Synthesis of Ethynylboron Halides

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Summary Two novel acetylenic organoboranes—ethynyldichloro- and ethynyldifluoro-borane—have been prepared by photochemical and metathetical routes and characterized by i.r., mass spectrometry, and by chemical cleavage.

ALKYNYLBORON HALIDES appear not to have been described previously, although corresponding alkyl, aryl, and alkenyl derivatives are well known, stable compounds.[1] We report the synthesis of two parent compounds of the alkynylboron dihalide series—ethynyldichloro- and ethynyldifluoro-borane. The existence of these compounds as stable, three-co-ordinate boron species is of particular interest in view of the apparent instability of most other ethynylboron compounds which necessitates their isolation in the form of co-ordination complexes.[2,3] The new organoboron halides are, moreover, the first examples of small, highly symmetrical molecules containing a boron atom adjacent to a carbon–carbon triple bond.

Ethynyldichloroborane, HC_2BCl_2, was initially obtained as a minor by-product of the previously described[4] photoisomerization of *cis*-bis(dichloroboryl)ethylene. Subsequently, we obtained useful quantities of the compound by irradiation of refluxing *trans*-2-chlorovinyldichloroborane with a medium-pressure mercury lamp (85% 2537 Å). Vinyldichloroborane, acetylene, boron trichloride, and hydrogen chloride were also observed among the photolysis products. The irradiated mixture was separated into its components by fractionation on a low-temperature Vigreaux column similar to the column described by Spanier.[5] The product, containing a few percent of vinyldichloroborane which could not be removed by this procedure, passed the column at −93°. From the size of the product fraction, we estimated that HC_2BCl_2 was produced at the rate of approximately 0·02 mmole/hr. under our experimental conditions.

Ethynyldifluoroborane, HC_2BF_2, was prepared by treating ethynyltrimethyltin with successive two- to three-fold excess portions of boron trifluoride at reaction temperatures from −80 to −63°. After a total of 5·42 mmole of BF_3 had been exposed to 0·60 mmole of the organotin reagent, fractionation of the mixture yielded 0·07 mmole of HC_2BF_2, passing the low-temperature column at −132°, together with 4·5 mmole of unreacted BF_3 and other, solid reaction products. Efforts to prepare HC_2BCl_2 by a similar procedure have so far been unsuccessful. Reaction of a two-fold excess of boron trichloride with ethynyltrimethyltin in the gas phase, in n-pentane, or in the condensed phase at −80°, gave only dark, intractable residues. Similar results were obtained in the reaction of an excess of boron trichloride with sodium acetylide in pentane, at room temperature.

The i.r. spectra of both compounds showed bands characteristic of monosubstituted acetylenes:[6,7] $\equiv$C–H stretch at 3310 cm.$^{-1}$ in both compounds, C$\equiv$C stretch at 2080 and 2120 cm.$^{-1}$ in the chloride and fluoride, respectively. Both compounds gave bands at 650—725 cm.$^{-1}$ in the general region of $\equiv$C–H bending modes in acetylene and its monosubstituted derivatives. Strong absorptions attributable to boron–halogen stretching modes were observed at 900—100 cm.$^{-1}$ in the chloride and 1300—1450 cm.$^{-1}$ in the fluoride.

The mass spectrum of the two compounds, obtained on a 180° sector, magnetic-deflection instrument (AEI MS-10, with sample inlet system modified in this laboratory) showed parent and all expected fragment peaks with no indication of di- or tri-ethynyl species. For the chloride, the intensity patterns in the diagnostic regions *m/e* 69—77 and 104—113 were analysed in detail using a computer program developed in this laboratory[8] for the interpretation of low-resolution polyisotopic mass spectra. In this treatment, the experimental mass spectrum was analysed by a least-squares fitting procedure as a superposition of the overlapping isotopically determined multiplet patterns of all possible contributing fragment species. At the resolution obtained, contributions of any peak in the observed spectrum to adjacent peaks were negligible. An experimental fragmentation pattern was utilized to take into account contributions from any vinyldichloroborane present as an impurity. In the regions indicated, 98% of the total ion current could be accounted for by the analysis. Application of the fitting procedure to the mass spectrum of the fluoride in the regions *m/e* = 53—58 and 72—77 accounted for 99% of the observed ion current in these regions using the fragments shown in the Table.

Treatment of the chloride with excess of propionic acid at 80° for 16 hr. gave acetylene and hydrogen chloride, identified from their i.r. spectra, together with some ethylene arising from the vinyldichloroborane impurity. Similarly, propionic acid cleavage of the fluoride (115°, 72 hr., borosilicate glass vessel) gave a mixture of acetylene and silicon tetrafluoride, identified by mass and i.r. spectra.

Further, unequivocal confirmation of the structure of the fluoride was obtained from preliminary measurements of the microwave spectrum.[9]

The two new alkynylboron dihalides can be manipulated in a glass vacuum line at room temperature without apparent decomposition, although some degradation was observed on prolonged standing at −80°. In view of the apparent stabilizing effect of co-ordinative saturation of the boron atom on ethynylboron derivatives,[2,3] the relative stability of these compounds, and of the formally similar dibutoxyethynylborane,[10] may be related to the presence of substituents with nonbonding electrons capable of delocalization into the vacant boron *p*-orbital.

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Relative contributions of ion multiplets

Fragment	*m/e* 53—58 Mass range	% Contribution[a]	Fragment	*m/e* 72—77 Mass range	% Contribution[a]
C_2BF^+	53—56	24·0	$C_2BF_2^+$	72—75	6·68
HC_2BF^+	54—57	75·7	$HC_2BF_2^+$	73—76	93·1
$H_2C_2BF^+$	55—58	0·28	$H_2C_2BF_2^+$	74—77	0·26

[a] As obtained from application of least-squares fitting procedure to the experimental spectrum.

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