diagram includes only the central portion of the spectrum. Proton nmr field markers are in kHz.

Table III. ESR Parameters for β -Oxygen Substituted *tert*-Butyl Radicals

Radical	Temp, $^\circ\text{C}$	$\langle g \rangle$	Hyperfine splitting, G			Solv. ^a
			$a_{\beta\text{H}}$	a_{CH_3}	a_δ	
$\text{CF}_3\text{OCH}_2\dot{\text{C}}(\text{CH}_3)_2$	-101	2.00256	10.02	23.45	3.08	F
$\text{CH}_3\text{OCH}_2\dot{\text{C}}(\text{CH}_3)_2^b$	-36	2.00258	18.40	22.97	NR	C
$\text{CH}_3\text{CH}_2\dot{\text{C}}(\text{CH}_3)_2$	-117	2.00278	17.94	22.80	<0.1	C

^a Solvent: F = Freon-12, C = cyclopropane. ^b Unpublished results (I. H. Elson). NR = not resolved.

Table IV. ESR Parameters of β -Thiylalkyl Radicals in Solution^a

Radical	Temp, $^\circ\text{C}$	$\langle g \rangle$	Hyperfine splitting, G			
			$a_{\alpha\text{H}}$	$a_{\beta\text{H}}$	$a^{\alpha\text{CH}_3}$	a_{F}
$\text{CF}_3\text{S}-\text{CH}_2\dot{\text{C}}\text{H}_2$	-127	2.00215	21.96	12.81	4.42	
$\text{CF}_3\text{S}-\text{CH}_2\dot{\text{C}}\text{HCH}_3$	-102	2.00277	21.43	11.84	24.30	4.39
$\text{CF}_3\text{S}-\text{CH}_2\dot{\text{C}}(\text{CH}_3)_2$	-96	2.00300		11.12	22.32	3.95
$\text{CH}_3\text{S}-\text{CH}_2\dot{\text{C}}\text{H}_2$	-124		21.68	13.50		NR
$\text{CH}_3\text{S}-\text{CH}_2\dot{\text{C}}\text{HCH}_3$	-81		21.36	12.94	24.13	NR
$\text{CH}_3\text{S}-\text{CH}_2\dot{\text{C}}(\text{CH}_3)_2$	-84			11.20	22.37	NR

^a In Freon-12. ^b From ref 6 in cyclopropane solution. NR = not resolved (<0.2 G) for δ -proton splitting.

photolysis of dialkyl disulfides was presented in a previous study.⁶ In the presence of alkenes, β -thiylalkyl adducts are generated in sufficiently high concentrations to obtain well-resolved ESR spectra. For example, the ESR spectra of the trifluoromethylthiyl adducts V to ethylene, propylene and isobutylene are obtained with excellent resolution and signal-to-noise ratio when reactions are carried out in the olefin as solvent or diluted

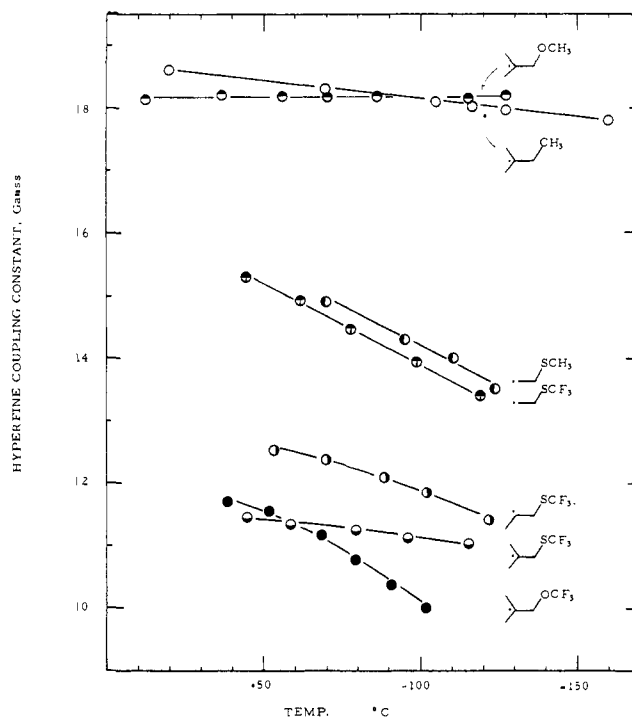
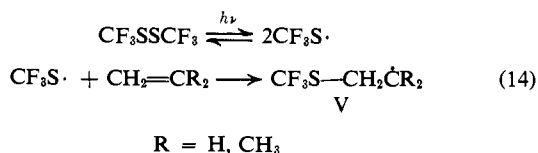


Figure 6. Temperature dependences of the β -proton hyperfine splittings for β -thiylalkyl radicals in solution. Comparison with the *tert*-amyl and the β -oxy analogs: (●) $\text{CF}_3\text{OCH}_2\dot{\text{C}}(\text{CH}_3)_2$; (⊖) $\text{CF}_3\text{SCH}_2\dot{\text{C}}(\text{CH}_3)_2$; (⊙) $\text{CF}_3\text{SCH}_2\dot{\text{C}}\text{HCH}_3$; (⊕) $\text{CF}_3\text{SCH}_2\dot{\text{C}}\text{H}_2$; (○) $\text{CH}_3\text{CH}_2\dot{\text{C}}(\text{CH}_3)_2$; (⊙) $\text{CH}_3\text{SCH}_2\dot{\text{C}}\text{H}_2$; (⊖) $\text{CH}_3\text{OCH}_2\dot{\text{C}}(\text{CH}_3)_2$.

with Freon-12 as shown in Figure 7 for the ethylene and propylene adducts.

The ESR parameters of the trifluoromethylthiyl adducts to alkenes are listed in Table IV, together with those of the corresponding methylthiyl adducts studied previously.⁶ It is noteworthy that the spectra obtained under these conditions show no indications of the presence of any other paramagnetic species.

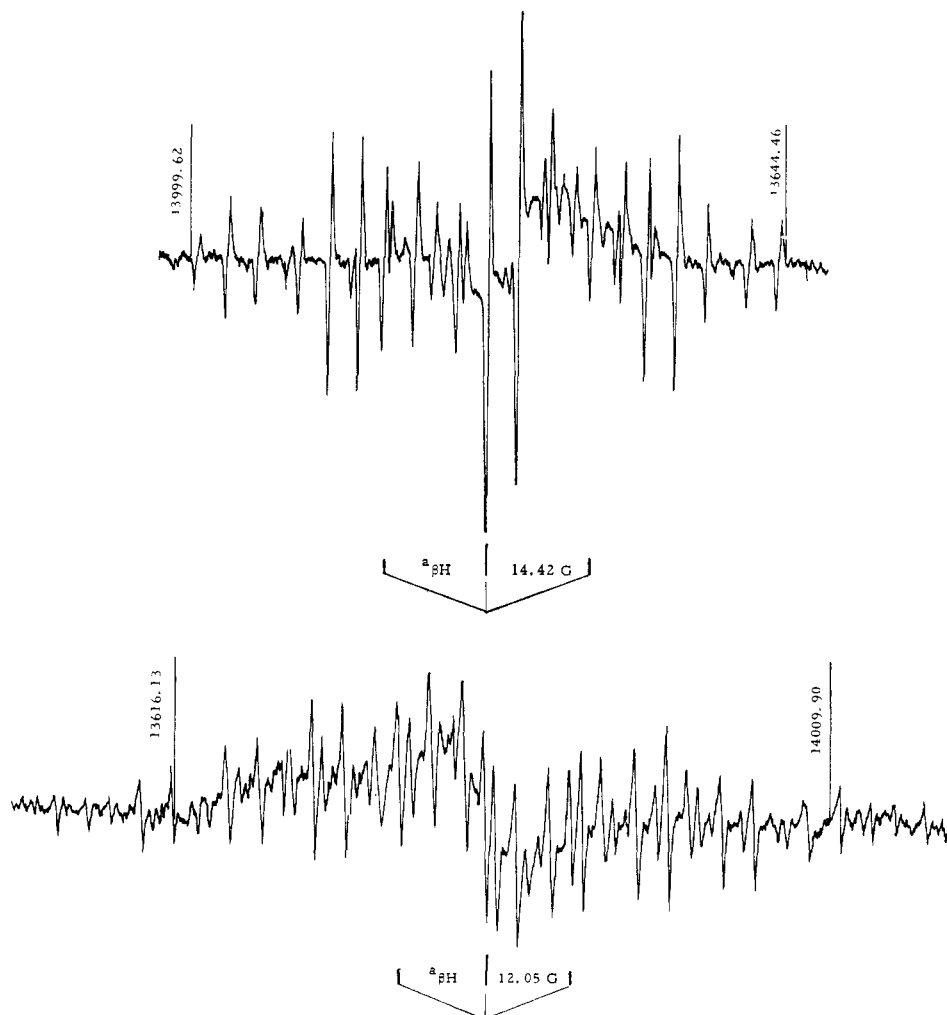
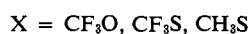
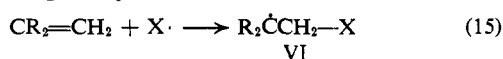


Figure 7. ESR spectra of (a) $\text{CF}_3\text{SCH}_2\dot{\text{C}}\text{H}_2$ and (b) $\text{CF}_3\text{SCH}_2\dot{\text{C}}\text{HCH}_3$ at -78 and -88° , respectively, in Freon-12 solutions. Proton nmr field markers are in kHz.

The hyperfine splittings due to the α protons and α -methyl groups in these adducts are comparable to those of the corresponding oxygen analogs. However, the β -proton splittings are all uniformly in the range of 11–13 G, which are small even for the β protons in the analogous *tert*-amyl radical. Furthermore, as shown in Figure 6, the temperature dependence of the β -proton splittings are all positive for the radicals containing tertiary carbon centers.

Discussion

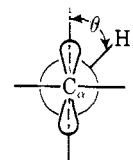
The esr spectrum of only one principal isomeric adduct is observed during the addition of trifluoromethoxy and alkylthiyl radicals to ethylene, propylene, and isobutylene. The structures VI correspond to an anti-Markovnikov orientation in these adducts, and they coincide with extensive chemical studies carried out on these and analogous systems.¹⁶



(16) (a) W. Stacey and J. F. Harris, Jr., *Org. React.*, **13**, 150 (1963); (b) C. Walling and E. S. Huyser, *ibid.*, **13**, 91 (1963); (c) G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry," MacMillan, New York, N. Y., 1964; (d) R. M. Kellogg, *Methods Free-Radical Chem.*, **2**, 1 (1969).

Esr studies provide unique insight into the structure and conformation of these β -substituted alkyl radicals. In the following discussion we wish to discuss (a) the conformation about the $\text{C}_\alpha\text{-C}_\beta$ bond and (b) bridging of the β -oxygen substituent to the radical center in these adducts.

Conformation of Alkyl Radicals. In *alkyl* radicals, the conformation about the $\text{C}_\alpha\text{-C}_\beta$ bond has been deduced from the magnitude of the β -proton splitting and its temperature dependence.^{6, 17} If θ describes the dihedral angle between the $\beta\text{-CH}$ bond and the principal



axis of the p orbital at the radical center at C_α , then the hyperfine splitting for the β proton is given by eq 16,

$$a_{\beta\text{H}} = A + B \cos^2 \theta \quad (16)$$

where A and B are constants. Alkyl radicals such as $\text{R}_2\text{C-CH}_2\text{R}'$ ($\text{R}, \text{R}' = \text{H}, \text{CH}_3$) exist in essentially two

(17) (a) P. J. Krusic, P. Meakin, and J. P. Jesson, *J. Phys. Chem.*, **75**, 3438 (1971); (b) R. W. Fessenden, *J. Chim. Phys. Physicochim. Biol.*, **61**, 1570 (1964).

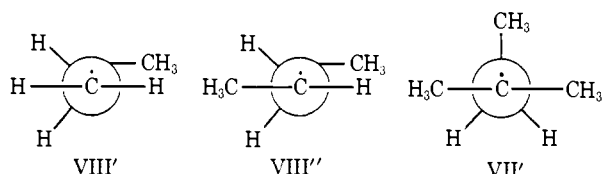
stable conformations VII and VIII,^{6,17} which are



R, R' = H, CH₃

designated as symmetric and unsymmetric, respectively.

A previous analysis^{4,6,17} of the temperature dependences of $a_{\beta H}$ for the *n*-propyl radical indicated that the stable conformation for this radical is VIII'. The



value of the hyperfine splitting for the pair of β protons in primary radicals in conformation VIII' such as *n*-propyl is typically 25–35 G and shows a *negative* temperature dependence (see Figure 3). Conformation VIII' is also consistent with the out-of-phase selective line broadening observed in the esr spectrum^{4,17a} due to restricted rotation about the C $_{\alpha}$ -C $_{\beta}$ bond leading to modulation of the hyperfine splitting of the two inequivalent α protons.

On the other hand, replacement of both α protons in the *n*-propyl radical by methyl groups alters the stable conformation to VII',^{4,17} and the *tert*-amyl radical and similar tertiary alkyl radicals show a greatly reduced β -proton splittings in the range of 15–18 G, which have *positive* temperature dependences (see Figure 6). The symmetric structure for the *tert*-amyl radical is further supported by the absence of selective line broadening in the spectrum at various temperatures.

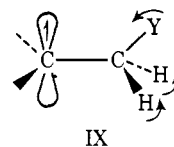
The change in the equilibrium conformation from the unsymmetric VIII' for *n*-propyl radical to the symmetric VII' for *tert*-amyl radical may be attributed to steric bulk imposed by two CH₃ α groups encumbering the radical center.¹⁸ The energy differences between VII' and VIII' are subtle, since the barrier of 0.6 kcal mol⁻¹ to hindered rotation about the C $_{\alpha}$ -C $_{\beta}$ bond in *tert*-amyl radical is not much larger than 0.3–0.4 kcal mol⁻¹ for *n*-propyl radical.¹⁷ Furthermore, the steric effects are highly cumulative since a single α -methyl substituent, as in the *sec*-butyl radical, is insufficient to alter the conformation of the *n*-propyl radical. Thus, the magnitude (27.20 G) of the β -proton splitting and the sign (negative, in Figure 3) of the temperature dependence indicate that the *sec*-butyl radical lies in a stable unsymmetric conformation, presumably VIII'' (in which the α and β methyl groups are anti) and not a symmetric one.

Criterion for Bridging in β -Substituted Alkyl Radicals.

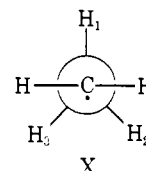
Bridging in β -substituted alkyl radicals implies an energy minimum at the conformation in which the dihedral angle, $\theta = 0^\circ$, is imposed by restricted rotation about

(18) (a) There is current disagreement as to the degree of nonplanarity of radical centers in tertiary alkyl radicals. (b) D. E. Wood, L. F. Williams, R. F. Sprecher, and W. A. Lathan, *J. Amer. Chem. Soc.*, **94**, 6241 (1972). (c) M. C. R. Symons, *Tetrahedron Lett.*, 207 (1973). (d) D. Griller and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 6459 (1973). (e) H. Paul and H. Fischer, *Helv. Chim. Acta*, **56**, 1575 (1973).

the C $_{\alpha}$ -C $_{\beta}$ bond. Radicals in conformation IX place the heteroatom Y directly behind the p orbital at the radical center and optimally located to interact with it. Bridging also implies *distortion* at C $_{\beta}$ which moves the heteroatom Y closer to the p orbital and H $_{\beta}$ closer to the nodal plane as shown in IX,⁶ although the latter is not a necessary consequence.

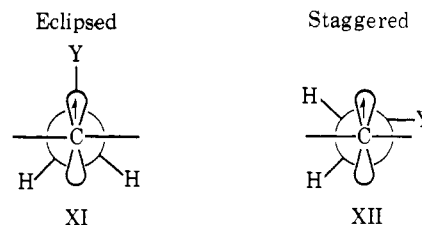


The value of the splitting expected for a pair of β protons in conformation VII, which is undistorted at C $_{\beta}$, can be obtained by considering an ethyl radical "frozen" in an analogous conformation X. The value



of the hyperfine splittings of 14.7 G is calculated for the equivalent H₂ and H₃ protons by the INDO molecular orbital method.¹⁹ Any distortion at C $_{\beta}$ such as that shown in IX would lead to values of the β -proton splittings lower than 15 G, and barriers to hindered rotation about the C $_{\alpha}$ -C $_{\beta}$ bond in excess of about 1 kcal mol⁻¹.^{6,17} Bridging in this context has also been discussed in radicals having heteroatom centers on Cl, Si, Sn, and P.^{20–22} Most of the bridged radicals examined heretofore exhibit only asymmetrical structures, that is, structures in which Y is not located midway between C $_{\alpha}$ and C $_{\beta}$.

The question now arises as to whether the change in conformation of a radical from VIII to VII is a necessary consequence of bridging. β -Oxyalkyl and β -thiylalkyl radicals provide a basis for comparison due to the unavailability of d orbitals and the higher electron affinity of oxygen compared to sulfur. In the following discussion we employ the foregoing analysis of the *magnitude* and *temperature dependence* of the β -proton splittings as probes for determining the conformation of β -substituted alkyl radicals as *eclipsed XI* or *staggered XII*, in which the β -substituent Y occupies an eclipsed or staggered position, respectively, relative to the p orbital at the α -carbon center, *i.e.*



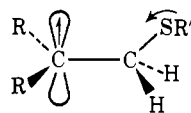
(19) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970, p 144.

(20) K. S. Chen, I. H. Elson, and J. K. Kochi, *J. Amer. Chem. Soc.*, **95**, 5341 (1973).

(21) (a) T. Kawamura, D. J. Edge, and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 1752 (1972); (b) T. Kawamura, P. Meakin, and J. K. Kochi, *ibid.*, **94**, 8065 (1972); (c) T. Kawamura and J. K. Kochi, *J. Organometal. Chem.*, **47**, 79 (1973).

(22) (a) A. R. Lyons and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 2*, **68**, 622 (1972); (b) W. Damerau, G. Lassman, and K. H. Lohs, *Z. Naturforsch. B*, **25**, 152 (1970).

Bridging by Sulfur in Alkyl Radicals. Judging by the values on the β -proton splittings and their temperature dependences, the adducts of methylthiyl radical to ethylene, propylene, and isobutylene all exist as eclipsed bridged structures XIII.⁶ The magnitudes of $a_{H\beta} = 11$ –13 G and their positive temperature dependences are largely independent of the degree of α -CH₃ substitution as listed in Table IV and shown in Figure 6. Furthermore, the similarity between the esr parameters in

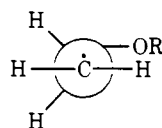


XIII, R' = CH₃, CF₃; R = H, CH₃

Table IV of the methylthiyl adduct and the trifluoromethylthiyl adduct suggests that the trifluoromethyl group does not impose additional large effects. The successively smaller values of $a_{\beta H}$ and the increase of the g factor ($\xi_p = 382 \text{ cm}^{-1}$)²³ suggest that distortion at C _{β} increases with α -methyl substitution. A similar trend was previously noted in the bridging by a β -chlorine substituent.²⁰

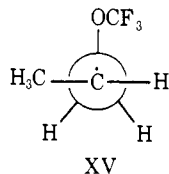
Since other primary n -alkyl radicals favor a staggered stable conformation, we ascribe the preference of the β -thiylethyl adducts R'SCH₂CH₂ for the bridged or eclipsed conformation to an interaction between the sulfur atom and the p orbital at the radical center which leads to stabilization of the eclipsed conformation. Hyperconjugative and homoconjugative interactions have been described previously,²¹ and the former is particularly noteworthy in view of the rather large (4 G) long-range fluorine splitting.

Bridging by β -Oxygen in Alkyl Radicals. A. Trifluoromethoxy Adducts to Olefins. The magnitude of 31 G for the β -proton splitting in the CF₃O adduct to ethylene is the same as that for the n -propyl radical (Table I), and its negative temperature dependence brackets that of n -propyl radical and other alkoxyethyl radicals as shown in Figure 3. We conclude, therefore, that CF₃OCH₂CH₂ exists in the same staggered conformation XIV as the n -propyl radical



XIV, R = H, CF₃, CH₃, n -Bu, ROC=O

Replacement of only a single α -CH₃ group in the CF₃O adduct is sufficient to alter the equilibrium conformation of XIV to XV, as indicated by the small value

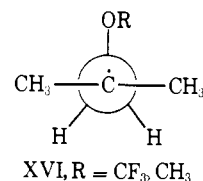


XV

of a $a_{H\beta} = 16$ G in Table II and the positive temperature dependence (Figure 4) for CF₃OCH₂CHCH₃. Finally, the α,α -dimethyl species, CF₃OCH₂C(CH₃)₂ (which is analogous to the *tert*-amyl radical), clearly exists in the

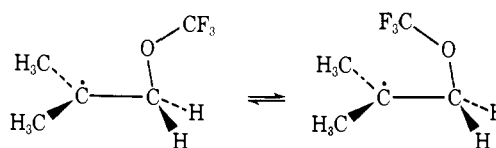
(23) E. U. Condon and G. M. Shortley, "Theory of Atomic Spectra," Cambridge University Press, New York, N. Y., 1953.

stable conformation XVI (R = CF₃) based on the unusually small value of the $a_{\beta H} = 10$ G in Table III and its sharply positive temperature dependence (Figure 6). The latter supports a structure for CF₃OCH₂C-



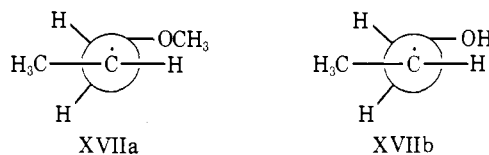
XVI, R = CF₃, CH₃

(CH₃)₂ in which distortion at C _{β} places the β -oxygen atom closer to the p orbital. The selective line broadening observed in the spectrum of CF₃OCH₂C(CH₃)₂ shown in Figure 5 is due to in-phase modulation of the β -proton hfs. Such a selective line-width effect²⁴ can be accounted for by hindered rotation about the C _{β} -OCF₃ bond, so that the pair of β protons always remains equivalent.



Thus, the change in the conformation of β -trifluoromethoxyalkyl radicals from the staggered XIV to the eclipsed XV and XVI with successive α -CH₃ substitution is also accompanied by increased bridging of the β -oxygen atom. The value of the long-range fluorine splitting due to the trifluoromethoxy group increases in this sequence from 1.47, 2.87 to 3.08 G in proceeding from the ethylene, propylene to the isobutylene adduct, and the trend is also consistent with bridging in this order. The change in g factor accompanying the bridging is not measurable due to the small spin-orbit coupling constant for oxygen ($\xi_p = 151 \text{ cm}^{-1}$).²⁵

B. Methoxy Adducts to Olefins. Simple replacement of the CF₃ group with CH₃ or H does not necessarily afford a β -methoxyalkyl or β -hydroxyalkyl radical with the same stable conformation. Thus, despite the eclipsed conformation of the CF₃O adduct to propylene, the CH₃O and HO analogs VIIa and VIIc exist in the stable staggered conformations XVIIa and XVIIb, judging from the same values of 23 G for the β -proton



splittings and their negative temperature coefficients listed in Table II. The difference in the esr spectra of the trifluoromethoxy and the methoxy adducts to propylene is graphically illustrated in Figures 1 and 2 which show the large difference in the β -proton triplets for these two adducts.

On the other hand, the esr spectra of the trifluoromethoxy and methoxy adducts to ethylene are quite similar (as shown in Figures 1 and 2, except for the additional CF₃ splitting), and we deduce that they both exist

(24) For a discussion, see P. D. Sullivan and J. R. Bolton, *Advan. Magn. Resonance*, **4**, 39 (1970).

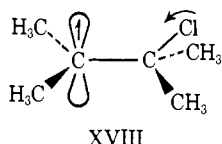
(25) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967.

in similar staggered conformations XIV. The isobutylene adducts IVa and IVb are also closely related and both favor the eclipsed conformation XVI as judged by the hyperfine splittings and temperature coefficients.

C. Substituent Effects on β -Oxygen Bridging in Alkyl Radicals. There exists, thus, an interesting dichotomy in the conformational preference imposed on the adducts by a β -CF₃O and a β -CH₃O group. In the ethylene and isobutylene adducts, CF₃O and CH₃O exert more or less the same influence, and the staggered conformation XIV of the ethylene adducts and the eclipsed conformation XVI of the isobutylene adducts are the same as those of the hydrocarbon analogs, *viz.*, primary normal alkyl and tertiary alkyl radicals. However, in the propylene adduct, CF₃O promotes the eclipsed conformation XV, whereas CH₃O favors the same staggered conformation XVII occupied by the analogous *sec*-butyl radical. We conclude from these results that a β -trifluoromethoxy group, unlike the β -methoxy group, is capable of partial bridging to the radical center in the propylene adduct XV. The magnitude of the interaction with the radical center, however, is insufficient to overcome the energy difference between the eclipsed and staggered conformations in the trifluoromethoxyethyl radical XIV, which still favors the staggered conformation.

Indeed, the esr parameters of the propylene adducts could *generally* provide the best probes to examine bridging by β substituents, since the energy difference between the eclipsed and staggered conformations is sufficiently well balanced at the secondary radical center and it will be affected by partial bridging.²⁶ At one extreme, the tertiary radical center always imposes an eclipsed conformation on the isobutylene adducts and β substituents can effect only limited conformational changes (although an increase in distortion at C _{β} is possible with certain bridging groups). On the other hand, the ethylene adducts usually favor the staggered conformation, barring *strong* interactions such as those experienced by chlorine, silicon, tin, and sulfur.^{5, 20-22}

In the latter regard, it is noteworthy that a β -sulfur substituent interacts relatively strongly with the radical center and always imposes an eclipsed conformation on the adduct, irrespective of whether it is ethylene, propylene, or isobutylene. Furthermore, in the ethylene adduct, the effect of a β -CF₃S substituent is only slightly more than that of a CH₃S group (compare Table IV and Figure 6). Bridging is even more important with a β -chlorine substituent and the eclipsed conformation is maintained even in the highly encumbered tetramethyl derivative XVIII.²⁰



A β -fluorine substituent appears to occupy an intermediate position like that of the β -CF₃O group in affecting stable conformations of alkyl radicals. Thus,

26) It would be highly desirable to obtain the barriers to hindered rotation in the propylene adducts by esr line-shape analysis.²⁷ However, the multiplicity of closely spaced lines in the spectra of the CF₃O adduct strongly discourages such a treatment.

(27) (a) *Cf.* ref 21b; (b) K. S. Chen and N. Hirota, "Investigation of Rates and Mechanisms," Part II, G. Hammes, Ed., Wiley, New York, N. Y., 1973, Chapter 13.

the β -fluoroethyl radical [$a_{H\beta} = 27$ G; $da_{H\beta}/dt$, negative]²⁸ shows no preference for an eclipsed conformation. On the other hand, we surmise from the esr parameters reported at only one temperature [$a_{H\beta} = 15.9$ G, -60°]²⁹ that the β -fluoroisopropyl radical prefers an eclipsed conformation.

Among β -oxygen substituents, trifluoromethoxy is not alone involved in bridging. Thus, the β -proton splittings in the benzoyloxy and propoxycarboxy adducts to propylene have values of 17.4 and 17.0 G, respectively, and positive temperature coefficients (see Figure 4) diagnostic of the eclipsed stable conformation.¹³ Contrariwise, the trimethylsiloxy adduct to propylene favors a staggered conformation ($a_{\beta H} = 27.1$ G; $da_{\beta H}/dt$, negative).³⁰

A relatively high group electronegativity of the substituents on oxygen (Table V) appears to be the single

Table V. Group Electronegativities^a

Group	Electronegativity (Pauling)	Group	Electronegativity (Pauling)
CF ₃	3.46	(CH ₃) ₃ C	2.29
C ₆ H ₅ C=O	<i>b</i>	(CH ₃) ₃ Si	2.27
CH ₃ OC=O	2.9 ^c	H	2.20
CH ₃	2.27		

^a From J. E. Huheey, *J. Phys. Chem.*, **69**, 3284 (1965). ^b Unknown. ^c Calculated by the method in *a*.

factor which oxygen-bridged adducts have in common. That is, those oxy groups with electronegative substituents such as CF₃, C₆H₅CO, and CH₃OCO are effective in inducing bridging. Alkyl groups, trimethylsilyl and H, with lower electronegativity, have essentially no strong influence on the conformation adopted by the alkyl radical.

On the basis of molecular orbital calculations,³¹ it has been suggested that β -substituted ethyl anions (X-CH₂CH₂⁻) favor the eclipsed conformation and the cations (XCH₂CH⁺) favor the staggered conformation when X is more electronegative than H due to hyperconjugative interactions. In the radical the difference was calculated to be small,³¹ but the concept has been recently applied to α,β -disubstituted ethyl radicals.³²

Differences in group electronegativity may indeed be a dominant factor in assessing the importance of bridging in a series of β -oxyalkyl radicals, R'OCH₂CR₂, since the substituent R' on oxygen may be simply treated as a perturbation. We tentatively suggest that the differences among β -oxy groups are due to homoconjugative interactions between the p orbitals on oxygen and the radical center, since the ability to bridge correlates with the substituent on oxygen rather than the oxy group itself. For example, the electronegativity³³ of HO (3.22) places it closer to CF₃O (3.74) than CH₃OCO (3.2) or CH₃O (2.68), yet HO is not involved

(28) D. J. Edge and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 6485 (1972).

(29) I. Biddles, J. Cooper, A. Hudson, R. A. Jackson, and J. T. Wiffen, *Mol. Phys.*, **25**, 225 (1973).

(30) D. J. Edge and J. K. Kochi, *J. Chem. Soc., Perkin Trans. 2*, 181 (1972).

(31) R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Amer. Chem. Soc.*, **94**, 6221 (1972).

(32) A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Magn. Resonance*, **11**, 100 (1973).

(33) J. E. Huheey, *J. Phys. Chem.*, **69**, 3284 (1965).

in bridging in radicals where CH_2OCO is. The extent to which these electronegativity values are questioned, however, lends doubt to this conclusion.

The role of hyperconjugative interactions in β -substituted alkyl radicals have been discussed previously with regard to second row elements as substituents.^{20, 21} The importance of hyperconjugative interactions in radicals with β -oxy substituents³² is not evaluated by the data at hand, although it is not required to explain the changes in conformation encountered in this study. The magnitudes of ^{17}O splittings would be highly informative in this regard.³⁴

Conclusion and Summary

Alkyl radicals with β heteroatoms exist in one of two conformations XI or XII in which the substituent Y is eclipsed or staggered, respectively, relative to the principal axis of the p orbital at the radical center. If Y contains a second row heteroatom such as Si, P, S, or Cl (or higher elements), the eclipsed conformation is preferred irrespective of whether the radical center is primary, secondary, or tertiary. In these radicals the values of the β -proton splitting less than that predicted for the minimum in a frozen eclipsed conformation can be accommodated by distortion at C_β such as those shown in XIII and XVIII.^{6, 20} In radicals containing β group IVB metals, the amount of distortion⁶ and the barrier to hindered rotation about the $\text{C}_\alpha\text{-C}_\beta$ bond^{21b} increase with atomic number due to hyperconjugative and homoconjugative interactions with the radical center.

If Y is a first row element, the equilibrium conformation depends on both the structure of Y and the presence of one or two α -methyl groups, *i.e.*, a primary, secondary, or tertiary radical center. In alkyl radicals where $\text{Y} = \text{CH}_3$, primary and secondary such as *n*-propyl (VIII') and *sec*-butyl (VIII'') exist preferentially in the staggered conformation in which the $\beta\text{-CH}_3$ group is displaced toward the nodal plane and away from the p orbital. On the other hand, tertiary radicals such as *tert*-amyl^{6, 17a} and α, α -di-*tert*-butylethyl radicals^{18d} prefer the eclipsed conformation such as VIII', largely due to steric bulk which forces the β -methyl group away from the nodal plane. The conformational preference shown by radicals with β -oxy substituents, OR, is intermediate between the wholly alkyl (hydrocarbon) radicals and those containing higher row elements; and these radicals show a high degree of dependence on the substituent R attached to oxygen. The effect is especially noticeable in β -substituted isopropyl radicals $\text{CH}_3\text{CHCH}_2\text{OR}$ in which the energy difference between the staggered and eclipsed conformations are sufficiently

(34) A referee has suggested an alternative or additional possibility involving nonbonded interactions between the β oxygen and an α hydrogen which stabilizes or destabilizes the staggered conformation depending on whether they are attractive (CH_3O , CH_3 , etc.) or repulsive (CF_3O , PhCO_2 , etc.). It should be mentioned, however, that $a_{\beta(\text{H})}$ in the sterically hindered $(\text{CH}_3)_3\text{CCH}_2\text{CH}_2\cdot$ is still 25 G.³⁵

(35) (a) T. Kawamura and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 648 (1972); (b) For a discussion of the effects of steric bulk at C_γ , see K. S. Chen, D. Y. H. Tang, L. K. Montgomery, and J. K. Kochi, *ibid.*, in press.

well balanced to be readily affected by changes in R. Thus, isopropyl radicals with $\beta\text{-CF}_3\text{O}$, PhCO_2 , and PrOCO_2 groups prefer the eclipsed conformation and those with $\beta\text{-CH}_3\text{O}$, *n*-BuO, HO, or $(\text{CH}_3)_3\text{CO}$ occupy the staggered conformation similar to that of *sec*-butyl radical. The change from a staggered to eclipsed conformation is attributed to an enhanced homoconjugative interaction between the β -oxygen substituent, OR, and the radical center, particularly when R is an electronegative group.

Bridging in β -substituted alkyl radicals in the absence of steric effects (such as those present in tertiary systems) is interpreted as a preference for the eclipsed conformation due to electronic interactions (*e.g.*, homoconjugative or hyperconjugative) between the substituent Y and the half-filled p orbital at the radical center. Distortion of the alkyl radical at C_β may be a consequence of this interaction (especially when it is strong), but it is not a necessary consequence of it.

Experimental Section

Materials. Di-*tert*-butyl peroxide was obtained from Shell Chemical Co., washed with water, dried, passed through an alumina column, and redistilled at reduced pressure prior to use. Triethylsilane was obtained from Columbia Chemicals Co., refluxed over molecular sieve and redistilled prior to use. Bistrifluoromethyl peroxide and bistrifluoromethyl disulfide were obtained from PCR, Inc. Bromoethane, 1-bromopropane, 2-bromopropane, 2-bromo-2-methylpropane, 2-bromobutane, 2-bromo-2-methylbutane obtained from Matheson Coleman and Bell were all washed with water, dried, and redistilled prior to use. 2-Bromoethyl methyl ether, 2-bromoethyl ethyl ether, 2-bromoethyl *n*-butyl ether, 2-bromo-1-propyl methyl ether, and 1-bromo-2-fluoroethane were prepared from the corresponding alcohols and phosphorus tribromide. *tert*-Butyl peresters of propionic acid, *n*-butyric acid, isobutyric acid, α -methylbutyric acid, α, α -dimethylbutyric acid, and β -fluoropropionic acid were prepared *via* the acid chlorides.³⁶ 2-Bromo-1-propanol was prepared from 2-bromopropionic acid by the method of Hohokabe and Yamazaki.³⁷ *tert*-Butylperoxy β -methoxypropionate was prepared in a previous study.¹³

Esr Measurements. The modified Varian X-band spectrometer, microwave frequency measurements, light source, and sample tubes are as described previously.^{6, 13}

To minimize the error in the *g* value determinations, all measurements were made on spectra recorded on the same day for increasing magnetic field. Perylene cation radical ($g = 2.00258$) was used as standard in the configuration employed. The accuracy of the measurements is estimated as ± 0.00003 . The temperature in the tube was calibrated with a thermocouple and accurate to $\pm 5^\circ$.

Sample Preparation. The peroxide or disulfide was transferred *in vacuo* to the suprasil quartz tube, followed by the olefin and solvent (cyclopropane or Freon-12). Oxygen was removed from the tube by a repeated freeze-pump-thaw cycle and the tube sealed *in vacuo*.

For photolytic reduction of alkyl halides, equal volumes of di-*tert*-butyl peroxide and triethylsilane were diluted with sufficient cyclopropane (and ethane) to give a final ratio of approximately 1:1:1:4 (v/v). For the photolysis of acyl peresters a small amount of peroxide (*ca.* 100 mg) was dissolved in a relatively large volume of alkene and/or alkane.

Acknowledgment. We thank the National Science Foundation for financial support of this research and Dr. I. H. Elson for helpful discussions.

(36) P. D. Bartlett and P. R. Hiatt, *J. Amer. Chem. Soc.*, **80**, 1398 (1958).

(37) Y. Hohokabe and N. Yamazaki, *Bull. Chem. Soc. Jap.*, **44**, 798 (1971).