

## Photochemistry of Alkyl Halides. II. Support for an Electron Transfer Process<sup>1</sup>

Sir:

It was recently reported from these laboratories that alkyl halides exhibit competing radical and ionic photo-behavior, with bromides affording almost exclusively radical products and the analogous iodides giving predominantly ionic products.<sup>1</sup> We wish now to record additional observations which (a) correlate these two modes of behavior, (b) reveal that certain alkyl bromides exhibit a substantial degree of ionic behavior, and (c) provide additional insight into the mechanisms by which ionic intermediates arise.

As shown in Table I (and Scheme I), irradiation of

**Table I.** Irradiation of 1-Bromo and 1-Iodonorbornane (1)<sup>a</sup>

Halide 1	Solvent	Time, hr	Yield, % <sup>b</sup>			
			1	3	6	8
X = Br	CH <sub>3</sub> OH <sup>c</sup>	8	3	30		55
	CH <sub>3</sub> OH <sup>c,d</sup>	8	10	19	40	30
	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> O <sup>c</sup>	24	66	7		17
	(CH <sub>3</sub> OH) <sub>2</sub> <sup>c,e</sup>	16	f	92		6
X = I	CH <sub>3</sub> OH <sup>c</sup>	2	3	72		15
	CH <sub>3</sub> OH <sup>g</sup>	2	4	76		12
	CH <sub>3</sub> OH <sup>d,g</sup>	2	11	41	47	f
	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> O <sup>g</sup>	4	18	63		19
	(CH <sub>2</sub> OH) <sub>2</sub> <sup>e,g</sup>	8	f	99		f

<sup>a</sup> Irradiations were conducted in a quartz vessel using 5-ml solutions containing 100 mg of halide. <sup>b</sup> Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. <sup>c</sup> The broad emission of a 450-W medium-pressure mercury arc was employed. <sup>d</sup> Solution saturated with oxygen; reductive work up using sodium borohydride. <sup>e</sup> Conducted using 10 ml of solution containing 100 mg of halide. <sup>f</sup> Trace. <sup>g</sup> Conducted at 254 nm.

1-iodonorbornane (**1b**)<sup>2</sup> in methanol or ether under an atmosphere of nitrogen affords predominantly the nucleophilic substitution product **3**, accompanied by a small amount of the reduction product norbornane (**8**). The corresponding bromide **1a**<sup>3</sup> has been found to exhibit similar behavior except that the reduction product norbornane (**8**) is formed predominantly. The discrepancy in behavior between iodides and bromides thus apparently involves differences in the relative rates of competing radical and ionic pathways rather than some more fundamental dichotomy involving mutually exclusive pathways.

The formation of ethers **3a** and **b** most likely involves nucleophilic trapping of the 1-norbornyl cation.<sup>4</sup> The formation of reduction products, such as norbornane (**8**), from alkyl halides was thought originally to involve only a radical intermediate.<sup>1</sup> However, a second, competing route for the reduction process has been uncovered by the finding that irradiation of **1a** or **b** in methanol-*O-d* resulted in the formation of norbornane (**8**) with substantial, but not complete, incorporation of deuterium

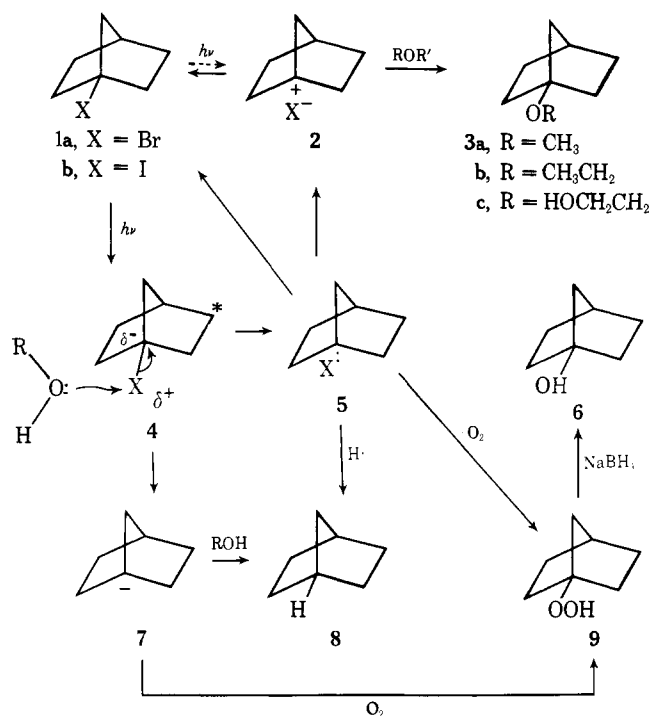
(1) For part I see P. J. Kropp, T. H. Jones, and G. S. Poindexter, *J. Amer. Chem. Soc.*, **95**, 5420 (1973).

(2) P. T. Lansbury, V. A. Pattison, J. D. Sidler, and J. B. Bieber, *J. Amer. Chem. Soc.*, **88**, 78 (1966).

(3) E. J. Kupchik and R. J. Kiesel, *J. Org. Chem.*, **29**, 764 (1964).

(4) For precedent for nucleophilic trapping of the 1-norbornyl cation by ether see E. H. White, R. H. McGirk, C. A. Aufdermarsh, Jr., H. P. Tiwari, and M. J. Todd, *J. Amer. Chem. Soc.*, **95**, 8107 (1973).

**Scheme I**



(18 and 30%, respectively) at the bridgehead position. Thus, in addition to the radical pathway for reduction there is apparently a competing process which we suggest involves nucleophilic attack by solvent on the  $n, \sigma^*$  excited state **4** to generate the carbanion **7**, in analogy with the previously observed photofragmentation of iodo lactones and ethers.<sup>1</sup>

When the irradiation of iodide **1b** was conducted in methanol saturated with oxygen, followed by a reductive work-up with sodium borohydride, the yield of norbornane (**8**) was reduced to a trace and the alcohol **6**<sup>3</sup> was obtained as a new product. This is consistent with trapping of both the radical **5** and the carbanion **7** by oxygen to afford the hydroperoxide **9**, followed by reduction to the alcohol **6**. Similar behavior was displayed by the bromide **1a** in the presence of oxygen.

Perhaps more significant, however, is the fact that the yield of ether **3a** from either halide was also reduced significantly, with the concomitant formation of additional alcohol **6**. Moreover, the rate of disappearance of halide **1** was not significantly changed in the presence of oxygen. These results are consistent with, and strongly support, our earlier proposal that cationic intermediates from alkyl halides arise *via* initial homolytic cleavage of the carbon-halogen bond to afford a radical pair, followed by electron transfer to generate an ion pair. In the presence of oxygen, trapping of the alkyl radical competes with the electron transfer process.

Also related is the observation that the amount of nucleophilic substitution product **3** formed is solvent dependent and is dramatically increased in viscous solvents such as ethylene glycol, as shown in Table I for halides **1a** and **b**.<sup>6</sup> This increase is most likely due in

(5) D. B. Denney and R. R. DiLeone, *J. Amer. Chem. Soc.*, **48**, 4737 (1962).

(6) Satisfactory analytical data have been obtained for all novel compounds.

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 bromides<sup>7</sup> 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.<sup>8</sup> 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 $\mu$ -Methylselenodiborane

Sir:

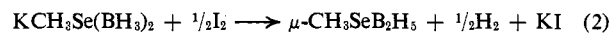
We wish to report the synthesis of a bisborane adduct of selenium and its conversion to the first example of a selenium substituted borane. A xylene slurry of  $\text{KSeCH}_3$  at 25° reacts with a stoichiometric amount of diborane over a period of 3 hr in agreement with eq 1.



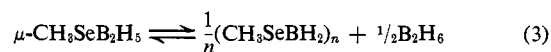
The colorless unsolvated solid product may be isolated by evaporation. *Anal.* Calcd (mmol/g):  $\text{B}(\text{OH})_3$ , 12.5;  $\text{H}_2$  (hydrolytic), 37.4. Found:  $\text{B}(\text{OH})_3$ , 12.0;  $\text{H}_2$  (hydrolytic), 35.0. The  $\text{KCH}_3\text{Se}(\text{BH}_3)_2$  is readily soluble 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  $\text{cm}^{-1}$ .

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  $\text{SeCH}_3$  singlet  $\tau$  8.91,  $^{11}\text{BH}$  1:1:1:1 quartet  $\tau$  7.94,  $J_{\text{BH}} = 140$  Hz, and bridge  $^{11}\text{BH}^{11}\text{B}$   $\tau$  11.33. The gas phase infrared spectrum shows terminal BH stretching bands at 2570 and 2485  $\text{cm}^{-1}$  and bridge BHB stretching absorptions at 1820 and 1735  $\text{cm}^{-1}$ . 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;  $\text{H}_2$  (hydrolytic), 41.5;  $\text{CH}_3\text{SeH}$ , 8.30. Found:  $\text{B}(\text{OH})_3$ , 17.4;  $\text{H}_2$  (hydrolytic), 42.3;  $\text{CH}_3\text{SeH}$ , 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  $(\text{CH}_3\text{SBH}_2)_n$ .<sup>1</sup>

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 radii<sup>2</sup>) and a B···B distance of 1.92 Å (from  $\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5$ )<sup>3</sup> 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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(2) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, p 45.

(3) K. Hedberg and A. J. Stosick, *J. Amer. Chem. Soc.*, **74**, 954 (1952).

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