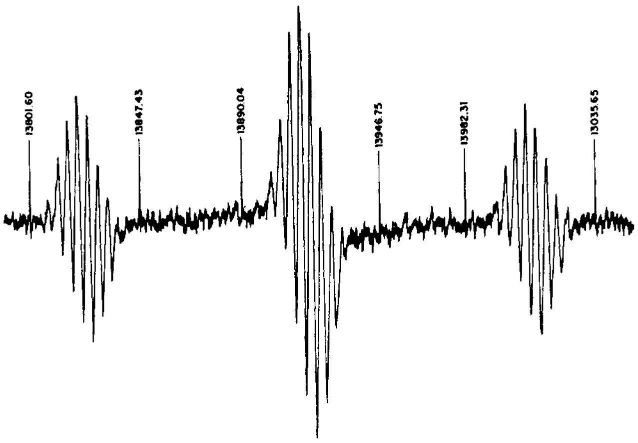

Figure 3. Esr spectrum of neopentyl radicals from the photolysis of *t*-butylacetyl peroxide at −58°.

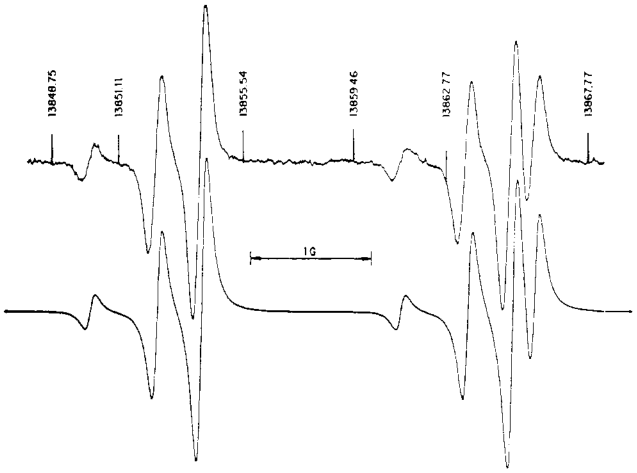

Figure 4. Experimental and calculated esr spectra of isopropyl radical: high-resolution sweep over the sixth and seventh "lines" of the spectrum showing the resolved second-order components.

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]

[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.

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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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).

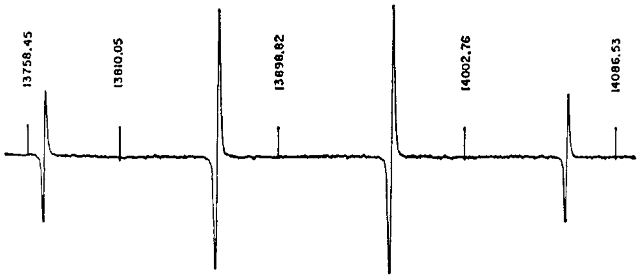

Figure 1. Esr spectrum of methyl radicals from trimethylboron and *t*-butoxy radicals at −138°. The proton nmr field markers are in kcps.

trum of the methyl radical was recorded when the di-*t*-butyl peroxide was omitted.[4]

The generation of methyl radicals in such high steady-state concentration in solution at these temperatures is a rather unusual phenomenon and indicates an extremely facile homolytic process. The esr spectrum of the methyl radical is reproduced in Figure 1. Furthermore, the high signal-to-noise ratio attainable under these conditions enabled us to record the ^{13}C species (a_C = 38.34 G, natural abundance *ca.* 1%) without deliberate isotopic enrichment.[5,6]

Similar intense esr spectra of ethyl (a_α = 22.37, a_β = 26.84 G, temperature −90°) and *n*-butyl radicals (a_α = 22.13, a_β = 29.09, a_γ = 0.73 G, temperature −101°) were also observed when triethylboron and tri-*n*-butylboron, respectively, were treated in the same manner.

The formation of alkyl radicals is not restricted to boron alkyls. Thus, triethylaluminum and tri-*n*-butylaluminum under these conditions also yield intense esr spectra of ethyl (Figure 2) and *n*-butyl radicals, respectively. The latter species has only recently been observed in solution.[7]

$$(CH_3CH_2CH_2CH_2)_3Al + \cdot OBu\text{-}t \longrightarrow (CH_3CH_2CH_2CH_2)_2AlOBu\text{-}t + CH_3CH_2CH_2CH_2\cdot \quad (2)$$

Diisobutylaluminum hydride, $[(CH_3)_2CHCH_2]AlH$, in analogous fashion, generated isobutyl radicals [a_α = 22.05, a_β = 35.15 G, a_γ (unresolved)]. As yet, we have been unable to detect the presence of any aluminum-centered radical such as I[8] which is expected to be derived from the aluminum hydride by hydrogen atom abstraction by *t*-butoxy radical (eq 3) in analogy with other studies.[3]

$$[(CH_3)_2CHCH_2]_2AlH + \cdot OBu\text{-}t \longrightarrow \underset{\text{I}}{[(CH_3)_2CHCH_2]_2Al\cdot} + t\text{-BuOH} \quad (3)$$

Since triethylgallium also produced high yields of ethyl radicals, the homolytic cleavage of alkyl–metal bonds by *t*-butoxy radical is a general process for group III organometallic derivatives. Indeed, it extends to other organometallics judging from our observations with *n*-butyllithium and di-*n*-butylmercury. We suggest that the production of alkyl radicals occurs by direct substitution of the alkyl moiety by *t*-butoxy radical on the metal (eq 4).

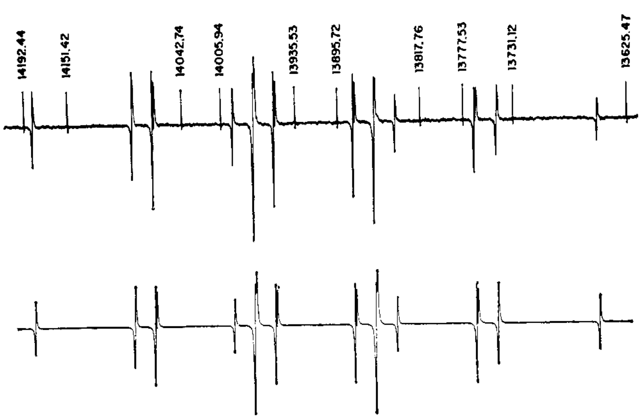

Figure 2. Experimental and calculated esr spectra of ethyl radicals from triethylaluminum and *t*-butoxy radicals at −114° with partially resolved second-order splittings.

$$R_3M + (CH_3)_3CO\cdot \longrightarrow R_2MOC(CH_3)_3 + R\cdot \quad (4)$$

It is conceivable that a substitution process such as (4) occurs by prior addition of *t*-butoxy radical to the organometallic species followed by ejection of an alkyl radical. However, if a four-coordinate organoboron or organoaluminum intermediate such as II or III were formed, it must have only a fleeting existence. Even at very low temperatures, we were unable to detect any paramagnetic species showing hyperfine structure by ^{11}B or ^{27}Al.

$$\underset{\text{II}}{R_3\bar{B}OBu\text{-}t} \qquad \underset{\text{III}}{R_3\bar{Al}OBu\text{-}t}$$

An SH2 displacement reaction[9] involving alkyl radicals has also been suggested during exchange between methyl radical and triethylboron[10] and dimethylmercury.[11] In a more direct example, the vigorous autoxidation of alkyl derivatives of group III elements[12] can be rationalized according to a radical chain process[13,14] in which the propagation steps 5 and 6 appear pertinent. Step 5, which is analogous to eq

$$RO_2\cdot + R_3M \longrightarrow RO_2MR_2 + R\cdot \quad (5)$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \text{ etc.} \quad (6)$$

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[4] Methyl radicals formed under these conditions were probably due to adventitious peroxides.

[5] T. Cole, H. O. Pritchard, N. R. Davidson, and H. McConnell, *Mol. Phys.*, **1**, 406 (1958).

[6] R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967).

[7] J. K. Kochi and P. J. Krusic, *J. Am. Chem. Soc.*, **91**, 3940 (1969).

[8] (a) Chemical studies suggest such species: R. Köster, G. Benedikt, and H. W. Schrotter, *Angew. Chem. Intern. Ed. Engl.*, **3**, 514 (1964); A. V. Grosse and J. M. Mavitz, *J. Org. Chem.*, **5**, 106 (1940); E. B. Milovskaya, E. I. Pokrovskii, and E. F. Fedorova, *Bull. Acad. Sci. USSR*, 1053 (1967). (b) An esr study of an unusual aluminum-centered radical has been reported by E. Müller, P. Ziemek, and A. Ricker, *Tetrahedron Letters*, 207 (1964).

[9] W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 9.

[10] J. Grotewohl and E. A. Lissi, *Chem. Commun.*, **21**, (1965); *J. Chem. Soc., B*, 264 (1968).

[11] R. E. Rebbert and P. Ausloos, *J. Am. Chem. Soc.*, **85**, 3086 (1963); (b) *cf.* also F. R. Jensen and H. E. Guard, *ibid.*, **90**, 3250 (1968).

[12] A. G. Davies, "Organic Peroxides," Butterworth & Co. (Publishers), Ltd., London, 1961, p 120 ff; S. B. Mirviss, *J. Am. Chem. Soc.*, **83**, 3051 (1961); R. L. Hansen and R. R. Hamann, *J. Phys. Chem.*, **67**, 2868 (1963); L. Partis and J. T. Miller, *Inorg. Chem.*, **3**, 1483 (1964); A. G. Davies and B. P. Roberts, *Chem. Commun.*, 298 (1966).

[13] (a) C. H. Bamford, and D. M. Newitt, *J. Chem. Soc.*, 688, 695 (1946); (b) J. E. Colman, Ph.D. Dissertation, Ohio State University 1959; (c) A. G. Davies, and B. P. Roberts, *J. Chem. Soc.*, *B*, 1074 (1968); (d) P. G. Allies and P. B. Brindley, *Chem. Ind.* (London), 319 (1967); (e) C. Walling, Advances in Chemistry Series, No. 75, American Chemical Society, Washington, D. C., 1968, p 166.

[14] The large preferential cleavage of the *t*-butyl moiety relative to isobutyl during autoxidation of *t*-butyldiisobutylboron is also consistent with a homolytic mechanism [A. G. Davies, D. G. Hare, and R. F. M. White, *J. Chem. Soc.*, 341 (1961)].

Table I. Hyperfine Coupling Constants of Radicals Derived from Trialkoxyboranes[a]

Trialkoxyborane	Radical	Temp, °C	Coupling constants, G a_α	a_B	a_β	a_γ
Trimethoxy	$(CH_3O)_2BOCH_2$	−34	20.14	0.35		
Triethoxy	$(C_2H_5O)_2BO\dot{C}HCH_3$	−54	18.55	0.66	23.52	
Tri-*n*-propoxy	$(C_3H_7O)_2BO\dot{C}HCH_2CH_3$	−48	18.5	0.4	23.4	0.4
Triisopropoxy	$(C_3H_7O)_2BO\dot{C}(CH_3)_2$[b]	−55		*c*	19.5	

[a] From photolysis of solutions containing 10% (v/v) di-*t*-butyl peroxide at 2500–3500 A. [b] In addition to a second paramagnetic species with hfs $a_H = 20.70$ G (quintet or septet) and $a_B = 5.45$ G. [c] Not determined due to complications from second-order effects.

4, differs from the molecular mechanism postulated earlier for the autoxidation of these compounds.[15,16]

The behavior of *trialkoxy*boranes toward *t*-butoxy radicals is entirely different from the *trialkyl*boranes discussed above. Thus, the esr spectrum obtained from the reaction of triethoxyboron and *t*-butoxy radical is shown in Figure 3, and there is no evidence for the formation of ethyl radicals. The radical species is identified as the radical IV, which is formed from triethoxyboron by abstraction of one of the methylene hydrogens by *t*-butoxy radical (eq 7). In addition to the doublet and quartet splittings due to the α and β protons, the esr spectrum shows a further quartet splitting due to the ^{11}B nucleus. The ^{11}B coupling constant shows a pronounced temperature variation of approximately 0.01 G/degree between −20 and −100°.

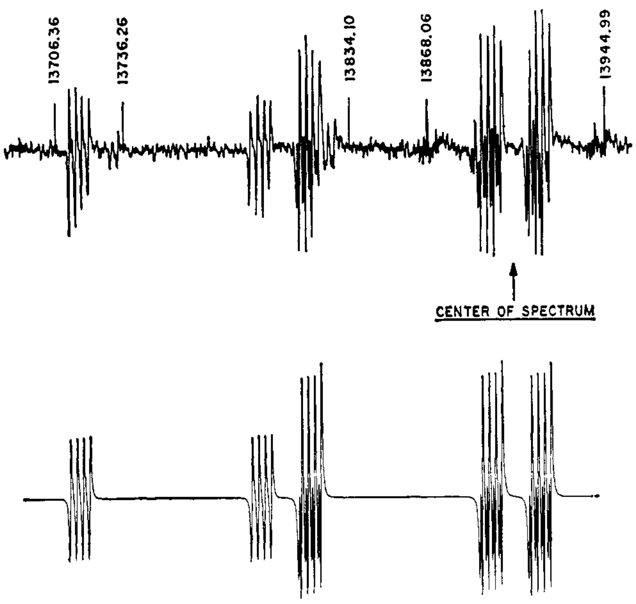

Figure 3. Experimental and calculated esr spectra of $(CH_3CH_2O)_2BO\dot{C}HCH_3$ from triethoxyboron at −54°. Part of the fine structure is due to second-order effects.

$$(CH_3CH_2O)_2BOCH_2CH_3 + \cdot OBu\text{-}t \longrightarrow (CH_3CH_2O)_2BO\underset{\text{IV}}{\dot{C}HCH_3} + t\text{-}BuOH \quad (7)$$

A variety of trialkoxyboranes (listed in Table I) also react with *t*-butoxy radicals to generate analogous species by abstraction of the protons α to the ethereal oxygen. The pertinent hyperfine coupling constants for these radicals are also included in Table I.

The abstraction of a hydrogen from trialkoxyboranes (eq 7) rather than a displacement (eq 4) can be, in part, attributed to the activating effect of a neighboring oxygen atom. Similar processes have been observed by esr in reactions of alcohols and ethers with hydroxy and *t*-butoxy radicals.[17]

Acknowledgment. We thank Mr. K. Eaby for technical assistance.

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(15) A. G. Davies, *Progr. Boron Chem.*, **1,** 276 (1964).

(16) (a) The autoxidation of organometallic derivatives of group I and II could also proceed *via* mechanism 3–4. However, these compounds are generally more ionic, and oxidation may occur *via* the carbanion [*cf.* G. A. Russell and A. Bemis, *J. Am. Chem. Soc.*, **88,** 5491 (1966)]. (b) For autoxidation of Grignard reagents, see R. C. Lamb, P. W. Ayers, M. K. Toney, and J. F. Garst, *ibid.*, **88,** 4262 (1966).

(17) (a) W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 3119 (1963); (b) R. Livingston and H. Zeldes, *J. Chem. Phys.*, **44,** 1245 (1966); **45,** 1946 (1966); *J. Am. Chem. Soc.*, **88,** 4333 (1966); (c) J. Q. Adams, *ibid.*, **90,** 5363 (1968); (d) P. J. Krusic, to be published.

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The Displacement of Alkyl Groups from Organophosphorus Compounds Studied by Electron Spin Resonance

Sir:

Organophosphorus compounds are involved in a variety of free-radical reactions.[1] Autoxidation generally exhibits radical chain character and as a class of reactions is particularly interesting because of its complexity.[2] Mechanisms involving alkyl, alkylperoxy, and alkoxy radicals as the principal reactive intermediates have been proposed. Alkoxy radicals have been postulated to react with alkylphosphines by either displacement (eq 1) or oxygen-atom transfer (eq 2).[1] Heretofore, no direct evidence has been brought forth to establish any of these homolytic processes.

$$R_3P + \cdot OR' \longrightarrow R_2POR' + R\cdot \quad (1)$$

$$R_3P + \cdot OR' \longrightarrow R_3PO + R'\cdot \quad (2)$$

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(1) (a) C. Walling and M. S. Pearson, *Topics Phosphorus Chem.*, **3,** 1 (1966); (b) J. I. G. Cadogan, *Advan. Free Radical Chem.*, **2,** 203 (1967); (c) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier Publishing Co., Amsterdam, 1967, p 158 ff; (d) J. I. G. Cadogan, *Quart. Rev.* (London), **16,** 208 (1962); (e) J. H. Boyer and J. D. Woodyard, *J. Org. Chem.*, **33,** 3329 (1968).

(2) (a) S. A. Buckler, *J. Am. Chem. Soc.*, **84,** 3093 (1962); (b) M. B. Floyd and C. E. Boozer, *ibid.*, **85,** 984 (1963); (c) F. R. Mayo, L. J. Durham, and K. S. Griggs, *ibid.*, **85,** 3156 (1963).