

part to an increased lifetime of the radical pair cage in the more viscous solvent, which increases the probability for the electron transfer process. Similarly the failure of most bromides to exhibit significant cationic behavior is perhaps due to a shorter lifetime of the radical pair cage. The increased cationic behavior exhibited by bridgehead bromides⁷ is then attributable to partial shielding by the cyclic structure, a sort of internal viscosity effect.

Interesting behavior has also been observed for 1-bromo- and 1-iodooctane. On irradiation in methanol the bromide affords only *n*-octane (83%) whereas the iodo analog gives rise predominantly to a mixture of 1- (56%), 2- (4%), and 3-octene (2%), along with some *n*-octane (38%). In ether solution the bromide similarly affords only *n*-octane (76%), whereas the iodide gives principally 1-octene (70%), accompanied by a mixture of 2- and 3-octene (9%) and some *n*-octane (18%). The predominance of elimination, accompanied by some prior rearrangement to internal positions, in preference to nucleophilic trapping by solvent is characteristic behavior for "free" cations formed *via* a high energy process with little or no solvent participation.⁸ By contrast treatment of the iodide with methanolic silver perchlorate affords exclusively methyl 1-octyl ether.

Further work is in progress to explore the synthetic potential, as well as mechanistic details, of the versatile photochemical behavior of alkyl halides.

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(7) 1-Bromo- and 1-iodoadamantane exhibit photochemical behavior closely analogous to that reported here for the 1-halonorbornanes; unpublished results.

(8) For a discussion of the concept of "free" ions, see J. T. Keating and P. S. Skell, *Carbonium Ions*, 2, 573 (1970).

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Potassium Bisboranemethylselenide(1-) and μ -Methylselenodiborane

Sir:

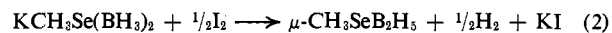
We wish to report the synthesis of a bisborane adduct of selenium and its conversion to the first example of a selenium substituted borane. A xylene slurry of KSeCH_3 at 25° reacts with a stoichiometric amount of diborane over a period of 3 hr in agreement with eq 1.



The colorless unsolvated solid product may be isolated by evaporation. *Anal.* Calcd (mmol/g): $\text{B}(\text{OH})_3$, 12.5; H_2 (hydrolytic), 37.4. Found: $\text{B}(\text{OH})_3$, 12.0; H_2 (hydrolytic), 35.0. The $\text{KCH}_3\text{Se}(\text{BH}_3)_2$ is readily soluble in tetrahydrofuran and is thermally stable at room temperature for a few hours. Boron-11 nmr shows a

quartet, 22.8 ppm (relative to $(\text{C}_2\text{H}_5)_2\text{OBF}_3$), $J_{\text{BH}} = 100$ Hz; infrared shows BH stretching at 2390, 2325, and 2290 cm^{-1} .

Treatment of a cumene slurry of $\text{KCH}_3\text{Se}(\text{BH}_3)_2$ with 0.5 mol of iodine at 25° produces $\mu\text{-CH}_3\text{SeB}_2\text{H}_5$ in ca. 10% yield according to eq 2. The liquid product



slowly passes a trap at -45° and stops at -78°. The bridge substituted structure is confirmed by boron-11 nmr which shows a triplet of doublets at 19.0 ppm with $J_{\text{BH}} = 140$ Hz and $J_{\text{BHB}} = 38$ Hz. Proton nmr shows SeCH_3 singlet τ 8.91, ^{11}BH 1:1:1:1 quartet τ 7.94, $J_{\text{BH}} = 140$ Hz, and bridge $^{11}\text{BH}^{11}\text{B}$ τ 11.33. The gas phase infrared spectrum shows terminal BH stretching bands at 2570 and 2485 cm^{-1} and bridge BHB stretching absorptions at 1820 and 1735 cm^{-1} . The mass spectrum is complex owing to the presence of six selenium isotopes in addition to boron-10 and -11, but the expected high mass peak at m/e 124 corresponding to $^{11}\text{B}_2^{12}\text{C}^{1}\text{H}_3^{82}\text{Se}^+$ is readily observable; the general envelope of peaks is consistent with the proposed structure. *Anal.* Calcd (mmol/g): $\text{B}(\text{OH})_3$, 16.6; H_2 (hydrolytic), 41.5; CH_3SeH , 8.30. Found: $\text{B}(\text{OH})_3$, 17.4; H_2 (hydrolytic), 42.3; CH_3SeH , 7.65. The thermal stability of $\mu\text{-CH}_3\text{SeB}_2\text{H}_5$ is poor; typically a sample decomposes within 10 min at 25° according to eq 3. In toluene reaction 3 is easily reversible at



25° so that under these conditions $\mu\text{-CH}_3\text{SeB}_2\text{H}_5$ is stable indefinitely in the presence of excess diborane, indicating that $(\text{CH}_3\text{SeBH}_2)_n$ is considerably more labile than its sulfur analog $(\text{CH}_3\text{SBH}_2)_n$.¹

The $\mu\text{-CH}_3\text{SeB}_2\text{H}_5$ molecule should possess considerable structural strain owing to the large selenium atom. Assuming a B-Se distance of 2.02 Å (sum of covalent radii²) and a B...B distance of 1.92 Å (from $\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5$)³ gives a highly acute B-Se-B angle of 57°. Relieving this strain by opening the angle should alternatively result in an unusually stretched B-H-B bridge.

We are currently investigating the chemistry of $\mu\text{-CH}_3\text{SeB}_2\text{H}_5$ and related compounds more fully and will report our findings in greater detail at a later date.

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