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Chlorination of Trimethylamine Borane. Synthesis of Trimethylamine Dichloroborane

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Trimethylamine borane can be chlorinated with a variety of halides and oxyhalides under mild conditions. Reactivity decreases in the order $SbCl_5 \sim SO_2Cl_2 > SbCl_3 > SOCl_2 > HgCl_2 > HCl > (CH_3)_3NH \cdot HCl$*, and correlates well with thermodynamic properties of the halogenating agents. Reactivity towards chlorination in the amine boranes decreases in the order* $(CH_3)_3NBH_3 > (CH_3)_3NBH_2Cl > (CH_3)_3NBHCl_2$*, and correlates well with B—H stretching frequencies and nmr shifts. Trimethylamine dichloroborane was synthesized and characterized for the first time. The weaker halogenating agents appear to react via a polar hydride transfer mechanism whereas the strongest ones are likely to halogenate by a free radical chain mechanism.*

Introduction

Halogen substitution on the boron atom in amine boranes has been accomplished previously by using hydrogen halides,[1,2] halogens,[2] or trihaloboranes[2,3] as halogenating agents. These reagents produced either substitution of a single hydrogen atom or proceeded to complete halogenation of the trifunctional BH_3 group. In this work, a variety of new chlorinating agents for –H bonds were explored which belonged to the class of metal or non-metal chlorides or oxychlorides. In the course of this work, a clean synthesis for dimethylamine dichloroborane was developed and the phsical and chemical properties of this compound were determined.

Experimental Section

Materials and Apparatus. Trimethylamine borane obtained from Callery Chemical Company was purified by vacuum sublimation. Reagent grade mercuric chloride was ground to a fine powder and used without further purification. Diethyl ether was distilled from calcium hydride before use. Thionyl chloride and sulfuryl chloride (Allied Chemical Company) were purified by trap-to-trap distillation in the vacuum line. Anhydrous hydrogen chloride (Matheson Company) and antimony pentachloride (Allied Chemical Company) were used without further purification. Trimethylamine hydrochloride (Eastman Organic Chemicals) was dried in a vacuum desiccator before use.

Where appropriate, an all pyrex glass vacuum system was used to manipulate the materials. In experiments involving the use of an autoclave, a 100 ml stainless steel autoclave was heated in a thermostated furnace. The change in pH with time was followed by using a Model SR Sargent Recorder equipped with a resistance-matching adapter (S-72172 Sargent pH Adapter) for measurement with Beckman glass and calomel electrodes. The apparatus was calibrated by standard buffer solutions to have a pH range of 0 to 12.5 pH units over a one millivolt range. The ^{11}B nuclear magnetic resonance spectra were obtained at 19.3 megacycles with a Varian DP 60 spectrometer, and ^1H resonance spectra with a Varian A-60 A instrument. The infrared spectra were taken of KBr pellets with a Beckman IR-10 spectrometer. Elemental analysis was done by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Infrared spectral analysis. The infrared spectra of the trimethylamine chloroborane adducts were sufficiently different that each could be distinguished in a spectrum taken of a mixture of the adducts. The most characteristic region of the spectrum was the 300-600 cm^{-1} region. A comparison of the absorptions of the adducts in this region is given in Table I. It was this region which allowed rapid positive identification of the various chloro-substituted adducts.

Reaction of Trimethylamine Borane and Mercuric Chloride. 1. *In diethyl ether.* Trimethylamine borane (0.137 mole) was placed in a two liter, three-necked round bottom flask containing one liter of diethyl ether. One neck of the flask contained a Soxhlet extractor with a filter thimble filled with mercuric chloride (0.553 moles); the center neck of the flask contained a Teflon wing-stirrer; the remaining neck contained a glass plug. As diethyl ether refluxed through the Soxhlet extractor dissolving the mercuric chloride, it gave slow addition of mercuric chloride solution to the trimethylamine borane-diethyl ether solution.

The progress of the reaction was followed by infrared analysis of the reaction mixture. After 18 hours at reflux and 12 hours at room temperature, the infrared spectrum was that of pure $(CH_3)_3NBHCl_2$. No change in the infrared spectrum was observed there-

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[1] H. I. Schlesinger, N. W. Flodin, and A. B. Burg, *J. Am. Chem. Soc.*, *61*, 1078 (1939).
[2] H. Noeth and H. Beyer, *Chem. Ber.*, *93*, 2251 (1960).
[3] S. Ratajczak, *Bull. Soc. Chim. France*, *3*, 487 (1960).

Table I. Infrared Spectra of $(CH_3)_3NBH_3$ and the Trimethylamine Chloroboranes in the 300-600 cm^{-1} Region

$(CH_3)_3NBH_3$	$(CH_3)_3NBH_2Cl$	$(CH_3)_3NBHCl_2$	$(CH_3)_3NBCl_3$
440 cm^{-1}	470 cm^{-1}	500 cm^{-1}	530 cm^{-1}
345	420	440	440
	330	345	375
	310	315	350

after on continuing reflux for 95 hours. Trimethylamine dichloroborane was extracted from the reaction mixture with warm diethyl ether and by an additional extraction with hot carbon tetrachloride. The ether and carbon tetrachloride solvents were removed with a rotating vacuum exaporator. The white solid was recrystallized from hot carbon tetrachloride to give a 80% yield.

Anal. Calcd. for $(CH_3)_3NBHCl_2$: C, 25.41; H, 7.11; N, 9.88; Cl, 50.00; B, 7.62. Found: C, 24.68; H, 6.89; N, 9.59; Cl, 47.77; B, 7.93.

The material had a sealed tube melting point of 144 to 149°C. The infrared spectrum agreed with that of $(CH_3)_3NBHCl_2$.

2. *At elevated temperatures.* Trimethylamine borane (30.8 mmoles) and mercuric chloride (61.6 mmoles) were placed into a stainless steel autoclave which was immediately sealed. After nine hours, during which time the temperature was raised from 35° to 100°, the autoclave was cooled to room temperature, The solid residue was extracted with hot carbon tetrachloride. An infrared spectrum of the extracted material showed that it was a mixture of $(CH_3)_3NBH_2Cl$, $(CH_3)_3NBHCl_2$, and $(CH_3)_3NBCl_3$. Mercury metal was present in the reaction residue.

Trimethylamine borane was also heated in the presence of an excess of mercuric chloride at 150° for three and one half hours. The material, extracted as above, was a mixture of $(CH_3)_3NBHCl_2$ and $(CH_3)_3NBCl_3$.

3. *In water or aqueous potassium chloride.* Trimethylamine borane, dissolved in water, was added to aqueous $HgCl_2$, or a solution of $HgCl_2$ in KCl. After stirring for five to thirty minutes, the mixture was extracted with an equal volume of benzene which was dried and evaporated at room temperature. The small quantity of recovered product in all instances proved to be $(CH_3)_3NBH_2Cl$, free of higher chlorides or starting material. The identity of the product was established by its infrared and nmr spectra. In a typical experiment, $(CH_3)_3NBH_3$ (5.18 mmole), $HgCl_2$ (36.0 mmole), and KCl (20.4 mmole) in 100 ml water yielded after twenty minutes 0.049 g of product (9%), mp 76-79°, ^1H mnr: singlet at $\delta = 2.67$ ppm. Without added KCl, but otherwise identical reaction conditions, only 2% of the trimethylamine borane was recovered as monochloroborane.

The change in pH with time for the reaction was also followed during such a reaction. The results are shown in Figure 1.

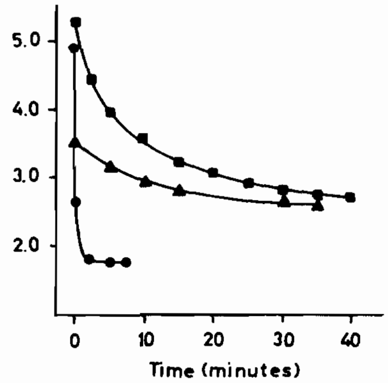

Figure 1. Reaction of $HgCl_2$ in water with $(CH_3)_3NBHCl_2$, ■; $(CH_3)_3NBH_2Cl$, ▲; $(CH_3)_3NBH_3$, ●.

Reaction of Trimethylamine Borane with Hydrogen Chloride. 1. *In benzene.* Trimethylamine borane (26.8 mmoles) was dissolved in 200 ml of benzene and hydrogen chloride was bubbled slowly through the solution for four hours at room temperature. After twenty four hours, the solution was filtered and the solvent removed with a rotating vacuum evaporator. The remaining solid material had a melting point of 85° (lit.:[2] 85°) and the infrared spectrum agreed with that of $(CH_3)_3NBH_2Cl$. The yield was 95%. This is a recommended method for preparation of $(CH_3)_3NBH_2Cl$.

2. *In water.* Saturated aqueous trimethylamine borane (15 ml) was added to aqueous concentrated hydrochloric acid (3 ml) and shaken vigorously for five minutes. The solution was neutralized by adding 6 *M* NaOH, and cooled to room temperature. The benzene extract of this solution was dried over potassium carbonate, filtered, and the solvent was removed. The infrared spectrum of the recovered product showed a trace of $(CH_3)_3NBH_2Cl$ to be present, but it also contained peaks similar to those of boric acid.

Competitive Reaction of Mercuric Chloride and hydrogen Chloride with Trimethylamine Borane. A solution of mercuric chloride (3.20 mmoles) and hydrogen chloride (1.60 mmoles) in 50 ml anhydrous ether was mixed on the vacuum line with trimethylamine borane (1.59 mmoles) in 15 ml ether and stirred at 0° for one hour. The non-condensable gas (H_2) was removed with a Topeler pump and measured. The amount of gas (0.36 mmole) corresponded to only 23% of the amount of hydrogen which could have been formed if all the HCl had reacted with trimethylamine borane. All the starting borane adduct had been converted to the monochloro compound.

Reaction of Trimethylamine Borane, Trimethylamine Monochloroborane, or Trimethylamine Dichloro-

borane with Trimethylamine Hydrochloride. General procedure. The appropriate amounts of the amine borane and trimethylamine hydrochloride were placed in the autoclave and heated for a set period of time at a desired temperature. After cooling the autoclave to room temperature, the gaseous products weree released. The solid residue was extracted with hot carbon tetrachloride, filtered, and the solvent was removed. The products were generally mixtures of $(CH_3)_3NBH_2Cl$ and $(CH_3)_3NBHCl_2$. However in one experiment, trimethylamine borane (16.5 mmoles) and trimethylamine hydrochloride (63.0 mmoles) were heated for twenty five hours at 150° to 185°. The gaseous products were then removed and heating was continued for an additional twenty two hours. This experiment gave trimethylamine dichlorobrane in 40% yield, with a melting point of 145-146°. *Anal.* Calcd. for $(CH_3)_3NBHCl_2$; C, 25.41; H, 7.11; N, 9.88; Cl, 50.00; B, 7.62. Found: C, 25.36; H, 7.06; N, 9.83; Cl, 50.09; B, 7.55.

Reaction of Trimethylamine Monochloroborane with Antimony Pentachloride. Antimony pentachloride (3.91 mmoles) was vacuum-distilled onto trimethylamine monochloroborane (2.10 mmoles) at −196°. On warming to −78°, no increase in pressure occurred in the system, whereas on warming slowly to 0° there was an immediate increase in pressure which continued on warming to room temperature. After 45 minutes at room temperature, the reaction mixture was cooled to −196° and a trace of non-condensible gas was noted. The condensible gaseous products were distilled from the reaction flask and the grey solid residue was washed with diethyl ether. The ether insoluble residue was extracted with hot ethanol. The ethanol-soluble material had an infrared spectrum which agreed with that of $(CH_3)_3NBCl_3$. The ether wash solutions remained colorless until the ether was removed and then the residue turned grey in color. A crystalline material was sublimed from this grev residue which had a melting point the same as that of antimony trichloride, m.p. 73-74°, lit.[4] 73.4°.

Reaction of Trimethylamine Borane with Thionyl Chloride. To a slurry of trimethylamine borane (1.020 g, 14.00 mmole) in 15 ml CCl_4, cooled at 0°, was added over a ten minute period 15.0 ml of thionyl chloride (208.6 mmole). The mixture was then kept at room temperature for 8 hours, with stirring and protection by a nitrogen atmosphere. A yellow solid precipitated during that time. After removal of all volatile components under vacuum, the remaining solid was extracted with benzene, and the benzene-soluble solid (2.579 g) was again extracted with methylene chloride to yield 1.584 g of fairly pure product (80% yield). Recrystallization by evaporation of a solution in methylene chloride-petroleum ether (60-110°) gave an over-all yield of 73% trimethylamine dichloroborane, which contained a small amount of trimethylamine boron trichloride.

A second crystallization from hot carbon tetrachloride gave 80% recovery, m.p. 143-146°, but did not remove the $(CH_3)_3NBCl_3$ impurity.

Reaction of Trimethylamine Borane and Sulfuryl Chloride. Trimethylamine borane (0.53 mmoles) was sublimed into a flask containing sulfuryl chloride (6.20 mmoles) at −196°. On warming to −63° for 30 minutes, a slow increase in pressure occurred; on warming to −23°, the pressure initially increased rapidly and continued to increase steadily. After one hour, the mixture was warmed to 0° and no increase in pressure was noted. On cooling the reaction flask to −196°, a trace of non-condensible gas was noted. All room temperature volatile materials were distilled from the flask and identified by their gas phase infrared spectra to be HCl (g), (1.50 mmoles), SO_2 (g), and SO_2Cl_2. The infrared spectrum of the solid residue was that of $(CH_3)_3NBCl_3$ containing a trace of $(CH_3)_3NBHCl_2$.

Results and Discussion

Trimethylamine Dichloroborane. Although the preparation of trimethylamine dichloroborane, $(CH_3)_3NBHCl_2$, had been implied by a brief mention in the literature,[1] no experimental evidence for its existence has been reported. The compound has been synthesised here by several routes and is doubtlessly also an intermediate in the chlorination of trimethylamine borane to trimethylamine boron trichloride.

The best methods of synthesis were the reaction of trimethylamine borane near room temperature with mercuric chloride or with thionyl chloride, both of which gave high yields; mercuric chloride gave the purer product. Other chlorinating agents, such as $(CH_3)_3N \cdot HCl$, HCl, $SbCl_3$, $SbCl_5$ or SO_2Cl_2 either gave mixtures with the monochloroborane adduct or produced complete substitution of all the hydrogen bonds in the BH_3 group.

Trimethylamine dichloroborane is a stable white solid, easily soluble in dichloromethane, diethyl ether, benzene, ethanol, and hot carbon tetrachloride, but practically insoluble in petroleum ether or water. It is decomposed by heating in concentrated acid or base, but is stable for days at room temperature in dilute acid or base in 50% aqueous ethanol, or in saturated iodine solution in this solvent.

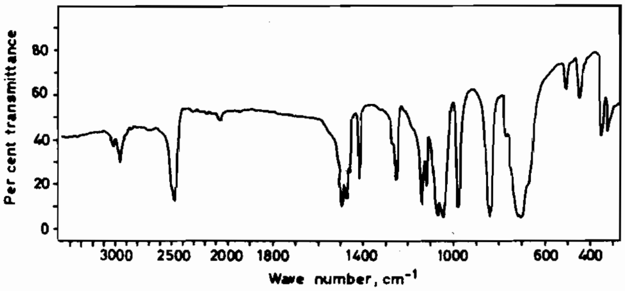

Figure 2. Infrared spectrum of $(CH_3)_3NBHCl_2$

The infrared spectrum of trimethylamine dichloroborane is given in Figure 2. It shows an intense single absorption at 2480 cm^{-1} expected for the B–H unit. Additional distinguishing intense bands appear

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(4) Chemical Rubber Publishing Co., Handbook of Chemistry and Physics, 40th ed., 1958-1959, p. 536.

at 1065 and 1040 cm^{-1}, and bands of lesser intensity at 500, 440, 345 and 315 cm^{-1}. The ^{11}B magnetic resonance was the expected 1:1 doublet centered at 13.3 ppm upfield from external trimethylborate with a B–H coupling constant of 148±5 hz. The ^{1}H magnetic resonance showed a sharp singlet corresponding to the methyl groups attached to nitrogen and a very broad quartet due to boron-attached hydrogen, which could be detected only at high amplification. The quartet was centered at –3.53 ppm from internal tetramethylsilane and had a coupling constant $J_{B-H} = 152 \pm 2$ hz.

Stoichiometry. Trimethylamine borane reacted with mercuric chloride in diethyl ether according to the following equations:

$$(CH_3)_3NBH_3 + 2HgCl_2 \rightarrow (CH_3)_3NBH_2Cl + Hg_2Cl_2 + HCl \qquad (1)$$

$$(CH_3)_3NBH_2Cl + 2HgCl_2 \rightarrow (CH_3)_3NBHCl_2 + Hg_2Cl_2 + HCl \qquad (2)$$

The hydrogen chloride liberated in both steps was demonstrated to react with trimethylamine borane in competition with mercuric chloride to give hydrogen gas.

$$(CH_3)_3NBH_3 + HCl \longrightarrow (CH_3)_3NBH_2Cl + H_2 \qquad (3)$$

Reaction 3 was at least four times slower than reaction 1, but fast enough to make it difficult to prepare pure trimethylamine monochloroborane merely by control of the borane/mercury(II) ratio; exact 1:2 ratios always gave small impurities of the dichloro compound. Large-scale preparation of the dichloroborane adduct from mercuric chloride was best accomplished by continuous addition of the salt in ether solution. Reactions by addition of the solid did not reproducibly go to completion, presumably because the crystals were soon covered with ether-insoluble Hg_2Cl_2, which was unreactive towards the boranes. In the absence of solvent, mercury metal was produced instead of mercury(I) chloride. Complete chlorination to trimethylamine boron trichloride did not occur at room temperature but proceeded readily at 100° when the solid reagents were heated in an autoclave; mercury metal again was the recovered reduction product.

Sufuryl chloride quantitatively converted trimethylamine borane to the boron trichloride adduct, according to equation 4,

$$(CH_3)_3NBH_3 + 3SO_2Cl_2 \longrightarrow (CH_3)_3NBCl_3 + 3SO_2 + 3HCl \qquad (4)$$

and did so without side reactions. Thionyl chloride reacted much more slowly and produced the dichloro adduct, according to the *idealized* equation

$$(CH_3)_3NBH_3 + 2SOCl_2 \rightarrow (CH_3)_3NBHCl_2 + S + SO_2 + 2HCl \qquad (5)$$

However, the amount of sulfur dioxide isolated was significantly smaller than predicted from equation 5, and the total weight of non-volatile reaction products was larger than predicted. Apparently, other sulfur compounds besides sulfur dioxide were formed in the reaction. Small amounts of trimethylamine boron trichloride were also present in the product and were detected by the characteristic proton magnetic resonance spectrum.[5]

Antimony pentachloride reacted vigorously with trimethylamine borane, trimethylamine monochloroborane, and trimethylamine dichloroborane to produce trimethylamine boron trichloride. Antimony trichloride was identified as one of the reaction products, and was demonstrated to react with the B–H containing boranes, though more slowly than $SbCl_5$. When less $SbCl_5$ than required for equation 6 was used, all B–H bonds were removed but the amount of HCl produced was somewhat less than required by equation 6 and 7

$$(CH_3)_3NBH_2Cl + 2SbCl_5 \rightarrow 2SbCl_3 + (CH_3)_3NBCl_3 + 2HCl \qquad (6)$$

$$(CH_3)_3NBH_2Cl + \frac{2}{3}SbCl_3 \rightarrow \frac{2}{3}Sb + (CH_3)_3NBHCl_2 + HCl \qquad (7)$$

It is probable that antimony-hydrogen compounds, in addition to metallic antimony, remained in the low-volatile products.

Reactivity of Borane Adducts. Selective chlorination obviously would not be possible if the reactivity of the remaining boron-hydrogen bonds remained unchanged on substitution. In fact, chlorination progressively deactivates the remaining B–H bonds towards further reaction. This was verified not only by isolating pure partially chlorinated adducts from reaction mixtures with excess chlorinating agent, but also by testing the reactivities of the borane adducts independently. Trimethylamine monochloroborane reacted with $SbCl_5$, SO_2Cl_2, $SOCl_2$, or $HgCl_2$, but less vigorously than trimethylamine borane. It did not react with HCl at room temperature, but required long heating at 100° to produce trimethylamine dichloroborane. Trimethylamine dichloroborane was chlorinated rapidly, as expected, with $SbCl_5$ and SO_2Cl_2 at room temperature, but was recovered in almost quantitative yield after one day in contact with excess $HgCl_2$ in ether. The order of reactivity $(CH_3)_3NBH_3 > (CH_3)_3NBH_2Cl > (CH_3)_3NBHCl_2$ is also maintained in the reactions with aqueous acids, iodine, or $HgCl_2$ (*cf.* Figure 1).

The change in the reactivity of the various borane adducts is accompanied by systematic changes in the infrared and nmr properties of the compounds. Increased chlorination increases the B–H stretching frequency, and displaces the chemical shifts to lower field strengths, in the ^{11}B spectrum as well as in the ^{1}H spectra for B–H or the CH_3 groups in the coordinated amine. The data are given in Table II.

These observations suggest that there is a general drift of electron density away from the boron-hydrogen bond region as chlorination proceeds and that the boron-hydrogen bonds simultaneously becomes less hydridic and more resistant to cleavage.

Reactivity of Chlorinating Agents. The reactivity of the various chlorinating agents was established to follow the order

$$SbCl_5 \sim SO_2Cl_2 > SbCl_3 > SOCl_2 > HgCl_2 > HCl > (CH_3)_3N \,.\, HCl$$

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(5) G. E. Ryschkewitsch and W. J. Rademaker, *J. Magnetic Resonance*, to be published September, 1969.

Table II. Infrared and NMR Data

	mean B—H stretch, cm^{-1}	Chemical Shifts, ppm.			J_{B-H} hz
		^{11}B [b]	$^{1}H-B$ [c]	$^{1}H_3-C$ [c]	
$(CH_3)_3NBH_2Cl$	2310 [a]	26.1	−1.73	−2.60	101
$(CH)_3NBHCl_2$	2340	20.3	−2.72	−2.67	123
$(CH_3)_3NBCl_3$	2480	13.3	−3.53	−2.77	152
$(CH_3)_3NBH_3$	—	8.3	—	−3.00 [d]	—

[a] Weighted average of symmetric and asymmetric modes; [b] *vs.* external $B(OCH_3)_3$; [c] *vs.* internal tetramethylsilane; [d] quartet.

Table III. Incremental Enthalpies for the Reaction

$$\equiv B-H+YCl_2(g) \longrightarrow \equiv B-Cl+Y(g)+HCl(g)$$

$Y\ Cl_2(g)$	Y	ΔH_1, kcal [a]	Product adduct
Cl_2	—	0	$-BCl_3$ [b]
$SbCl_5$	$SbCl_3$	19.2	$-BCl_3$
SO_2Cl_2	SO_2	16.1	$-BCl_3$
$\frac{2}{3}SbCl_3$	Sb (c)	50	$-BHCl_2$; $-BCl_3$ slowly
$SOCl_2$	SO	52.3	$BHCl_2$
$HgCl_2$	Hg	51.0	$BHCl_2$

[a] Calculated from data in ref. 9 and 10, as $\Delta H°$ for $YCl_2(g) \longrightarrow Y(g)+Cl_2(g)$; [b] ref. 2.

This assignment was based a) on the extent of substitution on boron when excess reagent was reacted with trimethylamine borane or a partially substituted adduct; b) on the results of reaction when two reagents were in competition; and c) on the conditions necessary to produce reaction.

Thus, both $SbCl_5$ and SO_2Cl_2 were capable of rapidly removing all boron-hydrogen bonds on the borane adduct below room temperature,[6] wheras $SOCl_2$ yielded predominantly the dichloro derivatives.[7]

The reaction of trimethylamine borane with thionyl chloride was more rapid than with mercuric chloride. Thionyl chloride yielded *no* non-condensible gas, while mercuric chloride always gave *some* hydrogen as a by-product. Both reactions produced hydrogen chloride, which subsequently could react with trimethylamine borane to give hydrogen, according to equation 3. This clearly demonstrates that thionyl chloride is more reactive than mercuric chloride, since hydrogen chloride cannot compete with the former compound in the first chlorination step, whereas it can do so, through not very effectively, with the latter. Finally, hydrogen chloride was capable of achieving only mono-substitution at room temperature and, when in competition with $HgCl_2$ for trimethylamine borane, reacted at less than one quarter the rate of $HgCl_2$. The trimethylammonium salt required elevated temperature for reaction.

The general reactivity of the chlorinating agents, and their selectivity in producing partial chlorination, roughly parallels their thermodynamic oxidizing power. Table III gives the enthalpy increments for the general

$$\equiv B-H+YCl_2(g) \longrightarrow \equiv B-Cl+Y(g)+HCl(g) \qquad (8)$$

reaction where the enthalpy of reaction with chlorine is taken as zero for reference. In effect, the numbers represent the enthalpy of reduction of the oxidizing agent in the gas phase per chlorine molecule removed from the reagent without further rearrangement of the resulting fragment; they are consequently a measure of oxidizing power relative to chlorine. The incremental enthalpies are thus conceptually similar to half-reaction potentials in aqueous redox reactions, and differ from the actual enthaplies by the appropriate bond energy terms for B—H, B—Cl, HCl and Cl_2. Taking the bond energies for B—H and B—Cl quoted by Muetterties[8] and standard literature values for HCl and Cl_2[9,10] this correction should amount to approximately −60 kcal/mole.[11]

The data in Table III indicate that the chlorinating agents become selective in their attack on the B—H bonds in adducts with BH_3, BH_2Cl, or $BHCl_2$ only when the net reaction approaches thermo-neutrality, *i.e.* for $HgCl_2$ and $SOCl_2$.

Mechanism. It is tempting to raise the question whether all the chlorinations reported here can be explained by fundamentally the same mechanistic steps. There are two alternatives worth immediate consideration: a polar reaction involving hydride loss or a free radical process.

A mechanism for halogenation of amine boranes with halogens and with boron trihalides has been discussed by Noeth and Beyer.[2] These authors pro-

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(6) SO_2Cl_2 may be somewhat less reactive since a small amount of trimethylamine dichloroborane was detected in the product.

(7) With undistilled technical $SOCl_2$ in reactions outside the vacuum line a slight impurity og $(CH_3)_3NBCl_3$ was always detected by means of its characteristic quartet in the proton resonance spectrum.

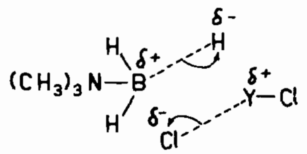
(8) E. L. Muetterties, « The Chemistry of Boron and its Compounds », E. L. Muetterties, ed., John Wiley and Sons, Inc., New York, 1967 p. 13.

(9) « Selected values of Chemical Thermodynamic Properties », Circular of the National Buerau of Standards 500. U.S. Dept, of Commerce, 1952.

(10) National Buereau of Standards, Technical Note 270-3, U. S. Government Printing Office, Washington, D. C., Jan. 1968.

(11) The B—Cl bond energy of 106 kcal/mole used here is based on BCl_3 as reference compound. This value is probably smaller in the borane adducts, because of the hybridization change and lack of π-bonding. If so, the ΔH correction would be numerically less than 60 kcal.

posed a heterolytic mechanism involving hydride transfer from boron to halogen, or boron trihalide, with a concerted halogen transfer in the opposite direction. The chlorinations investigated here plausibly could fit the hydride transfer mechanism. The chlorides of antimony(V), antimony(III) and mercury(II) are known acceptor molecules towards Lewis bases and thus could function, like the boron halides, as hydride acceptors and as chloride donors towards a cationic boron species (or in incipient cation, if the reaction is concerted). The sulfur oxyhalides or hydrogen chloride would, in this context, be mechanistic analogs of the halogens since they are susceptible to nucleophilic displacement of chloride from sulfur or from hydrogen, respectively.



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The halides, oxhyhalides, and hydrogen chlorides, in this view would differ from each other only in the extent to which the bond to hydrogen is made and the bond to chlorine is loosened in the transition state.

It is, however, not impossible that at least some of the oxidants chlorinate by a free radical mechanism. In view of the high B–H energy,[8] such a reaction would have to be initiated by the cleavage of the bond to chlorine in the oxidant

$$\mathrm{Cl{-}Y{-}Cl} \longrightarrow \mathrm{Y{-}Cl\cdot} + \mathrm{Cl\cdot} \qquad (9)$$

to be followed by hydrogen abstraction from B–H

$$\mathrm{B{-}H} + \mathrm{Cl\cdot} \longrightarrow \mathrm{B\cdot} + \mathrm{HCl} \qquad (10)$$

In a non-chain mechanism, the final products are then obtained by

$$\mathrm{B\cdot} + \mathrm{Y{-}Cl\cdot} \longrightarrow \mathrm{B{-}Cl} + \mathrm{Y} \qquad (11)$$

Since the atom abstractions represented by equations 10 and 11 are higly exothermic, they should proceed essentially without activation energy and should be very rapid.[12] Equation 9 therefore would represent the rate determining step. The reaction sequence 9 through 11 is, however, ruled out for general consideration on the grounds that the activation energies required for the cleavage of even the weakest bonds (SO_2Cl_2 and $SbCl_5$) are too large to produce the rapid reactions observed here.[13] A free radical mechanism at low temperature seems consequently possible only if there are long radical chains.

Thermally initiated chain reactions are quite possible for $SbCl_5$ and SO_2Cl_2. The latter compound is known to undergo thermal free radical dissociation with rather low activation energy in its irreversible decomposition in the gas phase.

$$\mathrm{SO_2Cl_2} \rightarrow \mathrm{SO_2Cl\cdot} + \mathrm{Cl\cdot} \quad E = 46.6^{14} \text{ or } 25^{15} \text{ kcal/mole} \qquad (12)$$

$$\mathrm{SO_2Cl\cdot} \rightarrow \mathrm{SO_2} + \mathrm{Cl\cdot} \quad E = 25.6 \text{ kcal/mole}^{14} \qquad (13)$$

Antimony pentachloride has an average bond dissociation energy for removal of the first two chlorine atoms of 38.7 kcal/mole, so that here again initiation and propagation by attack of the boryl radical on the halogen

$$\mathrm{B\cdot} + \mathrm{YCl_2} \longrightarrow \mathrm{B{-}Cl} + \mathrm{YCl\cdot} \qquad (14)$$

compound appear energetically quite feasible for reasonably frequent initiation as well as for the maintenance of long chains.

With HCl and $HgCl_2$, however, radical initiation (bond energies 103 and 85 kcal/mole[9,10] respectively) is highly unlikely, and chain propagation according to equations 1 0and 14 also becomes energetically much less favorable because the energy of the bond to halogen in the oxidizing agent approaches or even may exceed the boron-chlorine energy.

It is more likely that chlorination by mercuric chloride proceeds by hydride transfer with a transition state similar to I. Support for this view is found in the fact that the rate of reduction of mercury(II) is markedly diminished in saturated KCl, where the coordination sphere of mercury tends to be occupied by chloride ion. In pyridine solution radical cleavage as in equation 9 clearly is impossible since mercury(II) is complexed by the solvent, but reduction nevertheless takes place, albeit at elevated temperature.[16] The immediate product from transition state I would be a mercury(II) hydride complex. Such a compound should readily decompose into elemental mercury and HCl in analogy to the known instability of mercury hydride. It is pertinent to note that when reaction is carried out in the solid state metallic mercury is indeed the observed product at elevated as well as at room temperature. The metal is also formed initially when $HgCl_2$ is added to aqueous trimethylamine borane. Since Hg_2Cl_2 does not react with trimethylamine borane under these conditions, metallic mercury must be a primary product and the mercury(I) chloride obtained in ether or aqueous solution is therefore produced by a known fast secondary process, the reaction of mercury with mercury(II) chloride.

A number of experiments were made in an effort to explore the consequences of the hydride-transfer chlorination mechanism. This hypothesis demands that chlorinated borane adducts should form even in aqueous solution, if hydride transfer to mercury indeed proceeds simultaneous with chloride transfer to boron. The data in figure 1 show that the chlorinated borane adducts were kinetically substantially more stable to

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[12] For example, $CH_4 + Cl \rightarrow CH_3 + HCl$ is exothermic by 0.6 kcal and has less than 4 kcal activation energy [H. O. Pritchard *et al.*, *J. Am. Chem. Soc.*, *77*, 2629 (1955)]. The bond energies in ref. 8 predict $\Delta E = -12$ kcal/mole for reaction 10. Similarly the bond energy for B—Cl is at least 26 kcal/mole higher than the strongest Y—Cl bond (in $HgCl_2$), so that reaction 11 is also strongly exxothermic.

[13] An activation energy of 36 kcal/mole with the large pre-exponential factor of 10^{17} would yield a half life of about 10^{6} hours at room temperature.

[14] P. Huhn, T. Berces and Z. G. Szabo, *Z. Physik, Chem.* (Frankfurt), *23*, 70 (1960).

[15] Z. G. Szabo and T. Berces, *Z. Physik. Chem.* (Frankfurt), *12*, 169 (1957).

[16] G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, *89*, 3145 (1967).

aqueous $HgCl_2$ than trimethylamine borane, so that isolation of borane products should have been possible. Titration of a trimethylamine borane-$HgCl_2$ reaction mixture within minutes after mixing, and after a constant pH had been reached, produced 4.68 moles of H^+ per mole of borane, a little less than the 5 moles predicted for complete degradation according to

$$(CH_3)_3NBH_3+6HgCl_2(aq) \longrightarrow (CH_3)_3NH^+ + H_3BO_3 + 3Hg_2Cl_2 + 6Cl^- + 5H^+(aq) \qquad 15)$$

and far more than the 1 or 2 moles predicted for mono- or dichlorination, respectively. Nevertheless, it was possible to isolate from the reaction mixture a low yield of monochloroborane adduct, but no dichloro derivative. Yields were increased in the presence of large amounts of chloride ion or when mercury(II) was insufficient for complete reaction according to equation 15. If the reaction had produced a free cation $(CH_3)_3NBH_2^+$, the solvent would be expected to coordinate immediately and lead to rapid degradation.[17] On the other hand, coordination with Cl^- would trap the chloroborane as a species stable towards hydrolysis over the time period of the experiment. The results are consistent with the hypothesis that chloride ion is transferred before solvent can enter into bonding with boron. However, in aqueous, solution mercury(II) also has water in its coordination sphere, which could transfer to boron in competition with Cl^-. The yield of trimethylamine monochloroborane would then depend on the proportion of water and chloride ion in the coordination sphere of mercury and on the relative efficiencies of these two ligands in forming bridges to boron. An increase in coordinated chloride by addition of KCl indeed quadrupled the yield of monochloroborane adduct, but water apparently is so effective as a bridge, that the major portion of the reaction leads to degradation *via* water transfer. It is thus not surprising that no dichloroborane adduct was found, since this material would be formed by two successive unfavorable chloride transfers.

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(17) W. L. Jolly and Th. Schmitt, *J. Am. Chem. Soc.*, *88*, 4282 (1966) report rapid decomposition of the analogons ion $(H_2O)_2BH_2^+$ in aqueous acid above —20°.