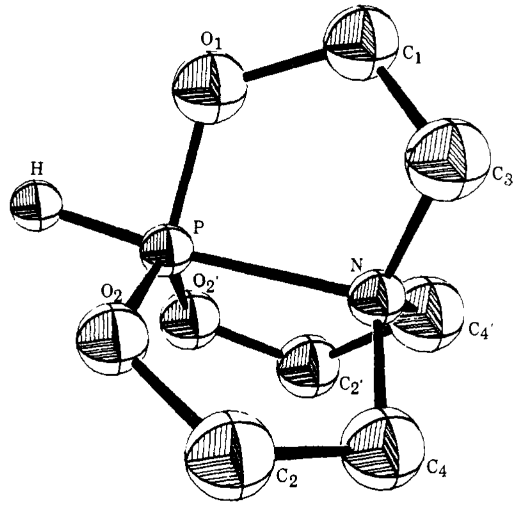


Figure 1. Computer drawing of the 1-hydro-2,8,9-trioxa-1-phospha-5-aza-tricyclo[3.3.3.0]undecane cation of **1**. Only the P-H hydrogen and one of the disordered conformations is shown.

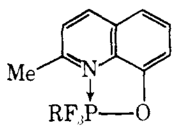
group ambiguity since they were intermediate between centrosymmetric (*Pnam*) and noncentrosymmetric ($Pna2_1$) in value and the presence of a heavy atom could easily give spurious results.

Solution of the crystal structure was begun by routine application of direct methods via a multiple solution weighted tangent formula[8] scheme in the noncentrosymmetric space group $Pna2_1$. All of the nonhydrogen atoms were easily located in the first phased *E* synthesis and all hydrogens located in subsequent difference *F* syntheses.[9] Full-matrix least-squares refinements proceeded uneventfully to a final cyrstallographic residual (*R*) of 6.2% for the 615 observed reflections and 183 variables. The geometry of this model was very poorly behaved with chemically identical bonds differing by five standard deviations. The molecular constitution was essentially that shown in Figure 1.

Refinement was then attempted in space group *Pnam* (alternate setting of *Pnma*). It became rapidly apparent that a model in which the molecule sat on a mirror plane would not refine and models in which C(3) and C(4) were disordered were tried. These refined satisfactorily to an *R* of 6.5% for the 135 variables used. Fractional coordinates, bond distances, bond angles, and observed and calculated structure factors for this model are given in the supplemental material to be found in the microfilm edition; see paragraph at end of paper regarding supplementary material. A drawing of this model is given in Figure 1.

The well-defined P←N dative bond in **1** (1.986 Å) is undoubtedly responsible for the unusual proton abstracting property of the bicyclic precursor. The phosphorus atom is clearly trigonal bipyramidal with O-P-O angles of 120°, O-P-N angles of 87°, and a H-P-N angle of 172°. This near trigonal bipyramidal symmetry of the five electron pairs around the phosphorus atom in 1 contrasts the relative instability of this electron pair configuration in: $PX_3 \leftarrow NR_3$ adducts[10] and intermediates involved in certain reactions of trivalent phosphorus compounds.[11] The P-H bond distance in **1** (1.35 Å) is about 0.1 Å shorter than the 1.41 to 1.45 Å realized in several phosphines and PH_4^+ [12] and is also somewhat shorter than the sum of the covalent radii (1.38 Å). It is interesting that although trigonal bipyramidal phosphoranes tend to orient the more electronegative substituents on the apices, molecular constraint appears to preclude this possibility in **1**. The similarity of the structure of phosphatrane **1** to that of silatranes ($RSi(OCH_2CH_2)_3N$)[13] with which it is isoelectronic is noteworthy.

The P-N bond distance found in **1** is quite comparable to those found in the six-coordinate systems below (1.91-1.98 Å) wherein the electronegative fluorines on the five-coordinate phosphorane moiety are effective in attracting the nitrogen lone pair to the acidic phosphorus.[14]



R = Ph, F

Acknowledgment. J.G.V. thanks the National Science Foundation for generous grant support of this research.

Supplementary Material Available: fractional coordinates, bond distances, bond angles, and structure factors (6 pages). Ordering information is given on any current masthead page.

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Directive Effects in the Electrophilic Substitution of Deltahedral Boranes and Heteroboranes. Halogenation of $1\text{-}SB_9H_9$. Unusually Long ^{11}B Spin-Lattice Relaxation Times

Sir:

There has been considerable interest in the stereochemistry of electrophilic substitution of closo(deltahedral) boranes[1] and heteroboranes, at least in part because many members of this class of molecules can be termed aromatic. For deltahedral heteroboranes like 1,2- and 1,7-$C_2B_{10}H_{12}$ and 2,4-$C_2B_5H_7$, ground-state charge distributions correlate nicely with the results of electrophilic halogenation.[2,3]

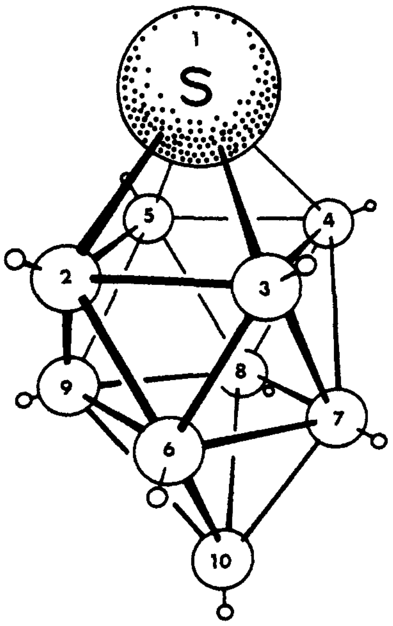

Figure 1. Structure and numbering convention for the thiadecaborane framework.

In the case of the deltahedral borane anions $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$ electrophilic halogenation[4] does not appear to correlate well with predictions for sequential substitution.[5] However, interpretation of the results was complicated somewhat by the ease of halogenation and the difficulty of isomer separation.[4] No evidence for the rearrangement of deltahedral boranes or heteroboranes during the course of halogenation has been presented. We report here results on the halogenation of $1\text{-}SB_9H_9$ which can be followed sequentially and thus provide a good probe for the theory of directive effects in substitution reactions in deltahedral boranes. The results suggest that cage rearrangement plays a role in the ultimate stereochemistry of the products. We also find that certain B sites in these halothiaboranes manifest unusually long spin-lattice relaxation times (T_1). Although our preliminary assessment indicates that the phenomenon is isolated to rather specific B sites, this communication is in part a caveat regarding the determination of ^{11}B NMR spectra, a task not usually plagued with difficulties due to saturation effects since relaxation is dominated by the very efficient quadrupolar mechanism.[6,7]

In keeping with previous observations for carboranes,[2,3] one would expect that those B sites furthest removed from the sulfur heteroatom would be most negative and most susceptible to electrophilic substitution. This assumes that the course of substitution is controlled by ground-state charge distribution and is also not subject to rearrangement of the framework. Our EHMO calculations corroborate this expectation and give the following atom charges from a Mulliken population analysis:[8] upper belt (ub) B(2,3,4,5) = 0.2524; lower belt (lb) B(6,7,8,9) = 0.0733; axial (ax) B(10) = −0.0734 (see Figure 1 for atom numbering convention).

When $1\text{-}SB_9H_9$ is treated with an equal amount of either I_2(200 °C) or Br_2 (25 °C) in a sealed tube (with or without aluminum halide) a mixture of $10\text{-}X\text{-}1\text{-}SB_9H_8$ and $6\text{-}X\text{-}1\text{-}SB_9H_8$ results.[11] The ratio of ax:lb substitution varies between about 2:1 and 1:1 depending on the run even though there is a four times greater statistical chance for lb vs. ax substitution. At first glance these results appear to be in accord with ground-state charge distributions; however, we suspect differently in view of the results of chlorination and isomerization experiments.

Table I. ^{11}B NMR Spectra of Halothiadecaboranes[a]

$6\text{-}I\text{-}1\text{-}SB_9H_8$: −71.2, d (1), J_{BH} = 175; 5.1, d (4), J_{BH} = 180; 16.8; d (2), J_{BH} = 135; 19.9, d (1), J_{BH} = 135; 24.1, s (1)
$10\text{-}I\text{-}1\text{-}SB_9H_8$: −50.1, s (1); 6.7, d (4), J_{BH} = 185; 16.2, d (4), J_{BH} = 165
$6\text{-}Br\text{-}1\text{-}SB_9H_8$: −69.3, d (1), J_{BH} = 175; 3.0, d (2), J_{BH} = 175; 6.9, d (2), J_{BH} = 190; 10.0, s (1); 15.4, d (2), J_{BH} = 180; 21.3, d (1) J_{BH} = 195
$10\text{-}Br\text{-}1\text{-}SB_9H_8$: −65.6, s (1); 8.3, d (4), J_{BH} = 175; 18.4, d (4), J_{BH} = 150
$6\text{-}Cl\text{-}1\text{-}SB_9H_8$: −68.7, d (1), J_{BH} = 175; 2.0, d (2), J_{BH} = 145; 4.2, s (1); 7.0, d (2), J_{BH} = 180; 14.6, d (2), J_{BH} = 170; 23.2, d (1), J_{BH} = 160
$10\text{-}Cl\text{-}1\text{-}SB_9H_8$: −73.4, s (1); 3.3, d (4), J_{BH} = 185; 17.3, d (4), J_{BH} = 160
$6,10\text{-}I_2\text{-}1\text{-}SB_9H_7$: −48.8, s (1); 5.5, d (4), J_{BH} = 180; 13.6, d (2), J_{BH} = 155; 15.7, d (1), J_{BH} = 180; 23.5, s (1)
$6,10\text{-}Br_2\text{-}1\text{-}SB_9H_7$: −64, s (1); 5.3, d (2), J_{BH} = 190; 7.6, d (2), J_{BH} = 175 10.4, s (1); 14.8, d (2), J_{BH} = 180; 20.6, d (1), J_{BH} = 185

[a] The chemical shift data are given in parts per million relative to external $Et_2O\cdot BF_3$ (− values downfield) followed by a description of the signal (d = doublet, s = singlet), its relative intensity (in parentheses), and observed coupling constant given in hertz. Spectra were determined at 32.1 MHz in $CDCl_3$ solution.

When $1\text{-}SB_9H_9$ is treated with Cl_2 in the manner used for bromination and iodination, only one isomer of chloro-1-thiadecaborane is observed, $6\text{-}Cl\text{-}1\text{-}SB_9H_8$, the lb isomer *not* the ax isomer predicted on the basis of charge distribution! Furthermore, when heated to 200 °C, $6\text{-}Cl\text{-}1\text{-}SB_9H_8$ isomerizes to an approximate 1:1 mixture of ax:lb isomers. We have also observed that after 20 h in a sealed tube at 200 °C the ratio of ax:lb $Br\text{-}1\text{-}SB_9H_8$ changes from 1:1 to 2:1 and for $I\text{-}1\text{-}SB_9H_8$ the ratio changes from 1.6:1 to 2:1, again indicating that the axial isomer is thermodynamically more stable.

These observations suggest but do not prove that initial attack is at the lower belt and that rearrangement occurs during the course of iodination and bromination. Certainly, the reaction temperature was high enough for rearrangement in the case of iodination and apparently either the vigor of attack by bromine or the nature of the transition state results in the formation of considerable axial isomer during bromination.

The course of sequential halogenation also appears to be complicated by rearrangement. Our EHMO calculations[8,12] suggest that both ax and lb isomers of $Cl\text{-}1\text{-}SB_9H_8$ should yield $6,10\text{-}Cl_2\text{-}1\text{-}SB_9H_7$ exclusively since for $6\text{-}Cl\text{-}1\text{-}SB_9H_8$ the axial site is most negative and for $10\text{-}Cl\text{-}1\text{-}SB_9H_8$ the lb sites are most negative. Indeed, the only dibromo and diiodo isomer observed in the reaction mixtures is the 6,10-isomer. However, no axial substitution has been detected in the case of the $Cl_2\text{-}1\text{-}SB_9H_8$ which appears to be a mixture of lb isomers as isolated from the reaction mixture.

Structural assignment is based on ^{11}B NMR spectroscopy (Table I). The structure of $2,2'\text{-}(1\text{-}SB_9H_8)_2$ is known[10] and allows the two doublets of relative intensity 4 in the ^{11}B spectrum of $1\text{-}SB_9H_9$[14] to be assigned. The lower-field doublet is due to the belt of four borons adjacent to the sulfur (ub) and the higher field doublet to the other belt of four borons (lb). In general for lb monosubstitution, the NMR signals for the unsubstituted ub borons displayed relatively little change from the corresponding region for $1\text{-}SB_9H_9$, but major shifts were evident in the lb region. In all cases, the barycenter for the ub and lb regions was maintained within ±1 and ±3 ppm, respectively, of the corresponding signal for $1\text{-}SB_9H_9$. The ax boron resonance is quite far downfield from the other signals and appeared as a doublet of relative intensity 1 for all lb-substituted products. For the ax isomers, the ^{11}B NMR spectra were quite simple and showed the expected downfield singlet[15] and two upfield doublets of relative intensity 1:4:4. However, as previously alluded to, the singlet was unusually hard to detect.

In the case of 10-X-1-SB_9H_8 (X = Cl, Br, I) we observe only two doublets of equal intensity when the ^{11}B NMR spectrum is determined with a short delay (10–100 ms) between $\pi/2$ pulses. The expected low-field singlet for the halogenated B site gradually grows in as the delay time is increased above 100 ms and reaches a limiting intensity (1 relative to 4 for the two doublets) at 8–10 s.[16] The intensity recovery for the singlet as the delay time increases follows first-order kinetics and was used to estimate[17] T_1 = 2.8, 3.9, and 2.6 s for X = Cl, Br, I, respectively. The π, τ, $\pi/2$ pulse sequence method of Vold[18] was used to determine the much shorter T_1's for the other B environments (ub = 10, 14, 8 ms; and lb = 24, 22, 19 ms for X = Cl, Br, I, respectively. For comparison, the T_1's for 1-SB_9H_9 are ax = 34, ub = 21, and lb = 40 ms, respectively. The halogen has a decided effect on the relaxation time of the axial B site. This seems even more remarkable in view of the T_1 results when the halogen is in a lb position, such as for 6-Br-1-SB_9H_8 where T_1 = 35 ms for the substituted boron and ranges from 11 to 22 ms for the other positions.

We do not feel that this effect is related to anisotropic molecular reorientation. For symmetric rotors, the relaxation time of a nucleus on the symmetry axis (such as the axial B site of 1-SB_9H_9) depends only on motion perpendicular to that axis.[19] As estimated from moments of inertia, such motion would give rise to longer correlation times (shorter T_1's) for 10-X-1-SB_9H_8 (X = Cl, Br, I) in comparison with 1-SB_9H_9. Moreover, for 6,10-Br_2-1-SB_9H_7, where the symmetric-top nature of 10-Br-1-SB_9H_8 has been removed by substitution of a second halogen on the lb, the ax- and lb-substituted borons still manifest the same large disparity in T_1 values.

The antipodal position of sulfur may somewhat influence T_1; however, we have found no saturation effects when running the spectrum of 12-Br-1-$SB_{11}H_{10}$, the icosahedral closo thiaborane with bromine substituted antipodal to the sulfur.[20] One perhaps salient difference between the axial positions in 1-SB_9H_9 and 1-$SB_{11}H_{11}$ is the coordination number of the deltahedral vertex, five in 1-SB_9H_9 and six in 1-$SB_{11}H_{11}$. However, we have no other axially halogenated 1-heterodecaboranes for comparison ($(\text{ax-I-}B_{10}H_9)^{2-}$ shows no saturation problems[21] but perhaps the unreported $(10\text{-X-1-}PB_9H_8)^-$ or $(10\text{-X-1-}CB_9H_9)^-$ would).

A comparison of T_1 values for ^{10}B and ^{11}B led Allerhand, Odom, and Moll to conclude that all contributions other than quadrupolar were negligible for B_2H_6, B_5H_9, and $B(C_2H_5)_3$; it was also estimated that electric field gradients at boron are relatively small.[6] It is our estimation that the electric field gradient is accidentally very small at the axial B site in 10-X-1-SB_9H_8 molecules even though this is not corroborated by EMHO calculations.[22]

In the absence of effective quadrupolar relaxation, it is entirely possible that scalar relaxation, caused by spin-spin interaction of the axial boron and the attached halogen, is dominant here. Since our present experiments only show that T_2 (effective) $\ll T_1$ rather than T_2 (actual) $\ll T_1$, the scalar mechanism cannot be established.[17]

Acknowledgment. We thank the National Science Foundation for partial support of this research (MPS74-0047 A01) and R. R. Sharp for helpful discussions.

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Trivalent Copper as a Probable Intermediate in the Reaction Catalyzed by Galactose Oxidase[1]

Sir:

Recently we reported[2] preliminary evidence that Cu(III), or Cu(II) in close proximity to an enzymic radical, may be an important catalytic intermediate in the reaction (eq 1) catalyzed by galactose oxidase (D-galactose: O_2 oxidoreductase; 1.1.3.9), and that a Cu(II) form of the enzyme is inactive catalytically. These conclusions were based especially on the following observations: (1) superoxide dismutase inhibits the galactose oxidase reaction and causes an increase in the intensity of the EPR signal given by the galactose oxidase,[3] and (2) the addition of superoxide or ferricyanide increases the rate of the galactose oxidase reaction, and ferricyanide causes an almost complete disappearance