The salts of $S_2PF_2^-$ readily oxidize with bromine to give the new compound $P_2S_4F_4$.[4] The $F^{19}$ and $P^{31}$ nmr spectra and the infrared data are consistent with the structure $F_2(S)PSSP(S)F_2$. This compound reacts with a variety of olefins; for example, it reacts with cyclohexene, to give $C_6H_{10}[SP(S)F_2]_2$,[5] a colorless liquid moderately stable to hydrolytic attack. Additionally, the cesium salt of $S_2PF_2^-$ reacts with a variety of organic halides to give compounds of the type $RSP(S)F_2$ where R is ethyl,[6] benzyl, or isopropyl.

Full details of this area of phosphorus–sulfur chemistry will be reported in a later paper.

**Acknowledgment.** We are indebted to Drs. M. T. Jones and D. R. Eaton for assistance in the esr interpretations.

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[4] *Anal.* Calcd for $P_2S_4F_4$: P, 23.3; S, 48.2; F, 28.5; mol wt, 266. Found: P, 23.5; S, 48.0; F, 28.3; mol wt (cryoscopic in benzene), 260; bp 58–60° (10 mm).

[5] *Anal.* Calcd for $C_6H_{10}S_4P_2F_4$: C, 20.7; H, 2.9; S, 36.8; P, 17.8; F, 21.8. Found: C, 20.9; H, 2.9; S, 37.3; P, 17.5; F, 22.0; bp 104° (0.5 mm).

[6] *Anal.* Calcd for $C_2H_5SPSF_2$: C, 14.8; H, 3.1; S, 39.5; P, 19.1; F, 23.4; mol wt, 162. Found: C, 15.3; H, 3.5; S, 39.1; P, 18.5; F, 23.0; mol wt (cryoscopic in benzene), 157; bp 124°.

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## $1\text{-}B_9H_9CH^-$ and $B_{11}H_{11}CH^-$

*Sir:*

The polyhedral boranes $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ are noted for their unusual stabilities and for the broad scope of their derivative chemistries.[1] The carborane $B_{10}C_2H_{12}$ which is isostructural and isoelectronic with $B_{12}H_{12}^{2-}$ has also received much attention because of its great thermal stability and extensive derivative chemistry.[2] The 1,6 and 1,10 isomers of $B_8H_8(CCH_3)_2$ which are isostructural and isoelectronic with $B_{10}H_{10}^{2-}$ have recently been reported.[3] The chemistry of $B_{10}C_2H_{12}$ differs from that of $B_{12}H_{12}^{2-}$, and the chemistry of $B_8C_2H_{10}$ can be expected to differ from that of $B_{10}H_{10}^{2-}$, both because of the charge differences and the localized effects of the carbon atoms.

**Table I.** Analyses

| Compound | Calculated, % B | C | H | N | H[a] | Found, % B | C | H | N | H[a] |
|---|---|---|---|---|---|---|---|---|---|---|
| $B_{10}H_{12}CNH_3$ | 72.5 | 8.0 | 10.1 | 9.4 | .... | 73.0 | 8.0 | 10.1 | 9.4 | .. |
| $(CH_3)_3NHB_{10}H_{12}CH$ | 56.0 | 24.9 | 11.9 | 7.2 | 2320 | 56.1 | 25.4 | 12.3 | 7.2 | 2358 |
| $B_9H_{11}CN(CH_3)_3$ | 54.2 | 26.8 | 11.3 | 7.8 | .. | 53.6 | 27.1 | 11.3 | 6.6 | .. |
| $(CH_3)_4NB_9H_9CH$ | 50.4 | 31.1 | 11.4 | 7.2 | 1970 | 50.7 | 31.4 | 11.9 | 7.2 | 2003 |
| $CsB_{11}H_{11}CH$ | 43.0 | 4.4 | 4.4 | ... | 1710 | 42.6 | 4.6 | 4.5 | ... | 1723 |
| $(CH_3)_4NB_{10}H_{10}CH$ | 52.7 | 29.2 | 11.2 | 6.8 | 2080 | 52.8 | 28.5 | 11.1 | 6.8 | 2090 |

[a] By evolution, ml/g.

This communication is concerned with the $1\text{-}B_9H_9CH^-$ and $B_{11}H_{11}CH^-$ anions. These species comprise the "missing links" in the $B_{10}H_{10}^{2-}$–$B_8C_2H_{10}$ and $B_{12}H_{12}^{2-}$–$B_{10}C_2H_{12}$ series, respectively. It is anticipated that these monobasic carboranes may exhibit some of the chemical properties of both their dibasic borane and neutral carborane analogs. This has already been demonstrated, in part, by the reactions of $1\text{-}B_9H_9CH^-$ and $B_{11}H_{11}CH^-$ with *n*-butyllithium to form $1\text{-}B_9H_9CLi^-$ and $B_{11}H_{11}CLi^-$, respectively. The reaction of $1\text{-}B_9H_9CLi^-$ with trimethylchlorosilane has given $1\text{-}B_9H_9CSi(CH_3)_3^-$. Analogous lithio derivatives have been prepared from $B_{10}C_2H_{12}$ and widely exploited.[2]

The preparations of $1\text{-}B_9H_9CH^-$ and $B_{11}H_{11}CH^-$ are outlined in the following equations.

$$Na_2B_{10}H_{13}CN^{4} \xrightarrow[\text{ion exchange}]{H^+} B_{10}H_{12}CNH_3 \xrightarrow[NaOH-H_2O]{(CH_3)_2SO_4} B_{10}H_{12}CN(CH_3)_3 \xrightarrow[\text{reflux}]{Na,\,THF} NaB_{10}H_{12}CH + NaB_{10}H_{10}CH \quad (1)$$

The sodium salt of $B_{10}H_{12}CH^-$ is much less soluble in tetrahydrofuran (THF) than is $NaB_{10}H_{10}CH$; separation is therefore readily accomplished.

$$2CsB_{10}H_{12}CH \xrightarrow{300\text{–}320^\circ} Cs\text{–}1\text{-}B_9H_9CH + CsB_{11}H_{11}CH + 2H_2 \quad (2)$$

Alternate syntheses include

$$CsB_{10}H_{12}CH \xrightarrow[180^\circ]{(C_2H_5)_3N\cdot BH_3} CsB_{11}H_{11}CH \quad (3)$$

$$NaB_{10}H_{12}CN\cdot S(CH_3)_2{}^{4} \xrightarrow[\text{ion exchange}]{H^+} B_{10}H_{11}(OH)CNH_3 \xrightarrow[NaOH]{(CH_3)_2SO_4} B_{10}H_{11}(OH)CN(CH_3)_3 \xrightarrow[H_2O,\ THF]{NaOH} B_9H_{11}CN(CH_3)_3 \xrightarrow[\text{reflux}]{Na,\ THF} \xrightarrow[H_2O]{(CH_3)_4N^+} H_2 + (CH_3)_4N\text{–}1\text{-}B_9H_9CH \quad (4)$$

If the acidification in eq 1 is accomplished with 12 *M* hydrochloric acid instead of by ion exchange, a mixture of $B_{10}H_{12}CNH_3$ and $B_9H_{11}CNH_3$ is obtained.

$$Na_2B_{10}H_{13}CN \xrightarrow[-H_2]{12\ M\ HCl} B_9H_{11}CNH_3 + B_{10}H_{12}CNH_3 \quad (5)$$

Analyses are given in Table I.

The postulate that $1\text{-}B_9H_9CH^-$ and $B_{11}H_{11}CH^-$ are isostructural with $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$, respectively, is supported by their $B^{11}$ nmr spectra. The spectrum of $Cs\text{-}1\text{-}B_9H_9CH$ in acetonitrile consists of three doublets of relative intensities 1:4:4 at −11.8 ($J$ = 152 cps), 37.4 ($J$ = 138 cps), and 43.8 ppm (J = 107 cps), respectively, referred to methyl borate. This is in accord with the spectrum expected for the $B_{10}H_{10}^{2-}$

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[1] W. H. Knoth, *J. Am. Chem. Soc.*, **88**, 935 (1966), and references therein.

[2] Carborane chemistry has recently been reviewed: T. P. Onak, *Advan. Organometal. Chem.*, **3**, 263 (1965).

[3] F. N. Tebbe, P. M. Garrett, D. C. Young, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **88**, 609 (1966).

[4] W. H. Knoth and E. L. Muetterties, *J. Inorg. Nucl. Chem.*, **20**, 66 (1961).

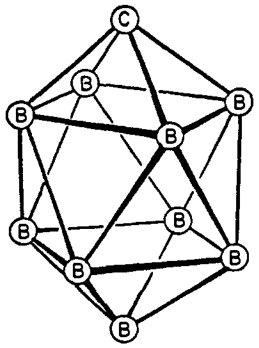

Figure 1. Skeletal Structure of 1-$B_9H_9CH$.

polyhedron with one apical boron atom replaced by a carbon atom (Figure 1). The $B^{11}$ spectrum of $CsB_{11}H_{11}CH$ in acetonitrile consists of three doublets which, though poorly resolved even at 32.1 Mc, appear to be of relative intensities 1:5:5 as required for an icosahedral monocarborane.

Todd and co-workers have recently reported the reaction of decaborane with isocyanides to form aminocarboranes of the general formula $B_{10}H_{12}CNH_2R$, and the N-alkylation of these compounds.[5] The melting point reported for $B_{10}H_{12}CN(CH_3)_3$ (344–345° dec) is close to that which we find (345–350°) for this compound as prepared in eq 1. The $B^{11}$ nmr spectrum at 32.1 Mc reported by Todd is compatible with one determined on our sample at 19.2 Mc. Additionally, and more conclusively, the benzylation of $B_{10}H_{12}CNH_3$ (from eq 1) gives $B_{10}H_{12}CNH_2CH_2C_6H_5$ which is identical by mixture melting point and infrared and powder X-ray analysis with $B_{10}H_{12}CNH_2CH_2C_6H_5$ as prepared from decaborane and benzyl isocyanide.[6] It is clear, therefore, that Todd's route and the mild acidification of $B_{10}H_{13}CN^{2-}$ lead to the same class of aminocarboranes. Boron[11] nmr analysis shows that the carborane skeleton is not affected by the deamination to $B_{10}H_{12}CH^-$. It appears probable from $B^{11}$ nmr spectroscopy that $B_{10}H_{11}(OH)CNH_3$ and its N-methylated derivative (eq 4) are also members of this structural class.

The aminocarboranes $B_9H_{11}CNH_3$ and $B_9H_{11}CN(CH_3)_3$ (eq 4 and 5) as well as $B_{10}H_{10}CH^-$ (eq 1) represent other new carborane series, which will be discussed in more detail in a subsequent paper. Boron[11] nmr analysis suggests a highly symmetrical structure for $B_{10}H_{10}CH^-$; this anion is isoelectronic with $B_9C_2H_{11}$.[7]

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(6) Acknowledgment for a sample of the decaborane–benzyl isocyanide product is made to Dr. W. R. Hertler, who independently discovered the decaborane–isocyanide reaction.

(7) (a) T. E. Berry, F. N. Tebbe, and M. F. Hawthorne, *Tetrahedron Letters*, **12**, 715 (1965); (b) C. Tsai and W. E. Streib, *J. Am. Chem. Soc.*, **88**, 4513 (1966).

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## Reactivity of Triplet States

*Sir:*

The relative reactivities of the n,π* triplet states of several ketones have been compared with that of *t*-butoxy radicals[1,2] in hydrogen abstraction reactions. We wish to report a comparison of the absolute reactivities of the triplet states of diethyl ketone and of benzophenone in hydrogen abstraction reactions under oxidative conditions. This comparison is made possible by the recent finding of Borkman and Kearns[3] that the triplet yield of acetone, like that of benzophenone,[4,5] is nearly unity.

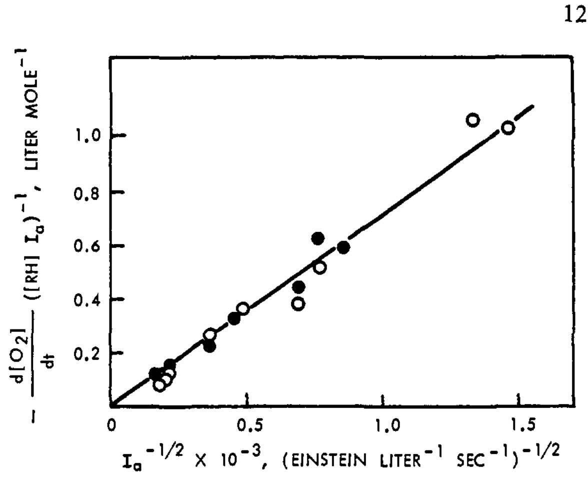

Figure 1. Photooxidations of cumene sensitized by benzophenone and by diethyl ketone, at 62.5° and 3130 A: ○, benzophenone; ●, diethyl ketone.

A solution of the ketone in 1:2 cumene–chlorobenzene was irradiated by either 3130- or 3650-A light under a constant oxygen pressure of 1 atm. The rate of oxidation was recorded automatically and the incident light intensity was measured before and after each irradiation. The purification of the compounds used, the optical system with associated filters, the oxygen absorption equipment, and the actinometry have been described elsewhere.[6] Over 95% of the light absorbed was absorbed by the ketone in all the experiments. Only the constant initial rates of oxidation, corresponding to less than 10% of the ketone reacted, were recorded. At very long irradiation times, the rates become faster or slower than the initial rate depending upon the amount of ketone initially present. The amount of unreacted benzophenone was determined spectrophotometrically; the amount of unreacted diethyl ketone was determined by gas chromatography. The results are summarized in Tables I and II.

Assuming quantitative intersystem crossing efficiencies for both diethyl ketone and benzophenone, using the usual mechanism for autoxidation,[6] we derive an expression for the initial rate of oxidation as

$$-\frac{d[O_2]}{dt} = \Phi^T I_a + \frac{k_p}{k_t^{1/2}}[RH](\Phi^T I_a)^{1/2} \qquad (1)$$

where $I_a$ is the absorbed light intensity, $\Phi^T$ is the quantum yield of initiation by the triplet state, $k_p$ and $k_t$ are the rate constants of propagation and termination, respectively, and [RH] is the cumene concentration. To calculate the values of $\Phi^T$, we plot $(-d[O_2]/dt)/[RH]I_a$ *vs.* $I_a^{-1/2}$ in Figure 1. The results

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