dihydrobatrachotoxin, R_f 0.55 in chloroform–methanol (7:1) on silica gel. Dihydrobatrachotoxin on treatment with dilute hydrochloric acid at room temperature easily changed to an equilibrium mixture containing a new isomer, R_f 0.39. The mass spectrum of isodihydrobatrachotoxin showed peaks at *m/e* 401, 314, 312, 296, 278, 263, 245, 235, 184, 139, 94, and 71. The mass spectra of dihydrobatrachotoxin showed peaks at 401, 386, 353, 341, 288, 285, 239, 95, and 71.

Borohydride Reduction of Homobatrachotoxin and Batrachotoxinin A. Analogously homobatrachotoxin and batrachotoxinin A were reduced to the corresponding dihydro derivatives. The R_f values of these products were as follows: homobatrachotoxin, 0.52; dihydrohomobatrachotoxin, 0.57; isodihydrohomobatrachotoxin, 0.45; batrachotoxinin A, 0.40; dihydrobatrachotoxinin A, 0.51; isodihydrobatrachotoxinin A, 0.26.

Hydrolysis of Batrachotoxin to Batrachotoxinin A. A solution of 0.5 mg of batrachotoxin was dissolved in 0.5 ml of 4.0 *N* aqueous methanolic (1:1) potassium hydroxide and heated to 60° in a sealed tube under a nitrogen atmosphere for 16 hr. Methanol was removed by a stream of nitrogen. The residue was extracted into chloroform. The chloroform solution was extracted with dilute hydrochloric acid. The acid solution was made alkaline by the addition of ammonia solution and extracted with chloroform.

The presence of batrachotoxinin A was confirmed by tlc (silica gel) in chloroform–methanol (7:1).

Anhydride II of 2,4,5-Trimethylpyrrole-3-carboxylic Acid and Ethyl Chloroformate. 2,4,5-Trimethylpyrrole-3-carboxylic acid (910 mg, 6×10^{-3} mol) and 0.60 g (6×10^{-3} mol) of triethylamine were dissolved in 10 ml of dry tetrahydrofuran. When the reaction mixture was kept below 0° a solution of 0.65 g (6×10^{-3} mol) of ethyl chloroformate in 3 ml of tetrahydrofuran was added dropwise and the reaction mixture was allowed to stand for 5 hr. After evaporation of the solvent *in vacuo*, the residue was extracted into benzene and washed with dilute hydrochloric acid and sodium bicarbonate. The solvent was removed by distillation and the residue was recrystallized from benzene–cyclohexane to give 1.15 g of the anhydride, mp 93°; ir spectrum in chloroform solution, ν (cm^{-1}) 1795, 1724 (CO); nmr spectrum (δ, $CDCl_3$, TMS), 2-CH_3, 2.44; 4-CH_3, 2.12; 5-CH_3, 2.10; ethoxyl group, 2.51 and 1.13.

Anal. Calcd for $C_{12}H_{15}NO_5$: C, 58.66; H, 6.71; N, 6.22. Found: C, 58.85; H, 6.46; N, 6.14.

The following acid anhydrides were prepared by the method described above: mixed anhydride of ethyl chlorocarbonate with (mp) 2,4-dimethylpyrrole-3-carboxylic acid (88–90°), 2,5-dimethylpyrrole-3-carboxylic acid (75–76.5°), 1,2,4,5-tetramethylpyrrole-3-carboxylic acid (oil), 2,4-dimethyl-5-ethylpyrrole-3-carboxylic acid (58°), and 2,4-dimethyl-5-acetylpyrrole-3-carboxylic acid (96–97°).

Acylations of Batrachotoxinin A. About 0.8 mg of batrachotoxinin A was used for each acylation experiment. Eight milligrams of the anhydride of the respective pyrrole-3-carboxylic acid (see footnotes to Tables III and IV) and ethyl chloroformate was added to a chloroform solution (1 ml) of batrachotoxinin A and, after the addition of 1 ml of 0.2 *N* sodium hydroxide solution, the mixture was stirred vigorously for 4 hr at room temperature. The chloroform layer was separated and washed with 0.3 *N* hydrochloric acid. The acid solution was made basic with ammonia and the reaction product was extracted into chloroform. The reaction products were purified by chromatography on a column (height 13 cm) containing 1.5 g of silica gel and eluted by a mixture of chloroform and methanol, 9:1. Fractions were collected after every 0.6 ml (60 drops). Batrachotoxinin A 20α esters (0.1–0.3 mg, 35%) appeared generally in fractions 11–13, while recovered batrachotoxinin A (~55%) showed up in fractions 16–23. The batrachotoxinin A 20α esters were identified by mass spectrometry.

With the anhydrides of 2,4,5-trimethyl-, 1,2,4,5-tetramethyl-, and 2,4-dimethyl-5-ethylpyrrole-3-carboxylic acids the yields in the esterification of batrachotoxinin A were quantitative. Esterification with the acid chloride of pyrrole-2-carboxylic acid gave about a 30% yield. The preparation of acid chlorides of 2,4- and 2,5-dimethylpyrrolecarboxylic acids, from a benzene solution of the acids with thionyl chloride, phosphorus oxychloride, and oxalyl chloride in the presence of triethylamine, failed. The symmetric anhydride of 2,5-dimethylpyrrole-3-carboxylic acid was prepared from the anhydride with ethyl chloroformate and excess free acid by heating in dioxane overnight with triethylamine present. The oily symmetric anhydride [ν (cm^{-1}) 3472 (NH), 1751, 1718 (CO); nmr (δ, $CDCl_3$), 2.13, 2.44, no signals for OCH_2CH_3] failed to esterify batrachotoxinin A in chloroform solution under Schotten–Baumann conditions.

Synthesis of Batrachotoxin. Eighteen milligrams of batrachotoxinin A and 170 mg of anhydride II (8.2 molar excess) were dissolved in 3 ml of chloroform and stirred vigorously with 3.0 ml of 0.2 *N* potassium hydroxide solution for 5 hr at room temperature. The chloroform layer was separated and extracted with 0.3 *N* hydrochloric acid. The aqueous phase was made basic with ammonia and was extracted with chloroform. The chloroform was removed *in vacuo* and the 16 mg of basic products was purified over a column containing 14 g of silica gel (height 18 cm). The eluting solvent consisted of a mixture of chloroform and methanol, 9:1. Each fraction consisted of 1.1 ml. Synthetic batrachotoxin (5 mg) appeared in fractions 21–24 and unreacted batrachotoxinin A (8 mg) was isolated after fraction 50. The synthetic batrachotoxin was identified by tlc, mass spectrometry, and nmr in deuteriochloroform and deuteriobenzene and by its unique toxicity, LD_{50} 2 μg/kg in mice.

Communications to the Editor

Electron Spin Resonance of Organosilyl Radicals in Solution

Sir:

Organosilicon chemistry encompasses a wide range of reactions and mechanisms.[1] Silicon-centered free radicals play important roles in a number of these processes,[2] particularly those involving the hydrosilation of unsaturated systems.[3] Except for silyl radicals[4] (which have only been observed in an argon or krypton matrix at 4.2°K), no direct evidence is available for these

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(1) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., New York, N. Y., 1965.

(2) C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London, 1960, pp 45 ff, 116; V. Bazant, J. Joklik, and J. Rathousky, *Angew. Chem.*, 80, 133 (1968); J. J. Zuckermann, *Advan. Inorg. Chem. Radiochem.*, 6, 383 (1964); D. Seyferth and R. B. King, *Ann. Survey Organometal. Chem.*, **2**, 110 (1966); J. Curtice, H. Gilman, and G. S. Hammond, *J. Am. Chem. Soc.*, **79**, 4754 (1957); H. Sakurai, A. Hosomi, and M. Kumada, *Bull. Chem. Soc. Japan*, 40, 1551(1967); L. E. Nelson, N. C. Agelotti, and D. R. Weyenberg, *J. Am. Chem. Soc.*, **85**, 2663 (1963); C. Eaborn, R. A. Jackson, and R. W. Walsingham, *Chem. Commun.*, 300 (1965); 920 (1967), *J. Organometal. Chem.*, **5**, 297 (1966); M. A. Nay, G. N. C. Woodall, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **87**, 179 (1965); N. J. Friswell and B. G. Gowenlock, *Advan. Free Radical Chem.*, **2**, 43 (1967); Y. Nagai, K. Yamazaki, *et al.*, *J. Chem. Soc., Japan, Pure Chem. Sect.*, **88**, 79 (1967); H. Sakurai, M. Murakami, and K. Kumada, *J. Am. Chem. Soc.*, **91**, 520 (1969).

(3) E. Y. Lukevits and M. G. Voronkov, "Organic Insertion Reactions of Group IV Elements," Consultants Bureau, New York, N. Y., 1966; T. G. Selin and R. West, *J. Am. Chem. Soc.*, **84**, 1860 (1962).

(4) (a) F. J. Adrian, E. L. Cochran, and V. A. Bowers, "Free Radicals in Inorganic Chemistry," Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962 p 50 ff; (b) R. L. Morehouse, J. J. Christiansen, and W. Gordy, *J. Chem. Phys.*, **45**, 1751 (1966); (c) the esr of stable radical ions containing Si has been reviewed recently: G. Urry, "Radical Ions," T. T. Kaiser and L. Kevans, Ed., Interscience Publishers, Inc., New York, N. Y., 1968, p 275 ff; (d) A. G. Brook and J. H. Duff, *J. Am. Chem. Soc.*, **91**, 2119 (1969); (e) H. Sakurai, M. Murakami, and K. Kumada, *ibid.*, **91**, 519 (1969).

Table I. Hyperfine Coupling Constants of Organosilyl Radicals

Silyl radical	Coupling constants, G			Temp, °C	Alkyl radical	Coupling Constants,[a] G		
	a_{SiH}	a_{CH_3}	$a_{^{29}\text{Si}}$			a_α	a_β	$a_{^{13}\text{C}}$
$\dot{\text{Si}}\text{H}_3$[b]	7.96[c]		266[d]	−153	$\dot{\text{C}}\text{H}_3$	23.04		38.34
$\text{CH}_3\dot{\text{Si}}\text{H}_2$	11.82	7.98		−121	$\text{CH}_3\dot{\text{C}}\text{H}_2$	22.38	26.87	39.07
$(\text{CH}_3)_2\dot{\text{Si}}\text{H}$	16.99	7.19	183.05	−123	$(\text{CH}_3)_2\dot{\text{C}}\text{H}$	22.11	24.68	
$(\text{CH}_3)_3\dot{\text{Si}}$		6.28	181.14	−120	$(\text{CH}_3)_3\dot{\text{C}}$		22.72	

[a] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); *J. Phys. Chem.*, **71**, 74 (1967). [b] Solution was *ca.* 30% by volume in ethane. [c] From ref 4b, $a_{\text{SiH}} = 8.1$ G. From ref 4a, $a_{\text{SiH}} = 7.2$ G (estimated). [d] Reference 4b.

species.[5] In this report we wish to present an electron spin resonance study of a series of transient silicon-centered free radicals in solution.

Figure 1. Esr spectrum of dimethylsilyl radical at −123°. The proton nmr field markers are in kcps.

The organosilyl radicals I were generated by abstraction of hydrogen from organosilanes with photochemically generated *t*-butoxy radicals.[6]

$$\text{R}_3\text{SiH} + (\text{CH}_3)_3\text{CO}\cdot \longrightarrow \underset{\text{I}}{\text{R}_3\text{Si}\cdot} + (\text{CH}_3)_3\text{COH} \qquad (1)$$

$$\text{R} = \text{CH}_3, \text{H}$$

The hyperfine coupling constants for a series of organosilyl radicals produced from silane, methylsilane, dimethylsilane, and trimethylsilane are given in Table I. Values of the known coupling constants for the carbon analogs are also given for comparison.

The esr spectra of the organosilyl radicals obtained under these conditions were well resolved, permitting positive assignment of the radical species. A typical spectrum is shown in Figure 1 for the dimethylsilyl radical obtained by reaction between dimethylsilane and *t*-butoxy radical. The attainable high signal-to-noise ratio allowed the observation of the ^{29}Si species without isotopic enrichment of the sample (^{29}Si natural abundance = 4.7%) as shown in Figure 2 for the trimethylsilyl radical. The technique is also applicable to other silicon hydrides. Thus, photolysis of di-*t*-butyl peroxide in triethylsilane yields a well-resolved spectrum of triethylsilyl radical ($a_{\text{CH}_2} = 5.69$ G, $a_{\text{CH}_3} = 0.16$ G at −90°).

The large values obtained for the ^{29}Si isotropic hyperfine constants in the methylsilyl radicals (Table I) imply considerable 3s character for the orbital occupied by the unpaired electron and hence a pyramidal structure for these radicals.[4b] With about 22% 3s character, $\cdot\text{SiH}_3$ has nearly maintained the tetrahedral geometry of the parent silane. This bent structure decreases, however, with increasing methyl substitution as indicated by the trend in the ^{29}Si coupling constants. The magnitudes and the trend displayed by the hyperfine constants of the α protons are also quite unusual and no doubt related to the varying geometry of the radicals in this series. Fessenden and Schuler[7] have adduced evidence which suggests that the α proton hyperfine constant in alkyl radicals should become more positive as the radical becomes more bent. Recent molecular orbital calculations[8] have confirmed their view. The trend displayed by the α protons in the methylsilyl series should be interpreted similarly. We suggest that the α proton coupling constants for $(\text{CH}_3)_2\dot{\text{Si}}\text{H}$ and $\text{CH}_3\dot{\text{Si}}\text{H}_2$ are negative, as is known to be the case for the carbon analogs which are planar or nearly so, but may be positive for the most bent $\cdot\text{SiH}_3$ radical.[9] Molecular orbital calculations bearing on this point are in progress. The recently reported high retention of configuration of silyl radicals[4d,e] is also consistent with a sizable barrier to inversion for these pyramidal radicals compared to the carbon analogs.

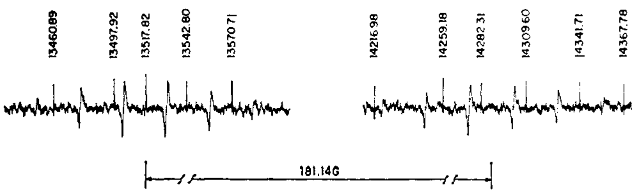

Figure 2. Esr spectrum of the ^{29}Si species of the trimethylsilyl radical in natural abundance at −120°. Only six of the ten lines can be detected for each multiplet.

Interestingly, the silicon-centered radical was the only species observed when mono-, di-, and trimethylsilanes were subjected to *t*-butoxy radicals. The esr spectra of the radical species generated by hydrogen abstraction from the methyl groups were never in evidence. However, when tetramethylsilane, which has no silicon–hydrogen bond, was examined under analogous conditions, a strong spectrum of trimethylsilylmethyl radical (II) was observed.[10] This high selec-

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(5) J. Roncin has reported the esr spectrum of $\cdot\text{CH}_2\text{Si}(\text{CH}_3)_3$ obtained by γ irradiation of $(\text{CH}_3)_4\text{Si}$ at 77°K (*Mol. Cryst.*, **3**, 117 (1967)). He incorrectly attributes some minor features of the spectrum to $\text{Si}(\text{CH}_3)_3$ with $a_{\text{H}} = 21.7$ G (*vide infra*).

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

(7) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965); R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967).

(8) D. L. Beveridge, P. A. Dobosh, and J. A. Pople, *J. Chem. Phys.*, **48**, 4802 (1968); K. Morokuma, L. Pedersen, and M. Karplus, *ibid.*, **48**, 4801 (1968).

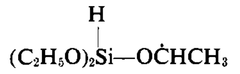
(9) Morehouse, Christiansen, and Gordy,[4b] who have also studied the esr of $\cdot\text{CH}_3$, $\cdot\text{GeH}_3$, and $\cdot\text{SnH}_3$ in a rigid argon matrix, proposed a negative spin density for SiH_3 to obtain a regular trend for the proton coupling constants in the group IV series. Urry[4c] questions the validity of their argument.

(10) P. J. Krusic and J. K. Kochi, to be published.

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



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

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 ($g_{(CH_3)_3C\cdot} - g_{(CH_3)_3Si\cdot} = -0.00024$).

(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)

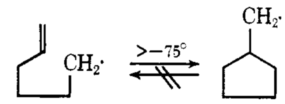
$$CH_3CH_2CH_2CH_2\cdot + RH \longrightarrow CH_3CH_2CH_2CH_3 + R\cdot \quad (2)$$

R = *t*-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



I II (3)

only II during photolysis of cyclopentylacetyl peroxide at temperatures even up to 0°.[5]

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).