Synthesis of Asymmetric Boron Cations and Resolution with $As(C_6H_4O_2)_3^-$ Anion

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Abstract: Boron cations in which trimethylamine and 4-methylpyridine are coordinated to BH_2^+, $BHCl^+$, and $BHBr^+$ have been synthesized in high yield, a number of salts have been prepared and characterized, and the interconversion of salts has been described. The halogenation of the boron–hydrogen bond in these cations is compared to other halogenations and a mechanism not involving free radicals is suggested. Resolution into pure *levo* isomers of the two asymmetric cations and into impure *dextro* isomers was accomplished with the *levo* complex anion of arsenic(V) with catechol. The optically active boron salts are the first examples of resolved simple asymmetric boron species. The cations are optically stable at room temperature and in acid, but are decomposed by base. The synthesis of the optically active resolving agent, $KAs(C_6H_4O_2)_3$, was substantially improved to give an anion of high optical purity.

In an earlier communication the partial resolution by the Pasteur method of an optically active boron cation, 4-methylpyridinetrimethylaminechlorohydroboron(1+), in the form of the hexafluorophosphate salt was described.[1] We now wish to report the synthesis of derivatives of this type of ion and their resolution into optical isomers by chemical means. These compounds represent the first pure optically active boron cations, and the first examples of stable optically active compounds with boron as the asymmetric center. Previously, only chelated boron-containing anions with salicylic acid[2] or catechol[3] had been partially resolved in the form of strychnine salts, but proved to be labile toward racemization by traces of water.

Experimental Section

Materials. Trimethylamine borane was used as supplied by Callery Chemical Company. All other materials were reagent grade. Solvents were dried over molecular sieves, although this was found not to be necessary except in the iodination of the borane, where moisture leads to hydrolysis of the intermediate.

Preparation of BH_2^+ Cation. Iodide. Trimethylamine borane (32.37 g, 0.444 mol) was dissolved in 450 ml of dry benzene in a conical flask. Solid iodine (51.25 g, 0.202 mol) was added in portions to the stirred solution over a 10-min period. On each addition, immediate exothermic reaction resulted with evolution of a nonacidic combustible gas (hydrogen). After 30 min of standing, with the solution protected from the atmosphere by a stream of nitrogen, 200 ml of benzene was added and 94 ml (90 g, 0.97 mol) of 4-methylpyridine, freshly distilled from calcium hydride, was added. Precipitation of a white solid started immediately and was finished after 1 hr standing in the refrigerator. After filtration and washing with benzene and diethyl ether (two 100-ml portions each) and drying overnight in a vacuum desiccator, the product weighed 115 g. This corresponds to a yield of 97% based on the equations

$$2(CH_3)_3NBH_3 + I_2 \longrightarrow 2(CH_3)_3NBH_2I + H_2$$

$$(CH_3)_3NBH_2I + H_3CC_5H_4N \longrightarrow [(CH_3)_3NBH_2CH_3C_5H_4N]^+, I^-$$

Anal. Calcd for $C_9H_{18}BIN_2$: I, 43.46. Found: I, 43.51. The compound started to melt with decomposition at 154°. It is soluble in water, methanol, acetone, and methylene chloride, and can be recovered in nearly quantitative yield from the latter solvent by addition of ether.

Hexafluorophosphate. To a warm solution of 8.70 g of the iodide (29.8 mmol) in 50 ml of water was slowly added 11.8 g (excess) of NH_4PF_6 in 75 ml of water. The hexafluorophosphate salt precipitated immediately, yield 8.59 g, 27.7 mmol, 93%, after washing with 50 ml of water, mp 145–146°. Recrystallization from a minimum of hot water gave nearly quantitative recovery of pure product, mp 146.5–147.0°. *Anal.* Calcd for $C_9H_{18}BF_6N_2P$: C, 34.87; H, 5.85; B, 3.49; F, 36.77; N, 9.04; P, 9.99. Found: C, 34.92; H, 5.96; B, 3.39; F, 36.56; N, 8.92; P, 9.80. The compound is soluble in chloroform, acetone, and methylene chloride.

Hexafluoroarsenate. In a procedure similar to the above, 1.08 mmol of the iodide in 10 ml of water was converted to the AsF_6^- derivative with $KAsF_6$. The yield of pure product recrystallized from 50 ml of water was 52%, mp 134.5–135°. *Anal.* Calcd for $C_9H_{18}BF_6N_2P$: C, 30.43; H, 5.13; N, 7.91. Found: C, 30.70; H, 4.96; N, 7.84.

Triiodomercurate. This salt was precipitated on addition of a solution of $HgCl_2$ in excess of KI to a boiling 0.2 *M* solution of the boronium iodide. The washed precipitate was recrystallized in long needles by slow cooling of a solution in the minimum quantity of 1:1 acetone–water, mp 149.5–150°. *Anal.* Calcd for $C_9H_{18}BHgI_3N_2$: C, 14.58; H, 2.43. Found: C, 14.80; H, 2.45. On boiling in water for several hours the compound dissolves completely with formation of metallic mercury and destruction of the cation.

A sample of the compound (0.1365 g) in 5 ml of 1:1 water–acetone was left for 1 day in contact with 0.15 g of aluminum foil. After dissolution of excess aluminum with sulfuric acid, the metallic mercury produced was weighed (0.0364 g, calcd 0.0366 g).

Chlorination of Iodide. Chlorine was slowly bubbled (3 to 5 cc/min) for 1 hr through a solution of 21.26 g of iodide salt (72.8 mmol) in 200 ml of methylene chloride while the solution was stirred in a tared round-bottomed flask immersed in an ice bath. The solvent was neutral to litmus at the end of reaction. On evaporation of the solvent at reduced pressure, there was produced a lemon yellow solid, 26.35 g, mp 118–120°. The weight expected on the assumption that only iodide was chlorinated to ICl_2^-, and no chlorination had occurred on boron, is 26.42 g. *Anal.* Calcd for $C_9H_{18}BCl_2IN_2$: C, 29.79; H, 5.00; Cl, 19.54; I, 34.97. Found: C, 29.61; H, 4.90; Cl, 19.28; I, 35.07.

The ^{11}B nmr spectrum showed a triplet at 15.8 ± 0.5 ppm indicating the presence of an intact BH_2 group. On heating in dry nitrogen the compound decomposed to give HCl instead of HI (acidic gas, no iodide, precipitate with $AgNO_3$). The compound was insoluble in water, but dissolved in acetone with formation of HCl. If chlorination was prolonged or carried out at room temperature, boron-hydrogen bonds were also chlorinated, as evidence by formation of HCl and changes in the infrared and nmr spectra consistent with the formation of a monochlorinated boron cation.

Tribromide. To an ice-cold solution of 3.105 g of $[(CH_3)_3NBH_2CH_3C_5H_4N]^+PF_6^-$ in 550 ml of water was added dropwise and with vigorous stirring 20 ml of an aqueous solution 1 *M* in Br_2

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(1) G. E. Ryschkewitsch and J. M. Garrett, *J. Am. Chem. Soc.*, **89**, 4240 (1967).

(2) J. Meulenhoff, *Z. Anorg. Allgem. Chem.*, 142, 373 (1925).

(3) J. Boeseken and J. A. Mijs, *Rec. Trav. Chim.*, **44**, 758 (1925).

and 2 M in NH_4Br. There formed a fine crystalline yellow precipitate which on washing and drying weighed 3.583 g (88.5% yield based on Br_3^- salt). The ^{11}B nmr showed a triplet at 16.4 ± 0.5 ppm, mp 117–118°. *Anal.* Calcd for $C_9H_{18}BBr_3N_2$: C, 26.70; H, 4.48; Br, 59.22. Found: C, 26.76; H, 4.40; Br, 59.26.

On heating 1.00 mmol of the solid on the vacuum line to 125°, the dark orange melt decolorized within 10 min and produced only 0.10 mmol of gas, identified as HBr by titration and test with Ag^+, and a white solid which partially sublimed. No further changes occurred on heating for 30 min. The remaining solid dissolved only partially in cold water and reacted with hydrogen evolution in hot water. With excess NH_4PF_6 only a small amount (0.037 g) of salt was isolated, mp 112–120°, decreased ir absorption at 1200 cm^{-1}, low intensity B–H stretch. The product apparently contained brominated cation and starting material. The water-insoluble tribromide was easily converted to the soluble bromide by warming 0.408 g (1.00 mmol) with 2.00 mmol of $Na_2S_2O_5$ in 10 ml of H_2O. The tribromide dissolved rapidly. On adding excess NH_4PF_6, 0.265 g of pure hexafluorophosphate of the BH_2 cation was isolated, mp 145–146°, 85% yield.

Preparation of $BHCl^+$ Cation. Chlorination of Hexafluorophosphate of BH_2^+ Ion. Into a solution of 3.256 g (10.50 mmol) of BH_2^+–PF_6^- salt at room temperature was bubbled excess gaseous chlorine for 30 min. On immediate evaporation at reduced pressure, 3.659 g of dry product was isolated (calcd for monochlorination, 3.618 g). The yield of the chlorinated salt was the same when the reaction was carried out in completed arkness. Recrystallization by addition of enough tetrahydrofuran and diethyl ether (1:1) to a warm solution of the salt in methylene chloride to just start precipitation,[4] followed by slow cooling in the refrigerator, yielded 3.539 g (97.8%) of pure $BHCl^+$ salt, mp 119.8–120.3°. Recrystallization from 125 ml of hot water by quick cooling gave 83% recovery. *Anal.* Calcd for $C_9H_{17}BClF_6N_2P$: C, 31.38; H, 4.97; B, 3.14; Cl, 10.29; F, 33.90; N, 8.13. Found: C, 31.52; H, 5.02; B, 3.06; Cl, 10.44; F, 33.30; N, 8.15.

When substantially longer reaction periods were used, or when the reaction mixture was not worked up immediately, the nmr spectrum indicated the presence of an impurity, presumably the dichlorination product.

Derivatives. The tribromide salt was prepared in 50% yield as described for the BH_2^+ compound, crude mp 118–121°; recrystallized by slow evaporation of a solution in 3:1 methylene chloride–petroleum ether (bp 30–60°), fine yellow needles, mp 121–121.5°. *Anal.* Calcd for $C_9H_{17}BBr_3ClN_2$: C, 24.61; H, 3.90; Br, 54.58; N, 6.38. Found: C, 24.80; H, 3.95; Br, 54.40; N, 6.49.

After conversion to the water-soluble bromide with $Na_2S_2O_5$, a picrate was precipitated with saturated $NH_4C_6H_2(NO_3)_3O$ as yellow needles, mp 124–125°. Another portion of the solution was converted to the hexafluoroarsenate, which, after recrystallization from boiling water, melted at 95–97°. *Anal.* Calcd for $C_6H_{17}AsBClF_6N_2$: C, 27.83; H, 4.41; B, 2.78; Cl, 9.13. Found: C, 28.08; H, 4.58; B, 2.95; Cl, 8.93.

Preparation of $BHBr^+$ Ion. The BH_2–PF_6 salt (44.5 mmol) was dissolved in 25 ml of methylene chloride (nearly saturated) and 6 ml of bromine (threefold excess) was added in portions within 10 min. After the first milliliter had been added, vigorous reaction started with evolution of hydrogen bromide. After 14 hr at room temperature, excess solvent and bromine was pumped off with a water aspirator while the flask was warmed to 45°. To the brown cake there was added in portions 85 mmol of $Na_2S_2O_5$ in 70 ml of water while the mixture was warmed to 70°. After all the bromine color had been discharged (30 min) and the mixture had cooled, 45 ml of 1 M NH_4PF_6 was added,[5] and the filtered product was recrystallized from 600 ml of boiling water, yield 14.11 g (81%), mp 143–145°. A second recrystallization of 1 g from 30 ml of water gave 87% recovery, mp 143–144°. *Anal.* Calcd for $C_9H_{17}BrBF_6N_2P$: C, 27.79; H, 4.41; B, 2.78; Br, 20.54; N, 7.20. Found: C, 27.53; H, 4.25; B, 2.91; Br, 20.64; N, 7.15.

Bromination was also carried out in hot water (30 ml, 7.5 mmol of BH_2 salt), driving off excess halogen by boiling. On cooling a 58% yield of monobrominated hexafluorophosphate was obtained. The filtrate yielded an additional 11% tribromide salt when 0.5 ml of Br_2 was added to the cold solution, mp 129–130° dec. *Anal.* Calcd for $C_9H_{17}BBr_4N_2$: C, 22.35; H, 3.54; Br, 66.08. Found: C, 22.50; H, 3.44; Br, 66.20.

The AsF_6^- salt was obtained in 53% yield of recrystallized product from the PF_6^- salt by conversion to tribromide, disulfite treatment, and precipitation with $KAsF_6$, mp 115.5–117.5°. *Anal.* Calcd for $C_9H_{17}AsBBrF_6N_2$: C, 24.97; H, 3.96; B, 2.50; N, 6.47. Found: C, 25.26; H, 3.89; B, 2.80; N, 6.50.

Addition of a solution of HgI_2 in excess KI to a hot solution of the PF_6^- salt precipitated the triiodomercurate. The light yellow salt was recrystallized by slow evaporation of a hot saturated solution in acetone–water, mp 118.5–120°. *Anal.* Calcd for $C_9H_{17}BBrHgI_3N_2$: C, 13.09; H, 2.08. Found: C, 13.13; H, 1.99.

Complex of Catechol and Arsenic(V), Potassium Salt. The optically active salt was prepared by a modification of the procedure of Rosenheim and Plato.[6] Since our synthesis gave higher yields and substantially higher optical purity, we report it here. The racemic acid of the catechol complex, $H[As(C_6H_4O_2)_3]\cdot H_2O$, was made in 87% yield by adding 1.00 mol of catechol to a boiling solution of 0.167 mol as As_2O_5 in 100 ml of water. The monohydrate was obtained after the cooled solution was seeded and the crystalline precipitate was dehydrated over $CaCl_2$ *in vacuo*.[7] To a saturated solution of cinchonine (0.116 mol) in boiling ethanol (1400 ml) was added 0.116 mol of the racemic arsenic complex; this resulted in the precipitation of the cinchonine salt of the acid. Three crops of crystals were collected: the initial precipitate (25.48 g), a second precipitate after concentration to 950 ml over 1.5 hr boiling (26.04 g), and a third after concentration to 500 ml (6.84 g). The specific rotations were $[\alpha]^{25}\mathrm{D}$ -258.2, -255.2, and $-264.0°$, respectively (lit.[6] $-253.5°$), total yield 71%. The cinchonine salt (26.21 g, 36.8 mmol) and 40 mmol of KOH in 325 ml of water were heated with vigorous mechanical stirring for 3 hr and the resulting cinchonine was filtered off hot. The filtrate and washings (three 50-ml portions of boiling water) yielded, after concentration to 80 ml and cooling, 11.70 g of pure dry potassium salt, $KAs(C_6H_4O_2)_3$ (72.6% yield). Nitrogen was blown over the solutions during these operations in order to avoid excessive darkening by oxidation. After drying under vacuum over H_2SO_4, the specific rotation was $[\alpha]^{25}\mathrm{D}$ $-580.9°$ (lit.[6] $-459.9°$). Other preparations yielded specific rotations up to $-583°$. A solution of the salt in 5 ml of acetone lost all rotation immediately after addition of one drop of concentrated HCl.[8] *Anal.* Calcd for $KAs(C_6H_4O_2)_3\cdot H_2O$: C, 47.37; H, 3.09. Calcd for $KAs(C_6H_4O_2)$: C, 49.32; H, 2.76. Found: C, 48.74; H, 2.66.

Resolution of Boron Cations. Chloro Derivative. The hexafluorophosphate (30.0 mmol) was converted to the tribromide by precipitation of a dilute, warm solution with excess aqueous NH_4Br–Br_2 and the moist crystals were converted to bromide by reaction at room temperature with 1-hexene (10 ml) in 75 ml of methylene chloride. After evaporation of excess olefin and solvent, the salt was dissolved in 125 ml of water and 4.73 g of optically pure potassium salt of *l*-As(cat)$_3^-$ (10.5 mmol) was added in small portions to the boiling, well-stirred solution. The precipitated complex arsenate salt was converted to the partially resolved hexafluorophosphate in the following way. The salt (1.2 mmol) was mixed with 6 ml of concentrated HCl, 6 ml of water, and 1 ml of methanol, and H_2S was bubbled through the heated mixture for 25 min. The cooled mixture was neutralized with excess $CaCO_3$ and filtered. Addition of excess NH_4PF_6 gave 82% yield of the hexafluorophosphate of the boron cation.[9] A recrystallized sample had an infrared spectrum identical with that of an authentic sample and a specific rotation $[\alpha]^{25}\mathrm{D}$ $-23.3°$.

In a similar experiment, 40 mmol of boron cation in 200 ml of water and 50 ml of acetone was mixed with 10.9 mmol of arsenic complex and precipitated slowly by evaporating the acetone in a stream of nitrogen. The solid (6.38 g) had a specific rotation $[\alpha]^{25}\mathrm{D}$ $-450°$ in acetone which was immediately decreased to $[\alpha]^{25}\mathrm{D}$ $-19.0°$ when a drop of concentrated HCl was added, yield 94%, mp 208–210°. *Anal.* Calcd for $C_9H_{17}BClAs(C_6H_4O_2)_3$: C, 54.16; H, 4.88; N, 4.68. Found: C, 54.49; H, 5.00; N, 4.69.

From the filtrate was isolated a total of 17.4 mmol of PF_6^- salt, 14.4 mmol by NH_4PF_6 precipitation and an additional 3.0 mmol *via* the Br_3^- salt recovered from the filtrate. Both hexafluorophosphate fractions had identical rotations, $[\alpha]\mathrm{D}$ $+19.8°$.

The arsenate salt was partially crystallized into five fractions from warm 3:1 acetone–water by slow evaporation of the acetone, with an over-all recovery of 94%. The weight per cents, $[\alpha]\mathrm{D}$ in pure acetone, and $[\alpha]\mathrm{D}$ in acidified acetone, respectively, were as follows:

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(4) The salt oils out if too much ether is added.

(5) If this step was omitted, the yield was reduced sharply.

(6) A. Rosenheim and W. Plato, *Chem. Ber.*, **58**, 2000 (1925).

(7) R. F. Weinland and J. Heinzler, *ibid.*, **52**, 1316 (1919).

(8) J. H. Craddock and M. M. Jones, *J. Am. Chem. Soc.*, **83**, 2839 (1961), report rapid loss of optical activity in aqueous acid.

(9) Yields in this step were not reproducible and ranged from 30 to 92%.

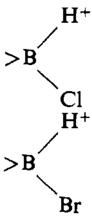
(1) 50%, −458°, −22.9°; (2) 25%, −456°, −23.0°; (3) 15%, −444°, −19.6°; (4) 2%, −431°, −10.7°; (5) 2%, −405°, +4.3°. A second similar fractional recrystallization of the first fraction produced no further increase in rotation (four fractions): (1) 12%, −452°, −23.0°; (2) 40%, −458°, −22.8°; (3) 34%, −451°, −22.0°; (4) 3%, −454°, −21.8°. Conversion to the hexafluorophosphate as above yielded a 27% yield of pure *levo*-boron cation, $[\alpha]_D$ −41.2°, identical in infrared and proton magnetic resonance spectrum with the racemic salt; the melting point of the optically active salt, 126.0–126.5°, was, however, higher than in the racemate.

Bromo Derivative. The racemic arsenate salt was prepared from the boronium tribromide by conversion of the latter salt to bromide with acetone, followed by precipitation with optically active $KAs(C_6H_4O_2)_3$ from aqueous acetone (97% yield). Under these conditions, the acid liberated in the bromination of acetone racemized the catechol complex completely. Recrystallization by slow evaporation of an aqueous acetone solution gave 79% recovery, mp 215–216° dec. *Anal.* Calcd for $C_9H_{17}BBrN_2As(C_6H_4O_2)_3$: C, 50.42; H, 4.54; N, 4.35. Found: C, 50.87; H, 4.64; N, 4.43.

Optically active compound was obtained as with the chloro derivative: 12.7 mmol of PF_6^- salt was converted to bromide and precipitated slowly from aqueous acetone with 4.75 mmol of *l*-$KAs(C_6H_4O_2)_3$. The filtrate yielded eventually 3.4 mmol of recrystallized incompletely resolved PF_6^- salt, $[\alpha]^{25}_D$ +35.1°, mp 141–143°, while the precipitate, dissolved in acidified acetone, had a specific rotation $[\alpha]^{25}_D$ −27.5°. Partial recrystallization from acetone–water gave four fractions whose weight per cent of starting material and specific rotations in pure and acidified acetone were as follows: 1.36%, −437°, −36.5°; 2.25%, −437°, −36.6°; 3.19%, −436°, −36.1°; 4.13%, −249°, +10.9°. A second recrystallization of the first three fractions with 89% recovery gave a small decrease in specific rotations (−437 and −35.8°). The hexafluorophosphate salt derived by destruction of the arsenate complex with acid and hydrogen sulfide had a specific rotation $[\alpha]_D$ −60.9 and was identical in infrared and proton magnetic resonance spectrum to the racemic salt, but melted at 136–137°.

Physical Properties. Measurements of optical rotation were made on 0.025 *M* solutions in acetone at 25° and at several wavelengths with a Perkin-Elmer Model 141 polarimeter with digital read-out. Specific rotations are based on measurements in 10-cm cells. Molecular rotations quoted in the discussion were calculated by multiplying the specific rotations by 1% of the formula weight, according to standard practice. The results are given in Table I.

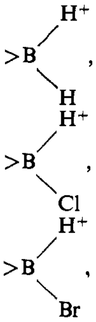
Table I. Specific Rotations of Boron Salts[a]

Compd	Wavelength, mμ 589 Specific rotations, deg	578	546	436	365
 , PF_6^-	−41.2	−42.8	−51.4	−93.6	−171
, PF_6^-	−60.9	−62.7	−73.0	−136	−240

[a] The experimental error is estimated at ± 1%.

Nmr data were obtained for ^{11}B at 19.3 Mc and for ^1H at 60 Mc in methylene chloride solutions. The boron spectra showed the expected multiplicities due to coupling to hydrogen. The proton spectra showed two low-field doublets corresponding to the two kinds of pyridine ring protons and two high-field singlets appropriate for the two different kinds of methyl groups present. Boron-attached hydrogens could not be detected. The integrated intensities were in excellent agreement with the expected values. The chemical shifts in parts per million (ppm) are listed in Table II.

Table II. Chemical Shifts[a] of Boron Salts

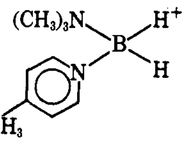
Compd	^{11}B[b] δ	^{11}B[b] J_{B-H}[d]	^1H[c] CH₃-py	^1H[c] N-CH₃	^1H[c] 3-py[e]	^1H[c] 2-py[e]
 , PF_6	15.8[f]	100	2.63	2.67	7.78	8.55
, PF_6^-	9.3	140	2.70	2.78	7.87	8.75
, PF_6^-	14.6	160	2.70	2.84	7.85	8.80

[a] All shifts in parts per million (ppm). [b] *vs.* external methyl borate. [c] *vs.* external tetramethylsilane, δ downfield. [d] Coupling constants, ±10 cps. [e] Doublets; J_{H-H} = 6–7 cps. [f] This resonance was erroneously reported as 17.8 ppm in ref 1.

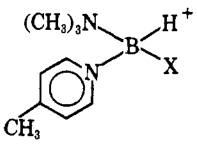
The most characteristic difference in the infrared spectra of the dihydro and the monohalo derivatives was the replacement of the symmetric and antisymmetric BH_2 valence stretch around 2500 cm^{-1} by a single vibration expected for BHX and the disappearance on halogenation of a strong band at 1200 cm^{-1}, which is near the 1160 cm^{-1} band in the bis(pyridine)dihydro cation previously assigned to the BH_2 deformation.[10]

Results and Discussion

The synthesis of two cations with an asymmetric boron center proceeded from the dihydro cation A and resulted in the eventual resolution of two pure optical isomers of the cations B, in the *levo* form. The syntheses were accomplished by the following sequence of steps.

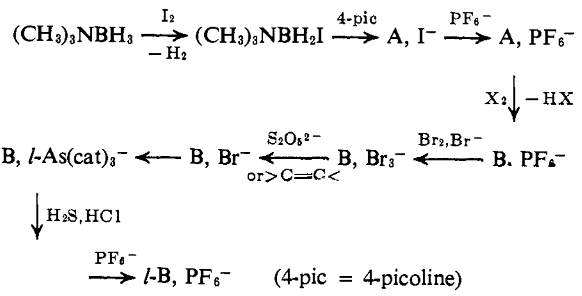


A



B

X = Cl, Br



All reaction steps and intermediate purifications were accomplished in high yield with the exception of the final step, removal of the resolving agent, which, on occasion, gave low recovery of cations.

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(10) G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, **89**, 3145 (1967).

The formation of the fundamental bis(amine) cation structure was easily accomplished by iodide displacement from trimethylamine monoiodoborane with 4-methylpyridine, a reaction which appears to have quite general applicability to other amines and haloboranes.[10–12] As has been pointed out elsewhere,[13] incorporation of a BH_2 group into a cationic structure sharply reduces its otherwise high reactivity toward hydrogen halides and halogens. Hydrogen chloride or hydrogen bromide do not react with the BH_2 cation, even in hot or concentrated solution, whereas the corresponding neutral adducts of BH_3 with trimethylamine[14] or pyridines[15] readily halogenate at the boron atom. The clean synthesis of the intermediate trimethylamine iodoborane also depends on the high reactivity of the neutral borane toward hydrogen iodide. Hydrogen iodide is formed in the direct iodination of the borane, but is completely reacted when an additional mole of the borane is present. Elemental chlorine and bromine do, however, react with BH_2 cation and give monohalo derivatives under relatively mild conditions. Chlorination on boron is nevertheless considerably slower than chlorination of iodide, as is demonstrated by the quantitative production of the ICl_2^- salt of the BH_2 cation. The essentially quantitative conversion of the polyhalides to simple halides with sulfite ion, acetone, or olefins without change in the substituents on boron indicates that the boron species are also substantially less reactive toward halogenation than are the former three reagents. The polyhalide salts prepared here are stable at room temperature indefinitely and halogenate on boron only at elevated temperatures where the cationic structure is no longer maintained. Only a small yield of hydrogen halide and partially halogenated cation was recovered from the pyrolysis of the BH_2 cation; the remainder of the product apparently was ammonium salt and halogenated neutral borane. Resistance toward halogenation is further increased by the introduction of one halogen substituent on boron in place of hydrogen, as evidence by the clean synthesis of monohalo cations, even in the presence of excess halogen: chlorine and bromine apparently deactivate an adjacent boron–hydrogen bond with respect to further reaction. The 4-methylpyridinetrimethylamine cation, however, seems to be chlorinated somewhat more readily than the bis(trimethylamine) cation. The latter ion was treated under drastic conditions and produced only a monochloro derivative,[16] whereas the 4-methylpyridine ion showed evidence of double halogenation on boron when exposure to chlorine was prolonged near room temperature.

It has been implied elsewhere that direct chlorination and bromination proceed *via* a free-radical mechanism.[13] This hypothesis was based on the slowness of the reaction of $[(CH_3)_3N]_2BH_2^+$ at 90°, and a qualitative comparison of this reaction with chlorination by known free-radical sources. The rather facile direct chlorination observed here, at low temperature and in the absence of light, suggests that the BH_2^+ cation might react with halogen by a different mechanism, *e.g.*, *via* electrophilic attack on the B–H bond, in analogy to the reactions of amine boranes.[10,14] Deactivation of the cations with respect to the neutral boranes and deactivation of the remaining B–H bond in the halogenated cations toward further reaction then can be interpreted in terms of inductive electron withdrawal from the B–H bond by substituents which are more electronegative than H^-, *i.e.*, $(CH_3)_3N$ and X^-, respectively. The ^{11}B chemical shifts parallel the reactivity toward halogens and decrease from 26.3 ppm in trimethylamine borane to 15.8 ppm in the BH_2 cation with 4-methylpyridine and further to 14.6 and 9.3 ppm in the $BHBr^+$ and $BHCl^+$ ions, respectively. Insofar as downfield shifts reflect a decrease in the availability of electrons on boron[17] for attack by an electrophilic reagent, this order is consistent with a hydride abstraction mechanism by halogen.

After a number of futile attempts to resolve the asymmetric boron cations with common anionic resolving agents, success was achieved with the anionic catechol complex of arsenic(V).[18] The *l,l* salt is apparently the less soluble diastereoisomer and is preferentially precipitated, especially when crystallization is carried out slowly by making use of the difference in solubility in water (insoluble) and acetone (soluble). Fractional crystallization eventually yielded samples where successive fractions had the same specific rotation, which was invariant on further recrystallization. Since the complex arsenate anion is easily destroyed by acid with loss of optical activity, acidified solutions directly gave the rotations due to the boron cation. The molecular rotations of the cations calculated from the measurements on these solutions were [M]D −139° for the chloro compound, and [M]D −236° for the bromo compound. These values are based on formula weights of 598.8 and 643.2 for the two anhydrous complex arsenate salts, appropriate to the results of the elemental analyses, and on the maximum values of the specific rotations in acidified acetone. The hexafluorophosphate salts derived after destruction of the arsenic complex in boiling acid and hydrogen sulfide gave essentially the same molecular rotations for the cations, −142 and −237° for the chloro and bromo derivative, respectively.

Isoelectronic and isosteric analogs of the boron compounds made here would be quaternary salts of pyridine and the haloneopentyl group, or of trimethylamine and the phenylhalomethyl group. None of these compounds has been resolved. The only reported optically active compound with some structural resemblance to the boron cations is 1-chloro-1-phenylethane, which has a molar rotation [M]D 71°.[19] The analogous bromo derivative, likely to be optically impure, has a reported [M]D ≥35°. It has been unequivocally demonstrated that the above organic halo compounds with like sense of rotation have the same configuration, since they both yield the same optically active alcohol by a demonstrated SN2 pathway.[20] It appears reasonable that the same relation holds for the boron deriva-

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tives, *i.e.*, the two *levo* compounds have the same configuration.

The proof that complete resolution was indeed achieved is supported by the following additional evidence. The rotation due to boron cation in the sample before fractional crystallization and the rotation calculated from the percentage-weighted average for the recovered fractions agree closely. This means that the cations do not racemize during the fractionation process. When the acetone solutions of various fractions of the boron cation–arsenate salt are acidified, the difference in $[\alpha]_D$ values before and after addition of acid is constant for a given cation, −431 and −400° for the chloro and bromo salts, respectively. These values correspond to the specific rotation due to the arsenic complex in the salt and correspond, well within experimental error, to identical molecular rotations for this ion, *i.e.*, −2580 and −2570°. The values also agree very well with the molar rotation of the anhydrous potassium salt of the arsenic complex, $[M]_D$ −2560°, calculated from the observed specific rotation. The constancy of these values implies that the anion was optically stable during fractionation. Finally, it is felt that the purity of the resolving agent was not a limiting factor in the resolution of the anion, since it was synthesized in substantially higher optical purity than previously reported and showed the highest molecular rotation of any compounds of the arsenic(V)–catechol anion reported so far.[6,8,21]

The salts containing optically active boron were stable in the solid state and in solution. For example, the hexafluorophosphate of the chloro derivative did not lose its optical activity on standing in methylene chloride for 8 months. Dissociation has been proposed as the first step in substitution reactions of $[(CH_3)_3N]_2BH_2^+$ by halide ions or amines at higher temperatures.[13] The optical stability of our compounds definitely excludes the possibility of a reversible dissociation of one of the boron substituents at room temperature. The recovery of optically pure salt from boiling HCl implies not only that decomposition of the cation is slow, if it occurs at all under these conditions, but that racemization, *e.g.*, by chloride ion, must be an even slower process. The chloro compound is stable for short periods in pyridine at room temperature, but loses activity rapidly on heating. Both cations react with dilute aqueous hydroxide with complete loss of rotation.

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