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# B-Halogenation of N,N,N′,N′-Tetramethylethylenediamine–Bisborane

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*N,N,N′,N′-tetramethylethylenediamine–bisborane (TMED·2BH$_3$) has been treated with HF, HCl, HBr, and Br$_2$ and the reactions monitored with pmr. The new compounds TMED·2BH$_2$X (X = F, Cl, Br) and TMED·2BHX$_2$ (X = Br) were isolated and characterized. The course of halogen substitution is believed to reflect the influence of an inductive effect in agreement with an earlier study. The probable mechanism of halogenation is discussed.*

## Introduction

The B-halogenation of amine–boranes has been studied fairly extensively and a number of derivatives reported.[1–7] Molecular halogens, hydrohalic acids, or certain other halogen compounds substitute one or more halogen atoms on boron replacing hydrogen in the process.

$$R_3NBH_3 \xrightarrow[-H_2]{+HX} R_3NBH_2X \xrightarrow[-H_2]{+HX} R_3NBHX_2 \xrightarrow[-H_2]{+HX} R_3NBX_3 \quad (1)$$

We have found this to be a very useful synthetic route with the single limitation that full sequential halogenation does not readily occur in all cases. For example, anhydrous HF converts trimethylamine–borane stepwise to $(CH_3)_3NBH_2F$, $(CH_3)_3NBHF_2$, $(CH_3)_3NBF_3$, and finally to $(CH_3)_3NH^+BF_4^-$,[5] but under the same conditions HCl produces only the monochlorinated derivative.[6,7] Anhydrous HBr, on the other hand, readily gives $(CH_3)_3NBH_2Br$, $(CH_3)_3NBHBr_2$, and then slowly $(CH_3)_3NBBr_3$.*

Wiggins and Ryschkewitsch[4] have suggested that a drift of electron density away from the B–H bonds in B-chlorinated trimethylamine–boranes accounts for the reduced reactivity of these compounds towards electrophilic agents. It is evident, however, that such an inductive effect does not fully account for the halogenation reactions mentioned in the foregoing, particularly the full B-fluorination of $(CH_3)_3NBH_3$ accomplished by HF. Thus we decided to further investigate the inductive effect and other factors which could influence the extent of halogenation achieved by selected halogen compounds.

One method by which the influence of the inductive effect could be studied is to halogenate a bisborane adduct of a diamine. The course of the halogenation between the two borane groups should be influenced by the inductive effect of halogen substituents on boron.

We wish to report here the results of our studies of the fluorination, chlorination and bromination of N,N,N′,N′-tetramethylethylenediamine–bisborane (TMED·2BH$_3$).

## Experimental

NMR spectra were obtained on a Varian HA–100 instrument for boron (32.1 MHz) spectra and a Varian T–60 instrument for proton spectra. Mass spectra were taken on an Hitachi–Perkin Elmer RMU–6H instrument. Melting points were measured in closed 1-mm capillaries on a heated block and are uncorrected.

### *Materials*

N,N,N′,N′-tetramethylethylenediamine–bisborane (TMED·2BH$_3$) was prepared by an adaptation of the method of Moore, White, and Kelly.[8] A tetrahydrofuran (THF) solution of a stoichiometric quantity of $Et_2O \cdot BF_3$ was added dropwise into a suspension of $NaBH_4$ in THF (cooled with an ice bath) to form THF·BH$_3$. Then a THF solution of the stoichiometric amount of TMED (Matheson Coleman and Bell) was added dropwise to the above mixture forming TMED·2BH$_3$. The solvent was stripped from the reaction mixture and the residue extracted with $CH_2Cl_2$. The white crystalline TMED·2BH$_3$ (m.p. 180–182° C) was then obtained by stripping off $CH_2Cl_2$. THF was dried and distilled from Na(Pb). All other solvents were spectroquality except dimethylformamide which was reagent grade. Anhydrous hydrogen fluoride, hydrogen chloride and hydrogen bromide (Matheson Gas Co.) and purified bromine (J.T. Baker Co.) were used as obtained.

Boron analyses were carried out by standard Parr bomb techniques.[9] Analyses for carbon, hydrogen, and nitrogen were done by PCR Inc., Gainesville, Florida.

* Molecular bromine accomplishes the same sequential bromination more rapidly.[7]

*Syntheses*

*Bromination of TMED·2BH$_3$. Preparation of TMED·2BH$_2$Br and TMED·2BHBr$_2$*

A solution of TMED·2BH$_3$ (0.72 g, 5.0 mmol) in $CH_2Cl_2$ (40 ml) was stirred magnetically while portions of a solution of $Br_2$ (2.76 g, 17.25 mmol) in $CH_2Cl_2$ (100 ml) were added dropwise and the reaction mixture monitored by pmr.[5,7] The addition of bromine was interrupted when only one brominated product was observable from the pmr spectrum. After the first addition, about 0.83 g (5.2 mmol) of $Br_2$ had been used and one third of the resulting solution was transferred out. The principal product from this solution was determined to be TMED·2BH$_2$Br, but at this point it contained impurities which appeared to be other brominated products and no suitable method was found to separate them. (Pure TMED·2BH$_2$Br was best obtained by using anhydrous hydrogen bromide which will be described later.) As more bromine was slowly added to the remaining TMED·2BH$_2$Br solution, precipitate began to form. At the second stop about 1.07 g (6.67 mmol) more of $Br_2$ had been used and almost all the solute had precipitated out. The precipitate was then collected and identified as TMED·2BHBr$_2$. The yield of TMED·2BHBr$_2$ (m.p. 183–185° C) was essentially quantitative with respect to amine–bisborane remaining in the reaction mixture. Anal. Calcd for $C_6H_{18}B_2Br_4N_2$: C, 15.69; H, 3.95; N, 6.10. Found: C, 15.93; H, 3.89; N, 6.21. The methyl proton resonance was observed at $\delta$ 2.90, but the methylene resonance could not be identified because of the low solubility of the product. The boron-11 resonance in dimethylformamide solution was a broad doublet ($J_{BH} \cong 141$ Hz) centered at +20.1 ppm with respect to external trimethylborate.

Pure TMED·2BH$_2$Br was obtained essentially quantitatively by rapidly bubbling anhydrous hydrogen bromide into a solution of TMED·2BH$_3$ (0.288 g, 2.00 mmol) in $CH_2Cl_2$ (40 ml) for 4 minutes and then stirring magnetically until $H_2$ bubbles were no longer observed. The melting point of the product obtained in this manner was 155.5–156.5° C. Anal. Calcd for $C_6H_{20}B_2Br_2N_2$: C, 23.89; H, 6.68; N, 9.29; B, 7.17. Found: C, 23.49; H, 6.76; N, 8.95; B, 7.05. The methyl proton resonance occurred at $\delta$ 2.75 and the methylene proton resonance at $\delta$ 3.29. The boron-11 resonance in acetonitrile solution was a broad triplet ($J_{BH} \cong 126$ Hz) at +22.6 ppm with respect to external trimethylborate.

*Fluorination of TMED·2BH$_3$. Preparation of TMED·2BH$_2$F*

B-fluorination was carried out using the method described in earlier papers.[5,7] For TMED·2BH$_3$, the only fluorinated compound which could be obtained by this method was TMED·2BH$_2$F. The yield of this product never exceeded 50% and the compound decomposed gradually without a sharp melting point when heated above 127° C. Anal. Calcd for $C_6H_{20}B_2F_2N_2$: C, 40.07; H, 11.12; N, 15.58; B, 12.02. Found: C, 39.40; H, 11.31; N, 14.82; B, 11.32. The methyl and methylene proton resonances occur at $\delta$ 2.52 and $\delta$ 3.11 respectively. The boron-11 resonance in methylene chloride is observed at +12.95 ppm with respect to external trimethylborate. The resonance appeared as a broad, ill-defined quartet apparently arising from proton and fluorine coupling to boron with an observed coupling constant of approximately 101 Hz.

The mass spectrum of TMED·2BH$_2$F was obtained by subliming the compound under high vacuum into the mass spectrometer through the solid sample inlet. The spectrum contained peaks for the parent ion (180), four peaks corresponding to the loss of hydrogens from the parent, and substantial peaks for the following fragments: $FH_2BN(CH_3)_2CH_2CH_2N(CH_3)CH_2$ (147), $H_2BN(CH_3)_2CH_2CH_2N(CH_3)_2$ (129), $(CH_3)_2NCH_2CH_2N(CH_3)_2$ (116), $(CH_3)_2NCH_2CH_2$ (72), $(CH_3)_2NCH_2$ (58), $NCH_2CH_2$ (42), BHF (31), and BF (30).

A further confirmation of the structure of the fluorinated product was obtained by reacting TMED and $(CH_3)_3NBH_2F$[5] in equimolar quantitities in methylene chloride solution. This method was used by Miller and Meutterties[10] to prepare TMED·2BH$_3$. If we assume that TMED and trimethylamine have similar base strengths, base competition as shown below should lead to displacement of about 50% of the trimethylamine:

$$2(CH_3)_2NCH_2CH_2N(CH_3)_2 + 2(CH_3)_3NBH_2F \rightarrow FH_2BN(CH_3)_2CH_2CH_2N(CH_3)_2BH_2F + (CH_3)_2NCH_2CH_2N(CH_3)_2 + (CH_3)_3N$$

Actually 47% of the possible $(CH_3)_3N$ was measured and a commensurate amount of TMED·2BH$_2$F, identical with the product of fluorination, was isolated.

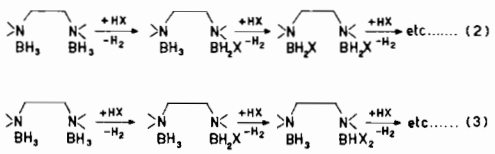
*Chlorination of TMED·2BH$_3$. Preparation of TMED·2BH$_2$Cl*

Using the same method as described above, TMED·2BH$_2$Cl was produced from the reaction of TMED·2BH$_3$ with anhydrous HCl. The yield was essentially quantitative and the product obtained in this manner was acceptably pure (m.p. 143–144° C). Anal. Calcd for $C_6H_{20}B_2Cl_2N_2$: C, 33.87; H, 9.47; N, 13.17; B, 10.16. Found: C, 33.35; H, 9.16; N, 13.08; B, 10.69. The methyl and methylene proton resonances occur at $\delta$ 2.67 and $\delta$ 3.21 respectively. The boron-11 resonance was a triplet ($J_{BH} = 121$ Hz) at + 19.98 ppm with respect to external trimethylborate.

## Discussion

The bisborane adduct of N,N,N′,N′-tetramethylethylenediamine was first prepared by Miller and Muetterties some time ago[10] as a precursor for certain boro-

nium salts. Relatively little work has apparently been done on this compound since that time. We chose to investigate the B-halogenation of TMED·$2BH_3$ in hopes that the sequence of halogenation might shed some light on the influence of the inductive effect in the halogenation reactions. If we consider the general stepwise halogenation, the first halogen may substitute on either borane group but the second step may give either a B,B′-dihalo or a B,B-dihalo product as shown below:




If a straightforward inductive effect of the added halogen is the dominate factor, pathway 2 is expected since the hydrogens of the unsubstituted borane group should remain more negative and therefore react more rapidly with HX (or $X_2$). If the inductive characteristics of the halogen substituent are not decisive, and no other factors are important, a statistical distribution of the two products would be expected {(2) and (3)}.

The progress of the halogenation reactions of TMED·$2BH_3$ was followed by pmr since it has been shown that symmetrically substituted TMED adducts exhibit only two singlet resonances corresponding to methyl and methylene protons, while unsymmetrical adducts exhibit four resonances.[11] Thus if the primary mechanism can be represented by pathway 2, sequential pmr spectra of the products of progressive halogenation should show only two peaks at times when B,B′-dihalo-, B,B,B′,B′-tetrahalo-, and finally the B-hexahalo-tetramethylethylenediamine–bisboranes are present. If pathway 3 or some combination of the two pathways are involved, then it is unlikely that the pmr spectra during the reaction would ever contain just two singlets expect by chance overlap of signals.

In Figure 1 is shown the bromination sequence of TMED·$2BH_3$ carried out using $Br_2$. Molecular bromine was used because rate of bromination with HBr became very slow after the second step. Inspection of Figure 1a shows the methyl ($\delta$ 2.60, [Lit.[11] 2.59]) and the methylene ($\delta$ 3.12 [Lit.[11] 3.12]) protons of TMED·$2BH_3$. Upon exposure to bromine new peaks appear downfield (Figure 1b) from these, probably representing parts of the spectra of the monobromo- and B,B′-dibromo-compounds. Further addition of $Br_2$ results in the spectrum shown in Figure 1c which represents principally B,B′-dibromo-tetramethylethylenediamine–bisborane with $\delta$ $CH_3$ = 2.75 and $\delta$ $CH_2$ = 3.29. Small peaks near $\delta$ 2.6 and $\delta$ 2.9 represent small quantities of starting material (or the first intermediate) and subsequent reaction product respectively. The dibromo-derivative was best isolated and characterized by carrying out the reaction to this point with HBr (see Experimental). Symmetrical bromination was confirmed by $^{11}B$ nmr which showed the expected triplet arising from spin coupling of the boron with the protons in the $BH_2Br$ groups.

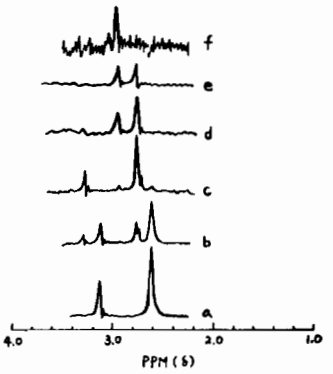



Figure 1. PMR Spectra of the Reaction of $Br_2$ with TMED·$2BH_3$.

Further bromination of the reaction mixture with $Br_2$ resulted in a decrease of the resonances associated with TMED·$2BH_2Br$ and the appearance of a new methyl resonance near $\delta$ 2.90 (the corresponding methylene peak was not identifiable because of overlap with satellites of the solvent resonance). The methyl peak was somewhat broadened perhaps representing two magnetically similar but not identical methyls in the expected tribromo intermediate (Figures 1d and 1e). A solid was evident in the reaction mixture during this time and eventually nearly all the product precipitated. The precipitate was characterized and identified as TMED·$2BHBr_2$. Figure 1f shows the methyl resonance of this compound ($\delta$ 2.90) at higher receiver gain because of its low solubility. The methylene resonance was again undetected because of overlap with solvent signal satellites. The $^{11}B$ spectrum consisted of a broad doublet confirming the symmetrical disposition of the bromines in the product.

The fluorination and chlorination of TMED·$2BH_3$ were carried out similarly, with the B,B′-dihalo-products being isolated and characterized in each case. The former case has some interesting features which should be mentioned; the pmr spectra of the fluorination sequence are shown in Figure 2. Notice that the chemical shift of the methyl proton resonance moves toward higher field as the fluorination proceeds. The methyl proton shift in TMED·$2BH_2F$ is $\delta$ 2.52 which represents a significant shift in the opposite direction to that produced by the other halogens. The general criterion of Lewis base alkyl proton chemical shifts has been used in some cases to estimate the strength of Lewis acid–base interactions.[12,13] In this context the

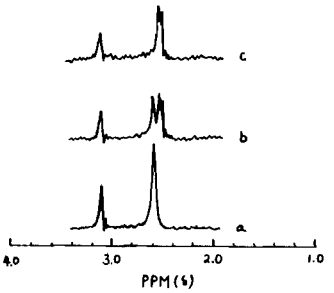



Figure 2. PMR Spectra of the Reaction of HF with TMED · $2BH_3$.

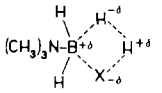
upfield shift of the methyl protons of TMED · $2BH_2F$ (Figure 2c) would suggest that fluorination weakens the B–N adduct bond [a similar shift was observed in $(CH_3)_3NBH_2F$[5]]. Such pmr evidence alone is probably not sufficient to warrant this conclusion because of the possibility of neighborhood anisotropy effects on the chemical shift.

A second point of interest concerns the doublet appearance of the methyl resonance of TMED · $2BH_2F$. In order to establish whether this represented spin coupling or some type of magnetic nonequivalence, another spectrum was obtained at 100 MHz to determine the effect on the magnitude of the splitting. A splitting of 1.5 Hz was measured in both spectra indicating that a spin coupling between the methyl protons and the fluorines, was responsible. The only similar couplings we are aware of are those reported by Heitsch,[14] who gives values of 0.65 ± 0.02 and 0.69 Hz for $J_{HcnbF}$ in trimethylamine– and triethylamine–trifluoroboranes.

When addition of HF to the reaction mixture containing TMED · $2BH_2F$ was resumed, a solid began to be deposited and eventually the pmr signals disappeared. The solid was found to be $[TMEDH_2^{2+}][BF_4^-]_2$ by comparison with an authentic sample prepared from TMED and fluoboric acid. No partially fluorinated intermediates could be detected in the pmr spectra.

The appearance of the tetrafluoroborate salt in lieu of fluorinated intermediates was surprising although we have observed small percentages of tetrafluoroborate salts continuously formed as byproducts in other amine–borane fluorinations.[15] It is possible that another mechanism is responsible for these products. perhaps involving an initial dissociation of the TMED · $2BH_2F$ adduct and rapid attack of the trigonal boron species by HF. If this were the case, fluorinated intermediates would probably not be observed, but more study would be required before a reliable conclusion could be reached on this point. In the chlorination reaction it was found that further attack of HCl on TMED · $2BH_2Cl$ could not be observed under the conditions of the experiment.

The fact that B-halogenation of TMED · $2BH_3$ does give the symmetrically substituted products in every case studied must be considered as evidence that the inductive effect caused by halogens on boron makes the remaining hydrogens less reactive towards electrophilic attack. Noeth and Beyer[2] have proposed a mechanism for the reaction of amine–boranes with hydrohalic acids involving a four-center transition state similar to the one shown below:




Wiggins and Ryschkewitsch[4] have discussed the chlorination of amine–boranes and concluded from their results that such a mechanism probably operates in the case of relatively weak chlorinating agents such as HCl and $HgCl_2$. They suggested that a free radical hydrogen abstraction process may be involved for stronger chlorinating agents, including $SbCl_5$ and $SO_2Cl_2$ on the basis of a thermodynamic argument. Species which readily undergo dissociation yielding halogen atoms are the most likely candidates for this mode of attack, so it is possible that the bromination with molecular bromine proceeds by a free radical mechanism.

The stability of the four-center transition state will depend to a substantial extent on the partial charges of the atoms involved. A strongly polar B–H bond will tend to stabilize the state through Coulombic attractions. Reduction of the bond polarity by the inductive influence of a halogen substituent will destabilize the transition state, thereby (in the absence of other factors) tending to reduce the rate of the reaction. Thus our results with HX molecules appear to be generally consistent with the proposed mechanism. Nevertheless these considerations do not fully account for the HF reactions with $(CH_3)_3NBH_3$ and TMED · $2BH_3$.

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