obtained 24.2 g of **23**·bitartrate, mp 209–210°; liberated base, $[\alpha]^{24}_{576}$ 0° (1 dm, *c* 2.96). This material was dissolved in refluxing MeOH–H_2O (1:1, 400 ml) and then allowed to stand for 1 hr at room temperature. The resultant solid was filtered off and the filtrate was concentrated *in vacuo* to about 100 ml. The solid was filtered off to give 9.5 g of (−)-**23**·bitartrate, mp 211–213°; liberated base, $[\alpha]^{24}_{546}$ −11.6° (1 dm, *c* 3.01), mp 198–200°. *Anal.* ($C_{31}H_{33}NO_8$): C, H, N, O.

Filtrate A from above was concentrated *in vacuo* to about one-fourth the original volume and the resultant solid was filtered off to give 19.8 g of **23**·bitartrate, mp 216–218°; liberated base, $[\alpha]^{24}_{546}$ +2.0 (1 dm, *c* 2.95). The solid was dissolved in refluxing Me_2CO–MeOH (1:1, 250 ml) and then allowed to stand about 18 hr at room temperature. Filtration gave 14.6 g of **23**·bitartrate, mp 213–215°; liberated base, $[\alpha]^{24}_{546}$ +4.7° (1 dm, *c* 2.85). This material was then recrystallized twice from MeOH–H_2O (1:1, 250 ml) to give 8.7 g of (+)-**23**·bitartrate, mp 209–212°; liberated base, $[\alpha]^{24}_{546}$ +12.3 (1 dm, *c* 2.90), mp 198–200°. *Anal.* ($C_{31}H_{33}NO_8$) C, H, N, O.

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The Alkylation and Acylation of $B_{10}H_9NH_3^-$ [1,2]

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The reaction of 2-$B_{10}H_9NH_3^-$ with ethylene oxide produced $H_3NB_{10}H_7(CH_2CH_2OH)_2^-$, several salts and derivatives of which were prepared. Treatment of 2-$B_{10}H_9NH_3^-$ with NaH followed by the addition of ethyl α-chloroacetate produced $B_{10}H_9NH(CH_2COOC_2H_5)_2^-$, which was subsequently reduced to $B_{10}H_9NH(CH_2CH_2OH)_2^-$. Benzoylation of 2-$B_{10}H_9NH_3^-$ was found to give the N-substituted in preference to the B-substituted derivative. Preliminary biological results reveal that whereas the N-β-hydroxyethyl derivative is not incorporated into brain, muscle, or tumor tissues the B-β-hydroxyethyl derivative and its phosphate ester appear to be strongly bound to tumor tissues and give very favorable tumor-blood boron ratios.

The low toxicity of polyhedral boranes and their derivatives[4] has stimulated a renewed interest in the B^{10} neutron capture therapy of brain tumors.[5] The discovery that these boranes can be readily substituted with a number of organic groups[6] opened up a search for convenient "handles" for the incorporation of these boron-rich ions into tumors. The search is still on, since with few exceptions[7] the derivatives prepared so far are either too toxic or are not selectively incorporated into tumor in adequate concentrations for therapy.[8]

We decided to begin an investigation of reactions which would enable us to build up "handles" on the boron cage containing a biochemical rationale for their incorporation into neoplasm. A stepwise synthetic scheme was chosen with functional groups as close to the cage as possible thereby eliminating intervening atoms which do not contribute to the biological activity of the organic side chain. Additionally the boron percentages of these compounds would be high. The choice of $B_{10}H_9NH_3^-$ [9] as a starting point was motivated not only by the fact that it offers a choice of two reactive sites, the nitrogen and the cage, but that its chemistry has not been even superficially explored. Alkylation and acylation reactions were the first to be examined since they can provide the starting points in the syntheses of derivatives having the borane attached to the hydrocarbon backbone of the organic molecule. Of course, only alkylations where the other end of the carbon chain had a functional group capable of undergoing additional reactions were explored.

Results and Discussion

Reactions.—The principal reactions discussed in this paper are represented in Scheme I.

The alkylation with ethylene oxide provides another example of the aromatic character of the polyhedral ions,[6] since it apparently resembles an analogous reaction with benzene.[10] What is somewhat surprising is the fact that no detectable amount of N-substituted product was isolated, despite the weakly acidic nature of the NH_3^+ protons which can be exchanged for deuterium in D_2O. Also the nitrogen can be easily methylated with Me_2SO_4.[9] The acidic medium should not have been a hindrance either, since analogous alkylation of primary amines occurs readily in acidic media.[11] However, as we have shown in this work under basic conditions acylation occurs almost exclusively at the nitrogen. In the absence of the NH_3^+ group the cage is readily benzoylated even without a Friedel–Crafts

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(3) To whom enquiries regarding the chemical aspects of this work should be addressed at the Department of Chemistry, Tufts University, Medford, Mass. 02155.

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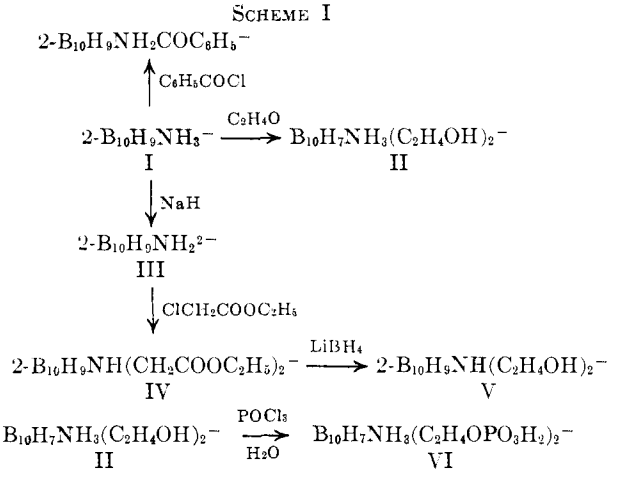
SCHEME I



catalyst.[12] A thorough mechanistic study will be required to explain the directional nature of the electrophilic substitutions of $B_{10}H_9NH_3^-$.

One of the reasons for studying the second sequence of reactions was to prepare a N-β-hydroxyethyl derivative of I for comparison with II. At the same time we wanted to see whether electrophilic substitution can be directed to the nitrogen exclusively by converting $B_{10}H_9NH_3^-$ into the strong nucleophile $B_{10}H_9NH_2^{2-}$ first. Our results indicate that by treating the appropriate α-halogenated esters with this nucleophile and hydrolyzing the product formed, a variety of N-substituted α-amino acids can be synthesized.

Once a suitable oxidizing agent has been found capable of converting II to the corresponding aldehyde and acid without degrading the boron cage it will also be possible to make α-amino acids with the polyhedron attached to the α carbon. The problems encountered in our attempts to oxidize II suggest that the effect of the β-hydroxyethyl groups are analogous to the effects of simple hydroxyl groups, which greatly reduce the oxidative stability of polyhedral boranes.[12] The acetylation of II proceeds normally, except that the acetyl chloride, or the HCl produced *in situ* also catalyze the addition of nitriles to the cage. Hydrolysis of such adducts yields N-cage amides of the type isolated in our work. Similar addition and hydrolysis have been observed when $B_{10}H_{10}^{2-}$ was refluxed with *p*-toluenesulfonic acid in nitriles.[13] We found that if II is acetylated in the presence of triethylamine only the acetyl derivative of the alcohol is formed. Except in very basic solutions the N-cage amides retain an extra proton on the nitrogen, which explains why our product with two quaternary nitrogens attached directly to the cage was a neutral species. Where the CH_2CH_2OH group in II differs from an ordinary aliphatic alcohol is in its reaction with $POCl_3$ which fails to proceed beyond the formation of the intermediate C–O–P bond to give the expected halide.

Products.—The B^{11} nmr spectrum of II resembles in its gross features that of I except that in addition to the peaks belonging to 2-$B_{10}H_9NH_3^-$ (doublet at 20.6 ppm, singlet at 33.4 ppm, multiplet with a maximum at 46.4 ppm)[9] there was a small peak at 2.6 ppm and a shoulder at 41.2 ppm. The resolution was too poor to permit any definite conclusions with regards to the stereochemistry of II but since the peak at 2.6 ppm represented less than one-tenth of the total area a mixture of isomers is suspected. That in II the carbons are attached directly to the cage and not to N is shown quite conclusively by the comparison of its pmr spectrum with that of V, where the mode of attachment is known unequivocally. In the spectrum of II the triplet at τ 5.95 is assigned to the β protons (on the carbon adjacent to the OH group) and the high-field triplet at τ 8.37 to the α protons. The assignment of the two triplets is based on the following facts: (1) esterification shifts the low-field triplet much more than it does the high-field triplet, about 20 and 4 cps downfield, respectively; (2) the corresponding protons in the analogous aromatic systems are centered at about τ 6 and 7. For example, protons on CH_2 adjacent to the oxygen and one carbon removed from the phenyl ring show up at τ 6.3 and 5.7, respectively, in $(CH_3)_2C_6H_3CH_2CH_2OH$ and $C_6H_5CH_2CH_2OCOCH_3$.[14] In the same two organic compounds the α protons show up at τ 7.3 and 7.1, respectively. That in II the α protons show up about 1 ppm higher than they do in the two aromatic compounds listed above provides additional evidence for the B–CH_2CH_2OH sequence of atoms, since this unusually large upfield shift is quite consistent with the effects of the cage on the ir frequency of adjacent carbonyls.[12] At the same time the effect on a CH_2 one carbon removed should be less pronounced since the electrons released by the cage produce a much smaller shift in the C=O frequency of esters of the $B_{10}H_9OCO$ type.[12] Of the four ionizable protons expected in VI only two could be titrated below pH 12. The titration yields $pK_1 = 5.1$ and $pK_2 = 9.3$ for the first two ionization constants.

The pmr spectra of V and VI show how effectively the quaternary N screens the alkyl protons from the cage. As a matter of fact N has enough positive charge around it to shift the protons on adjacent α-methylenes downfield from their normal position in $C_6H_5N(C_2H_5)(CH_2CH_2OH)$, for example, while leaving the β-CH_2 unaffected. Thus, in the organic compound shown above the two triplets appear at τ 6.60 and 6.30, respectively,[14] whereas in VI they appear at 5.62 and 6.32. In V the α protons appear as a singlet at τ 5.68 (in D_2O). In nonaqueous media, when protons attached to N cannot exchange with solvent protons, they split this singlet into a doublet centered at τ 5.88 in DMSO-d_6 and themselves show up as a broad quintet at τ 3.42. On the other side of the C=O, the C_2H_5 in IV yields the expected quartet and triplet at τ 5.28 and 8.23, respectively. This can be compared with the corresponding set of peaks in EtOAc, for example, which show up at τ 5.88 and 8.75.[14]

The ir spectrum of VII resembles very closely that of $B_{10}H_9NH_2COC_6H_5^-$ made from $B_{10}H_{10}^{2-}$ and PhCN,[13] but the melting point of the latter was higher, 232–233° as against our 218–219°. The difference appears greater than one could attribute to impurities on the basis of the elemental analysis, hence, it is very likely that the material made by Muetterties, *et al.*,[13] is a different isomer. Our material, of course, is the 2-amido

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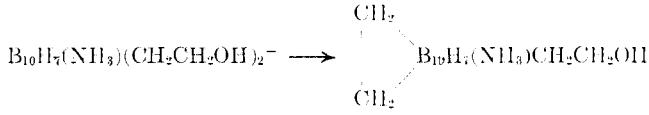
derivative, *and* hence the direct addition of PhCN to $B_{10}H_{10}^{2-}$ probably gives the apically substituted amide. This would be consistent with the observation that MeCN definitely adds at the apex.[13]

Biological Results and Discussion.—The results for the two anions $B_{10}H_9NH(CH_2CH_2OH)_2^-$ and $B_{10}H_7NH_3(CH_2CH_2OH)_2^-$ are strikingly dissimilar. Whereas the former shows little if any boron accumulation in tumor, brain, muscle, and blood of C_3H mice bearing a subcutaneously transplanted ependymoblastoma,[15] the latter and its derivatives are incorporated to a marked extent, with tumor–blood boron ratios ranging from 2.1 to 13.3. This is entirely comparable to results observed with the $B_{12}H_{11}SH^{2-}$ and $B_{10}Cl_8(SH)_2^{2-}$ which have appeared to be of potential use in neutron capture therapy.[7]

It is highly probable that the reason for the incorporation of this promising new class of boron hydride anions is based upon the alkylating properties of the β-hydroxyethyl group on the boron cage. This must be the case since $B_{10}H_9NH_3^-$ itself shows no evidence of such selective binding. Alkylation by such an alcoholic function was wholly unexpected. However, on closer examination, the hydroxyl in such a position next to a potent nucleophile may be susceptible to an elimination reaction by reason of a neighboring-group mechanism generating a reactive species of the following structure. This internally compensated neutral moiety



may then be capable of alkylating both proteins and nucleic acids and in this manner may become incorporated into tumor. This postulation is speculative but is supported by the biological data obtained to date. Further work is needed to elucidate the precise mechanism of the reaction which is occurring.

Experimental Section

Preparation of $H_3NB_{10}H_7(CH_2CH_2OH)_2^-$.—Ethylene oxide was bubbled for 6 hr through a vigorously stirred solution (3 g in 75 ml) of $[(CH_3)_4N]B_{10}H_9NH_3$ in 20% aqueous AcOH. The solution changed from colorless to brown. After the addition of ethylene oxide was discontinued the reaction mixture was stirred for 12 hr and filtered and the filtrate was concentrated in a rotary evaporator to a syrupy residue, which when stirred with 100 ml of EtOH yielded a finely divided tan solid. The solid was removed by filtration, washed several times with absolute EtOH and Et_2O, dissolved in H_2O, and reprecipitated from a concentrated aqueous solution by the addition of EtOH. After it was redissolved in H_2O and reprecipitated for a second time, washed with absolute EtOH, and dried (P_2O_5), it weighed 1.6 g (a yield of 37.5%): ir spectrum, prominent bands at 3500, 3225, 2980, 2870, 2470, 1600, 1470, 1410, 1145, 1045, and 945 cm^{-1}; pmr spectrum in D_2O, singlet at τ 6.35 and two triplets (J = 7 cps) at 5.95 and 8.37, with an area ratio of 3:1:1. In several solvents the low-field triplet splits into a quintet with J = 3–4 cps.

Anal. Calcd for $[(CH_3)_4N]B_{10}H_7NH_3(CH_2CH_2OH)_2$: C, 32.4; H, 10.9; N, 9.45; B, 36.5; mol wt, 296. Found: C, 32.6; H, 10.3; N, 9.61; B, 36.4; mol wt, 285.

The $(CH_3)_4N^+$ salt was converted into H_3O^+, Na^+, and K^+ salts by passage through appropriate cation-exchange resins. Solution of the free acid was evaporated to near dryness at room temperature and left over P_2O_5 *in vacuo* for 4 days. Titration of the solid residue with KOH gave equiv wt 247 (calcd for $[H_3O]B_{10}H_7(CH_2CH_2OH)_2$, 240). Both the Na^+ and K^+ salts were very hygroscopic.

Anal. Calcd for $KB_{10}H_7NH_3(CH_2CH_2OH)_2 \cdot H_2O$: C, 17.1; H, 7.85; N, 5.06; B, 38.8. Found: C, 16.9; H, 7.09; N, 4.70; B, 38.7.

Phosphorylation of $H_3NB_{10}H_7(CH_2CH_2OH)_2^-$.—A 3.5-g (12 mmoles) sample of the bis-β-hydroxyethyl derivative was refluxed for 12 hr in 120 ml of $POCl_3$. The reaction mixture was filtered, the unreacted $POCl_3$ was removed in a rotary evaporator, and the gummy brown residue was stirred with dry Me_2CO. The Me_2CO solution was filtered, the filtrate was evaporated to dryness under reduced pressure, and the residue was dissolved in 50% EtOH. At this stage a considerable amount of HCl was liberated in solution. The solution was filtered and evaporated to dryness under reduced pressure and the residue was dissolved in 95% EtOH. Addition of Et_2O to the alcoholic solution yielded a tan precipitate which was removed by filtration, washed with absolute EtOH and Et_2O, and dried over P_2O_5 *in vacuo*. The product, $[(CH_3)_4N]B_{10}H_7NH_3(CH_2CH_2OPO_3H_2)_2$, is very hygroscopic. The yield was 2.6 g (45%).

Anal. Calcd for $[(CH_3)_4N]B_{10}H_7NH_3(CH_2CH_2OPO_3H_2)_2$: C, 21.0; H, 7.51; N, 6.14; B, 23.7; P, 13.6; mol wt, 456. Found: C, 21.1; H, 7.55; N, 5.82; B, 23.0; P, 13.2; mol wt, 465.

The ir spectrum of the diphosphate ester resembled that of the parent dialcohol, except for the presence of two very broad bands in the region around 3000 and 1000–1200 cm^{-1}. Pmr spectrum in D_2O contained two triplets (J = 7 cps) at τ 5.50 and 8.31, respectively. Aqueous solutions of the salt were weakly acidic and could be titrated with strong bases. The pH at the 0.5 and 1.5 equivalent points was 5.1 and 9.3, respectively. Passage of the salt through a cation-exchange resin in the H_3O^+ form yielded a solution which was concentrated to a syrupy residue by evaporation under reduced pressure at room temperature, and the residue was dried (P_2O_5) *in vacuo* to constant weight. Titration of this material with NaOH yielded equiv wt 201 (calcd for $[H_3O]H_3NB_{10}H_7(CH_2CH_2OPO_3H_2)_2$, 200). The pmr spectrum of the free acid in H_2O looked similar to that of the various salts except that the two triplets were shifted downfield by 10 and 3 cps, respectively.

Acetylation of $H_3NB_{10}H_7(CH_2CH_2OH)_2^-$.—A solution containing 0.53 g (1.8 mmoles) of $[(CH_3)_4N]B_{10}H_7NH_3(CH_2CH_2OH)_2$ and 5 ml of AcCl in 30 ml of MeCN was refluxed for 30 min and stirred at room temperature for 4 hr. The reaction mixture was filtered and the filtrate was treated with Et_2O. The resulting brown precipitate was washed repeatedly with H_2O until the ir spectra of the water-insoluble portion became unaffected by additional washings. The aqueous washings contained the starting material and its acetate ester, identified by a prominent C=O band at 1730 cm^{-1} and the characteristic C–O– band at 1240 cm^{-1}. The water-insoluble product after recrystallization from H_2O–MeCN weighed 0.3909 g. Its ir spectrum differed from that of the water-soluble component by the *absence* of bands characteristic of the Me_4N^+ cation (1485 and 950 cm^{-1}) and the presence of an additional, acetamide-type, CO band at 1650 cm^{-1}.

Anal. Calcd for $H_3NB_{10}H_6(NH_2COCH_3)(CH_2CH_2OCOCH_3)_2$: C, 32.9; H, 7.69; N, 7.69; B, 29.7. Found: C, 32.4; H, 7.45; N, 7.46; B, 30.2.

Oxidation and Halogenation of $H_3NB_{10}H_7(CH_2CH_2OH)_2^-$.—Attempts to convert the dialcohol to either the corresponding aldehyde or acid were unsuccessful. Even at 0° the compound reacts very vigorously with acidic or neutral $Cr_2O_7^{2-}$. The reaction is accompanied by the evolution of H_2 and yields H_3BO_3 as the only B-containing product. Oxidation with MnO_4^- gave similar results. Both aqueous Br_2 and Cl_2 instead of halogenating the cage decompose it to H_3BO_3 at 0° and higher temperatures.

Preparation of $[(CH_3)_4N]B_{10}H_9NH(CH_2COOC_2H_5)_2$.—A solution of $[(CH_3)_4N]B_{10}H_9NH_3$ (2.08 g, 10 mmoles) in 15 ml of dry DMF was added dropwise with stirring to a cooled (10°) slurry of NaH in mineral oil (0.95 g of a 50% dispersion). After all the amine was added the slurry was stirred until the evolution of H_2 ceased. About 9 mmoles of H_2 were liberated. The reaction mixture was cooled to 0° and 2.46 g (20 mmoles) of $ClCH_2CO_2C_2H_5$ was added to it dropwise. The mixture was stirred for 2 hr, allowed to warm to room temperature, and filtered. The precipitate consisted almost exclusively of NaCl. Treatment of the filtrate with anhydrous Et_2O yielded a gummy brown precipitate which was removed by filtration and redissolved (H_2O). After the brown aqueous solution was decolorized with activated charcoal

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it was first concentrated to near saturation under reduced pressure, then permitted to evaporate slowly at room temperature. The evaporation yielded a white crystalline solid, mp 196–198°. After recrystallization (H_2O) 1.60 g (4.3 mmoles, 43%) of $[(CH_3)_4N]B_{10}H_9NH(CH_2COOC_2H_5)_2$, mp 197–198°, was obtained. The yield can be increased to about 70% by repeatedly concentrating the Et_2O–DMF filtrate to progressively smaller volumes and precipitating the product by the addition of Et_2O after each volume reduction; ir spectrum, strong C=O band at 1745 cm^{-1}; pmr spectrum in D_2O, quartet (J = 7 cps) at τ 5.28, singlet at 5.68, another singlet at 6.35, and triplet (J = 7 cps) at 8.23, area ratio 2:2:6:3; pmr spectrum in DMSO-d_6, broad quintet (J = 4.5 cps) at τ 3.42, a quartet at 5.48, a doublet (J = 4.5 cps) at 5.88, a singlet at 6.49, and a triplet at 8.40.

Anal. Calcd for $[(CH_3)_4N]B_{10}H_9NH(CH_2COOC_2H_5)_2$: C, 37.9; H, 9.97; N, 7.37; B, 28.4; mol wt, 380. Found: C, 38.0; H, 9.63; N, 7.15; B, 28.6; mol wt, 376.

Preparation of $B_{10}H_9NH(CH_2CH_2OH)_2^-$.—To a solution of $[(CH_3)_4N]B_{10}H_9NH(CH_2COOC_2H_5)_2$ in dry diglyme (0.75 g, 2 mmoles, in 20 ml) about 7 mmoles of $LiBH_4$ was added and the mixture was heated with stirring for 5 hr at 95–100°, then stirred for 12 hr at room temperature. The reaction mixture was acidified with 25% aqueous AcOH until the evolution of H_2 ceased and the resulting clear solution was washed with several 50-ml aliquots of Et_2O. The aqueous layer was passed through a cation-exchange resin in the H_3O^+ form and concentrated in a rotary evaporator. Addition of a saturated solution of TlF precipitated a white solid which was separated by filtration and washed with ice-cold H_2O. Recrystallization (H_2O) yielded 0.703 g (83%) of $TlB_{10}H_9NH(CH_2CH_2OH)_2$: mp 100–102°; ir spectrum, bands at 3570, 3448, 3226, 3058, 2475, 1613, 1470, 1453, 1430, 1070, 1045, 1013, 971, 905, 850, and 815 cm^{-1}. The salt is insoluble in EtOH and Me_2CO but dissolves readily in DMSO and hot H_2O.

Anal. Calcd for $TlB_{10}H_9NH(CH_2CH_2O\mathbf{H})_2 \cdot H_2O$: C, 10.8; H, 4.94; N, 3.14; B, 24.2; Tl, 45.9. Found: C, 10.7; H, 4.96; N, 3.53; B, 24.6; Tl, 45.8.

The Tl^+ salt was dissolved in a large volume of H_2O and passed through a cation-exchange resin in the Na^+ form. The solution was evaporated to dryness and dissolved in D_2O; pmr spectrum of the Na^+ salt, two triplets (J = 5 cps) of equal area at τ 5.62 and 6.32, respectively; equiv wt of the salt, 250 (calcd for $NaB_{10}H_9NH(CH_2CH_2OH)_2$, 245).

Benzoylation of $B_{10}H_9NH_3^-$.—A solution of $[(CH_3)_4N]B_{10}H_9NH_3$ (3.5 g, 17 mmoles) and C_6H_5COCl (18 g, 128 mmoles) in 200 ml of 10% NaOH was stirred for 24 hr at room temperature. The reaction mixture was concentrated to 100 ml under reduced pressure, treated with 3 l. of Me_2CO to precipitate $C_6H_5CO_2Na$, and filtered. The filtrate was concentrated under reduced pressure to near dryness and treated with 100 ml of H_2O. The resulting suspension was cleared by extracting the suspended solid with five 50-ml aliquots of Et_2O. Acidification of the clear aqueous solution with HCl to pH 2 precipitated a solid which was redissolved in MeCN. Addition of Et_2O to the MeCN solution yielded a mixture of brown and white solids. The brown solid was washed out with a small amount of cold MeCN, and the remaining white solid dissolved in Me_2CO. Addition of Et_2O to the Me_2CO solution yielded $[(CH_3)_4N]B_{10}H_9NH_2COC_6H_5$, mp 218–219°. The yield after recrystallization from Et_2O–MeCN was 0.9 g (17%); ir spectrum, bands attributable to the phenyl ring, the cation, and the boron cage, and a very strong amidic carbonyl peak at 1640 cm^{-1}.

Anal. Calcd for $[(CH_3)_4N]B_{10}HN_9H_2COC_6H_5$: C, 42.3; H, 9.0; N, 8.9; B 34.6. Found C, 41.9; H, 8.6; N, 9.2; B, 33.2.

Reagents, Apparatus, and Techniques.—Except for $B_{10}H_9NH_3^-$, which was made by the reaction of $B_{10}H_{10}^{2-}$ with hydroxylamine-O-sulfonic acid,[9] commercially available reagent grade chemicals were used throughout this work. In the case of diglyme only the fraction boiling at 161–162° at 740 mm was collected after 3 hr of reflux over $LiAlH_4$. DMF was distilled over CaH_2, whereas MeCN was distilled over P_2O_5.

The ir spectra were recorded in KBr pellets or Nujol mulls on a Perkin-Elmer Model 337 spectrometer, the pmr spectra on a Varian DA-60 spectrometer at 60 Mc (TMS). Molecular weights of salts which had no additional ionizable H were obtained by exchanging the cation in a weighed sample of a salt for H_3O^+ and titrating the resulting acid with KOH. The titration was monitored with a Leeds and Northrup pH meter. Elemental analyses were performed at commercial laboratories.

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