This simple technique for the production of alkyl radicals for esr study enjoys the advantages of ease and especially selectivity over the classic radiolytic method of Fessenden and Schuler.[5] The esr spectrum generally observed belongs to that alkyl radical produced by abstraction of hydrogen from the weakest bond (*i.e.*, allyl, benzyl > *t*-alkyl > *sec*-alkyl ≫ *p*-alkyl). Radicals produced by scission of the carbon chain inherent in electron radiolysis are absent. Except where several hydrogens have nearly the same reactivities (*e.g.*, 2- and 3-pentyl from pentane), the esr spectrum is generally uncomplicated by the presence of several radical species. A typical example (Figure 1) is the spectrum of the *sec*-butyl radicals produced from *n*-butane. A variety of free radicals produced from some representative hydrocarbons is given in Table I, with the appropriate coupling constants.

Isotropic spectra characteristic of freely tumbling alkyl radicals in solution can be obtained even for the higher melting or readily polymerizable hydrocarbons. Methane, ethane, and cyclopropane, which do not produce radicals in sufficient concentrations to be observed under these conditions, can be conveniently employed as solvents or diluents.[6,7] The esr spectrum of cyclopentadienyl radical in cyclopropane solution (Figure 2) illustrates the characteristic narrow lines attainable.[9,10]

The highly selective production of alkyl radicals by this method offers a potentially valuable tool for the detailed study of a variety of free-radical structures and dynamics.[11]

Acknowledgments. J. K. K. expresses his gratitude to the Central Research Department for the hospitality extended to him during the course of this work.

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(5) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 39, 2147 (1967).

(6) Under these conditions we have not observed the methyl radicals formed by fragmentation of *t*-butoxyls.

(7) Radicals have recently been observed in the γ radioloysis of di-*t*-butyl peroxide in rigid matrices.[8] Broad lines and a mixture of radical species were reported, apparently by an electron-transfer process.

(8) T. Shida, *J. Phys. Chem.*, **72**, 723 (1968).

(9) Cyclopentadienyl radicals in solution have also been observed previously by R. W. Fessenden, *et al.* (*J. Am. Chem. Soc.*, **86**, 3591 (1964); "Radiation Research," G. Silini, Ed., North Holland Publishing Co., Amsterdam 1967, p 99).

(10) The complete equivalence of the five protons precludes a static Jahn–Teller distortion of the molecule at this temperature (*cf.* G. F. Liebling and H. M. McConnell, *J. Chem. Phys.*, **42**, 3931 (1965)).

(11) After this work was accepted for publication J. Q. Adams (*J. Am. Chem. Soc.*, 90, 5363 (1968)) reported an esr study of α-hydroxy alkyl radicals generated by photolysis of di-*t*-butyl peroxide in the presence of alcohols. A flow technique similar to that of R. Livingston and H. Zeldes (*J. Chem. Phys.*, **44**, 1245 (1966)) was employed.

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Isomerization and Electron Spin Resonance of Allylic Radicals

Sir:

The photolysis of a propylene solution of di-*t*-butyl peroxide produces allyl radicals (I). The esr spectrum of the allyl radical is shown in Figure 1. The spectral assignments are based on internal consistency with the methyl-substituted allyl radicals (*vide infra*).[1] Our

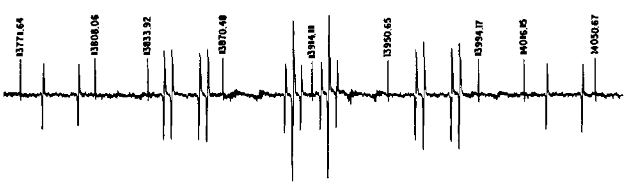
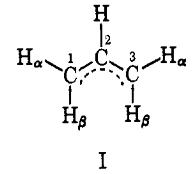


Figure 1. Esr spectrum of the allyl radical at −130°. The nmr frequency markers are in kcps.

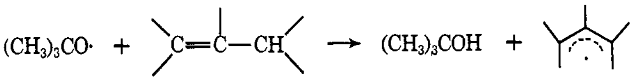


coupling constants, G
$a_{1,3\alpha H} = 14.81$
$a_{1,3\beta H} = 13.90$
$a_{2H} = 4.06$

I

coupling constants agree with those of Fessenden and Schuler,[3] who were able to extract the allyl lines from a complex spectrum obtained from the radiolysis of cyclopropane.[4]

Hydrogen atoms in the allylic position can also be selectively abstracted from a series of butenes by the technique described in the previous communication.[5] Thus, the esr spectrum obtained from isobutylene can

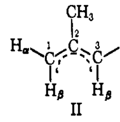
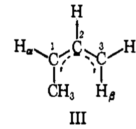
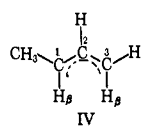


(1)

be unambiguously assigned to the 2-methallyl radical (II). *cis*-Butene-2 affords the *cis*-1-methallyl radical (III) (Figure 2). Similarly, *trans*-butene-2 gives *trans*-1-methallyl radical (IV) (Figure 3).[6]

The esr spectrum of *cis*-1-methallyl from the pho-

Table I. Methallyl Radicals from Butenes

Butene	Methallyl radical	Coupling constants, G
Isobutylene	 II	$a_{CH_3} = 3.19$ $a_{1,3\alpha H} = 14.68$ $a_{1,3\beta H} = 13.82$
cis-Butene-2	 III	$a_{CH_3} = 14.01$ $a_{1\alpha H} = 14.17$ $a_{2H} = 3.83$ $a_{3\alpha H} = 14.94$ $a_{3\beta H} = 13.52$
trans-Butene-2	 IV	$a_{CH_3} = 16.43$ $a_{1,3\beta H} = 13.83$ $a_{2H} = 3.85$ $a_{3\alpha H} = 14.78$

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(1) It is to be noted that Hinchliffe and Atherton's semiempirical calculations[2a] lead to $a_{\beta H} > a_{\alpha H}$ for the methylene protons. More recent calculations by Pople, *et al.*,[2b] lead to the same prediction but with a much smaller difference between the two positions.

(2) (a) A. Hinchliffe and N. M. Atherton, *Mol. Phys.*, **13**, 89 (1967); (b) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Am. Chem. Soc.*, **90**, 4201 (1968).

(3) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(4) The spectrum was successfully dissected into six radical components: cyclopropyl, isopropyl, allyl, methyl, and two unidentified species formed in minor amounts.[3]

(5) P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, **90**, 7155 (1968).

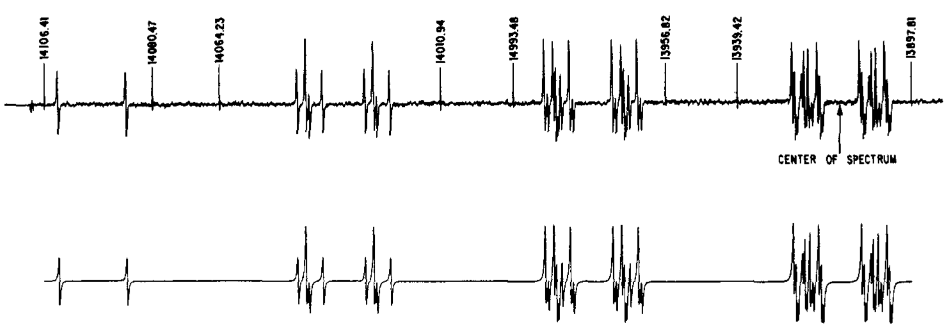

Figure 2. Experimental and calculated high-field halves of the esr spectrum of *cis*-1-methallyl radical at −140°. The line widths are *ca.* 0.07 G. Part of the fine structure is due to second-order effects.

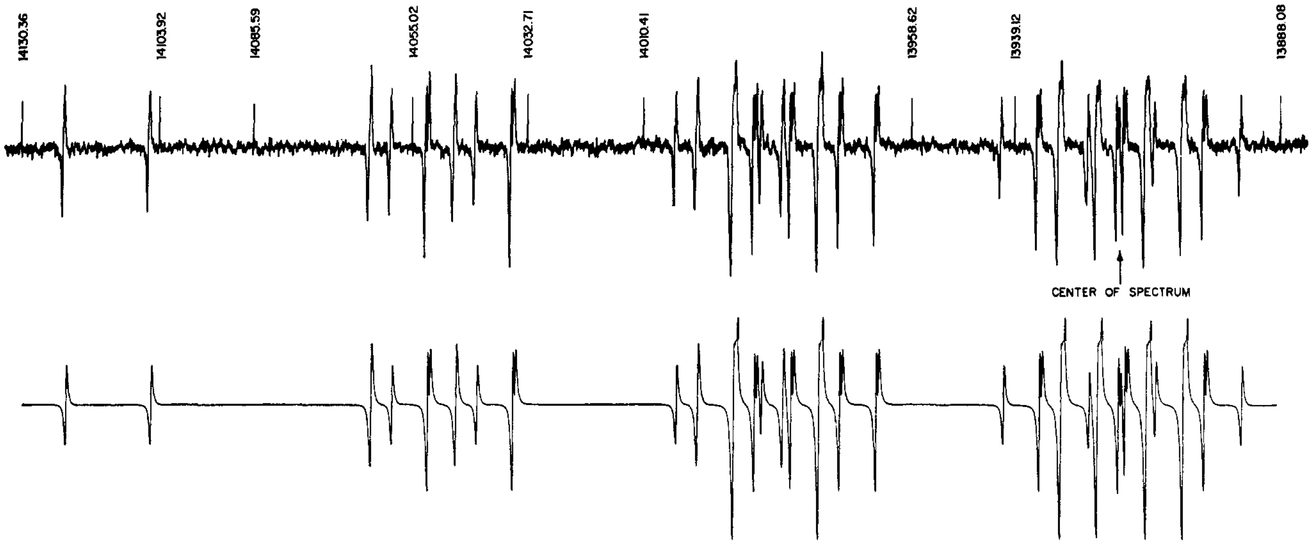

Figure 3. Experimental and calculated high-field halves of the esr spectrum of *trans*-1-methallyl radical at −110° with partially resolved second-order splittings.

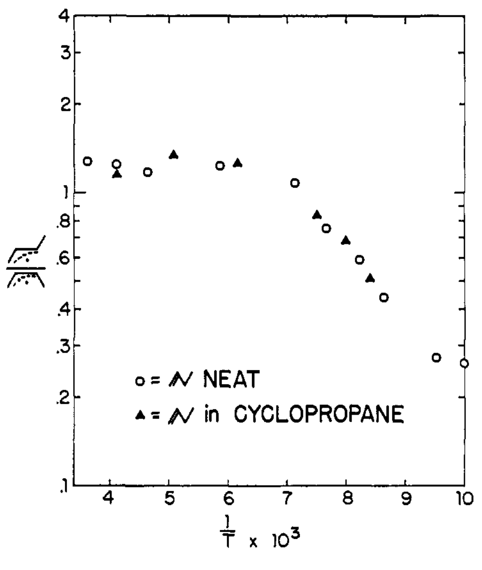

Figure 4. Temperature dependence of the relative concentrations of *trans*-1-methallyl and *cis*-1-methallyl resulting from butene-1 by hydrogen atom abstraction.

tolysis of *cis*-butene-2 solutions was examined from 0 to −130°. We could find no evidence for the presence of the isomeric IV under these conditions. Reexamination of the recovered butene showed <0.5% *trans*-butene-2. We estimate[7] that the first-order rate constant for the isomerization of *cis*-methallyl to *trans*-methallyl is less than 10^2 sec^{-1}.

The esr spectra from various molar mixtures of *cis*- and *trans*-butene-2 consisted simply of the superposition of the individual spectra of III and IV. The clearly separated doublets ($a_{2\text{H}}$ splittings) in the wings of the spectra were used for quantitative analysis. After normalization, the relative concentration of IV and III under competitive conditions was IV/III = 1.2 ± 0.3. The ratio diminished slightly from 0 to −160°. The steady-state concentrations of III and IV thus observed can be compared with the relative rates (k_t/k_c = 0.95 at 40°) of hydrogen abstraction from *cis*- and *trans*-butene-2 by *t*-butoxy radicals during radical-chain chlorination with *t*-butyl hypochlorite.[8,9]

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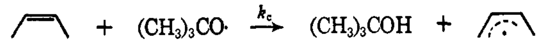
(6) R. W. Fessenden has also obtained the esr spectrum of IV by electron radiolysis of *trans*-butene-2 (156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 9, 1968, Abstracts, No. ORGN-85).

(7) The calculation is based on the steady-state approximation, an assumed concentration of the principal radicals of 10^{-6} *M*, rates of self- and cross-combination of methallyl radicals of 10^9 M^{-1} sec^{-1}, and the assumption that the steady-state concentration of the isomeric radical is no more than 10% of the principal species.

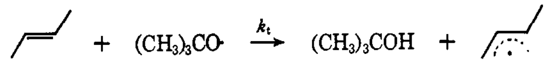
(8) C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961).

(9) (a) The relative steady-state concentrations of III and IV are not necessarily related to their relative rates of formation (eq 2 and 3). However, since radicals in our system probably disappear by mutual interaction, these quantities should show a 1:1 correspondence. (b) The stability of *cis* and *trans* methallyl radicals has been discussed qualitatively [S. Bank, *J. Am. Chem. Soc.*, **87**, 3245 (1965)].



(2)

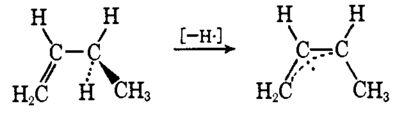
III



(3)

IV

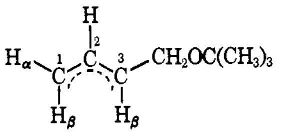
Examination of the esr spectra obtained from butene-1 shows the presence of only III and IV. The relative amounts of these isomeric radicals are temperature dependent (Figure 4). At relatively high temperatures between 0 and −100°, only slightly more *trans*-1-methallyl is formed than *cis* isomer. Since stereoisomeric integrity is maintained under these conditions, the mixture of radicals cannot arise by interconversion. We tentatively interpret the drop-off of the *trans* isomeric radical at temperatures less than −130° to an increased conformational preference of a *gauche* structure such as V for butene-1 at lower temperatures.[10–13] Further studies on steric effects are in progress.



V

(4)

The importance of the conformation of the reactant is shown further by the *addition* of *t*-butoxy radical to 1,3-butadiene. At −137° the esr spectrum of only the *trans* allylic radical VI is observed.[14] The coupling constants are highly consistent with the assignments for the other allylic radicals. The 1β and 3β hydrogens have degenerate coupling constants as in the analogous *trans* methallyl radical.



VI

coupling constants, G
$a_{1\alpha H} = 14.83$
$a_{1,3\beta H} = 13.74$
$a_{2H} = 3.88$
$a_{CH_2} = 16.97$

Acknowledgment. J. K. K. expresses his gratitude to the Central Research Department for the hospitality extended to him during the course of this work.

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[10] An examination of nmr coupling constants in butene-1 shows that the rotational conformers are about equally populated at ambient temperatures.[11] Recent calculations by N. L. Allinger, *et al.* [*J. Am. Chem. Soc.*, **90**, 5773 (1968)], indicate, however, that the *gauche* rotamer of butene-1 is 0.69 kcal/mol more stable than the *anti* form. Similarly, in propionaldehyde, a reasonable model, the *cis* rotamer is approximately 1 kcal/mol more stable than the *gauche* form, and the barrier to rotation is 2.3 kcal/mol.[12]

(11) A. A. Bothner-By, C. Naar-Colin, and H. Gunther, *J. Am. Chem. Soc.*, **84**, 2748 (1962).

(12) S. S. Butcher and E. B. Wilson, Jr., *J. Chem. Phys.*, **40**, 1671 (1964).

(13) A mixture of two isomeric 1-hydroxyallyl radicals was obtained from the photolysis of hydrogen peroxide in allyl alcohol by R. Livingston and H. Zeldes [*J. Chem. Phys.*, **44**, 1245 (1966)]. The relative concentrations of the isomers were temperature dependent, but they were unable to make structural assignments.

(14) The esr spectrum does not distinguish between VI and the oligomeric radicals resulting from further addition to butadiene. There is no doubt, however, that the configuration of all of these allylic radicals is *trans*. The broader lines observed in this case (*ca.* 0.5 G) may be due to either unresolved hyperfine interactions or a mixture of radicals.

Radical Mechanism of Alkylation of Sodium Naphthalenide

Sir:

The potential competition between electron-transfer and nucleophilic displacement reactions is especially interesting for organic radical anions. In order to elucidate the factors which influence this competition, it is imperative that those reactions of radical anions which might proceed by either mechanism be correctly classified. Both pathways have been suggested for alkylations of sodium naphthalenide with alkyl halides. Data reported herein rule out the nucleophilic displacement mechanism for such alkylations with primary alkyl halides.

Reactions of sodium naphthalenide (:Naph·⁻) with alkyl halides (RX) in 1,2-dimethoxyethane (DME) lead to reduction products (RH)[1–3] and alkylation products.[4–6] The reduction products arise through successive electron-transfer reactions (eq 1–3).[1–3] Radical (eq 1 followed by eq 4) and S_N2 (eq 5) mechanisms have been suggested for the initial step of alkylation.[5,7] Subsequent alkylation probably proceeds from the anion which is the product in eq 6.[5]

$$:\text{Naph}\cdot^- + \text{RX} \longrightarrow :\text{Naph} + \text{R}\cdot + \text{X}^- \qquad (1)$$

$$:\text{Naph}\cdot^- + \text{R}\cdot \longrightarrow :\text{Naph} + \text{R}:^- \qquad (2)$$

$$\text{R}:^- \xrightarrow{\text{DME}} \text{RH} \qquad (3)$$

$$:\text{Naph} + \text{R}\cdot \longrightarrow \cdot\text{Naph-R} \qquad (4)$$

$$\cdot\text{Naph}:^- + \text{RX} \longrightarrow \cdot\text{Naph-R} + \text{X}^- \qquad (5)$$

$$\cdot\text{Naph-R} + :\text{Naph}\cdot^- \longrightarrow :\text{Naph-R}^- + :\text{Naph} \qquad (6)$$

A direct answer to the question of the alkylation mechanism was sought by investigating the effects of halogen variation on the yields of reduction products, using primary (5-hexenyl) halides. Since the reduction and alkylation products are formed competitively, the yield of reduction product would vary from one halogen

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(1) (a) J. F. Garst, P. W. Ayers, and R. C. Lamb, *J. Am. Chem. Soc.*, **88**, 4260 (1966); (b) *Preprints, Div. Petrol. Chem.*, **13**, D65 (1968).

(2) G. D. Sargent, J. N. Cron, and S. Bank, *J. Am. Chem. Soc.*, **88**, 5363 (1966).

(3) J. F. Garst and F. E. Barton, II, unpublished work documenting the successive electron-transfer mechanism for production of 1-hexene and methylcyclopentane in reactions of 5-hexenyl fluoride with sodium naphthalenide in DME.

(4) N. D. Scott and J. F. Walker, U. S. Patent 2,150,039 (March 7, 1939); *Chem. Abstr.*, **33**, 4602^6 (1939).

(5) D. Lipkin, F. R. Galiano, and R. W. Jordan, *Chem. Ind.* (London), 1657 (1963); see also D. Lipkin, G. J. Divis, and R. W. Jordan, *Preprints, Div. Petrol. Chem.*, **13**, D60 (1968), and further references therein.

(6) The alkylation products are principally dialkyldihydronaphthalenes and alkylnaphthalenes.[4,5]

(7) G. J. Hoijtink, *Chem. Ing. Tech.*, **35**, 333 (1963).