The toluene data give a good Arrhenius plot indicating $E_a + E_b - E_{t12} = 8.35$ kcal/mole (a reasonable value), and from Table I it is evident that ϕ $(=(k_{t12}/2(k_{t1}k_{t2})^{1/2})$ is much larger than unity in all systems. A small value for $2k_{t1}/k_a{}^2$ for cyclohexane is expected because of its high reactivity toward *t*-butoxy radicals (7.63 × toluene by direct competition, although there are apparently complicating solvent effects[4]). If our ratio in toluene (0.77) is accepted we can make a rough estimate of k_a for the toluene reaction. The rate of recombination of iodine atoms in hexane is approximately 2×10^{10} at 30°, and when produced photochemically some 70% escape from the initial solvent cage.[5] Efficiency of *t*-butoxy radical escape in the decomposition of di-*t*-butyl peroxalate is apparently 96% in pentane.[6] Since the two radicals are rather similar in size and shape, we assume them to have similar diffusion rates, and estimate $k_{t1} = (^4/_{96})(^{70}/_{30}) \times (2 \times 10^{10}) = 20 \times 10^8$, whence $k_a = 7.2 \times 10^4$. This result seems consistent with the high reactivity of *t*-butoxy radicals, the rapidity of *t*-butyl hypochlorite chlorinations, and the value of 9×10^3 for the reaction of toluene with the benzophenone triplet,[7] an electronically rather similar but slightly more selective[8] species.

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Two New Undecaboranes

Sir:

Muetterties[1] and co-workers reported the preparation of $NaB_{11}H_{14}$ and its rapid degradation on treatment with aqueous acids. We have carefully studied the nature of the acidification reaction in several nonaqueous solvents and have successfully identified the parent borane, $B_{11}H_{15}$, as a disolvated material.

The reaction of the dioxanate, $NaB_{11}H_{14} \cdot xC_4H_8O_2$ (*x* is variable between 2 and 3), with an equimolar quantity of HCl proceeds over a several-hour period as represented by the equation

$$NaB_{11}H_{14} \cdot 2.5C_4H_8O_2 + HCl \longrightarrow B_{11}H_{15} \cdot 2.0C_4H_8O_2 + NaCl + 0.5C_4H_8O_2$$

No hydrogen loss is observed when the reaction is carried out at room temperature in dioxane or *n*-pentane or at 0° in dimethyl sulfide. In THF, slow H_2 loss occurs after 4 hr at room temperature and yields a solvated $B_{11}H_{13}$ derivative at the end of approximately 24 hr. Similarly, when the HCl treatment is conducted in dimethyl sulfide at room temperature, hydrogen is slowly but continuously evolved to yield solvated product, which on recrystallization corresponds to $B_{11}H_{13}(CH_3)_2S$.

When no hydrogen is evolved, both products of the acidification reaction are essentially insoluble in the liquid medium; separation of the solvated borane from the NaCl has not yet been completely satisfactory. The existence of $B_{11}H_{15} \cdot 2C_4H_8O_2$ and its relationship to the starting sodium salt has, however, been unequivocally demonstrated. Thus, the solvated $B_{11}H_{15}$ product reacts quantitatively with sodium hydride in diethyl ether to regenerate the original sodium salt and evolve the stoichiometric quantity of hydrogen demanded by the equation

$$B_{11}H_{15} \cdot 2C_4H_8O_2 + NaH \longrightarrow NaB_{11}H_{14} \cdot 2C_4H_8O_2 + H_2$$

In this respect, these B_{11} derivatives appear remarkably similar to the quantitative reactions that we observed with decaborane.[2]

$$B_{10}H_{14} + NaH \longrightarrow NaB_{10}H_{13} + H_2$$
$$NaB_{10}H_{13} + HCl \longrightarrow NaCl + B_{10}H_{14}$$

In a typical experiment $NaB_{11}H_{14} \cdot 2.5C_4H_8O_2$ (10 mmoles) was allowed to react with a stoichiometric quantity of gaseous HCl in dimethyl sulfide at 0° over a 6-hr period. The insoluble product of reaction after recovery and drying was best represented as an equimolar mixture of NaCl and $B_{11}H_{15} \cdot 2C_4H_8O_2$. X-Ray diffraction confirmed the presence of NaCl and showed additional diffraction lines not characteristic of the starting material. *Anal.* Calcd for NaCl + $B_{11}H_{15} \cdot 2C_4H_8O_2$: C, 26.0; Cl, 9.62; Na, 6.25; B, 31.4. Found: C, 24.9; Cl, 9.43; Na, 6.20; B, 31.4.

As the bisdioxanate derivative, $B_{11}H_{15}$ appears to exhibit reasonably good thermal stability with respect to hydride degradation since a solvent-free borane has been obtained by sublimation techniques at 100° without loss of hydrogen. Characterization of the sublimed product is not yet complete. Solvated $B_{11}H_{15}$ yields a solvated $B_{11}H_{13}$ derivative by loss of 1 mole of H_2 upon treatment with water, alcohol, or thioethers. In fact, the disolvated $B_{11}H_{13}$ is readily prepared by the acidification of the sodium salt with anhydrous HCl in dimethyl sulfide at ambient temperature, followed by filtration of the insoluble NaCl and recovery of the desired product from the filtrate by volatilization of the solvent. In contrast to the higher hydrogen analog, the $B_{11}H_{13}$ derivative is not reactive toward water or alcohol unless the solvent contains added quantities of HCl. The observed rapid degradation of $NaB_{11}H_{14}$ by aqueous acids may be the result of a sequence of reactions involving borane species similar to those herein reported.

When the reaction of $NaB_{11}H_{14}$ dioxonate with gaseous HCl is carried out in dimethyl sulfide at room temperature, the stoichiometric quantity of hydrogen is evolved for the formation of $B_{11}H_{13}$. Simple filtration techniques can be used to remove the insoluble NaCl from the reaction mixture, and the solvated $B_{11}H_{13}$ remains in the dimethyl sulfide solution. Purification of the $B_{11}H_{13}$ product was accomplished by dissolving the residue, obtained from a vacuum removal of volatiles, in methanol and subsequent crystallization from water; a white product formed. *Anal.* Calcd for $B_{11}H_{13} \cdot (CH_3)_2S$: B, 61.25; C, 12.36; H (total),

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[1] V. D. Aftandilian, H. C. Miller, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, **1**, 734 (1962).

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9.86; S, 16.51. Found: B, 59.8; C, 12.01; H (total), 9.9; S, 15.5.

Structural studies on the two new solvated B_{11} derivatives have not been completed. We believe, however, that $NaB_{11}H_{14}$ can be best pictured as possessing an electron pair in a bridge position; an available proton would be expected to attack this basic site to yield the parent borane species, $B_{11}H_{15}$. This view is supported by many observations of acid character of bridge hydrogens and the fact that the $B_{11}H_{15}$ product exhibits a significant increase in bridge hydrogen absorption in its infrared spectra at 1918 cm^{-1} in comparison to the sodium derivative. The loss of 1 mole of hydrogen from $B_{11}H_{15}$ to form $B_{11}H_{13}$ is accompanied by a substantial decrease in the bridging absorption in the infrared region of 1918 cm^{-1}, suggesting that $B_{11}H_{13}$ is derived through loss of at least one bridge hydrogen. Both of these boranes exhibit a new band of medium intensity at 820 cm^{-1}, not found in the sodium derivative.

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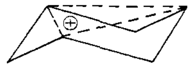
Monohomocyclooctatetraene Anion Radical. A Homoaromatic Nine-Electron System[1,2]

Sir:

A number of homoaromatic species with delocalized two- or six-electron systems have been reported and discussed. Examples are trishomocyclopropenyl[1] cations such as I[3a] and II,[3b] monohomotropylium ions[1] such as III,[4] and the 1,3-bishomocyclopentadienide ion[1,5] IV. We now report an example of a homoaromatic nine-electron system.



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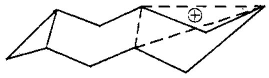

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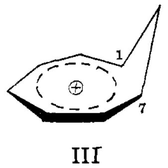
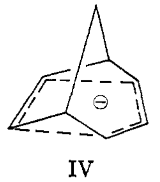


III



IV

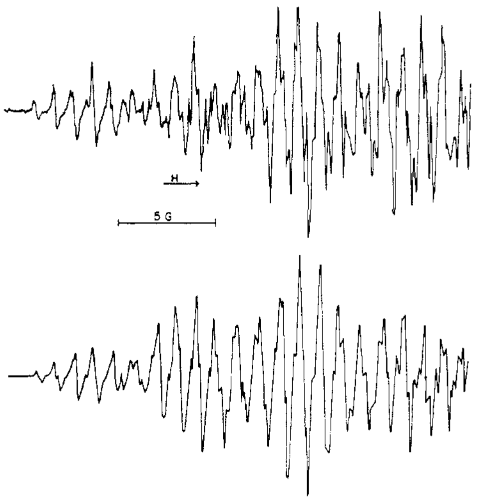


Figure 1. Esr spectra of VII: upper, observed; lower, calculated using 0.150-gauss line width and Lorentzian line shape; only half-spectra shown.

Instead of entering an antibonding olefinic molecular oribital, an additional electron supplied to tub cyclooctatetraene prefers to go into a nonbonding molecular orbital of a planar cyclooctatetraene.[6] The HMO delocalization energy of cyclooctatetraene anion radical V is so large (2.66β) that aromatization is induced by donation of an electron to cyclooctatetraene. Analogously, we have now observed that donation of an electron to the cyclooctatetraene monomethylene adduct[7] VI (monohomocyclooctatetraene) gives rise to monohomocyclooctatetraene anion radical VII.

Treatment of VI with a small amount of potassium in glyme at −80° gives an anion radical whose esr spectrum has been observed at −84°. Compared to cyclooctatetraene anion radical V with a nine-line esr spectrum due to spin coupling of the odd electron with eight equivalent protons (a_H = 3.209 gauss), the monohomocyclooctatetraene anion radical displays a relatively complex esr spectrum showing eight major groups each split into seven lines (Figure 1). The observed spectrum is appropriate for a species with the symmetry of VII. The spectrum indicates a large hyperfine splitting constant (a_H) of 16.8 gauss assigned to one of the C_9 protons and an a_H value averaging 5.6 gauss for four protons. Further, the septet splitting averages *ca.* 1 gauss. The interpretation of the spectrum is further substantiated with the aid of the dideuterio analog of VII, namely VIID, prepared from VID containing two deuterium atoms on C_9. The latter was prepared by the use of CD_2Cl_2 in the reaction of cyclooctatetraene dianion with methylene chloride.[7b]

From the relative widths and other features of the spectra of the ordinary and dideuterio anion radicals VII and VIID, shown in Figures 1 and 2, it is clear that the sum of the hyperfine coupling constants of the two C_9 methylene protons is *ca.* 19 gauss, making a_H *ca.* 2 gauss for the second of the two C_9 protons. Setting

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[2] (a) Research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgement is hereby made to the donors of this fund. (b) Research was supported in part by the National Science Foundation.

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