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Relative Acidities of the Trifluorovinylchloroboranes

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A relative acidity scale based on the proton shifts of the diethyl etherates of the Lewis acids BCl_3 and BF_3 has been developed by Deters, *et al.*[2] Since the trifluorovinylboranes $(C_2F_3)_3B$, $(C_2F_3)_2BCl$, and $C_2F_3BCl_2$ are among the few stable fluorocarbon boranes,[3] it is of interest qualitatively to compare their acidities with those of the boron halides.

Experimental Section

The fluorocarbon boranes were handled exclusively in a glass vacuum system while all other materials were handled to exclude moisture.

Materials. Diethyl ether was distilled from calcium hydride under a nitrogen atmosphere. Boron trichloride was purified by fractional condensation in the vacuum system with the material used that stopped in a −111° trap. The vapor pressure was 477 Torr, lit. value 477 Torr at 0°. Boron trifluoride etherate was distilled under nitrogen and the fraction boiling at 126° was collected. The $(C_2F_3)BCl_2$ and $(C_2F_3)_2BCl$ were prepared as described in the literature.[2] The procedure for $(C_2F_3)_3B$[2] was modified by the addition of Du Pont E-5 fluorinated ether to the reaction mixture in order to moderate the vigor of the reaction. In the absence of the ether we obtained only polymers.

Nmr Measurements. The samples were prepared either on the vacuum system or in a drybox. Weighed amounts of ether and acid were allowed to react with the latter in excess and tetramethylsilane was added as an internal reference. The sample tubes were sealed off and kept in liquid nitrogen until being warmed immediately before measurement on a Varian A-60 spectrometer. The methylene proton shifts for the 1:1 ether–acid complexes were measured relative to those of the pure ether[4] and are as follows (Hz): BCl_3, 79.8; $(C_2F_3)BCl_2$, 73.5; $(C_2F_3)_2BCl$, 64.5; $(C_2F_3)_3B$, 59.0; BF_3, 50.5.

Discussion

On the basis of the relative shifts of the complexes the Lewis acidities fall in the order $BCl_3 > C_2F_3BCl_2 > (C_2F_3)_2BCl > (C_2F_3)_3B > BF_3$. A more quantitative set of values may be assigned by plotting the chemical shifts in hertz against the relative acidities for a series of Lewis acids as assigned by Deters, *et al.* When this is done, the relative values are 100, 92, 82, 74, and 63 Hz in the order given above. The relatively linear decrease in acid strengths as trifluorovinyl groups are substituted for chloride suggests that the effects are solely electronic and steric factors do not play any role. Although it is well known that fluorine is more electronegative than chlorine, this is more than offset by the back-donation of electron density by the former, making BCl_3 a stronger acid than BF_3. Based on the relative acid strengths the trifluorovinyl group falls between fluorine and chlorine in its composite inductive–back-donation effect. It is interesting that the trifluorovinyl group shows so little interaction between its π electrons and the boron p_z orbital despite its well-known ability to react with transition elements.[5]

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Registry No. $BCl_3 \cdot Et_2O$, 2102-03-6; $(C_2F_3)BCl_2 \cdot Et_2O$, 42886-05-5; $(C_2F_3)_2BCl \cdot Et_2O$, 42886-06-6; $(C_2F_3)_3B \cdot Et_2O$, 42886-07-7; $BF_3 \cdot Et_2O$, 109-63-7.

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(1) Abstracted from a portion of the Ph.D. thesis of N. W.

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(4) A referee has raised the objection that the chemical shifts maybe affected by intermolecular effects. However, both Deters and ourselves have observed that a plot of the chemical shifts as a function of acid:base ratio gives a straight line up to the 1:1 pure adduct ratio. Thus intermolecular effects must be small.

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Oxidations of Partially Fluorinated Alkyl Sulfides. Preparation of Methyl Trifluoromethyl Sulfoxide and Methyl(trifluoromethyl)sulfur Tetrafluoride

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Traditionally, sulfoxides are formed by the oxidation of sulfides. Although there are many oxidations of this nature reported in the literature,[2-6] these occur with sulfides containing nonfluorinated alkyl or aryl groups. An exception was the reported oxidation of methyl trifluoromethyl sulfide with hydrogen peroxide or HNO_3 in glacial acetic acid.[7] In attempts to repeat this oxidation, the reaction product was invariably methyl trifluoromethyl sulfone. While our work was in progress, a study of the oxidation of various methyl polyfluoroalkyl sulfides was reported.[8]

Completely fluorinated alkyl sulfides have been shown to be totally inert to the normal oxidative methods.[9] However, oxidation with chlorine monofluoride has yielded bis(perfluoroalkyl)sulfur difluorides or bis(perfluoroalkyl)sulfur tetrafluorides.[10-13] The difluorides, when treated with anhydrous HCl in Pyrex glass, resulted in sulfoxide formation. In contrast to bis(perfluoroalkyl) sulfides, when CH_3SCF_3 was treated with ClF, no methyl(trifluoromethyl)sulfur difluoride was formed. However, good yields of methyl(trifluoromethyl)sulfur tetrafluoride were obtained. Oxidation of CF_3SCH_3 with *m*-chloroperoxybenzoic acid at 0° gave high yields of methyl trifluoromethyl sulfoxide. At 25° or above, the sulfide was oxidized to sulfone. In similar fashion, $(CF_3S)_2CH_2$ was slowly oxidized by *m*-chloroperoxybenzoic acid to $CF_3SCH_2S(O)CF_3$ and other unidentified oxidation products.

Results and Discussion

The controlled reaction of methyl trifluoromethyl sulfide

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