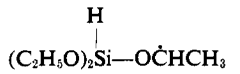
tivity is consistent with our earlier observations of the behavior of *t*-butoxy radicals toward hydrocarbons[6]

$$(CH_3)_4Si + (CH_3)_3CO\cdot \longrightarrow \underset{\text{II}}{(CH_3)_3SiCH_2\cdot} + (CH_3)_3COH \quad (2)$$

and generally reflects the lower bond dissociation energy of the silicon–hydrogen bond relative to its carbon–hydrogen analog.[11] In the presence of an activating atom, however, such as oxygen in triethoxysilane, the abstraction of the hydrogen atom from the silicon was not observed. Abstraction occurred predominantly from the methylene group to produce a carbon-centered radical, III. The magnitudes of the α and β coupling constants in III are similar to the analogous coupling



$$(C_2H_5O)_2\overset{\overset{\large H}{|}}{Si}\text{—}O\dot{C}HCH_3$$

III

$a_{CH} = 17.76$ G ($-97°$)
$a_{CH_3} = 23.35$ G
$a_{SiH} = 0.21$ G

constants in α-hydroxy and α-alkoxyalkyl radicals derived from alcohols and ethers.[12] The splitting due to the γ proton attached to the silicon atom, on the other hand, is significantly smaller than that observed for the corresponding hydrogen across the ether linkage, *e.g.*, $a_\gamma = 1.4$ G in α-ethoxyethyl radical.[12] Interestingly, photolysis of di-*t*-butyl peroxide in triethyl orthoformate, the carbon analog of triethoxysilane, yields only the spectrum of triethoxymethyl radical, $(CH_3CH_2O)_3C\cdot$ ($a_{CH_2} = 0.40$ G).

It is also possible to generate simultaneously a silyl and an alkyl radical by irradiating di-*t*-butyl peroxide in a silane–hydrocarbon mixture. For example, a superposition of *t*-butyl and trimethylsilyl spectra was obtained from an isobutane–trimethylsilane system. The *g* values of these radicals do not differ appreciably ($g_{(CH_3)_3C\cdot} - g_{(CH_3)_3Si\cdot} = -0.00024$).

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[11] N. J. Friswell and B. G. Gowenlock, *Advan. Free Radical Chem.*, 1, 39 (1965).

[12] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 3119 (1963); W. T. Dixon, R. O. C. Norman, and A. Buley, *ibid.*, 3625 (1964); T. Shiga, A. Boukhors, and P. Douzou, *J. Phys. Chem.*, 71, 3559 (1967).

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Electron Spin Resonance of Primary Alkyl Radicals. Photolysis of Acyl Peroxides

Sir:

We wish to report a general technique for producing a *specific* alkyl radical in solution for electron spin resonance (esr) study. When diacyl peroxides are photolyzed (2500–3500 Å) at low temperatures directly in the cavity of the spectrometer, an intense esr spectrum of even a primary alkyl radical can be observed. As an example, the spectrum of *n*-butyl radical, previously unobserved, was obtained from the photolysis of a solution of *n*-valeryl peroxide in cyclopropane (Figure 1). The resolution and signal-to-noise ratio of this spectrum are typical for these systems. We attribute the selective broadening of the lines corresponding to $M = 0$ for the β hydrogens in Figure 1 to restricted rotation about the C_β–C_γ bond. The details of the temperature dependence of the broadening of the central group of multiplets is shown in Figure 2.

Carbon dioxide accompanies the formation of *n*-butyl radicals, and the photochemical reaction is represented by eq 1.[1] The photolyses[2,3] were also carried out in

$$(CH_3CH_2CH_2CH_2CO_2)_2 \xrightarrow{h\nu} 2CH_3CH_2CH_2CH_2\cdot + 2CO_2 \quad (1)$$

isopentane, propylene, or silane as solvent at various temperatures. No evidence for *t*-amyl, allyl, or silyl radicals formed by secondary reactions such as (2)

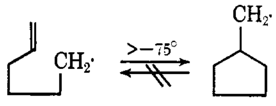
$$CH_3CH_2CH_2CH_2\cdot + RH \longrightarrow CH_3CH_2CH_2CH_3 + R\cdot \quad (2)$$

$$R = t\text{-amyl, allyl, silyl}$$

could be found. However, in the more reactive cyclopentene solvent, a weak spectrum of cyclopentenyl was observed coincidentally with that of *n*-butyl radical. We conclude that reactions such as (2) are too slow to generate radicals (R·) in adequate steady-state concentration to be observed. Fortunately, this allows for a wide choice of solvents.

The esr spectrum of neopentyl radical (Figure 3) shows a well-resolved hyperfine structure due to nine γ hydrogens.[4] A wide variety of other primary alkyl radicals listed in Table I have been examined by this technique. Moreover, the esr spectra of various fluorinated alkyl radicals have also been recorded.

The method is applicable to highly metastable species. For example, the esr spectrum of 5-hexenyl radical (I) from 6-heptenoyl peroxide can be observed directly at −75°. At slightly higher temperatures (−35°), the esr spectrum of only cyclopentylmethyl radical II was detected. Both species I and II were present at intermediate temperatures (−55°). The irreversibility of the rearrangement (eq 3) is shown by the observation of only II during photolysis of cyclopentylacetyl peroxide at temperatures even up to 0°.[5]



I II (3)

β-Phenethyl and some of its ring-substituted analogs were produced from the photolysis of hydrocinnamoyl peroxide and its derivatives. The homologous δ-

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[1] The equation is not intended to establish stoichiometry, but only that alkyl radicals are produced. Product and quantum yield studies are in progress (R. A. Sheldon).

[2] (a) The *photosensitized* decomposition of diacyl peroxides was reported by C. Walling and M. J. Gibian (*J. Am. Chem. Soc.*, 87, 3413 (1965)). Only slight or no decomposition was noted in unsensitized reactions at >3050 Å. (b) A product study of the photolysis of *t*-butyl peresters has been recently published (W. H. Simpson and J. G. Miller, *ibid.*, 90, 4093 (1968)).

[3] The photodecomposition of diacyl peroxides and peresters, unlike di-*t*-butyl peroxide, probably occurs *via* a n–π^* transition similar to carboxylic acids and esters (<2500 Å): J. C. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 427 ff.

[4] Neopentyl radical was originally observed by R. W. Fessenden and R. H. Schuler (*J. Chem. Phys.*, 39, 2147 (1963)) by electron radiolysis of neopentane. However, they were unable to resolve the hyperfine splittings due to γ hydrogens. See also J. Lin and F. Williams, *J. Phys. Chem.*, 72, 3707 (1968).

[5] The rate of rearrangement (eq 3) has been evaluated as 10^5 M^{-1} sec^{-1} at 25° (D. J. Carlson and K. U. Ingold, *J. Am. Chem. Soc.*, 90, 7047 (1968).

Table I. Hyperfine Coupling Constants of Alkyl Radicals from Acyl Peroxides[a]

Alkyl radical	Temp, °C	Hyperfine coupling constants, G a_α	a_β	a_γ
$CH_3\cdot$	−97	22.83		
$CH_3CH_2\cdot$	−85	22.30	26.81	
$CH_3CH_2CH_2\cdot$	−105	22.14	30.33	0.27
$(CH_3)_2CH\cdot$	−105	22.06	24.74	
$CH_3CH_2CH_2CH_2\cdot$	−106	22.12	29.07	0.71
$(CH_3)_2CHCH_2\cdot$	−57	21.93	30.02	[b]
$(CH_3)_3CCH_2\cdot$	−58	21.81		1.00
$CH_2{=}CH(CH_2)_2\cdot$	−105	22.17	28.53	0.61, 0.35[c]
$CH_2{=}CH(CH_2)_3\cdot$	−63	22.13	28.84	0.59
$CH_2{=}CH(CH_2)_4\cdot$	−82	21.93	28.58	0.69
c-$C_5H_9CH_2\cdot$	−90	21.3[d]	21.3[d]	[e]
$C_6H_5CH_2CH_2\cdot$	−33	22.00	29.27	
p-$CH_3OC_6H_4CH_2CH_2\cdot$	−20	22.04	29.50	
m-$CH_3OC_6H_4CH_2CH_2\cdot$	−37	22.2[f]	29.5[f]	
p-$CH_3C_6H_4CH_2CH_2\cdot$	−25	22.00	29.35	
$C_6H_5CH_2CH_2CH_2CH_2\cdot$	−75	22.06	28.66	0.78
$C_6H_5CH_2CH_2CH_2CH_2CH_2\cdot$	−44	22.07	28.12	0.69
$C_6H_5C(CH_3)_2C(CH_3)_2\cdot$[g]	−88		22.61	[e]

[a] Solutions *ca.* 0.1–1 *M* peroxide in cyclopropane or cyclopentane solvent. [b] Unresolved. [c] One δ hydrogen. [d] Near-degenerate coupling constants for α and β protons leading to broadened quartet. Envelope of each multiplet *ca.* 4 G wide, due also to unresolved γ-hyperfine interactions. [e] Unresolved. [f] Approximate value due to low solubility. [g] From photolysis of di-*t*-butyl peroxide in 2,3-dimethyl-2-phenylbutane (*cf.* ref 7).

phenylbutyl and ε-phenylpentyl radicals were also generated from δ-phenylvaleryl and ε-phenylcaproyl peroxides, respectively, in an analogous manner. The esr spectra (Table I) of these radicals were all triplets of triplets similar to that of *n*-butyl radicals and showed no resolvable hyperfine interaction with the aromatic hydrogens. Thus, we obtained no evidence for bridged radical structures such as III and IV variously postulated earlier from chemical studies.[6] Moreover, the esr spectrum of the tetramethyl analog obtained from the photolysis of di-*t*-butyl peroxide in 2,3-dimethyl-2-phenylbutane[7] is simply a septet broadened by partially resolved γ interactions. Thus, the bridged structure V is also to be excluded for this substituted β-aralkyl radical.

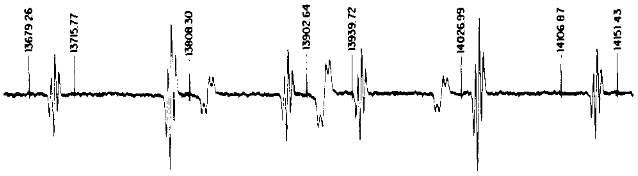
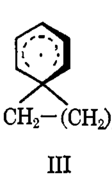
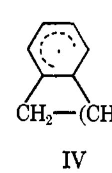
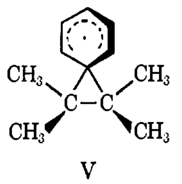


Figure 1. Esr spectrum of *n*-butyl radical from the photolysis of a solution of *n*-valeryl peroxide in cyclopropane at −105°. The proton nmr field markers are in kcps.


III


IV


V

The method is also applicable to other peroxidic derivatives such as peresters. Thus, the photolysis of *t*-butyl peracetate[8] in cyclopropane produces an intense esr spectrum of methyl radicals (eq 4). The spectrum

$$CH_3CO_2OC(CH_3)_3 \xrightarrow{h\nu} CH_3\cdot + CO_2 + \cdot OC(CH_3)_3 \qquad (4)$$

of *t*-butoxy radical is not observed under these conditions, in agreement with earlier studies.[7] Radicals

Figure 2. The selective broadening of the central triplet in the spectrum of *n*-butyl radicals at various temperatures.

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(6) For a review see R. Kh. Friedlina, *Advan. Free Radical Chem.*, **1**, 211 (1965); W. H. Urry, D. J. Trecker, and H. D. Hartzler, *J. Org. Chem.*, **29**, 1663 (1964); R. Scheppele and S. Seltzer, *J. Am. Chem. Soc.*, **90**, 367 (1968); D. I. Davies and C. Waring, *J. Chem. Soc., C*, 1865 (1968).

(7) *Cf.* P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, **90**, 7551 (1968).

(8) After this work was completed, we learned that the esr spectrum of methyl radicals has been observed from the photolysis of *t*-butyl peracetate (H. Fischer and H. Hefter, *Z. Naturforsch.*, **23**, 1763 (1968)).

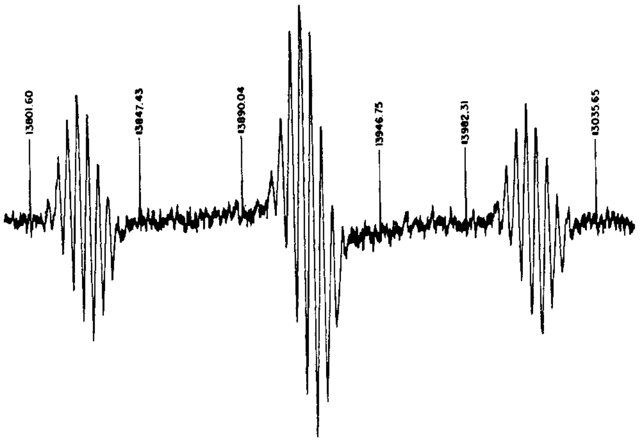

Figure 3. Esr spectrum of neopentyl radicals from the photolysis of *t*-butylacetyl peroxide at −58°.

formed secondarily, however, can be observed if the photolysis is carried out in a solvent more readily attacked by *t*-butoxy radical. For example, the esr spectrum obtained during photolysis of a solution of *t*-butyl peracetate in cyclopentane is a composite of methyl and cyclopentyl radicals. The photolyses of *t*-butylperoxy *n*-butyrate and isobutyrate under analogous conditions yield well-resolved spectra of *n*-propyl and isopropyl radicals, respectively. The high quality of the spectra obtained under these conditions is illustrated in Figure 4 for the isopropyl radical (eq 5). The esr spectrum of methyl radicals from the frag-

$$(CH_3)_2CHCO_2OC(CH_3)_3 \xrightarrow{h\nu} (CH_3)_2CH\cdot + CO_2 + \cdot OC(CH_3)_3 \quad (5)$$

mentation of *t*-butoxy radicals was not observed in the latter cases. However, well-resolved esr spectra of ethyl and isopropyl radicals, in addition to methyl radicals, were obtained from the photolysis[9] of *t*-amyl and 2,3-dimethyl-2-butyl peracetates (eq 6), respectively.

$$CH_3CO_2OC(CH_3)_2CH(CH_3)_2 \xrightarrow{h\nu} CH_3\cdot + CO_2 + OC(CH_3)_2 + (CH_3)_2CH\cdot \quad (6)^1$$

The photolysis of diacyl peroxides, peresters, and related compounds[11] thus constitutes a convenient method of generating a *specific alkyl radical* in solution for esr study. It is particularly adapted to radicals which have more stable or more readily formed isomers, such as *n*-butyl (*sec*-butyl), 3-butenyl (α-methallyl), β-phenethyl (α-phenethyl), etc., in which alternative procedures dependent on hydrogen abstraction from the parent hydrocarbon are not applicable.[7]

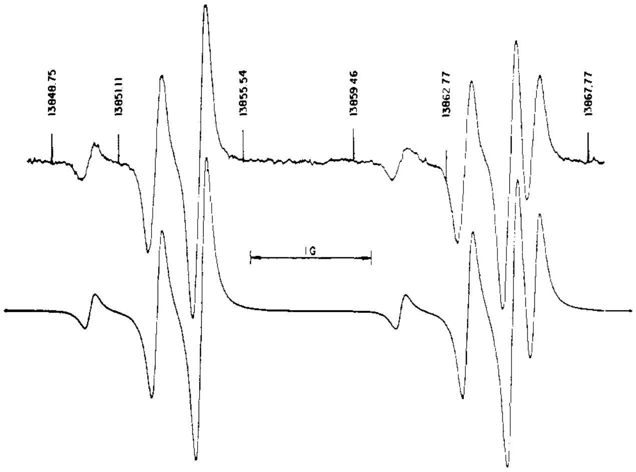

Figure 4. Experimental and calculated esr spectra of isopropyl radical: high-resolution sweep over the sixth and seventh "lines" of the spectrum showing the resolved second-order components.

Acknowledgments. We thank Mr. C. L. Jenkins for the preparation of heptenoyl and cyclopentylacetyl peroxides and Dr. R. A. Sheldon for *t*-amyl and 2,3-dimethyl-2-butyl peracetates and helpful discussions.

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[9] In the photolysis of these peresters, the esr spectrum of isopropyl radicals can be observed to much lower temperatures (−130°) than ethyl radicals (−60°). These observations are, no doubt, related to the ease of fragmentation of the corresponding alkoxy radicals[10] and are supported by product studies (R. A. Sheldon, unpublished results). Methyl radicals are probably formed in the primary photochemical process, and, as expected, the intensity of the methyl spectrum increases with decreasing temperatures.

(10) F. D. Greene, *et al.*, *J. Am. Chem. Soc.*, **81**, 2688 (1959); *J. Org. Chem.*, **28**, 55 (1963); C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1593 (1963); J. D. Bacha, and J. K. Kochi, *J. Org. Chem.*, **30**, 3272 (1965); *J. Am. Chem. Soc.*, **84**, 1193 (1962).

(11) Alkyl radicals can also be produced for esr study by the photolysis of azoalkanes. However, the quantum yields are significantly lower and the quality of the spectra is correspondingly poorer.

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Electron Spin Resonance Studies of Homolytic Substitution Reactions. Organoboron, -aluminum, and -gallium Compounds

Sir:

The high chemical reactivity of the organometallic derivatives of the group III elements is generally attributed to their electron deficiency caused by the vacant orbital on the metal.[1] The resultant Lewis acid character of these compounds constitutes their principal mode of reaction.[2] We wish to report an esr study on the *homolytic* reactions of these compounds in which the alkyl–metal bond is readily ruptured and the alkyl radicals are observed in solution.

When stationary solutions of trimethylboron react with photochemically generated *t*-butoxy radicals in the cavity of the spectrometer,[3] a high steady-state concentration of methyl radicals (a_H = 22.89 G, temperature −110°) is generated as evidenced by an intense esr spectrum of these species. No methyl radicals were observed in the absence of irradiation or when the irradiation was interrupted. Only a very weak spec-

$$(CH_3)_3B + \cdot OBu\text{-}t \longrightarrow (CH_3)_2BOBu\text{-}t + CH_3\cdot \quad (1)$$

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(1) G. E. Coates and K. Wade, "Organometallic Compounds," Vol. 1, Methuen and Co., Inc., New York, N. Y., 1967, p 177 ff.

(2) (a) J. J. Eisch, "The Chemistry of Organometallic Compounds," The MacMillan Co., New York, N. Y., 1967, p 18 ff; (b) R. Koster and P. Binger, *Advan. Inorg. Radiochem.*, 7, 263 (1965).

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