5-Nitrospiro(cyclopentane-1,1'-indan). The nitration of spiro-(cyclopentane-1,1'-indan) (0.01 mol) with nitric acid and acetic anhydride in methylene chloride was carried out at about 5° by the procedure used for other spiro compounds.[17] The 5- and 6-nitro compounds obtained in nearly equal amounts were separated by vpc. 5-Nitrospiro(cyclopentane-1,1'-indan) (mp 60–62°, 10% yield) was purified by sublimation. The nmr spectrum (1.77 (8 H, s), 2.0 (2 H, t, J = 7 Hz), 2.90 (2 H, t, J = 7 Hz), 7.14 (1 H, d, J = 9 Hz), 7.97–8.10 (2 H, m)) and the mass spectrum (calcd for $C_{13}H_{15}NO_2^+$, 217.1103; found, 217.1109) establish the structure. For comparison, the nmr spectrum of the 6-nitro derivative exhibited the following signals: 1.77 (8 H, s), 2.0 (2 H, t, J = 7 Hz), 2.90 (2 H, t, J = 7 Hz), 7.13–7.37 (1 H, m), 7.85–8.06 (2 H, m). The m/e value observed for this isomer was 217.1096.

Electron Paramagnetic Resonance Spectra. The anion radicals of the nitrobenzene derivatives were generated electrolytically. In a typical experiment, 4-(1-methylcyclopropyl)nitrobenzene (2.0 mg, 9.013 mmol) was dissolved in acetonitrile containing tetra-1-propylammonium perchlorate. This solution was placed in the bulb section of an electrolytic cell[34] and degassed. The solution was then introduced into the capillary portion of the cell which contained 0.5 cm of mercury (D. F. Goldsmith). The solution was continuously electrolyzed at −1.8 V. The spectrum was recorded in the usual way. The spectrum was analyzed by computer simulation.

Acetonitrile was washed with saturated potassium hydroxide solution. The nitrile was decanted and dried over sodium carbonate for 12 hr. The dry material was refluxed for 8 hr over phosphorus pentoxide in a nitrogen atmosphere. Acetonitrile was then collected by distillation and stored under nitrogen. Tetra-1-propylammonium perchlorate was prepared by the neutralization of the ammonium hydroxide (10% solution, 50 ml) with perchloric acid (70% solution, 7.5 ml) at 0°. The white crystals were collected and washed with water. The product was then recrystallized twice from 80:20 water–acetonitrile and dried at 80° over phosphorus pentoxide.

Computations. Program 141, Quantum Chemistry Program Exchange, Indiana University, was used for the INDO calculations. The bond lengths and angles used in these calculations are based on known structural data.[35] The general structures of 4-cyclopropyl-nitrobenzene (W) and cyclopropylcarbinyl radical (X) are shown in Figure 1, ref 17.

(34) C. P. Poole, "Electron Spin Resonance, A Comprehensive Treatise on Experimental Techniques," Interscience, New York, N. Y., 1967, p 628.

(35) (a) R. G. Ford and R. A. Beaudet, *J. Chem. Phys.*, 48, 4671 (1968). (b) R. W. G. Wyckoff, *Crystal Struct.*, 6, 11 (1969). R. W. G. Wyckoff, "Crystal Structures," John Wiley and Sons, Inc., New York, New York, 1969.

Homolytic Rearrangements and the Conformations of Alkyl Radicals by Electron Spin Resonance

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Abstract: Homolytic rearrangements are studied by esr in the allylcarbinyl, ω-hexenyl, β-acetoxyethyl, neophyl, and 4-phenylbutyl systems, which have been scrutinized previously in chemical studies. The presence and location of unsaturation (vinyl, acetylenyl, carbonyl, or phenyl) in the alkyl chain are employed as possible probes for conformational effects on cyclizations in these systems. The magnitude and the temperature dependence of the hyperfine splitting of the β protons, together with the observation of alternating line widths in the esr spectra, are used as guides to deduce equilibrium conformations. A carbonyl group specifically located in the 4 position relative to the radical center has a unique effect on the selective broadening of only the M_1 = ±1 lines of the β-proton triplets caused by in-phase modulation of the coupling constants. The effects of C=C unsaturation and phenyl groups on the conformation of alkyl radicals are also discussed.

E lectron spin resonance spectroscopy (esr) has been used in a direct study of homolytic rearrangements. For example, the esr spectrum of the cyclopropylcarbinyl radical from the photolysis of cyclopropylacetyl peroxides can be readily observed at low temperatures ($< -140°$), whereas only that of the allylcarbinyl radical can be obtained above $-100°$.[1] At intermediate temperatures the esr spectrum consists of a superposition of these two individual spectra. The reverse process, *viz.* the ring closing of allylcarbinyl

$$\text{(1)}$$
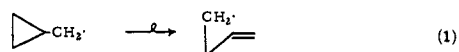
radical to cyclopropyl carbinyl radical, on the other hand, cannot be observed by esr, since only the spectrum of the allylcarbinyl radical is obtained from the photolysis of allyl acetyl peroxides even at $-140°$. The

kinetic analysis of the vinyl rearrangement of allylcarbinyl radicals, however, indicates that it proceeds *via* cyclization.[2] The latter is not inconsistent with the esr studies since the concentration of the cyclopropylcarbinyl intermediate may be too low to observe. Similar results have been obtained in an esr examination of the irreversible cyclization of the ω-hexenyl radical to the cyclopentylmethyl radical.[3] Both of these systems are unusual for alkyl radicals, since they proceed at relatively high rates. For example, the first-order rate constant for ring opening in eq 1 is in excess of 10^8 sec^{-1} and that for cyclization of the ω-hexenyl radical is approximately 10^5 sec^{-1} at 25°.[4]

Generally, the rearrangement of organic free radicals is less common than that of the analogous carbonium ions.[5] Homolytic cyclizations, when they have been

(1) J. K. Kochi, P. J. Krusic, and D. R. Eaton, *J. Amer. Chem. Soc.*, 91, 1877 (1969).

(2) L. K. Montgomery, J. W. Matt, and J. R. Webster, *ibid.*, 89, 923 (1967).

(3) R. A. Sheldon and J. K. Kochi, *ibid.*, 92, 4395 (1970).

(4) D. J. Carlsson and K. U. Ingold, *ibid.*, 90, 7047 (1968).

Table I. Esr of δ-Keto-Substituted Alkyl Radicals in Solution

Radical	T, °C	$\langle g \rangle$	A_α, G	A_β, G	A_γ, G	$A_\beta(T)$, G/deg
$CH_3C(=O)CH_2CH_2CH_2\cdot$	−106	2.00266	22.18	29.69	0.32	0.032
$EtOC(=O)CH_2CH_2CH_2\cdot$	−104	2.00268	22.22	29.53	0.37	0.029
$CH_3C(=O)OCH_2CH_2\cdot$	−108	2.00259	22.26	28.44		0.042

observed, are usually associated with unsaturated centers, probably due to the presence of antibonding π* orbitals. However, rearrangement *per se* is not an adequate criterion to probe for orbital overlap between the radical site and the unsaturated center, since the driving force provided by such an electronic interaction may not be sufficient to overcome the activation energy required to reorganize the σ framework.

Conformational changes in the alkyl radicals, however, involve much smaller energy differences and are well suited for the study of any subtle electronic effects in the ground state. The well-resolved esr spectra which are obtainable for transient free radicals have been used to describe the conformations of a variety of alkyl radicals in solution.[6,7] In this study we examined the effects of aryl, vinyl, and carbonyl substituents on the conformations of alkyl radicals at various positions along the chain in order to explore the possibility of relating the conformation of the free radical to the occurrence of homolytic rearrangement.

Results and Discussion

Conformational Effects of Carbonyl Substituents. Chemical evidence has been recently presented for 1,2-acetoxy migration in alkyl radicals.[8] An addition–

$$AcO-C(CH_3)_2-CH_2\cdot \xrightarrow{a} (CH_3)_2\dot{C}-CH_2-OAc \quad (2)$$
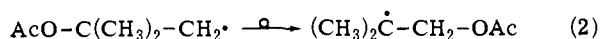
elimination mechanism as well as a symmetrically bridged intermediate have been ruled out. The esr
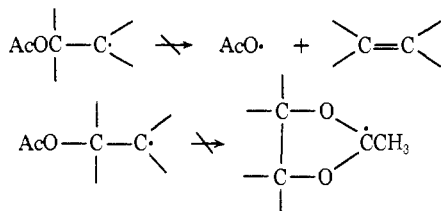
spectra of both radical species in eq 2 have also been observed when *tert*-butyl acetate reacted with hydroxyl radicals.[9]

The esr parameters are listed in Table I for the β-acetoxyethyl radical **1** generated from β-bromoethyl acetate and photochemically[10] generated triethylsilyl

(5) (a) J. W. Wilt, "Free Radicals," Wiley-Interscience, New York, N. Y., in press; (b) C. Walling, "Molecular Rearrangements," Vol. 1, P. deMayo, Ed., Interscience, New York, N. Y., 1963, Chapter 7; (c) A. L. J. Beckwith, *Chem. Soc., Spec. Publ.*, No. 24, 239 (1970).

(6) R. W. Fessenden, *J. Chim. Phys.*, **61**, 1570 (1964).

(7) (a) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971); (b) P. J. Krusic, P. Meakin, and J. P. Jesson, *J. Phys. Chem.*, **75**, 3438 (1971); (c) J. K. Kochi and P. J. Krusic, *Chem. Soc., Spec. Publ.*, No. 24, 147 (1970).

(8) (a) D. D. Tanner and F. C. P. Law, *J. Amer. Chem. Soc.*, **91**, 7535 (1969); (b) J. M. Surzur and P. Teissier, *Bull. Soc. Chim. Fr.*, 3060 (1970); (c) S. N. Lewis, J. J. Miller, and S. Winstein, *J. Org. Chem.*, **37**, 1478 (1972); (d) for 1,2-acyl migrations see: C. L. Karl E. J. Maas, and W. Reusch, *J. Org. Chem.*, **37**, 2834 (1972).

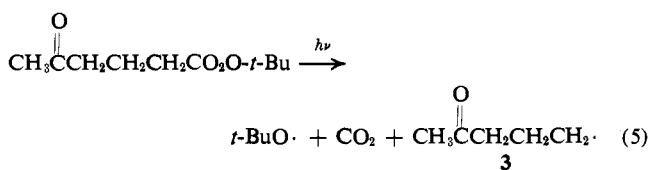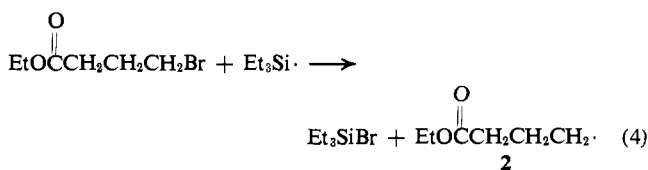(9) A. L. J. Beckwith and P. K. Tindal, *Aust. J. Chem.*, **24**, 2099 (1971).

(10) *Cf.* A. Hudson and R. A. Jackson, *Chem. Commun.*, 1327 (1969).

radicals in cyclopropane solutions (eq 3). The value

$$CH_3COCH_2CH_2Br + Et_3Si\cdot \longrightarrow Et_3SiBr + CH_3\overset{O}{\overset{\|}{C}}OCH_2\dot{C}H_2 \quad (3)$$
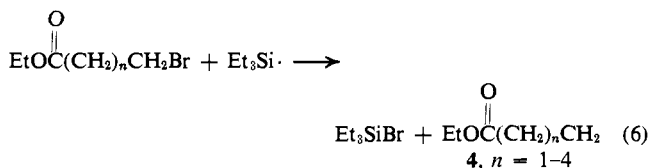**1**
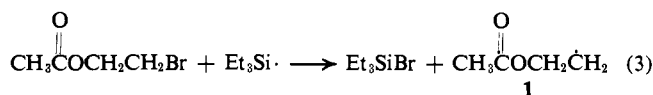
of the hyperfine coupling constant (hfs) of the α protons in this radical was invariant with temperature. The hfs of the β protons increased with decreasing temperature, and it became apparent that the *outer* ($M_I = \pm 1$) pairs of lines of the triplet splittings in the spectrum due to the β protons appeared with reduced peak to peak amplitudes. The selective line broadening was noticeable at −120° and became progressively more pronounced at lower temperatures.

The unusual alternative line width behavior observed in the esr spectrum of the β-acetoxyethyl radical was also observed with the 3-carbethoxypropyl (**2**) and 3-acetylpropyl (**3**) radicals, which both have their carbonyl group in the same (*i.e.*, δ) position relative to the radical center. Radicals **2** and **3** were generated by bromine transfer from ethyl 4-bromobutyrate to the triethylsilyl radical[10] and photolysis of *tert*-butylperoxy 5-ketohexanoate,[11] respectively, in cyclopropane solutions (eq 4 and 5).

$$EtO\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2Br + Et_3Si\cdot \longrightarrow$$
$$Et_3SiBr + EtO\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2\cdot \quad (4)$$
2

$$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CO_2O\text{-}t\text{-Bu} \xrightarrow{h\nu}$$
$$t\text{-BuO}\cdot + CO_2 + CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2\cdot \quad (5)$$
3

The esr spectra of alkyl radicals with the carbonyl function in different positions along the carbon chain were also examined. The homologous series of radicals **4** listed in Table II were all produced from the corresponding ethyl bromo esters (eq 6). The esr

$$EtO\overset{O}{\overset{\|}{C}}(CH_2)_nCH_2Br + Et_3Si\cdot \longrightarrow$$
$$Et_3SiBr + EtO\overset{O}{\overset{\|}{C}}(CH_2)_nCH_2 \quad (6)$$
4, $n = 1–4$

parameters for the corresponding alkyl radicals are also listed in Table II for comparison. All of the radicals listed in Table II with the exception of **2** showed a different alternating line width behavior in which the *central* ($M_I = 0$) lines of the triplet splittings due to the β protons are now broadened.[12] The shaded por-

(11) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3940 (1969).

(12) *n*-Propyl radical is the other exception. The selective broadening of the central ($M_I = 0$) line of the triplet splitting due to the α protons has been discussed.[7]
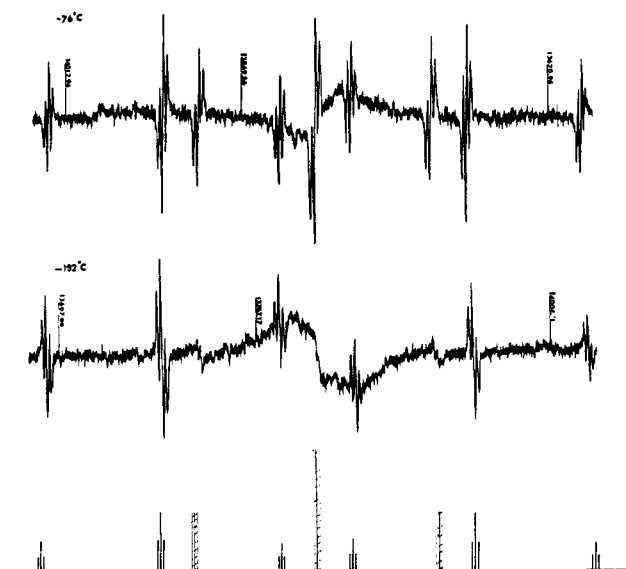
Figure 1. Alternating line width effect in the temperature-dependent esr spectrum of the 4-carbethoxybutyl radical in cyclopropane solution. Shaded portions of the stick spectrum correspond to selective line broadening due to the *out-of-phase* modulation of the β-proton hfs.
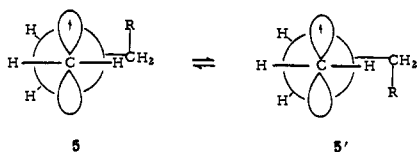
Table II. Esr of Carbethoxyalkyl Radicals. Comparison with n-Alkyl Radicals[a]

Radical	T, °C	$\langle g \rangle$	A_α, G	A_β, G	A_γ, G	$A_\beta(T)$, G/deg
EtO₂C(CH₂)ₙĊH₂						
$n = 1$	−108	2.00274	22.62	31.77		0.031
$n = 2$	−104	2.00268	22.22	29.53	0.37	0.029
$n = 3$	−106	2.00266	22.11	29.18	0.73	0.019
$n = 4$	−100	2.00265	22.14	29.24	0.70	0.023
AcOCH₂CH₂ĊH₂	−105	2.00265	22.29	28.83	0.75	0.015
CH₃(CH₂)ₙCH₂·						
$n = 1$	−104	2.00265	22.18	30.93	0.27	0.024
$n = 2$	−105	2.00267	21.98	29.54	0.72	0.022
$n = 3$	−109	2.00266	22.15	29.67	0.69	0.021
$n = 6$	−104	2.00265	21.98	29.25	0.70	0.023

[a] In cyclopropane solutions.

Figure 2. Alternating line width effect in the temperature-dependent esr spectrum of the 3-carbethoxypropyl radical in cyclopropane solution. Shaded portions of the stick spectrum correspond to selective line broadening due to the *in-phase* modulation of the β-proton hfs.

tions of the stick spectrum of the δ-carbethoxybutyl radical **4** shown in Figure 1 typically illustrate this type of alternating line width behavior.

The selective line broadening described above is associated with the *out-of-phase* modulation of the hfs of the pair of β protons in these radicals. An internal rate process in these radicals exchanges the inequivalent β protons between different environments. Hindered rotation about the Cβ–Cγ bond shown in **5** is consistent with this exchange.[7]

The presence of a carbonyl group specifically in the δ position, however, dampens these conformational changes. Thus, the esr spectra of the radicals **1**, **2**, and **3** listed in Table I all show selective (outer) line broadening associated with *in-phase modulation* of the hfs of the pair of β protons. Rate processes in which
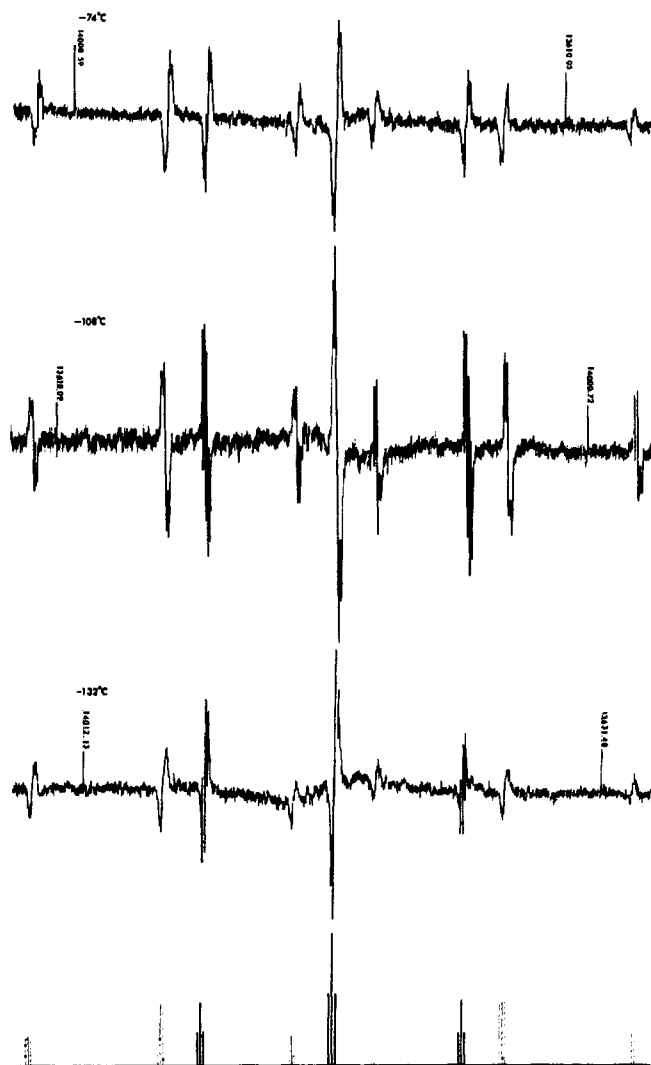
the two β protons have hfs which are instantaneously equivalent at all times but modulated between two or more limiting values are consistent with this observation, since the width of a particular line would be proportional to $(M_H)^2$.[13] The latter would lead to selective broadening of only the "outer" pairs of lines of the triplets associated with the β protons and is indicated by the shaded portions of the stick spectrum in Figure 2. Therefore, in radicals **1**, **2**, and **3** restricted rotation of the Cβ–Cγ bond as in **5** must be replaced by conformational changes in which the β protons are always magnetically equivalent. Furthermore, the magnitude and temperature dependences of the β hfs indicate that the conformation about the Cα–Cβ bond in these radicals is the same as those for other alkyl radicals (see Tables I and II). The γ-carbon atom in these radicals must, therefore, lie in the equatorial plane.

(13) (a) G. K. Fraenkel, *J. Phys. Chem.*, **71**, 139 (1967); (b) P. D. Sullivan and J. R. Bolton, *ibid.*, **73**, 4387 (1969). (c) There are few previous examples of selective line broadening attributable to in-phase modulation of the coupling constants. For a lucid discussion of alternating line width effects, see (d) P. D. Sullivan and J. R. Bolton, *Advan. Magn. Resonance*, **4**, 39 (1970), and A. Hudson and G. R. Luckhurst, *Chem. Rev.*, **69**, 191 (1969).

With this information available, we propose that a conformation (6) in which the δ-carbon atom (which has the carbonyl function) lies close to the equatorial plane represents one of the potential minima.[14] Other conformational changes are possible but must be limited


6   6'
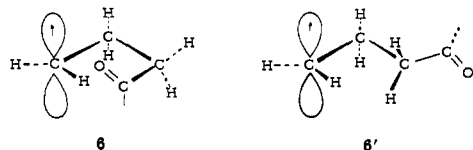
to those in which the hfs of the β protons remains equivalent.[15]

The conformation of the trimethylene chain shown in 6 and 6' is rather unusual, and so far we have found it only in one other system. Thus, the esr spectrum of either the γ-bromo- or γ-chloropropyl radical exhibits a similar temperature-dependent selective broadening of lines, from which we have deduced a stable conformation (7).[16] The unusually high g values for these

7
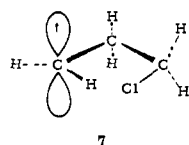
γ-halopropyl radicals indicate a significant interaction between the halogen and the odd-electron orbitals, which could contribute to the stabilization of this conformation. The π orbitals on the carbonyl group in conformation 6 are also suitably located to overlap with the p orbital at the radical center.[17] Furthermore, the similarity in the behavior of a 3-halo and a 4-keto function on the conformation of alkyl radicals precludes a mechanism involving a dipolar interaction between the radical center and the substituent.

Conformational Effects of Vinyl Substituents. The effects exerted by a δ-keto function on the conformation of alkyl radicals disappear when it is replaced by a vinyl group. Thus, the well-resolved esr spectrum of the 4-pentenyl radical 8 shows only a very slight broad-

$$CH_2=CHCH_2CH_2CH_2Br + Et_3Si \cdot \longrightarrow$$
$$Et_3SiBr + CH_2=CHCH_2CH_2CH_2 \quad (7)$$
8
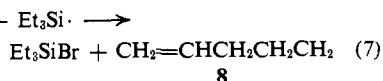
ening of the $M_I = 0$ lines due to the β-proton triplet as the temperature is lowered (eq 7). The esr parameters given in Table III for the 4-pentenyl radical exhibit no unusual trend. The dissimilar conformational effects conferred by C=C in contrast to C=O unsaturation at the δ carbon may be attributable to the presence of a pair of terminal vinylic hydrogens in 8 which pre-

(14) Such a conformation, however, places the β- and γ-methylene hydrogens in an unfavorable eclipsed conformation depending on how close the δ carbon is to the equatorial plane.

(15) It is interesting to note that the conformation presented in 6 for δ-ketoalkyl radicals lies close to that required for 1,2-acetoxy migration in eq 2, the ring closure observed during reduction of γ-chlorobutyrophenone with tributyltin hydride [L. W. Menapace and H. G. Kuivila, J. Amer. Chem. Soc., 86, 3047 (1964)] and the unusual 1,4-hydrogen transfer shown by the γ-formylpropyl radical [T. J. Wallace and R. J. Gritter, J. Org. Chem., 26, 5256 (1961)]. However, it is not clear whether 1,2-acetoxy migration is a [2,3]- rather than a [2,1]dioxy sigmatropic rearrangement. Oxygen labeling studies would be illuminating.

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

(17) The dependence of the g factor on the spin delocalization in these radicals is not a sensitive measure of this interaction and is encompassed within the experimental uncertainty.

Table III. Vinyl- and Acetylenyl-Substituted Alkyl Radicals in Solution[a]

| $CH_2=CH(CH_2)_nCH_2 \cdot$	T, °C	$\langle g \rangle$	A_α, G	A_β, G	A_γ, G	$A_\beta(T)$, G/deg
$n = 1$	−102	2.00266	22.18	28.79	0.62[b]	0.018
$n = 2$	−99	2.00265	22.12	29.69	0.61	0.031
$n = 3$	−105	2.00264	21.98	29.25	0.74	0.019
n-$C_4H_9C{\equiv}C(CH_2)_2\dot{C}H_2$	−104	2.00266	22.09	29.14	0.74	0.025
n-$C_4H_9C{\equiv}C(CH_2)_3\dot{C}H_2$	−103	2.00266	21.97	29.08	0.79	0.039

[a] Cyclopropane. [b] $A_{H\delta} = 0.37$ G for one proton.

vents it from assuming a conformation such as that shown in 6.

Although there is no evidence for the cyclization[18] of the pentenyl radical 8, the higher 5-hexenyl homolog 9 readily rearranges to the cyclopentylmethyl radical 10.[19] The esr spectrum of 9 can be observed during


9   10

the photolysis of 6-heptenoyl peroxide or the reaction of triethylsilyl radicals with 5-hexenyl bromide at temperatures less than −35°. At higher temperatures

$$[CH_2=CH(CH)_4CO_2]_2 \longrightarrow$$
$$CH_2=CH(CH_2)_4Br + Et_3Si \cdot \longrightarrow$$
$$CH_2=CHCH_2CH_2CH_2CH_2 \cdot$$
9
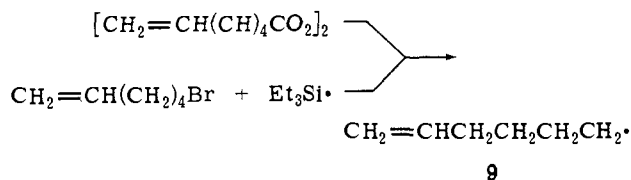
only the spectrum of the rearranged radical 10 is obtained.[3] The esr spectrum of the 5-hexenyl radical shows the largest temperature-dependent changes. The $M_I = 0$ lines due to the β-proton triplets are severely broadened in the spectrum, and the effect is pronounced even at relatively high temperatures as shown in Figure 3. The drastic line broadening may be associated with a coiled conformation 11 in which the terminal unsaturated linkage lies over the radical center.[13c,d]


11
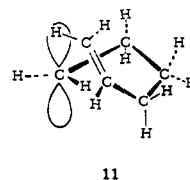
It is not necessary for a direct relationship to exist between the stable conformation of a radical and its propensity for cyclization. Thus, the preferred conformation for cyclization of the 3-butenyl radical 12


12
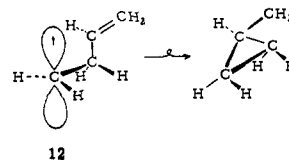
(18) C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, J. Amer. Chem. Soc., 88, 5361 (1966); R. F. Garwood, G. J. Scott, and B. C. L. Weedon, Chem. Commun., 1, 14 (1965); K. W. Watkins and D. K. Olsen, J. Phys. Chem., 76, 1089 (1972).

(19) (a) M. Julia, Accounts Chem. Res., 4, 386 (1971); (b) R. C. Lamb, P. W. Ayers, and M. K. Toney, J. Amer. Chem. Soc., 85, 3483 (1963).

places the γ carbon in an eclipsed position relative to the radical center.[1,2,5,20] However, the esr parameters of the 3-butenyl radical clearly indicate that the conformation about the C_α–C_β bond is similar to that of the higher homologs, *viz.* 13. The esr spectrum of the

13
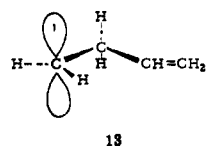
3-butenyl radical shows a temperature-dependent broadening of the $M_I = 0$ lines of triplets associated with the α protons. There is no obvious line broadening in the spectrum associated with the β protons like that previously presented for the saturated (*n*-butyl) analog, and hindered rotation about the C_β–C_γ is apparently absent due to homoconjugation.[21] Interestingly, p–p homoconjugation due to a vinyl group in conformation 13 is opposed to that shown in 14 for radicals with sub-

14, X = Cl, S, Sl, Ge, Sn, etc.
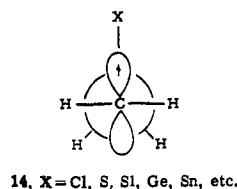
stituents in the β position consisting of heteroatoms with available d orbitals.[7a,22] The esr spectrum of the 3-butenyl radical generated from 3-butenyl bromide and triethylsilyl radicals showed no evidence of the isomeric cyclopropylcarbinyl radical even at the lowest temperatures studied, in agreement with the earlier investigation utilizing peroxides.[1]

Phenyl as a Substituent on Alkyl Radicals. Chemical studies show that the rearrangement of the neophyl radical 15 favors the tertiary isomer 16 (eq 8).[5,23]

$$PhC(CH_3)_2\dot{C}H_2 \xrightarrow{\quad a \quad} (CH_3)_2\dot{C}CH_2Ph \qquad (8)$$

15   16
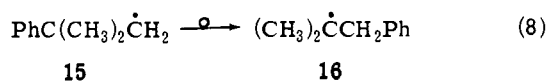
However, the rate of isomerization must be relatively slow, since neophyl radicals generated from neophyl chloride and triethylsilyl radicals do not afford 16 in sufficient concentrations to observe the esr spectrum at temperatures as high as $-60°$.[24] At all temperatures studied, the esr spectrum consisted only of a triplet further split into a septet (Table IV), which is clearly associated with the neophyl radical 15. In some experiments a weak spectrum of even the tri-

(20) (a) *Cf.* M. Simonetta and S. Winstein, *ibid.*, 76, 18 (1954); (b) E. H. Howden and J. D. Roberts, *Tetrahedron*, *Suppl.*, 2, 403 (1963); (c) L. Salem, *Chem. Brit.*, 5, 449 (1969).

(21) For homoconjugation in 13 there are at least two conformations (syn and anti) for the vinyl group (carbon-3 of) which must lie close to the equatorial plane. A choice must take into account long-range coupling to the γ and (one) δ protons.

(22) T. Kawamura and J. K. Kochi, *J. Amer. Chem. Soc.*, 94, 648 (1972); T. Kawamura, D. J. Edge, and J. K. Kochi, *ibid.*, 94, 1752 (1972).

(23) W. H. Urry and M. S. Kharasch, *ibid.*, 66, 1438 (1944); H. Meislick, J. Costanza, and J. Strelitz, *J. Org. Chem.*, 33, 3221 (1968).

(24) (a) For example, the esr spectra of the rearranged radicals derived from cyclopropylcarbinyl and ω-hexenyl radicals are readily observed under comparable conditions. (b) The barrier to rearrangement of the neophyl radical is >8 kcal/mol [J. Wilt and C. A. Schneider, *ibid.*, 26, 4196 (1961)].
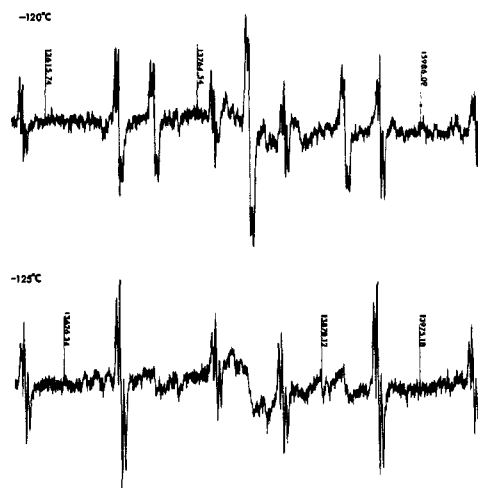
Figure 3. Comparison of the selective line broadening in the esr spectra of the 4-pentenyl (upper) and 5-hexenyl (lower) radicals in cyclopropane solution. Proton nmr field markers are in kilohertz.

Table IV. Esr of Phenyl-Substituted Alkyl Radicals in Solution

Radical	T, °C	$\langle g \rangle$	$A_{\alpha H}$, G	$A_{\beta H}$, G	$A_{\gamma H}$, G
$PhC(CH_3)_2\dot{C}H_2$	-96	2.00263	21.80	1.05[a]	
$PhCH_2\dot{C}H_2$	-100	2.00268	22.10	30.94	
$PhCD_2\dot{C}H_2$	-107	2.00271	22.19	4.75[b]	
	-25		22.19	4.18	
p-$CH_3OC_6H_4CH_2\dot{C}D_2$	-63	2.00271	3.40[b]	30.40	
	-25		3.40	28.60	
$Ph(CH_2)_2\dot{C}H_2$	-99	2.00262	22.11	28.65	0.71
$Ph(CH_2)_3\dot{C}H_2$	-90	2.00263	22.18	29.04	0.69
$PhOCH_2\dot{C}H_2$	-99	2.00261	22.29	32.50	
$PhO(CH_2)_2\dot{C}H_2$	-104	2.00262	22.19	29.02	0.73
$PhO(CH_2)_3\dot{C}H_2$	-102	2.00261	22.17	29.51	0.68

[a] Methyl septet. [b] Deuteron splitting.

ethylsilyl radical[25] was observed, and it became the dominant feature at lower temperatures ($< -110°$).

The parent β-phenethyl radical 17 and the deuterated analog 18 were readily generated from the photolysis of hydrocinnamoyl peroxide and β,β-dideuteriohydrocinnamoyl peroxide, respectively.[11] The parameters obtained from the esr spectrum observed in the latter case were the same as those derived from β-phenethyl radical 17 with the exception that the β hfs were 6.6 times smaller due to the presence of deuterium.[26] There was no evidence of the presence of the isomeric α,α-dideuteriophenethyl radical. The α,α-dideuterated p-methoxy analog 19 showed similar behavior. Thus,

18   19
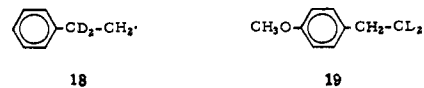
in none of the β-aralkyl systems did we find any evidence for rearrangement by an examination of the esr

(25) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 91, 3938 (1969).

(26) (a) Interestingly, the ratio of the β-proton hfs in 17 to the β-deuteron hfs in 18 at the same temperature ($-88°$) is 6.695 in comparison to the predicted ratio 6.514 based on the magnetic moments of the two nuclei. (b) The same ratio in the parent $CH_3\dot{C}H_2$ and $CD_3\dot{C}D_2$ is 6.586 [R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 39, 2147 (1963); see also ref 6]. (c) The ratio of the α-proton hfs in 17 to the α-deuteron hfs in 19 is 6.509, which compares with 6.507 for the same ratio in the ethyl radicals (ref b above).
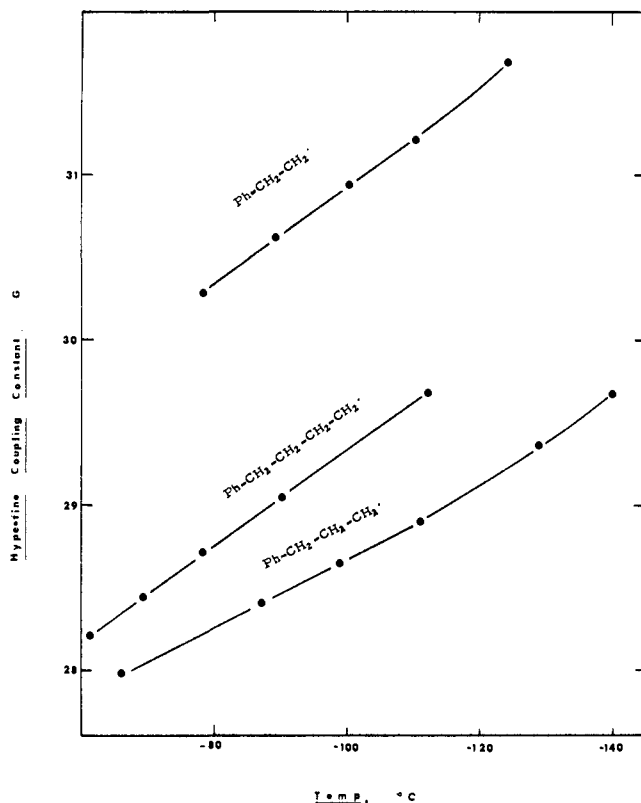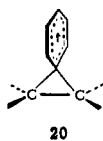
Figure 4. Temperature dependence of the hfs for the β protons in β-phenethyl, γ-phenylpropyl, and δ-phenylbutyl radicals in solution.

spectra. The possibility of rearrangement,[27] of course, is not precluded by these studies, since we only observe under our conditions the species present in highest steady-state concentrations.

Our inability to detect 16 or intermediates such as 20[5a, 28] is in accord with the earlier studies.[11] Therefore, the β-phenethyl radical itself was examined in order to use the pair of β protons as probes for conformational effects exerted by a potential interaction between the radical center and the aromatic ring.

The magnitude of the β-proton hfs in Table IV suggests that the phenyl group lies closer to the equatorial plane as in a homoconjugative model 21 rather than one such as 21' involved in bridging. The esr param-

21   21'
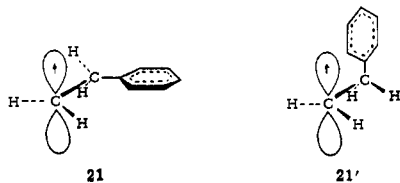
eters of the higher homologs and the oxygen analogs also listed in Table IV suggest that all of these radicals

(27) The barrier to rearrangement of the β-phenethyl radical is in excess of 11 kcal/mol (ref 5a).
(28) R. Kh. Friedlina, Advan. Free-Radical Chem., 1, 211 (1965); D. I. Davies and C. Waring, J. Chem. Soc. C, 1865 (1968).

exist in similar conformations about the C_α–C_β bond. However, the temperature dependence of the hfs of the β protons for these radicals varies considerably but not monotonically with molecular weight. Thus, the slopes in Figure 4 for the 2-, 4-, and 5-phenyl-substituted alkyl radicals are greater than that for the 3-phenyl-propyl radical.

The alternating line width effect in these radicals selectively broadens only the $M_I = 0$ lines of the β-proton triplets. The broadening increases progressively as the phenyl substituent is moved along the alkyl chain and is considerably more severe in the 4-phenylbutyl radical (Figure 5) than that observed for the n-butyl radical and its higher homologs. The lines in the spectrum of 17 had their predicted amplitudes (taking into account the resolved second order splittings) at all the temperatures studied.

The selective line broadening observed in these radicals is associated with hindered internal rotation about the C_β–C_γ bond, in which the β protons are exchanged between two or more different environments.[13d] The degree of line broadening and the magnitude of the β-proton hfs in closely related radicals should reflect the height of the barrier to such internal motions.[6,7b] The quantitative relationship among these, however, also depends on the configuration of the radical particularly at the β-carbon atom. Distortion of the radical at this site from a tetrahedral geometry can cause deviations from the calculated curves of $A_{\beta H}(T)$ based on a $\cos^2 \theta$ angular dependence.[7]

Chemical evidence amply demonstrates the migration of 4- and 5-phenyl groups in free radicals, via an intermediate such as 22,[29] whereas there is no evidence for

22

the migration of 3-phenyl groups. We expected to interrelate the migratory aptitudes of phenyl groups in these radicals to their conformations. Unfortunately, the lack of quantitative tools at hand to derive activation barriers from $A_{\beta H}(T)$ prevents us from assessing the magnitude of interaction between the aromatic ring and the radical center. However, it is clear qualitatively that the location of the phenyl group in an alkyl chain affects the conformation in a much more significant manner than that imposed by an alkyl group of equivalent size.

Experimental Section

Esr spectra were taken with a modified Varian X-band spectrometer utilizing 100-kHz modulation. The microwave bridge was designed around a three-port ferrite circulator. A backward diode (Philco L4154B) was employed as detector in conjunction

(29) (a) S. Winstein, R. Heck, S. Lapporte, and R. Baird, Experientia, 12, 138 (1956); (b) Cf. L. H. Slaugh, E. F. Magoon, and V. P. Guinn, J. Org. Chem., 2643 (1963); L. H. Slaugh, J. Amer. Chem. Soc., 80, 1398 (1958); (c) J. K. Kochi and R. D. Gilliom, ibid., 86, 5251 (1964); (d) M. Julia and B. Malassine, Tetrahedron Lett., 987 (1971); (e) J. W. Wilt, R. A. Dabek, and K. C. Welzel, J. Org. Chem., 37, 425 (1972). (f) The reactivity of ω-phenylalkenes to homolytic addition has also been found to be dependent on the chain length [M. M. Martin and G. J. Gleicher, J. Amer. Chem. Soc., 86, 239 (1964)].

with a low-noise, wide-band preamplifier (Philico P301). The latter was provided with an impedance-matching input circuit and a simple dc circuit to monitor the crystal current by means of a sensitive galvanometer. The input transformer was wound in a ferrite pot core (Ferroxcube Inc.) and was carefully shielded with many layers of high magnetic permeability foil. An attenuator was placed before the tunable detector mount and was used during tuning to avoid excessive microwave power on the detector. The field of a Varian V3600 12-in. magnet was swept very linearly by a Varian V3508 magnet flux stabilizer and slow-sweep unit. The spectral scans were accurately calibrated by means of a field marker operating in conjunction with a Harvey-Wells G502 nmr gaussmeter and a Hewlett-Packard frequency counter. The field marker causes the superposition of markers at accurately known field values directly onto the spectral record. The microwave frequency was determined directly using a Hewlett-Packard 5255A frequency converter and a Hewlett-Packard X281A microwave adapter in conjunction with a Hewlett-Packard 5248L frequency counter. The g factors were determined with the perylene cation radical ($g = 2.00258$)[30] as a daily standard in the configuration employed. A correction, usually 5×10^{-5}, was made to the measured values. The accuracy of such measurements is thought to be ± 0.00003, and g factors made under these conditions were in agreement with those obtained by Fessenden and Schuler.[26b] In most cases hfs were determined by positioning each line precisely, applying second-order corrections,[31] and then recomputing the distance between each line.

The light source, variable temperature equipment, and the sample tubes are as described previously.[7] The temperature in the tube was calibrated with a thermocouple and accurate to $\pm 5°$. The photolyses were carried out in typical cases as follows.

For the photolysis of diacyl peroxides or acyl peresters,[11] a small amount of the peroxide (ca. 100 mg) was dissolved in a relatively large volume (15:1) of cyclopropane or cyclopropane–ethane mixtures. For diacyl peroxides it was also possible to employ diethyl ether or ether–pentane mixtures as solvent to enable lower temperatures to be obtained before crystallization became a problem.

For photolytic reduction of alkyl halides,[10] 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. The halide was usually the bromide, but chlorides could also be used. In the latter case, good spectra of alkyl radicals could only be observed at certain temperatures, above and below which the spectrum of triethylsilyl radicals was also observed. All samples were thoroughly degassed using a freeze–pump–thaw cycle. When spectra were weak or not observed, the amounts of the various components were varied to obtain optimum concentrations.

The esr spectra of other substituted alkyl radicals were also examined. Since they are related but not directly tied in with the principal radicals reported here, they are presented separately in Table V.

Materials. Di-tert-butyl peroxide was obtained from the Shell Chemical Co., washed, and redistilled at reduced pressures prior to use. Triethylsilane, ethyl 4-bromobutyrate, 4-bromobut-1-ene, 5-bromopent-1-ene, and 6-bromohex-1-ene were obtained from Columbia Organic Chemicals Co. Phenethyl bromide was obtained from Matheson Coleman and Bell; 3-phenylpropyl bromide, 3-phenoxypropyl bromide, and 2-bromoethyl acetate were from Eastman Kodak. Ethyl 3-bromopropionate and ethyl 5-bromovalerate were obtained from Aldrich Chemical Co. Samples were redistilled before use.

The bis-5-phenylvaleryl peroxide was prepared using a previously described method;[32] the tert-butyl perester of 4-acetylbutyric acid (Aldrich) was prepared by the carbonyldiimidazole method.[33] Ethyl 6-bromocaproate was prepared from the corresponding 6-bromocapronitrile (Columbia) by treatment with ethanol and hydrogen chloride,[34] bp 41–42° (1 mm). 3-Acetoxypropyl bromide was prepared from 3-bromopropanol-1 (Columbia) by acetylation with acetic anhydride.[35] Neophyl chloride prepared by chlorina-

(30) B. G. Segal, M. Kaplan, and G. K. Fraenkel, *J. Chem. Phys.*, **43**, 4191 (1965).
(31) R. W. Fessenden, *ibid.*, **37**, 747 (1962).
(32) J. K. Kochi, *J. Amer. Chem. Soc.*, **85**, 1958 (1963).
(33) R. Hecht and C. Ruchardt, *Chem. Ber.*, 1281 (1963).
(34) B. K. Campbell and K. N. Campbell, *J. Amer. Chem. Soc.*, **60**, 1372 (1938).
(35) J. K. Kochi and D. M. Singleton, *J. Org. Chem.*, **33**, 1027 (1968).

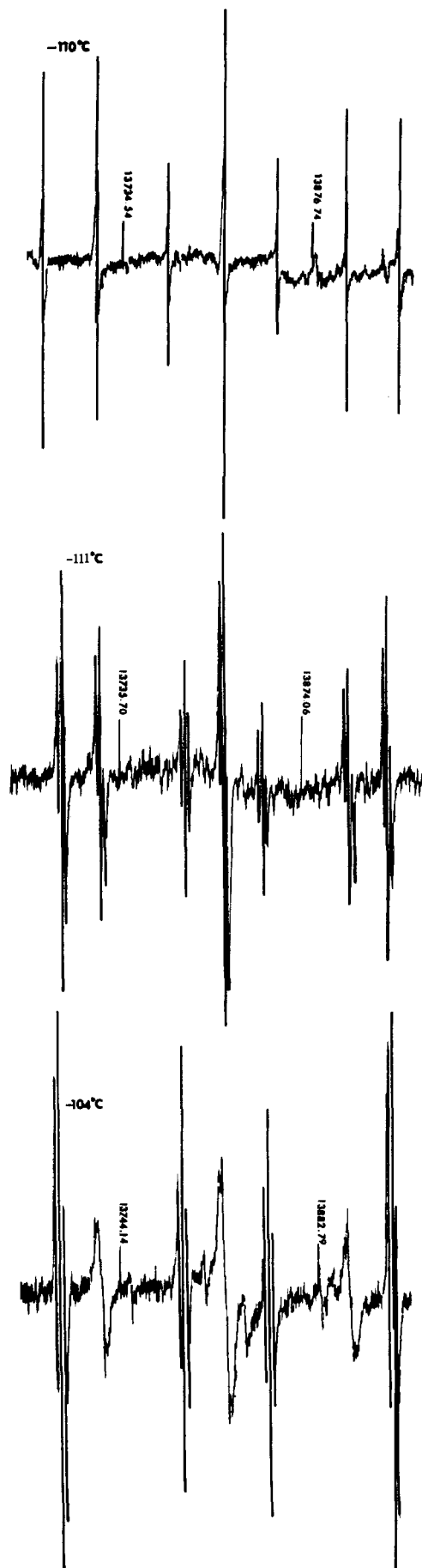Figure 5. Esr spectra (central portion) of β-phenylethyl (top), γ-phenylpropyl (center), and δ-phenylbutyl (bottom) radicals in cyclopropane showing differences in the selective line broadening with chain length.

Table V. Esr of Substituted Alkyl Radicals in Solution

Radical	T, °C	$\langle g \rangle$	A_α, G	A_β, G	A_γ, G
$\dot{C}H_2CH_2OCH_2CH_3$	−111	2.00257	22.15	33.76	
	−136		22.13	34.68	
$\dot{C}H_2CH_2OSi(CH_3)_3$	− 98	2.00258	22.11	34.01	
	−135		22.12	35.63	
$\dot{C}H_2CH_2CH(CH_3)_2$	− 70	2.00259	22.06	27.59	0.94
	−121		22.07	28.24	0.97
$\dot{C}H_2CH_2C(CH_3)_3$	−105	2.00268	22.06	24.71	0.1[a]
$\dot{C}H(CH_3)CH(CH_3)OAc$	−104	2.00258	22.12	25.53 (CH₃)	0.70[b]
				15.71 (H)	
$\dot{C}H_2(CH_2)_2C{\equiv}C\text{-}n\text{-}C_4H_9$	−104	2.00266	22.09	29.14[c]	0.74
$\dot{C}H_2(CH_2)_3C{\equiv}C\text{-}n\text{-}C_4H_9$	−103	2.00266	21.97	29.06[c]	0.79

[a] δ protons (decet). [b] Selective broadening of the $M_I = \pm^1/_2$ lines observed at lower temperatures resulting in reduced amplitude and much poorer resolution compared to the α-methyl quartets. [c] Central line ($M_I = 0$) of the triplet severely broadened.

tion of *tert*-butylbenzene was kindly supplied by Dr. L. F. Friedman. Hydrocinnamoyl peroxide, the β,β-dideuterio compound, and *p*-methoxyhydrocinnamoyl peroxide-α,α-d_2 were described[36]

(36) J. K. Kochi, A. Bemis, and C. L. Jenkins, *J. Amer. Chem. Soc.*, 90, 4038, 4616 (1968).

earlier. 9-Bromononyne-5 and 10-bromodecyne-5 were prepared and kindly donated to us by Drs. W. Michaely and J. K. Crandall.

Conformations of 7,12-Dihydropleiadene Radical Anions. Electron Spin Resonance and Electron Nuclear Double Resonance Studies

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Abstract: The radical anions of 7,12-dihydropleiadene, 1-methyl-7,12-dihydropleiadene, and 7,12-(*o*-phenylene)-7,12-dihydropleiadene have been prepared and their esr spectra interpreted with the aid of endor spectroscopy. The hyperfine coupling constants for the bridge protons in the seven-membered ring have been used to determine the conformation of this ring. Contrary to previous suggestions, the conformation of the methyl-substituted anion is found to be the same as for the unsubstituted radical anion, *i.e.*, two equivalent axial and two equivalent equatorial protons on the seven-membered ring.

The conformationally labile 7,12-dihydropleiadenes (DHPs) have proven to be ideal molecules for studying ring inversion of seven-membered rings[2] (*e.g.*, A $\rightleftarrows$ E (k_r) with R = H) using dynamic nmr techniques.

pleiadene
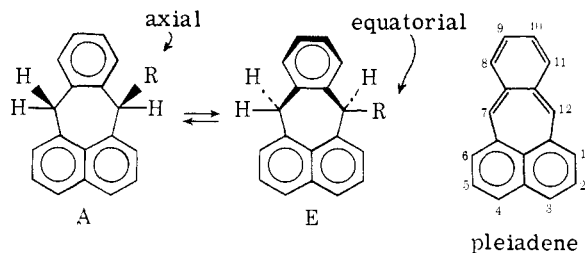
Since $\Delta G^{\pm}$ for inversion is usually *ca.* 13–15 kcal/mol, it was quite easy to measure T_c and $\Delta\nu_{AB}$ for a number

of aryl-substituted DHPs (with R = H) and also to "freeze out" diastereomeric conformers A and E (above) when R was a substituent whose steric preference we wished to assess.[3a] From a study of various seven-substituted DHPs (assessing K_{eq} for A $\rightleftarrows$ E with R $\neq$ H), we found relative steric bulks of "similar" alkyl groups (on cyclohexanes) to change quite drastically[3b] when on the ring. Complementing these stereochemical studies was the discovery of several hydride rearrangements across the seven-membered ring.[4]

When C_1 substituents were present on the DHP nucleus, low-temperature nmr studies in most cases revealed two AB quartets for the C_7 and C_{12} methylene groups,[4] with the C_{12} quartet invariably exhibiting the smaller $\Delta\nu_{AB}$, as in 1-Me-DHP (below). C_8 and/or C_{11} substituents also reduced $\Delta\nu_{AB}$ of the neighboring CH_2

(1) State University of New York at Buffalo, Graduate School Fellow, 1969–1970.
(2) (a) P. T. Lansbury, J. F. Bieron, and M. Klein, *J. Amer. Chem. Soc.*, 88, 1477 (1966); (b) F. D. Saeva, Ph.D. Dissertation, State University of New York at Buffalo, 1968.

(3) (a) P. T. Lansbury, J. F. Bieron, and A. J. Lacher, *J. Amer. Chem. Soc.*, 88, 1482 (1966); (b) P. T. Lansbury, A. J. Lacher, and F. D. Saeva, *ibid.*, 89, 4361 (1967).
(4) P. T. Lansbury, *Accounts Chem. Res.*, 2, 210 (1969).