apical nuclei. The large triplet in benzyldecaborane shows a considerable perturbation which also points to the direct substitution by the benzyl group of one of the protons attached to a basal boron atom. These data, therefore, strongly suggest that benzyldecaborane is substituted at a basal boron atom.

Acknowledgments.—The authors are indebted to Dr. George Wilmot for the infrared spectrum of benzyldecaborane, Mrs. Phyllis Wheeler for the elemental analyses and Dr. Sol Skolnik for valuable advice. LeRoy Johnson of Varian Associates obtained the nuclear magnetic resonance spectra.

INDIAN HEAD, MARYLAND

[CONTRIBUTION NO. 423 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

Reactions of Hydrogen Fluoride with Some Boron–Oxygen Compounds

BY EARL L. MUETTERTIES

RECEIVED APRIL 11, 1958

Advantage has been taken of the facile cleavage of the boron–oxygen bond by hydrogen fluoride to prepare boron trifluoride–oxygen base complexes. The alcohol complexes of boron trifluoride, $2ROH \cdot BF_3$, formed essentially quantitatively in the reaction of trialkyl borates with hydrogen fluoride at 30°. Similarly, $2CH_3COOH \cdot BF_3$ was obtained in good yield from boric oxide, acetic anhydride and hydrogen fluoride. Attempts to extend these syntheses to organoboron fluoride complexes were unsuccessful. In reactions of such compounds as $C_6H_5B(OC_2H_5)_2$ and $ClC_3H_6B(OH)_2$ with hydrogen fluoride, there was not only cleavage of boron–oxygen bonds but also extensive cleavage of the boron–carbon bonds.

Introduction and Discussion

Complexes of boron trifluoride with organic oxygen compounds such as ethers, alcohols, esters and acids are a well established class of compounds.[1] Usually these compounds are prepared by the reaction of boron trifluoride or its etherate with the organic base.[1] Because boron–oxygen bonds are easily cleaved by hydrogen fluoride, we have explored the reactions of various boron–oxygen compounds with hydrogen fluoride as direct routes to boron trifluoride complexes.

Hydrogen fluoride converted trialkyl borates rapidly and cleanly to the dialcoholates

$$B(OR)_3 + 3HF \longrightarrow ROH + 2ROH \cdot BF_3$$

These dialcoholates were purified readily provided that the amount of hydrogen fluoride used was not in excess of the amount required to convert the borate to the complex (it was found difficult to free the dialcoholates of excess hydrogen fluoride). Triphenyl borate appeared to behave similarly to the alkyl borates, but a rigorous purification of the product was not achieved. Trimethoxyboroxine, $(CH_3OBO)_3$, was converted by hydrogen fluoride to a product that could not be vacuum distilled without decomposition and that appeared to be a labile mixture of $2CH_3OH \cdot BF_3$, $2H_2O \cdot BF_3$ and possibly $H_2O \cdot CH_3OH \cdot BF_3$. Several attempts were made to modify the borate reactions in order to obtain other boron trifluoride complexes. Acid anhydrides were employed here as alcohol acceptors, and the idealized reactions were represented in the two equations

$$B(OCH_3)_3 + 3(C_2H_5CO)_2O + 3HF \longrightarrow 2C_2H_5COOCH_3 + 3C_2H_5COOH + C_2H_5COOCH_3 \cdot BF_3$$

$$B(OCH_3)_3 + 3(CF_3CO)_2O + 3HF + (C_2H_5)_2O \longrightarrow 3CF_3COOH + 3CF_3COOCH_3 + (C_2H_5)_2O \cdot BF_3$$

In these two systems, the reactions were apparently more complex than indicated in the equations, and only low yields of the desired addition compounds were realized.

The 1:2 boron trifluoride complex with acetic acid formed directly and in good yield from the reaction of boric oxide, hydrogen fluoride and excess acetic anhydride

$${}^1/_2B_2O_3 + {}^3/_2(CH_3CO)_2O + 3HF \longrightarrow CH_3COOH + 2CH_3COOH \cdot BF_3$$

Use of tetraacetyl diborate, $(CH_3COO)_4B_2O$, in place of the boric oxide–acetic anhydride mixture led to products that, like those from the methoxyboroxine, were not purified readily.

Both trimethoxyboroxine[2,3] and tetraacetyl diborate[4,5] have boron–oxygen–boron bonds, and consequently, in the reactions of these compounds with hydrogen fluoride, water must in effect be formed. This water would emerge from the reaction as some type of boron trifluoride hydrate. For example, the boroxine might be expected to form the dialcoholate and the dihydrate

$${}^2/_3(CH_3OBO)_3 + 6HF \longrightarrow 2CH_3OH \cdot BF_3 + 2H_2O \cdot BF_3$$

However, if such a mixture were obtained and if there were no strong interactions between the components, distillation should permit isolation of the dialcoholate. Low molecular weight dialcoholates, as demonstrated in this work, can be *vacuum* distilled without significant decomposition but the hydrates cannot be distilled.[6] However, in the case of the products from the boroxine and the tetraacetyl diborate reactions, temperatures (~25-38°)

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(1) H. S. Booth and D. R. Martin, "Boron Trifluoride and Its Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 61-74.

(2) G. L. O'Connor and H. R. Nace, THIS JOURNAL, **77**, 1578 (1955).

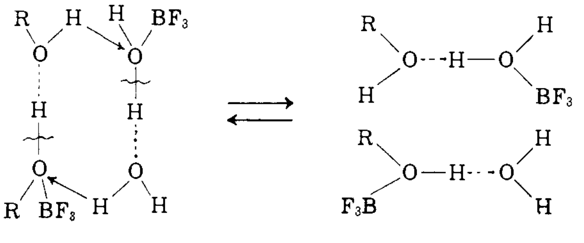
(3) J. Goubeau and H. Keller, *Z. anorg. allgem. Chem.*, **267** (1951).

(4) R. G. Hayter, A. W. Laubengayer and P. G. Thompson, THIS JOURNAL, **79**, 4243 (1957).

(5) The contrasting behavior of tetraacetyl diborate and the boric oxide–excess acetic anhydride in the hydrogen fluoride reaction appears to be further evidence that "boron acetate" is $(CH_3COO)_4B_2O$ and not $(CH_3COO)_3B$.

(6) J. S. McGrath, G. G. Stack and P. A. McCusker, THIS JOURNAL, **66**, 1263 (1944).

effective for vacuum distillation of the pure complexes yielded no distillate, and higher temperatures resulted in decomposition of the material. It is suggested that this behavior is due to a gross interaction of the alcohol or acid complexes with the hydrate. An exchange process might proceed as shown in the speculative[7] equation. Evidence for



an exchange that at least produces OH proton equivalence was found in the proton magnetic resonance spectra of synthetic mixtures of $2H_2O{\cdot}BF_3$ with $2CH_3OH{\cdot}BF_3$, with $2CH_3COOH{\cdot}BF_3$ and with $2C_6H_5OH{\cdot}BF_3$. If there were no interaction in these mixtures, two OH proton resonances would be expected (each of the pure complexes has a characteristic single OH proton resonance, and these OH proton resonances occur at measurably different frequencies). However, each of the three mixtures produced a single, concentration-dependent OH proton resonance.[8]

Hydrogen fluoride reacted with $C_6H_5B(OC_2H_5)_2$ at 20–50° to form $2C_2H_5OH{\cdot}BF_3$ and benzene. Similarly, chloropropylboronic acid was largely converted to *n*-propyl chloride and boron trifluoride dihydrate, and nonylboronic acid underwent some cleavage of the boron–carbon bond. Thus, this hydrogen fluoride system is at best not a general route to organoboron fluoride complexes. It should be noted that in these cleavages of boron–carbon bonds, hydrogen fluoride is not necessarily the active species. In fact, it is more probable that the alcohol or water produced in the cleavage of the boron–oxygen bonds serves as an ionization medium for hydrogen fluoride and the resulting solvated proton is the intermediate that attacks the boron–carbon bond.[9] There is, in related systems, evidence that this may be the case. Hydrogen chloride and hydrogen bromide cleave neither the boron–oxygen bonds (thermodynamically unfavored) nor the boron–carbon bonds in esters of phenylboronic acid and *n*-butylboronic acid.[10] However, hydrochloric acid does cleave the boron–carbon bond in phenylboronic acid to produce benzene.[11] Alkylboronic acids appear to require more rigorous conditions for deboronation than do the arylboronic acids, but heating of the hydrated sodium salt of *n*-butylboronic acid does yield *n*-butane.[12]

Experimental

Materials and Procedure.—Commercial samples of the borate esters were dried with sodium and then distilled. Boric oxide was prepared by dehydration of boric acid.[13] The organic reagents and a commercial sample of trimethylboron were purified by distillation. Phenylboronic acid was prepared by hydrolysis of the product from the reaction of trimethylborate and phenylmagnesium bromide. The crude product was recrystallized from ether (m.p. 218–220°). The ethyl ester of phenylboronic acid was prepared by direct esterification of the acid with ethanol with sulfuric acid as a catalyst. This ester was separated from the reaction mixture by distillation (b.p. 87–89° (8 mm.)). Commercial samples of boron acetate, obtained from American Potash and Chemical Corporation, and of trimethoxyboroxine, nonylboronic and chloropropylboronic acids, obtained from Callery Chemical Company, were used without further purification.

The general procedure for the fluorination reactions was as follows. Reactants, with the exception of the hydrogen fluoride, were placed in a stainless steel-lined vessel of 400-ml. internal capacity. After the vessel was cooled with a Dry Ice–acetone mixture and evacuated, the required amount of hydrogen fluoride was condensed in the vessel. Slightly less than the theoretical amount of hydrogen fluoride was employed in all cases. It was found that the complexes could not be freed of excess hydrogen fluoride by prolonged evacuation or by fractional freezing, and distillation of such products in glass columns led to exceptionally rapid attack of the glass. To ensure completeness of reaction the vessel was heated to ~80° for 1 hr. (This proved unnecessary, at least for the alkyl borates, since it was later found that these esters were converted to the alcoholates merely by passing a hydrogen fluoride–nitrogen gas stream through the esters at room temperature.) After cooling to room temperature, the vessel was re-evacuated and the residual products were recovered.

The methyl, ethyl and *n*-propyl borates (0.5 mole) and hydrogen fluoride (1.45 moles) gave nearly quantitative yields (85–95%) of the dialcoholates. These liquid products were purified by vacuum distillation at ~30° in a spinning-band (platinum) column and by fractional freezing. The products of both purification procedures were identical as judged by the proton magnetic resonance spectra.

Anal. Calcd. for $2CH_3OH{\cdot}BF_3$: B, 8.23; F, 43.19. Found: B, 8.24; F, 43.27. Calcd. for $2C_2H_5OH{\cdot}BF_3$: B, 6.76; F, 35.62. Found: B, 6.80; F, 35.31.

Trimethoxyboroxine (0.2 mole) and hydrogen fluoride (1.75 moles) yielded a mixture that severely etched the glass distillation column; no separation of products was achieved. Triphenyl borate (0.5 mole) and hydrogen fluoride (1.45 moles) gave the bis-(phenol) complex but a rigorous purification was not achieved.

Trimethyl borate (0.5 mole), propionic anhydride (1.8 moles) and hydrogen fluoride (1.45 moles) gave a mixture, and distillation of the mixture gave a low yield (~5%) of $C_2H_5COOCH_3{\cdot}BF_3$. However, as infrared and elemental analysis indicated, a complete separation of the complex and propionic acid was not achieved.

Anal. Calcd. for $C_2H_5CCOCH_3{\cdot}BF_3$: B, 6.94; F, 36.5. Found: B, 6.47; F, 34.49.

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[7] A considerable amount of evidence has been cited for the fractional ionization of $2ROH{\cdot}BF_3$ and $2H_2O{\cdot}BF_3$ to $ROH_2{}^+BF_3(OR)^-$ and $H_3O^+BF_3(OH)^-$, respectively (N. N. Greenwood and R. L. Martin discuss this subject in a review, *Quart. Rev.*, **8**, 1 (1954)). A rapid equilibrium between the complexes and the ions also could be used to describe the exchange of OH protons. The available data do not permit a precise description of the exchange mechanism. It should also be noted that P. Diehl and R. A. Ogg, Jr., *Nature*, **180**, 1114 (1957), have reported that there is effective CH_2 proton equivalence in $2CH_3CH_2OH{\cdot}BF_3$, and this equivalence may well be the result of an exchange process.

[8] Exchange phenomena of sufficiently high frequency have been shown capable of collapsing a two-line spectrum into a single, concentration-dependent resonance; H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

[9] It was established that hydrogen fluoride alone is capable of cleaving the boron–carbon bond. At 60°, trimethylboron was converted to methylboron difluoride and dimethylboron fluoride. The fact that cleavage in methylboron difluoride did not proceed under these conditions does, however, suggest that a solvated proton may be more active than a hydrogen halide in these cleavage reactions.

[10] P. B. Brindley, W. Gerrard and M. F. Lappert, *J. Chem. Soc.*, 824 (1956).

[11] A. D. Ainley and F. Challenger, *ibid.*, **2171** (1930).

[12] M. F. Lappert, *Chem. Revs.*, **56**, 994 (1956).

[13] "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. **22**.

Formation of the relatively non-volatile propionic acid complex, $2C_2H_5COOH \cdot BF_3$, may be responsible for the low yield of the ester complex.

Trimethyl borate (0.5 mole), trifluoroacetic anhydride (1.8 moles), ethyl ether (0.8 mole) and hydrogen fluoride (1.45 moles) gave trifluoroacetic acid, methyl trifluoroacetic acid and low (28%) yields of boron trifluoride etherate.

Anal. Calcd. for or repd. for $(C_2H_5)_2O \cdot BF_3$: F, 40.2; B, 7.62; b.p. 90°/(150 mm.), $n^{25}D$ 1.348. Found: F, 38.65; B, 8.23; b.p. 88° (147 mm.), $n^{25}D$ 1.347.

Boric oxide (0.25 mole), acetic anhydride (1.8 moles) and hydrogen fluoride (1.45 moles) gave $2CH_3COOH \cdot BF_3$ in yields as high as 80%. The crude product was purified by vacuum distillation.

Anal. Calcd. for $2CH_3COOH \cdot BF_3$: B, 5.76; F, 30.32. Found: B, 5.26; F, 30.58.

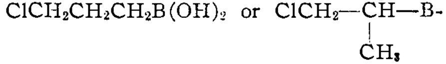
"Boron acetate," $(CH_3COO)_4B_2O$ (0.25 mole) and hydrogen fluoride (1.45 moles) gave a liquid product that attacked the distillation column and displayed the general behavior of the product from trimethoxyboroxine and hydrogen fluoride. The liquid showed a pronounced tendency to supercool and attempted purification by fractional freezing was unsuccessful.

The ethyl ester of phenylboronic acid (0.1 mole) and hydrogen fluoride (0.2 mole) gave a liquid product. Volatile materials were removed by evacuation to <1 mm. at 25°. Elemental analysis of the liquid suggested that it was $2C_2H_5OH \cdot BF_3$ rather than $2C_2H_5OH \cdot C_6H_5BF_2$.

Anal. Calcd. for $2C_2H_5OH \cdot C_6H_5BF_2$: B, 4.96; H, 7.80; C, 55.09. Calcd. for $2C_2H_5OH \cdot BF_3$: B, 6.76; H, 7.80; C, 30.25. Found: B, 6.27; H, 7.67; C, 28.62.

The formation of benzene in this reaction was established by mass spectrometric analysis of the volatile reaction products.

Tenth mole quantities of $ClC_3H_7B(OH)_2$ and $C_9H_{19}B(OH)_2$ were placed in separate gas storage vessels (stainless steel). About 0.5 mole of hydrogen fluoride was distilled into each vessel, and then these vessels were heated to 50° for a period of 1 hr. After about 100 hr. at 25°, the gas phase in each vessel was characterized by mass spectrometric analysis. *n*-Propyl chloride and hydrocarbons were detected in the samples from $ClC_3H_7B(OH)_2$ and $C_9H_{19}B(OH)_2$, respectively. The nonylboronic acid apparently was a mixture of alkylboronic acids because the mass spectrometer detected hydrocarbons ranging from C_6 to C_9. Boron–carbon bond cleavage was not complete here as indicated by the fact that the non-volatile (at 25°) product still contained 24% carbon. (Theory for $C_9H_{19}BF_2 \cdot 2H_2O$ is 51.5%.)



The formation of *n*-propyl chloride from the chloropropylboronic acid indicates that the structure of the parent acid is either $ClCH_2CH_2CH_2B(OH)_2$ or $ClCH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}B(OH)_2$. The proton magnetic resonance spectrum of the fused acid and of aqueous solutions of the acid supported the *n*-propyl structure in that three peaks of roughly equal intensity were found in the C–H region; however, differences in intensities of these three peaks were sufficient to preclude a rigorous assignment of structure.

Trimethylboron (2.0 g.) and hydrogen fluoride (5.0 g.) were condensed in a gas storage cylinder and then heated to 50° for 1 hr. The reaction mixture stood at ~25° for a period of about two weeks before it was analyzed by mass spectrometry. At that time, the gaseous products consisted of hydrogen fluoride, methane, methylboron difluoride and dimethylboron fluoride. Neither trimethylboron nor boron trifluoride were present in amounts sufficient to be detected by the analytical technique

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