

107. The Reaction of Diborane with the Alkyl Derivatives of Some Group VB Elements.

BY F. HEWITT and A. K. HOLLIDAY.

With Group VB trialkyls M, diborane yields borine co-ordination compounds $\overset{+}{M}-\bar{B}H_3$. The effect of change of donor atom and of alkyl group on the thermal stability of these compounds is discussed, and their reaction with hydrogen chloride is investigated.

ALTHOUGH borine normally exists only as the dimer diborane, the latter can undergo fission in the presence of a donor molecule M to give compounds $\overset{+}{M}-\bar{B}H_3$ in which the borine group is stabilised by co-ordination. Known compounds of this type include those with $M = Me_3N$, CO, and Me_2O (Schlesinger and Burg, *J. Amer. Chem. Soc.*, 1937, **59**, 780; 1938, **60**, 290). The trialkyls of the Group VB elements generally act as donor molecules to form 1 : 1 co-ordination compounds with electron-acceptor molecules BX_3 (other than borine), *e.g.*, $Me_3\overset{+}{P}-\bar{B}Me_3$ (Brown and Harris, *ibid.*, 1949, **71**, 2751), $Me_3\overset{+}{P}-\bar{B}Br_3$ (Holliday and Mowle, unpublished work), $Et_3\overset{+}{N}-\bar{B}F_3$ (Kraus and Brown, *J. Amer. Chem. Soc.*, 1929, **51**, 2690): similar compounds with the Group III analogues of BX_3 have been obtained. The relative stabilities of the 1 : 1-compounds of trimethylgallium with the trimethyl derivatives of all the Group VB elements have been discussed by Coates (*J.*, 1951, 2003). We have, therefore, investigated the reactions of diborane with several Group VB trialkyls, with the object of obtaining co-ordination compounds of borine and, if possible, of studying the effect on stability and other properties of (a) change of donor atom and (b) change of alkyl groups in the donor molecule.

TABLE 1.

Compound	M. p.*	V. p. (25°), mm.	Temp. of decomn.	Products of decomn., 120°	Moles of H ₂ per 100 moles of compound
$Me_3\overset{+}{N}-\bar{B}H_3$ †	94°	0.9	>125°	Unchanged	0
$Me_3\overset{+}{P}-\bar{B}H_3$ ‡	100 *	40	80—90	H ₂ , CH ₄	2.6
$Me_3\overset{+}{As}-\bar{B}H_3$	72 *	~3	40—50	H ₂ , CH ₄	5.4
$(Me_3\overset{+}{Sb}-\bar{B}H_3)$	-35 *	—	-35	H ₂	~26
$Et_3\overset{+}{P}-\bar{B}H_3$	46	62	60—70	H ₂	7.4
$Et_3\overset{+}{As}-\bar{B}H_3$	40 *	~1	30—40	H ₂	14.8
$(n-Pr_3\overset{+}{P}-\bar{B}H_3)$	~11	10	40—50	H ₂	~20

* Indicates decomposition.

† Data from Schlesinger and Burg, *loc. cit.*‡ Also prepared recently (1951) by Burg *et al.* (unpublished), who find hydrogen and methane in the thermal decomposition products.

When excess of diborane was condensed on the solid trialkyl at liquid-nitrogen temperature, and the temperature allowed to rise, reaction commenced and crystals appeared at the liquid-liquid interface. When reaction had ceased, unchanged reactants were removed, and the remaining solid purified by sublimation. Analysis and molecular-weight determination showed that for each trialkyl used, a 1 : 1-compound $\overset{+}{M}-\bar{B}H_3$ was formed. When tri-*n*-propylphosphine was used, separation of the 1 : 1-compound was incomplete, and an impure product resulted. With trimethylstibine, crystals were formed which melted at -35°, but completely dissociated above this temperature. The compounds obtained, together with some of their properties, are listed in Table 1. With the two exceptions noted, all the compounds formed well-defined crystals, with an appreciable vapour pressure at room temperature, soluble in most organic solvents, insoluble in, but slowly hydrolysed by, cold water, and readily attacked by aqueous oxidants, *e.g.*, hydrogen peroxide and nitric acid. When they are heated *in vacuo*, irreversible decomposition occurs, often

below the m. p. To determine the temperature range over which decomposition begins, vapour-pressure measurements were made for 10° increments, the temperature being increased and decreased over each 10° range before the next increment was made. The lowest range over which the ascending and descending v. p.-*T* curves were non-concurrent gave the decomposition range (see Table 1). Thermal decomposition was further studied by heating the compounds in a sealed tube for 3 hours at 120°. From those containing methyl groups, hydrogen and a little methane were identified as volatile products; the other compounds yielded no hydrocarbon. Small amounts of other volatile products were obtained but not identified; some evolved hydrogen on storage, and it is probable that they were higher hydrides of boron.

A quantitative criterion of stability—the dissociation constant for the reaction $\overset{+}{M}-\bar{B}H_3 \rightarrow M + BH_3$ —cannot be obtained from the above data because of irreversible secondary decomposition; but it is reasonable to suppose that this dissociation must be the important initial step in decomposition: and as the donor part of the molecule is thermally stable, the decomposition products must be chiefly those formed by interaction of the borine radicals. In Table 1, therefore, the hydrogen produced per mole of each compound is given, as a measure of the extent of thermal decomposition at 120°. This, together with the temperature of initial decomposition, gives two qualitative stability criteria which may be used to compare the compounds listed.

Effect of Change of Donor Atom on Stability.—For the trimethyl compounds, both criteria indicate an order of stability $N > P > As > Sb$, *i.e.*, decreasing with increasing size of donor atom; the same order was observed for compounds of Group V trialkyls with trimethylgallium (Coates, *loc. cit.*), trimethylaluminium (Brown and Davidson, *J. Amer. Chem. Soc.*, 1942, **64**, 316) ($N > P$), and trimethylboron (Brown, unpublished; see Chatt, *J.*, 1951, 652) ($N > P > As$) as acceptors.

Effect of Change of Alkyl Groups on Stability.—For the phosphorus compounds, both criteria indicate a stability sequence $Me > Et > Pr^n$, and for arsenic $Me > Et$ (the low stability of $PPr^n-\bar{B}H_3$ and its appreciable dissociation at ordinary temperature is responsible for the difficulty of isolating this compound). These results may be compared with those of Brown, Taylor, and Sei Sujishi (*J. Amer. Chem. Soc.*, 1948, **70**, 2878; 1951, **73**, 2464) for trimethyl boron with alkylamines as donors, *i.e.*, $R_3\bar{N}-\overset{+}{B}Me_3$, where a stability order $Me > Et < Pr^n < Bu^n < \dots$ was found. These authors suggest that conflicting steric requirements of the amine alkyl and the boron-attached methyl groups become important with the triethylamine compound, leading to a fall in stability; with larger alkyl groups the effect is modified by the increased inductive effect of the alkyls, and stability increases again, although rather slowly. In the present case, the greater size of the donor atom (P or As) and the presence of boron-attached hydrogen rather than methyl may make steric factors less important for methyl and ethyl than for *n*-propyl and higher alkyls. At the same time, the smaller inductive effect which the alkyls can exert, owing to the larger donor atom, may make the steric factors generally of predominant importance, bringing about the observed regular fall in stability with increasing size of alkyl.

The formation of a trace of methane in the decomposition of the trimethyl compounds may arise from the reaction $xMe_3\overset{+}{P}-\bar{B}H_3 \rightarrow (Me_2P, BH_2)_x + xMeH$ occurring simultaneously with dissociation [cf. the decomposition $R_3\overset{+}{N}-\bar{B}R_3 \rightarrow R_2N:BR_2 + R'R$ (Wiberg, F.I.A.T. Review 1949, Inorganic Chemistry, Part I, p. 129)]. In support of this mechanism, $Me_2\overset{+}{HP}-\bar{B}H_3$, when heated to 150° yields hydrogen and the trimer and tetramer of $Me_2\overset{+}{P}, \bar{B}H_2$ —both of these are chemically inert and thermally stable (Burg *et al.*, unpublished). The triethyl compounds $Et_3\overset{+}{P}-\bar{B}H_3$ and $Et_3\overset{+}{As}-\bar{B}H_3$ do not yield ethane on decomposition, possibly because the dissociation into borine and donor molecule is more readily achieved than the removal of an ethyl group from the donor atom.

The phosphorus and arsenic compounds listed in Table 1 all reacted vigorously with excess of hydrogen chloride on being warmed from liquid-nitrogen temperature. Hydrogen was evolved and, for the four compounds given in Table 2, the amount was measured

TABLE 2.
C.c. at N.T.P.

Compound	Amount used	H ₂ evolved = x	Amt. reacted = $x/3$	HCl used = y	$3y/x$
Me ₃ P ⁺ -BH ₃ ⁻	7.10	12.8	4.27	16.0	3.75
Me ₃ As ⁺ -BH ₃ ⁻	5.41	13.1	4.37	18.6	4.25
Et ₃ P ⁺ -BH ₃ ⁻	3.80	7.77	2.59	11.4	4.38
Et ₃ As ⁺ -BH ₃ ⁻	2.80	8.10	2.70	16.2	6.00

after one week at room temperature, together with the amount of hydrogen chloride used. The results show that the amount of hydrogen was less, and the amount of hydrogen chloride greater, than that required by the equation $\text{Et}_3\text{P}^+\text{-BH}_3^- + 3\text{HCl} \rightarrow \text{Et}_3\text{P}^+\text{-BCl}_3 + 3\text{H}_2$. No other gas or volatile product was formed. If the above equation is assumed to represent the main reaction, and if it is also assumed that the extent of this reaction is given by the amount of hydrogen evolved, then the last column of Table 2 shows that the molar excess of hydrogen chloride is approximately equal to the number of mols. of $\text{M}^+\text{-BCl}_3$ compound formed, for the first three of the listed compounds. It is difficult to account for this fact other than by assuming the formation of a hydrochloride, *i.e.*, $\text{M}^+\text{-BCl}_3 + \text{HCl} \rightarrow [\text{MH}]^+[\text{BCl}_4]^-$. There is some indirect evidence for the formation of the $[\text{BCl}_4]^-$ ion in the compounds $\text{NOCl}, \text{BCl}_3$ and $\text{PCl}_5, \text{BCl}_3$ which may exist in the solid state as $[\text{NO}]^+[\text{BCl}_4]^-$ and $[\text{PCl}_4]^+[\text{BCl}_4]^-$ respectively (cf. Martin, *J. Phys. Chem.*, 1947, **51**, 1400). In addition, Wiberg and Heubaum (*Z. anorg. Chem.*, 1935, **222**, 98) have prepared the stable, crystalline, involatile compound $\text{CPh}_3\text{Cl}, \text{BCl}_3$ which may be formulated as $[\text{CPh}_3]^+[\text{BCl}_4]^-$. Simple alkali chloroborates, *e.g.* NaBCl_4 , have never been prepared, in contrast to the well-known fluoroborates; the presence of a large cation may therefore be an essential prerequisite to the formation of a chloroborate.

The initial product $\text{M}^+\text{-BCl}_3$ believed to be formed in the reaction with hydrogen chloride is readily prepared by direct addition of the trialkyl donor molecule to boron trichloride (*e.g.*, $\text{Me}_3\text{P}^+\text{-BCl}_3$; Phillips, Hunter, and Sutton, *J.*, 1945, 146). If the reaction product, containing the presumed hydrochloride and unchanged $\text{M}^+\text{-BH}_3$, was gently heated *in vacuo*, the latter sublimed off, and the residue was found to have approximately the same m. p. as the corresponding $\text{M}^+\text{-BCl}_3$ compound formed by direct addition (*e.g.*, with triethylphosphine as donor, the product had m. p. 62°; $\text{Et}_3\text{P}^+\text{-BCl}_3$ prepared by direct addition had m. p. 65°). Hence, if a hydrochloride was formed, loss of hydrogen chloride occurred on heating it; the amount lost was not, however, determined. No reaction was observed when hydrogen chloride was condensed on $\text{Me}_3\text{As}^+\text{-BCl}_3$, all the hydrogen chloride being recovered on warming the mixture to room temperature. Evidence for hydrochloride formation is therefore inconclusive, and further study is required.

The reverse reaction, *i.e.*, reduction of compounds $\text{M}^+\text{-BCl}_3$ to $\text{M}^+\text{-BH}_3$, was attempted by using lithium aluminium hydride in ethereal solution. No reaction was observed even after 24 hours at room temperature with any of the compounds. Now boron trichloride is readily reduced by lithium aluminium hydride *in the presence of ether* to give diborane. In the absence of ether, reduction is difficult and the yield of diborane poor, suggesting that the ether is a necessary participant in the reduction (Paddock, *Nature*, 1951, **167**, 1070). However, in ethereal solution boron trichloride is present as the moderately stable etherate $\text{Et}_2\text{O}^+\text{-BCl}_3$, and the reduction can be represented as $\text{Et}_2\text{O}^+\text{-BCl}_3 \xrightarrow{\text{LiAlH}_4} \text{Et}_2\text{O}^+\text{-BH}_3$, followed by decomposition of the unstable borine etherate $2\text{Et}_2\text{O}^+\text{-BH}_3 \rightarrow \text{B}_2\text{H}_6 + 2\text{Et}_2\text{O}$. This may explain why the reduction of boron trichloride in ethereal solution proceeds to virtual completion. But when boron trichloride is co-ordinated to a Group V trialkyl, solution in ether yields no etherate, *i.e.*, the ether does not displace the trialkyl donor molecule.

More important, a strong donor molecule M greatly reduces the reactivity of the boron-attached halogens in $M^+-\bar{B}X_3$ compounds; *e.g.*, in boron trichloride or its etherate, chlorine atoms are readily replaceable by hydroxyl groups, by the action of water or alcohol; but these reagents have no action on boron trichloride-trimethylamine $Me_3N^+-\bar{B}Cl_3$. The non-reactivity of $M^+-\bar{B}Cl_3$ compounds towards lithium aluminium hydride in ethereal solution may thus be accounted for.

EXPERIMENTAL

The compounds described were prepared and studied in a vacuum apparatus as described by Stock ("The Hydrides of Boron and Silicon," Cornell, 1933) and by Sanderson ("Vacuum Manipulation of Volatile Compounds," Wiley, 1948). The two reactants were condensed in a tube (Sanderson, *op. cit.*), the latter was sealed off, and reaction allowed to proceed. The contents were then frozen in liquid nitrogen, the tube opened to the vacuum apparatus, and any non-condensable gas pumped off and transferred to a gas burette with a Töpler pump. Other volatile products of reaction were then removed and fractionated, and the amounts measured. The reaction tube was again sealed, transferred to a dry box, and opened to allow removal of the solid or liquid product for analysis or for study of reactions.

Analysis.—Where the trialkyl component of the compound was sufficiently volatile, the amounts of reactants and products could be determined and a material balance was obtained. With less volatile trialkyl components, analysis for boron and the donor atom was carried out, and this analysis was also made on the compounds formed with volatile trialkyls as a check. The molecular weight of each compound was determined by a cryoscopic method using a thermistor and benzene as solvent (Holliday and Sowler, *J.*, 1952, 11). Analysis for phosphorus was by fusion with sodium peroxide, precipitation of the resulting phosphate as ammonium phosphomolybdate, and alkalimetric titration of the latter. For arsenic, fusion with the peroxide was followed by acidification and reduction to the As(III) state with potassium iodide; the liberated iodine was boiled off, glycerol added to prevent decomposition of excess of iodide, and the neutral solution titrated with standard iodine. Boron analyses were by hydrolysis of the compound in a sealed tube, followed by titration of the liberated boric acid in presence of mannitol.

Vapour-pressure-Temperature Curves.—These were determined in an apparatus similar to that of Stock and Küss (*Ber.*, 1914, 47, 3115). The products of thermal decomposition were analysed in the vacuum apparatus; methane and hydrogen mixtures were determined by combustion with oxygen over a platinum spiral attached to the Töpler pump gas burette; from the contraction in volume after combustion the relative amounts of methane and hydrogen were calculated.

Materials.—The diborane was obtained by reduction of boron trichloride (v. p. 3–4 mm. at -78°) with lithium aluminium hydride in ether (Finholt, Bond, and Schlesinger, *J. Amer. Chem. Soc.*, 1947, 69, 1199). After fractionation in the vacuum apparatus it had v. p. 228 mm. at -112° ; hydrogen was evolved on storage, and this was pumped off and the residue re-fractionated to give the same v. p. before use. In all reactions of diborane, a little hydrogen was produced, owing to surface reaction (Emeléus and Stone, *J.*, 1950, 2755). The Group V trialkyls were prepared by reaction of the appropriate trichloride in ether with the requisite Grignard reagent, followed by destructive distillation at 200° (for trimethyl- and triethyl-phosphine) or by hydrolysis (for the other trialkyls). The ethereal distillates or extracts were then shaken with a solution of silver iodide in potassium iodide to form the corresponding complexes (Mann, Wells, and Purdie, *J.*, 1937, 1828), and the latter were filtered off and dried (P_2O_5). The free trialkyl compounds were then regenerated by heating the complex in a tube attached to the vacuum system.

The following exemplify the methods used in studying the compounds listed in Table 1:

Preparation of trimethylphosphine-borane. 112.6N-c.c. (5.02 mmol.) of trimethylphosphine and 110.5N-c.c. (4.93 mmol.) of diborane were condensed in a reaction tube and sealed off from the vacuum line. The temperature was brought to $\sim 20^\circ$, and the tube left for 24 hours to allow completion of the reaction. The tube was then cooled in liquid nitrogen and opened to the vacuum system, and the small amount of hydrogen pumped off and measured (0.12N-c.c.). Excess of diborane was then removed at -78° and unreacted trimethylphosphine was evaporated off as rapidly as possible at room temperature to prevent volatilisation of the addition

compound. 52.4N-c.c. of diborane were found to have reacted with 108.4N-c.c. of trimethylphosphine [Found: B, 11.6; P, 39.9%; P:B = 1.03:1; *M*, 91.4. $\text{Me}_3\text{P}^+\text{BH}_3^-$ requires B, 12.0; P, 34.5%; *M*, 89.7].

Thermal decomposition of trimethylarsine-borine. 0.1059 G. (17.75N-c.c.) of the compound, heated at 120° for 3 hours, yielded 2.49N-c.c. of gas non-condensable at liquid-nitrogen temperature; on combustion with oxygen, it gave carbon dioxide, and the oxygen consumed corresponded to 2.25N-c.c. of hydrogen and 0.24N-c.c. of methane. A small amount of material volatile above -78° was also formed, and evolved hydrogen on storage, but after fractionation there was too little for identification.

Reaction with hydrogen chloride. Excess of hydrogen chloride was condensed on a small amount of the compound in a tube, which was sealed at liquid-nitrogen temperature; a vigorous reaction occurred on warming it to room temperature. After 24 hours, 0.0051 g. (0.85N-c.c.) of the compound reacted with 2.94N-c.c. of hydrogen chloride yielding 1.49N-c.c. of hydrogen; after 170 hours, 0.0323 g. (5.41N-c.c.) of product reacted with 18.6N-c.c. of hydrogen chloride, giving 13.1N-c.c. of hydrogen. No other volatile product was found. The acid left in the reaction tube was warmed gently to free it from any unchanged complex, and then had m. p. > 170°. A specimen of trimethylarsine-boron trichloride, prepared by Phillips, Hunter, and Sutton's method (*loc. cit.*) (Found: Cl, 45.4. Calc. for $\text{Me}_3\text{As}^+\text{BCl}_3^-$: Cl, 44.9%), also had m. p. > 170°. Addition of lithium aluminium hydride to this compound dissolved in ether gave no visible reaction, and no precipitate after 24 hours at room temperature. The lithium aluminium hydride was destroyed by careful addition of water and the ether layer rapidly separated, dried, evaporated, and extracted with benzene to remove any lithium chloride. The evaporated extract gave a solid, m. p. > 170°.

DEPARTMENT OF INORGANIC AND PHYSICAL CHEMISTRY,
THE UNIVERSITY OF LIVERPOOL.

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