# REACTION OF BASES WITH 1,2,3,4-TETRAKIS(DICHLOROBORYL)-1,2,3,4-TETRAHYDRONAPHTHALENE

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Abstract – The reaction of group VA and VIA bases with 1,2,3,4-tetrakis(dichloroboryl)-1,2,3,4-tetrahydronaphthalene (I) is studied. Stable complexes are formed with composition,  $I \cdot 3Me_3N$ ,  $I \cdot 3Et_3N$ ,  $I \cdot 2i$ -Pr<sub>3</sub>N,  $I \cdot 3Me_3P$ ,  $I \cdot 2Me_2S$ ,  $I \cdot 2Et_2S$ . Unstable 1:2 complexes are obtained with  $Me_2O$ ,  $Et_2O$  and *i*-Pr<sub>2</sub>O. The ether complexes,  $I \cdot 2R_2O$ , decompose under mild conditions to eliminate all the *R* groups as *RCl*. A structure for the decomposition product is proposed.

### INTRODUCTION

IT is well known that chloroboranes react readily with Group VA ( $R_3X$ ; X = N, P) and group VIA ( $R_2Y$ ; Y = O, S) Lewis bases to form relatively stable 1:1 coordinate complexes (Equations (1) and (2))[1].

$$BCl_3 + R_3 X :\to Cl_3 B \leftarrow XR_3 \tag{1}$$

$$\mathrm{BCl}_3 + R_2 \ddot{Y} :\to \mathrm{Cl}_3 \mathrm{B} \leftarrow \ddot{Y} R_2.$$
<sup>(2)</sup>

In the particular case where Y = O, the complexes are known to decompose under fairly mild conditions with cleavage of the carbon-oxygen bond and the formation of the boron ester and the corresponding alkyl chloride (Equation (3))[1d]. It is interesting that no more than two B-Cl bonds may be cleaved in this manner (Equation (4)).

$$Cl_3B \leftarrow OR_2 \rightarrow Cl_2BOR + RCl$$
 (3)

$$\operatorname{Cl}_2\operatorname{BOR} + R_2\operatorname{O} \to \operatorname{Cl}_2(R\operatorname{O})\operatorname{B} \leftarrow \operatorname{OR}_2 \to \operatorname{ClB}(\operatorname{OR})_2 + R\operatorname{Cl}$$
 (4)

Additionally, the replacement of a chlorine atom by an alkyl or aryl substituent greatly reduces the ability of the boron compound to either attract bases or split ethers [1f]. For the  $R_3X$  and Y = S bases, comparable complexes have been reported; however, cleavage reactions have not been observed [1e].

Our recent studies into the substitutive chemistry of organo-dichloroboranes required a knowledge of the acid-base interaction of these same bases when several  $BCl_2$  groups are bound to adjacent carbon atoms on a single hydrocarbon

a. H. Steinberg and A. L. McClosky, Prog. boron Chem. 1, 83 (1964); b. W. Gerrard and M. F. Lappert, J. chem. Soc. 1486 (1952); c. E. Wiberg, Z. anorg. allg. Chem. 195, 288 (1931); d. E. Muetterties, The Chemistry of Boron Compounds p. 617. Wiley, New York (1967); e. H. L. Morris, N. I. Kalevsky, M. Tamres and S. Searles, Jr., Inorg. Chem. 5, 124 (1966); f. S. H. Dandegaonker, W. Gerrard and M. F. Lappert, J. chem. Soc. 2872, 2893 (1957).

framework. It is expected that a sterically crowded environment of boron groups should affect both the coordination ability of the available acid sites as well as the propensity for subsequent base cleavage reactions. In the present investigation, the reaction of 1,2,3,4-tetrakis(dichloroboryl)-1,2,3,4-tetrahydronaphthalene (I) with tertiary amines, trimethyl phosphine, dialkylethers and dialkylthioethers is reported[2].



### **RESULTS AND DISCUSSION**

# Reaction with group VA bases

A known excess of tertiary amine or trimethyl phosphine was condensed *in* vacuo, at liquid nitrogen temperature, into a vessel containing a preweighed quantity of I. A white solid formed in each case as soon as the mixture was warmed above the melting point of the base. The solids were allowed to sit in excess base for several hours whereupon the volatile materials were removed by pumping.

Table 1 summarizes the reaction data in terms of the reactant ratio (B/I), recovered base, and reaction ratio (b/I). It is evident from the reaction ratio that,

	Base	Rx. Mixt. (B/I)*	Recvd. Base (m-moles)	Recvd. RCl (m-moles)	Rx. Ratio (b/I)-	RCl/I
II	Me <sub>3</sub> N	16.8	2.87		3.03†	
ш	Et <sub>3</sub> N	9.43	1· <b>69</b>		3.06	
IV	<i>i</i> Pr <sub>3</sub> N	10.5	1.62		2-15	
V	Me <sub>3</sub> P	10.5	1.50		2.96	
VI	Me <sub>2</sub> O	10.4	2.56	1.21	2.10	3.90
		14.6	2.66	0.829	2.04	3.93
VII	Et <sub>2</sub> O	11.4	2.92	1-24	1.95	4.02
	-	12.6	2.76	1.08	1.96	4.15
VIII	<i>i</i> Pr <sub>2</sub> O	10.9	1.86	0.831	2.00	3.96
		12.5	2.18	0.816	2.02	3.92
IX	Me <sub>2</sub> S	8-41	1.33		2.10	
х	Et <sub>2</sub> S	9.64	2.35		2.13	

Table	1.	Summary	of	Lewis	base	reaction	data
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\*B/I = (m-moles of starting base)/m-moles I; b/I = (m-moles of base consumed)/I.

 $^{\dagger}A$  value of 3.14 is reported by W. B. Fox, Ph.D. Thesis, Pennsylvania State University (1960).

 a. M. Zeldin and T. Wartik, J. Am. chem. Soc. 88, 1336 (1966); b. W. B. Fox and T. Wartik, J. Am. chem. Soc. 83, 498 (1961). even for relatively small bases (trimethylamine, triethylamine and trimethylphosphine), only 3 of the 4 acid-coordination sites on the  $BCl_2$  groups can accept electron density from the base. The reduction in coordination ability of I is not unexpected based on examination of molecular models[3]. In fact, steric inhibition associated with the  $BCl_2$  groups is so severe in the models that coordination of more than two group V base molecules, regardless of organic substituent, can be considered difficult. It is not surprising, therefore, that the reaction ratio for the bulkier amine, *i*- $Pr_3N$ , decreases to two.

It is notable that the complex between I and *i*-Pr<sub>3</sub>N (IV) is as thermally stable as the smaller base molecules in spite of the fact that "front" and "back" strain effects should be larger with the isopropyl substituents [4]. That some dissociation does occur in IV is indicated by the isolation of small quantities of the free base on heating to 150°. Additionally, a white solid is obtained which has been identified as the complex,  $BCl_3 \cdot iPr_3N$ , by comparison with the authentically prepared material. Similar results are observed for the other base complexes.

The i.r. spectra of all the group VA complexes (Compounds II-IV, Table 3) show a remarkable similarity to each other and resemble that of pure I[2a]. All the spectra have a broad absorption between  $800-950 \text{ cm}^{-1}$  which is characteristic of symmetric and asymmetric BCl<sub>2</sub> stretching modes [5a]. The broadness of this band and the extension of the absorption envelop to a slightly lower energy from the comparable band in I is probably the result of vibrations from both the free and nitrogen coordinated BCl<sub>2</sub> groups. No absorption owing to a  $B \leftarrow N$  vibration is detected below 700 cm<sup>-1</sup> [5b].

The elemental analyses for the complexes are given in Table 2. All the solids decompose prior to melting and are insoluble in polar and non-polar organic solvents. They are sensitive to air and react with water to give an aqueous solution of the base hydrochloride and the same organic polyboronic acid that is obtained by hydrolysis of I.

### Reaction with group VIA bases

Using the same techniques as described above, an excess of an ether ( $Me_2O$ ,  $Et_2O$  or *i*- $Pr_2O$ ) was added to a known quantity of I. On warming the mixture to room temperature the reactants formed a clear yellow solution which remained unchanged for several hours. Subsequently, all volatile materials were removed by pumping and quantitatively analyzed either by conventional fractional condensation techniques or by glp chromatography.

Clearly, the results recorded in Table 1 indicate the formation of an initial 1:2 addition complex. In addition, the degree of complexation seems to be independent of the size of the hydrocarbon substituent on the ether as evidenced by a constant reaction ratio for R = Me, Et and *i*-Pr.

All attempts to detect the  $Me_2O$  or  $Et_2O$  complex in solution were unsuccessful. The proton resonance spectrum of I in an excess of the ether was taken

- 3. Fisher-Hirschfelder-Taylor models.
- 4. a. H. C. Brown, J. chem. Soc. 1248 (1956); b. H. C. Brown and S. Kujishi, J. Am. chem. Soc. 70, 2878 (1948).
- 5. a. L. J. Bellamy, J. Gerrard, M. F. Lappert and R. L. Williams, J. chem. Soc. 2412 (1958); b. W. Sawodny and J. Goubeau, Z. phys. Chem. 44, 227 (1965).

immediately after mixing and showed the normal chemical shifts of the ether protons and the protons on the two rings of I[2]. On standing, the spectra became too complicated for interpretation owing to the presence of reactants, intermediates and products.

Regardless of experimental conditions, a pure ether addition complex was never isolated. The removal of excess ether from the reaction mixture always was accompanied by the corresponding alkyl halide, RCl. On prolonged pumping (with mild heating for dimethyl and diethylether and at ambient temperature for diisopropylether) enough of the alkyl chloride was obtained to quantitatively account for all the ether organic groups in the complex (RCl/I  $\approx$  4). It is noteworthy that the relative rate of alkyl chloride elimination decreases in the order *i*-Pr > Et > Me which can be rationalized in terms of steric effects, the decreased carbon-oxygen bond energy and the increased stabilizing effect of a possible carbonium ion intermediate[6].

The residues from the total evaporation of the ether and the alkyl chloride were bright yellow crystalline solids (VI-VIII). These solids were stable to 300° in the absence of air and insoluble in either the parent ether or other organic solvents. VI, VII and VIII oxidized slowly in air and hydrolyzed readily to give HCl and a white solid, which was the corresponding polyboronic acid.

The analytical data for VI, VII and VIII are summarized in Table 2. The fact that all analyses fit the same empirical formula suggest that a common structural unit is obtained in each ether reaction. The uniqueness of structure is further supported by the i.r. spectra which are identical for all the products. In addition to the characteristic broad B-Cl stretching mode at 955 cm<sup>-1</sup>[5], a 1380 cm<sup>-1</sup> band, tentatively assigned to a B-O-B stretching vibration, is observed [7]. No such band is present in the spectrum of I.

Base		С	Н	В	Cl	N(P)
Me₀N	Calcol for CueHarBrCleNa	36.08	5.58	6.84	44.85	6.64
	Found	36.53	5.35	6.52	44.66	6.80
Et <sub>3</sub> N	Calcd. for $C_{28}H_{13}B_4Cl_8N_3$	44.33	7.04	5.70	37.39	5.54
0	Found	43.88	7.21	5.51	37.90	5.10
<i>i</i> Pr <sub>3</sub> N	Calcd. for $C_{28}H_{50}B_4Cl_8N_2$	45.35	6.80	5.83	38.24	3.78
-	Found	<b>46</b> ·10	6.26	5.56	38.33	3.53
Me <sub>3</sub> P	Calcd. for $C_{19}H_{35}B_4Cl_8P_3$	33-40	5.16	6.33	41.51	(13.60)
	Found	33.61	5.09	6.09	41.53	(13.47)
Me <sub>2</sub> O	Calcd. for $C_{10}H_8B_4Cl_4O_2$	34.79	2.34	12.53	<b>41</b> .08	
-	Found	35.06	2.11	12.33	40.65	
$Et_2O$	Found	35-43	2.16	12.40	41.31	
<i>i</i> Pr <sub>2</sub> O	Found	34.91	2.52	12.28	40.84	
$Me_2S$	Calcd. for $C_{14}H_{20}B_4Cl_8S_2$	29.02	3.48	7.46	48.96	
	Found	29.63	4·01	7.30	<b>48</b> ·81	
Et <sub>2</sub> S	Calcd. for C <sub>18</sub> H <sub>28</sub> B <sub>4</sub> Cl <sub>8</sub> S <sub>2</sub>	34.02	4.44	6.81	44.64	
	Found	34.37	4·12	6.76	<b>45</b> ∙08	

Table 2. Analytical data for addition compound of group VA and group VIA bases

6. W. Gerrard and M. F. Lappert, J. chem. Soc. 1020 (1951).

7. W. Gerrard, The Organic Chemistry of Boron p. 225. Academic Press, New York (1961).

The reaction stoichiometry can best be represented by the following equations:

$$C_{10}H_8(BCl_2)_4 + 2R_2O \rightleftharpoons C_{10}H_8(BCl_2)_4 \cdot 2R_2O$$
 (5)

$$\times C_{10}H_8(BCl_2)_4 \cdot 2R_2O \to [C_{10}H_8(BCl)_4O_2]_x + 4xRCl.$$
(6)

Assuming no gross carbon-skeleton rearrangements, the structure of the product can be postulated as either a polymeric material with inter-and/or intramolecular B-O-B bridges between tetralin-like rings  $(x \ge 2)$  or, more likely, owing to steric requirements, a monomeric species containing two intramolecular heterocyclic rings (x = 1). Both structures can be stabilized by extensive  $p\pi - p\pi$  delocalization of the lone pair electrons on oxygen and chlorine through the vacant p orbitals on the borons. Further structural studies of this compound are currently underway.



Contrary to the ether reaction products, the thioethers,  $Me_2S$  and  $Et_2S$ , formed relatively stable 1:2 adducts with I (Table 1: compounds IX and X respectively); however, neither of the complexes showed any tendency to decompose by C-S bond cleavage at room temperature. On heating the solid complexes above 130°, volatile decomposition products were produced which were identified as the boron trichloride complexes,  $BCl_3 \cdot Me_2S$  and  $BCl_3 \cdot Et_2S[1e]$ . Only small quantities of the free base and a trace of the alkyl chloride were identified.

The thioether complexes were white powders that decomposed prior to melting and showed no solubility in non-protonic organic solvents. The analyses are recorded in Table 2.

The i.r. spectra of IX and X (Table 3) were poorly resolved; however, the usual broad absorption between  $850-1000 \text{ cm}^{-1}$  characteristic of BCl<sub>2</sub> groups was present[5]. Interestingly, there is a lack of reactivity with dimethyl or diethylether, despite the general acceptance that O-ethers are more basic than S-ethers. This has been interpreted in terms of (a) the possibility that sulfur may be acting as a bifunctional donor which coordinately saturates all available acid sites (see structure on following page), and (b) steric effects which inhibit the substitution reaction.

The S-ether adducts reacted with ethanol in a complex manner. In addition to the liberation of the thioether, a mixture of chlorinated products (HCl and EtCl) was obtained. Although care was taken to maintain a constant set of reaction conditions, the product ratio was not reproducible. The reaction residues were white polymeric materials which presumably were formed by a mixture of both inter- and intramolecular elimination processes.



Table 3. I.R. spectra of reactant and products

Compound	Frequencies and relative intensities* (cm <sup>-1</sup> )			
$C_{10}H_8(BCl_2)_4[2a]$	3050 m, 3000 sh, 2890 m, 2830 m, 1960 vw,			
	1930 vw, 1625 m, 1600 m, 1560 m, 1500 m,			
	1455 m, 1400 m, 1343 m, 1308 sh, 1273 s, 1200 s,			
	1125 w, 1100 d, 930 br, 853 sh, 825 m, 783 s, 753 d,			
	726 m, 705 m			
$C_{10}H_8(BCl_2)_4$ . 3 Me <sub>3</sub> N	3040 w, 2995 vs, 2850 vs, 1630 m, 1615 w, 1470 s,			
	1400 m, 1350 sh, 1265 s, 1195 s, 1180 sh, 1120 br,			
	~900 vbr, 830 m, 780 m, 735 s, 700 m			
$C_{10}H_8(BCl_2)_4$ . 3 $Et_3N$	3045 w, 2990 vs, 2960 sh, 1630 w, 1600 m, 1480 m,			
	1425 m, 1330 w, 1255 s, 1195 br, 1060 br, ~900 vbr,			
	810 m, 800 sh, 770 m, 735 m, 705 w			
$C_{10}H_8(BCl_2)_4 . 2 i - Pr_3N$	3045 w, 2990 vs, 2860 vs, 2840 sh, 1950 vw, 1650 w,			
	1630 m, 1595 m, 1495 m, 1455 s, 1365 sh, 1265 (s),			
	1105 s, 1070 d, ~900 vbr, 850 sh, 810 m, 765 m,			
	730 s, 725 sh			
$C_{10}H_8(BCl_2)_4$ . 3 Me <sub>3</sub> P	3040 w, 2990 vs, 2890 sh, 2870 vs, 1940 vw, 1860 vw,			
	1660 m, 1600 m, 1500 m, 1435 d, 1235 m, 1180 br,			
	955 br, 905 sh, 810 m, 760 w, 740 m, 705 m			
$C_{10}H_8(BCl)_4O_2$	3070 w, 2995 vw, 1620 w, 1600 m, 1585m, 1495 m,			
	1430 sh, 1380 s, 1345 sh, 1255 m, 1210 sh, 1195 m,			
	1105 s, 1095 sh, 955 br, 880 m, 820 w, 795 vw, 755 s,			
	745 sh			
$C_{10}H_8(BCl_2)_4$ . 2 Me <sub>2</sub> S	3060 w, 2990 s, 2850 sh, 1630 w, br, ~1500 vw,			
	1350 m, d, 1230 br, 1150 br, sh, ~950 vbr, 800 m,			
	750 br, d, 725 m			
$C_{10}H_8(BCl_2)_4$ . 2 $Et_2S$	3060 w, 2990 s, 2860 sh, 1625 w, br, 1510 w, 1410 w,			
	1355 m, 1320 sh, 1260 br, 1170 vbr, ~950 vbr, 810 m, <750 vbr			

\*vs, very sharp; s, sharp; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad; vbr, very broad; d, doublet.

# EXPERIMENTAL

The preparation of I has been previously described[2]. All bases were purchased as reagent grade chemicals. They were dried over 3A molecular series and used without further purification. Conventional high-vacuum techniques were employed for gas manipulation. A Perkin-Elmer Model 337 Grating Spectrometer was used to record i.r. spectra. The spectra were taken as a KBr pellet,

### Reaction of bases

a Nujol mull and a hexachlorobutadiene mull. An F & M 700 glp chromatograph was used for the ether-alkyl chloride composition. C, H, B and P analyses were made by Schwarzkopf Microanalytical Laboratory. Cl analyses were made in this laboratory by hydrolysis of a weighed sample of adduct in an acid solution of known concentration of  $AgNO_3$  and subsequent back titration of the excess silver ion. All air-moisture sensitive compounds were handled in a dry nitrogen glove-bag.

### Preparation of group VA base complexes

In typical experiment, trimethylamine (3.50 m-moles) was condensed at  $-196^{\circ}$  into a hook breakerseal ampule containing I (0.208 m-moles). The vessel was sealed from the line and slowly warmed to room temperature. A white solid, II, precipitated as soon as the base melted and contacted I. The mixture was allowed to stand for 12 hr at room temperature without noticeable change. The ampule was opened under vacuum at the breaker seal and the unreacted base (2.87 m-moles) was removed by pumping into a liquid N<sub>2</sub> trap.

The analysis of the solid residue is given in Table 2. Table 3 records the i.r. spectrum.

A portion of II was heated to 150° for 3 hr with pumping. A white solid was condensed at  $-80^{\circ}$  and was identified as Me<sub>3</sub>N·BCl<sub>3</sub> by comparison of the i.r. and melting point with the authentic compound prepared from Me<sub>3</sub>N and BCl<sub>3</sub> (m.p. = 238-240°; lit. 243°[8]).

The reaction of I with  $Et_3N$  gave III. III was decomposed to  $Et_3N \cdot BCl_3$  (m.p. = 96–98°; lit. 93° [9]). The reaction of I with *i*-Pr<sub>3</sub>N gave IV, which when decomposed afforded *i*-Pr<sub>3</sub>N  $\cdot BCl_3$ . The latter was verified by comparison of the i.r. spectrum with the authentically prepared material. Decomposition of V gave Me<sub>3</sub>P  $\cdot BCl_3$  (m.p. = 245°; lit. 242 [10]).

Separate samples of II, III, IV and V were hydrolyzed with excess water. Vacuum removal of all volatile materials left a white solid which was identical, by i.r., to the hydrolysis product of I.

#### Reaction with diethylether

A measured excess of Et<sub>2</sub>O (3.52 m-moles) was condensed into a vacuum ampule containing I (0.308 m-moles) at  $-196^{\circ}$ .

The reactants were warmed to room temperature whereby the ether dissolved the adduct to form a clear yellow solution. After 12 hr and no observable change in the solution, the ampule was opened and the unreacted ether and other volatile products were removed by pumping through traps at  $-95^{\circ}$  and  $-196^{\circ}$ . Occasional warming was necessary to effect complete removal of volatile materials. The unreacted Et<sub>2</sub>O (2.93 m-moles) and EtCl (1.24 m-moles) were collected in the two traps, respectively.

The residue was a bright yellow crystalline solid VII which was found to be insoluble in the parent ether, chloroform, carbon tetrachloride, toluene and pentane. The elemental analysis of VII and the residues from the Me<sub>2</sub>O and *i*-Pr<sub>2</sub>O experiments (V and VIII) are given in Table 2. The i.r. spectra are recorded in Table 3.

A sample of VII (0.0981g) was treated with acidified  $AgNO_3$  solution (10 ml, 0.1M). The AgCl (0.1638 g) that was precipitated from solution agreed with the back titration data of the excess  $Ag^+$  (Cl = 41.31 per cent).

Hydrolysis of VII at 80° gave a white solid which was identical to the hydrolysis product of I.

### Preparation of dimethylsulfide complex

In a typical experiment  $Me_2S$  (1.77 m-mole) was condensed onto I (0.210 m-mole) at -196°. A white precipitate IX formed on warming the mixture to room temperature.

The volatile components were fractionated through  $-95^{\circ}$  and  $-196^{\circ}$  traps. The only observed product was the excess base (1.33 m-moles) retained at  $-95^{\circ}$ . There was no indication of the formation of MeCl. The analysis and i.r. spectrum of IX are recorded in Tables 2 and 3, respectively.

IX (0.098 m-moles) was heated to 130° for several hours. The volatile products, after fractionation, were identified as the complex,  $BCl_3 Me_2S$  (white solid; m.p. = 88-90°, lit. 85-90° [1e]), free  $Me_2S$  (0.016 m-mole) and a trace of MeCl as detected by i.r.

IX (0.122 m-mole) was stirred with EtOH ( $\sim 5$  ml) at room temperature for 2 hr. The gaseous components were removed and fractionated. Besides HCl (0.363 m-mole), appreciable quantities of EtCl

8. E. Wiberg and W. Sütterlin, Z. anorg. allg. Chem. 202, 31 (1931).

9. W. Gerrard, M. F. Lappert and C. A. Pearce, J. chem. Soc. 381 (1957).

10. G. M. Phillips, J. S. Hunter and L. E. Sutton, J. chem. Soc. 146 (1945).

(0.270 m-mole) were obtained. This corresponded to approximately 64 per cent recovery of halogen.

Hydrolysis of IX (~0.1 g) with  $H_2O$  (~ 5 ml) and evaporation of volatile materials gave a white residue which was identical to the hydrolysis product of I.

Decomposition of the Et<sub>2</sub>S complex, X, gave a white solid ( $Et_2S \cdot BCl_3$ ) at  $-23^{\circ}$  and melted near 15° on warming to room temperature (lit. 10-11°,[1e]).

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