646. *The Chemistry of Boron. Part VI.*[1] *New Preparative Methods and Decomposition Studies Relating to Methyldiboranes*

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Methyldiboranes, $B_2H_{6-n}Me_n$, have been prepared in a single-stage process by the interaction of trimethylborane under pressure with a metal borohydride and either hydrogen chloride or boron trichloride. If sodium borohydride is admixed with aluminium chloride, yields rise to >80% (based on total boron) with hydrogen chloride, but remain rather poor with boron trichloride. Lithium borohydride, however, gives yields of 90—95% with either hydrogen chloride or boron trichloride. Methane is liberated in the reactions involving sodium borohydride, but not with the lithium salt.

The thermal decomposition of tetramethyldiborane has been studied quantitatively with respect to disproportionation.

IN view of the importance of alkyldiboranes as derivatives of diborane and as possible reaction intermediates, surprisingly little has been published regarding their preparation and properties. The five possible methyldiboranes, $B_2H_{6-n}Me_n$ (where $n = 1$—4), including the two isomeric dimethyl compounds, were first prepared and characterised by Schlesinger and his co-workers,[2] who made use of the equilibration reaction $(6\text{-}n)B_2H_6 + 2n\,BMe_3 \rightleftharpoons 6B_2H_{6-n}Me_n$. Further methods of preparation have been reported relatively recently (for literature see Part V), the yields being invariably low. These compounds have also been prepared from the hydrogenolysis of trimethylborane under pressure at 80—200° [3] and from the action of diborane on the hydrazine adduct of trimethylborane.[4] For reasons discussed below, all these preparations yield a mixture of methyldiboranes, although it is possible to isolate the individual members of the series by fractionation at reduced temperatures.

In the present study, already briefly reported,[5] the earlier work with ethyldiboranes (see Part V) has been followed up and extended. It has been possible to show that the methyldiboranes can be prepared [6] in a single-stage reaction from trimethylborane by reaction under pressure with sodium borohydride (preferably admixed with aluminium chloride) and either hydrogen chloride or boron trichloride. Hydrogen chloride is much more effective than boron trichloride and yields may exceed 80% base on total boron. Methane is also a major product of the reaction, which is best carried out at 150—175°.

$$(n + 2)BMe_3 + (6\text{-}n)NaBH_4 + (6\text{-}n)HCl \xrightarrow{AlCl_3} 4B_2H_{6-n}Me_n + (6\text{-}n)NaCl + (6\text{-}n)CH_4$$

With lithium borohydride, no aluminium chloride is necessary and the reaction proceeds at lower temperatures; hydrogen chloride and boron trichloride are about equally effective and no methane is released:

$$nBMe_3 + (6\text{-}n)LiBH_4 + (6\text{-}n)HCl \longrightarrow 3B_2H_{6-n}Me_n + (6\text{-}n)LiCl + (6\text{-}n)H_2$$

$$4nBMe_3 + (18\text{-}3n)LiBH_4 + (6\text{-}n)BCl_3 \longrightarrow 12B_2H_{6-n}Me_n + (18\text{-}3n)LiCl$$

Yields of well over 90% can be obtained. These methods thus constitute a real advance.

EXPERIMENTAL

Preparation of Trimethylborane.—The usual method of preparing trimethylborane from ethereal methylmagnesium iodide and boron trifluoride involves the separation of large

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[1] Part V, L. H. Long and M. G. H. Wallbridge, *J.*, 1963, 2181.

[2] H. I. Schlesinger and A. O. Walker, *J. Amer. Chem. Soc.*, 1935, **57**, 621; H. I. Schlesinger, N. W. Flodin, and A. B. Burg, *ibid.*, 1939, **61**, 1078.

[3] R. Klein, A. Bliss, L. Schoen, and H. G. Nadeau, *J. Amer. Chem. Soc.*, 1961, **83**, 4131.

[4] W. G. Paterson and M. Onyszchuk, *Canad. J. Chem.*, 1961, **39**, 2324.

[5] L. H. Long and M. G. H. Wallbridge, *Chem. and Ind.*, 1959, 295.

[6] M. G. H. Wallbridge and L. H. Long, B.P. 853,063/1960; U.S.P. 3,118,950/1964.

quantities of trimethylborane from ether in vacuum apparatus and was found to be time-consuming and inconvenient. Accordingly a method due in essence to Ruthruff,[7] employing (as modified) methyl iodide, aluminium foil, and triethyl borate, and giving a yield of 80%, was adopted, but this in turn was later rejected in favour of a more rapid preparation [8] from trimethylaluminium (similar to that since used elsewhere for triethylborane [9]).

Trimethylaluminium (80 g.) from a cylinder was run into the bottom of a 1-litre three-necked flask previously filled with nitrogen. An approximately equimolecular quantity of redistilled triethyl borate (167 g.) was run in dropwise from a tap-funnel, while the flask was cooled in ice. The reaction, at first vigorous, soon moderated after the addition of a small fraction of the triethyl borate, and the rest could be added more rapidly. Trimethylborane (b. p. $-20°$) was smoothly evolved and trapped at $-78°$. At the end of the reaction the flask was warmed to drive off all the trimethylborane. The yield was 55 g., or 89% of theory according to the reaction $AlMe_3 + B(OEt)_3 \longrightarrow Al(OEt)_3 + BMe_3$. It was purified before use by vacuum condensation and stored in a cooled reservoir.

Action of Hydrogen Chloride on Sodium Borohydride.—Sodium borohydride (8·9 g.) and anhydrous hydrogen chloride (5·3 g.) were heated together in a stainless steel autoclave (internal vol. 625 ml.) at 180° and ~6 atm. pressure for 4 hr. After cooling, both reactants were recovered apparently unchanged and no diborane was detected.

Action of Boron Trichloride on Lithium Borohydride.—Excess of lithium borohydride (11·0 g., 0·5 mole) and boron trichloride (14·9 g., 0·13 mole) were placed in the autoclave. A slow reaction occurred at room temperature and the pressure rose gradually, reaching 7 atm. after 65 hr. Analysis of a small sample of the gas revealed that chlorine was still present in the gas phase at this stage. The temperature was raised slowly and samples taken at various temperatures, but only after 1·5 hr. at 145° was the reaction complete and the gas phase chlorine-free. The volatile products were diborane, hydrogen, and a trace of a colourless liquid which distilled from the autoclave under vacuum, but the amount of the liquid was too small to permit identification, except to show that it contained boron. The solid recovered (22·2 g.) consisted of lithium chloride and unreacted lithium borohydride.

Reactions of Trimethylborane.—(*a*) *Trimethylborane with sodium borohydride.* No reaction occurred when trimethylborane (18·1 g.) and sodium borohydride (16·0 g.) were heated at 160—170° for 7 hr. in the autoclave. The trimethylborane was also recovered unchanged from a repeat experiment in which aluminium chloride (9·4 g.) had been added (intimately mixed with the borohydride) as catalyst.

(*b*) *Trimethylborane with sodium borohydride and hydrogen chloride.* Excess of commercial sodium borohydride (22·1 g., 0·58 mole) of approximately 95% purity was placed in the autoclave and trimethylborane (27·2 g., 0·49 mole) and hydrogen chloride (17·8 g., 0·49 mole) introduced. No reaction was apparent at room temperature, and the pressure remained constant at 10 atm. On raising the temperature, a rather rapid rise in pressure revealed that a reaction set in just below 100°. Heating was continued for 4 hr., with the temperature during the final period kept constant at 175°, when the pressure was observed to be steady at 56 atm., indicating reaction to be complete. On allowing the autoclave to resume room temperature, the pressure fell to 23 atm. The autoclave was cooled to below 0° by means of ice–salt and the gases released slowly through two traps cooled to $-150°$, which trapped out every constituent except methane and hydrogen. The portion not condensing was analysed by means of a Bone–Wheeler apparatus and found to consist of 6·16 g. of methane and 0·48 g. of hydrogen. The remainder of the volatile material in the autoclave was brought over into the cooled traps by reducing the pressure, ultimately to 0·1 mm. The contents of the traps (30·3 g.) were separated by high-vacuum technique, whereupon the following products were positively identified by means of the analytical technique described below: tetramethyldiborane 6·0 g.; trimethyldiborane 0·39 g.; dimethyldiborane 0·67 g.; diborane 0·35 g.; trimethylborane 0·3 g.; dimethylchloroborane 15·6 g.; hydrogen chloride 1·18 g. The solid recovered from the autoclave (27·7 g.) was not further examined beyond showing that it contained 45·9% of sodium chloride by chlorine analysis (Volhard's method) and 41·2% of unchanged sodium borohydride by hydrogen evolution on hydrolysis.

These results show that most of the hydrogen chloride and all the trimethylborane had

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[7] R. F. Ruthruff, U.S.P. 2,247,821/1941.

[8] M. G. H. Wallbridge, Ph.D. Thesis, Exeter, 1958.

[9] R. Köster, *Annalen*, 1958, **618**, 31.

reacted, for the very small amount (0·3 g.) recovered was not more than expected to be present in the disproportionation equilibrium of the tetramethyldiborane. The total yield of methyldiboranes and their dissociation products is 28·2% based on boron according to the equation $(n + 2)BMe_3 + (6\text{-}n)NaBH_4 + (6\text{-}n)HCl \longrightarrow 4B_2H_{6\text{-}n}Me_n + (6\text{-}n)NaCl + (6\text{-}n)CH_4$, but it is clear that the reaction $BMe_3 + HCl \longrightarrow BMe_2Cl + CH_4$ is highly important under the experimental conditions, almost as much boron being found as dimethylchloroborane.

Two attempts were made in repeat experiments to improve the yield of methyldiboranes. (1) By raising the temperature to 200—220° and prolonging the time of heating to 18 hr. it was hoped that more methyldiboranes would be formed according to the reaction $Me_2BCl + NaBH_4 \longrightarrow NaCl + B_2H_4Me_2$. However, the total yield of methyldiboranes fell sharply and considerable quantities of methyldichloroborane resulted, apparently by disproportionation of the dimethylchloroborane, since the amount of methane was not increased. The amount of hydrogen, however, was considerably increased and after evacuation of the autoclave a considerable amount of a nearly white sublimate of relatively low volatility and indefinite composition was found on the interior walls of the autoclave, showing that cracking of the substituted diboranes had occurred. The sublimate, probably a mixture, could not be identified; it contained 25% of boron and detectable quantities of chlorine and (surprisingly) sodium, and gave an alkaline solution on hydrolysis with water.

(2) In the second attempt it was hoped to facilitate the completion of the reaction at slightly lower temperatures by the use of aluminium chloride. The sodium borohydride (22·6 g., 0·60 mole) was intimately mixed with anhydrous aluminium chloride (6·6 g., 0·05 mole) and placed in the autoclave before introducing the trimethylborane (33·3 g., 0·60 mole) and hydrogen chloride (21·8 g., 0·60 mole). At room temperature the initial pressure was 10 atm., but on heating, the rate of rise showed a sharp increase at about 90°, indicative of rapid reaction. The temperature was maintained at 150° for 4 hr., but the pressure rapidly became constant at 87 atm., and fell to 47 atm. when the autoclave resumed room temperature. The volatile products were separated and identified as before. Tetramethyldiborane (15·6 g., 0·186 mole) was subsequently isolated almost pure at −65°, m. p. −72·5 to −72·0° (lit.,[2] −72·5°), v. p. 15·5 mm. at −20° and 50·0 mm. at 0° (lit.,[2] 15·6 and 46·8 mm., respectively). Other products recovered were: trimethyldiborane (5·0 g., 0·072 mole); dimethyldiborane (5·8 g., 0·104 mole); monomethyldiborane (0·15 g., 0·004 mole); diborane (0·2 g., 0·007 mole); trimethylborane (0·1 g., 0·002 mole); dimethylchloroborane (4·8 g., 0·063 mole); hydrogen chloride (1·15 g., 0·032 mole); methane (5·0 g., 0·31 mole); hydrogen (1·4 g., 0·69 mole). The yellowish-white solid recovered from the autoclave contained 18·6 g. of chlorine (Volhard) and 3·8 g. of unchanged sodium borohydride (hydrogen evolution), but liberated no volatile material at 280° under vacuum.

With aluminium chloride the yield of methyldiboranes and their dissociation products is much higher (80·9% based on boron), and so it was used also in most of the remaining experiments in this series.

(*c*) *Trimethylborane with lithium borohydride and hydrogen chloride.* Lithium borohydride (15·3 g., 0·70 mole), mixed with aluminium chloride (12·2 g., 0·91 mole), was treated with trimethylborane (31·9 g., 0·57 mole) and hydrogen chloride (20·9 g., 0·57 mole) in the autoclave. The reaction, which proceeded differently from the foregoing, set in at room temperature, as indicated by a rise in pressure to 42 atm. over a fairly short interval before heating. Reaction may already have been virtually complete, because after heating at 143° for 2 hr. the pressure was still only 44 atm. on cooling to room temperature. Another difference was that no methane was produced in the reaction, although the amount of hydrogen was much greater (1·88 g., 0·93 mole). The remaining volatile products (40·9 g.), after fractionation in vacuum apparatus, were shown to contain tetramethyldiborane (11·7 g., 0·14 mole), trimethyldiborane (5·95 g., 0·085 mole), dimethyldiborane (13·4 g., 0·24 mole), and monomethyldiborane (5·75 g., 0·138 mole), the last of these probably containing a little diborane and trimethylborane by disproportionation. The only other volatile product detected was a small quantity of dimethylchloroborane (∼2 g.). The solid recovered from the autoclave (35·0 g.) contained 28·8 g. of chlorine and was mainly a mixture of lithium and aluminium chlorides, together with a little unchanged lithium borohydride. The combined yield of methyldiboranes and their dissociation product according to the equation $nBMe_3 + (6\text{-}n)LiBH_4 + (6\text{-}n)HCl \longrightarrow 3B_2H_{6\text{-}n}Me_n + (6\text{-}n)LiCl + (6\text{-}n)H_2$ amounts to 94·8%, based on boron.

(*d*) *Trimethylborane with sodium borohydride and boron trichloride.* Sodium borohydride

(32·1 g., 0·85 mole), mixed with aluminium chloride (9·5 g., 0·71 mole), was treated with trimethylborane (31·6 g., 0·56 mole) and boron trichloride (33·2 g., 0·28 mole) in the autoclave. On heating to 155° reaction slowly set in and the pressure rose to 87 atm. After 6 hr. the autoclave was allowed to cool to room temperature, when the pressure fell to 42 atm. The volatile products were recovered and separated as before, except for a slight modification necessary owing to the presence of methyldichloroborane. Yields of diborane derivatives were: tetramethyldiborane (1·0 g., 0·012 mole), trimethyldiborane (2·4 g., 0·034 mole), dimethyldiborane (4·2 g., 0·075 mole), and monomethyldiborane (0·3 g., 0·007 mole). Yields of other products were: methane (7·7 g., 0·48 mole), hydrogen (1·2 g., 0·6 mole), hydrogen chloride (1·2 g., 0·033 mole), dimethylchloroborane (8·9 g., 0·12 mole), and methyldichloroborane (5·4 g., 0·056 mole). The solid recovered from the autoclave (66·0 g.) contained 27·8 g. of chlorine (Volhard) and 5·1 g. of unchanged sodium borohydride (hydrogen evolution). However, the total boron (4·0 g., estimated as methyl borate) was considerably higher than required by sodium borohydride, indicating that the solid contained some other boron-rich compound, possibly sodium triborohydride,[10] NaB_3H_8. The combined yield of methyldiboranes according to the general equation $4nBMe_3 + (7n + 12)NaBH_4 + (n + 4)BCl_3 \longrightarrow 8B_2H_{6-n}Me_n + (3n + 12)NaCl + 4nNaB_3H_8 + 4nCH_4$ amounts to 27·3%, based on boron.

(*e*) *Trimethylborane with lithium borohydride and boron trichloride.* As the reaction proceeded at room temperature, no aluminium chloride was added. The quantities of reactants introduced into the autoclave were: lithium borohydride (21·8 g., 1 mole), trimethylborane (33·5 g., 0·6 mole), and boron trichloride (35·2 g., 0·3 mole). At room temperature the pressure rapidly rose to 8 atm., which probably means that reaction was near completion, since the pressure was still only 10 atm. after raising the temperature to 140° and cooling again. The only non-condensable product at −150° was hydrogen (~0·45 g.), and no methane was detected. The other volatile products pumped from the autoclave were chlorine-free and weighed 44·1 g. After fractionation, the yields of substituted diboranes were: tetramethyldiborane (15·3 g., 0·183 mole), trimethyldiborane (6·4 g., 0·092 mole), dimethyldiborane (14·5 g., 0·260 mole), monomethyldiborane (5·9 g., 0·141 mole), though again the last-named is likely to have contained a little diborane and trimethylborane by disproportionation. The solid recovered from the autoclave (~38 g.) contained only a trace of lithium borohydride and can be regarded as almost pure lithium chloride, as chlorine analysis (Volhard) showed it to contain 31·2 g. of chlorine. The over-all yield of methyldiboranes according to the equation $4nBMe_3 + (18-3n)LiBH_4 + (6-n)BCl_3 \longrightarrow 12B_2H_{6-n}Me_n + (18-3n)LiCl$ amounts to 92·8%.

Identification and Analysis of the Methyldiboranes.—Physical properties of the individual methyldiboranes after isolation were compared with those already reported.[2] For analysis, samples were weighed either as liquids or vapours and hydrolysed in order to measure the volume of hydrogen evolved in a gas burette. The boron in the resultant aqueous solution was determined, after heating with concentrated nitric acid to ensure its complete oxidation to boric acid, by distilling it as trimethyl borate from a small platinum still according to the usual volumetric procedure.[11] Combination of the hydrogen and boron figures identified the compound, and confirmation was forthcoming from the physical measurements.

Because of ready disproportionation, which is complete in a few hours at room temperature, the compounds isolated at low temperatures were stored at −78° until immediately before conducting the physical measurements. Typical results are given below for tetramethyldiborane. Observed values of the vapour pressure are compared in Table 1 with those calculated from published data.[2] The new values are well represented by the equation log p (mm.) = $7·96 - 1727/T$, according to which the b. p. (extrapolated) is 67·2°, the heat of vaporisation 7·80 kcal. mole^{-1}, and the Trouton constant 22·8, but measured values above about −5° are

TABLE 1

Vapour pressure of $B_2H_2Me_4$

Temp.	−30·0°	−24·4°	−20·0°	−17·1°	−14·0°	−10·0°	−5·0°	0·0°	+3·0°
p_{mm} (obs.)	8·2	12·0	15·0	18·0	21·9	28·0	37·3	49·0	56·5
p_{mm} (calc.)	8·4	12·0	15·5	18·4	22·1	27·6	36·0	46·8	54·2

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[10] W. V. Hough, L. J. Edwards, and A. D. McElroy, *J. Amer. Chem. Soc.*, 1956, **78**, 689; 1958, **80**, 1828.

[11] E. Schulek and G. Vastagh, *Z. analyt. Chem.*, 1931, **84**, 167.

unavoidably high because of an increasing rate of disproportionation. M. p.s were −72·5 and −72·3°, respectively (lit., −72·5°). Vapour density measurements gave *M* 84·0 and 84·9, respectively ($B_2H_2Me_4$ requires *M* 83·7).

Identification and Analysis of Other Volatile Products.—The methylchloroboranes, BMe_2Cl and $BMeCl_2$, were characterised by v.p. and v.d. measurements and analysed by hydrolysing weighed samples and determining the chloride ion (Volhard) and the boron as already described. The observed v.p. of dimethylchloroborane was 55 mm./−50·2° and 633 mm./0° (lit.,[12] 55 mm./−51·1°; 634 mm./0°). Diborane, trimethylborane, and hydrogen chloride were likewise identified by determining the v.p., v.d., and products of hydrolysis, while methane–hydrogen mixtures were analysed by combustion over cupric oxide in a Bone–Wheeler apparatus.

Decomposition Studies with Tetramethyldiborane.—The change in pressure with time of a confined volume of tetramethyldiborane vapour was studied in a constant-volume system at three different temperatures (0, 20·8, and 39·35°, respectively). The system (volume 204·0 ml.) consisted of a small thin-walled glass globe joined by capillary tubing to a mercury cut-off. The mercury was raised at intervals to a constant-volume mark on the capillary tubing of the limb attached to the globe, while the other limb was evacuated. The difference in levels of the mercury in the two limbs provided a direct measure of the pressure of the vapour in the globe. A calculated quantity of highly purified tetramethyldiborane vapour was introduced into the globe and traces of disproportionation products removed by pumping for a few minutes with the sample frozen out and held at −75°, at which temperature it is still solid and in the form of long needles. The mercury in the cut-off was then raised and the globe surrounded by a constant-temperature bath. The time was noted and the pressure measured as soon as possible after the sample had completely vaporised and assumed the temperature of the bath. Because disproportionation was proceeding during the time required to make the readings, it was necessary to correct the first reading to obtain the initial pressure p_i by extrapolating back to zero time, but the correction was in general only significant at the highest temperature. The pressure at constant volume increased with time because of reversible disproportionation processes such as $3B_2H_2Me_4 \rightleftharpoons 2B_2H_3Me_3 + 2BMe_3$, and was measured at intervals until equilibrium was established. The time beyond which no further change in pressure occurred was noted, as was the final pressure, p_f. The percentage of boron in tetramethyldiborane converted into trimethylborane is readily calculated from the pressure increase. The results of typical runs, adjusted for a small capillary correction of the mercury levels, are summarised in Table 2.

TABLE 2

Disproportionation of $B_2H_2Me_4$ vapour at constant volume

Temp.	p_i (mm.)	p_f (mm.)	Time (min.)	% B converted to BMe_3
0·0°	40·4	46·3	1500	14·6
0·0	43·3	49·6	1400	14·5
20·4	53·8	63·4	158	17·8
20·8	54·9	65·0	192	18·4
20·65	45·8	54·4	175	18·8
38·75	56·1	68·4	30	21·9
39·35	53·5	65·3	32	22·1

DISCUSSION

An unexpected feature in the present investigation is the very marked difference in behaviour between the borohydrides of sodium and lithium. This is so pronounced that different mechanisms must be postulated to account for the observations in the two cases. Thus the sodium borohydride reaction gives rise to methane, where the lithium compound gives only hydrogen. The methane does not arise from the interaction of the trimethylborane with the sodium borohydride, since it has been shown that no reaction occurs at 170° even in the presence of aluminium chloride. Rather it must arise by interaction with the hydrogen chloride, when present:

$$BMe_3 + HCl \longrightarrow Me_2BCl + CH_4 \qquad (1)$$

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[12] E. Wiberg and co-workers, as reported by J. Goubeau, F.I.A.T. Review of German Science 1939—1946, Inorg. Chem., Part I, p. 235.

This reaction is known [12] to occur at 150° and above, and in the present work there is the additional evidence that almost 1 mole of methane was produced for every mole of trimethylborane consumed. Further, the reaction may be catalysed by aluminium chloride (although the observed sudden rise in temperature slightly below 100° when aluminium chloride is present is probably not caused by this reaction, since it was also observed when hydrogen chloride was absent). These considerations lend support to the suggestion that the ethane observed in the earlier series of experiments with triethylborane [1] arose from a similar reaction, although in this case slightly more than 1 mole of ethane was formed for every mole of trialkylborane consumed.

It therefore appears that the initial product is dimethylchloroborane, which reacts in turn with the sodium borohydride by reactions of the type:

$$Me_2BCl + NaBH_4 \longrightarrow NaCl + B_2H_4Me_2 \qquad (2)$$

In practice an equilibrium of polymethyldiboranes results, since further equilibration reactions cannot be avoided, for example:

$$B_2H_4Me_2 + 2BMe_3 \rightleftharpoons 2B_2H_2Me_4 \qquad (3)$$

However, in the absence of aluminium chloride reaction (2) is not very efficient; considerable quantities of dimethylchloroborane and sodium borohydride were recovered even after several hours at 175°. Possibly the formation of solid reaction products on the surface of the sodium borohydride hinders further reaction. However, in the presence of sufficient aluminium chloride the reaction proceeds more efficiently and much less dimethylchloroborane was recovered after a similar period of heating at a lower temperature (150°). Tentatively it can be suggested that the aluminium chloride enters into the reaction to form $NaAlCl_4$ (m. p. 156°), thus adding propulsion to the formation of methyldiboranes. At all events, the aluminium chloride cannot afterwards be sublimed out of the solid reaction products on heating under vacuum. At the same time, its presence causes the yield of methyldiboranes to rise to >80% based on total boron, thus proving beyond question that boron from the sodium borohydride enters the vapour phase. The foregoing observation confirms an earlier finding [13] that aluminium chloride enhances the reactivity of sodium borohydride. The weight of methane recovered in the experiments involving aluminium chloride is within 3% of that predicted by the over-all equation cited in the introduction, provided a correction is made for the unreacted dimethylchloroborane. The hydrogen produced will arise from side-reactions, probably from cracking of the diborane which occurs in the equilibrium mixture or from its interaction with the sodium borohydride, *e.g.*:

$$NaBH_4 + B_2H_6 \longrightarrow NaB_3H_8 + H_2 \qquad (4)$$

With lithium borohydride still better yields of methyldiboranes are obtained, the main difference being that no methane is formed and the reaction proceeds at room temperature. The different reaction path is doubtless to be attributed to direct reaction with the hydrogen chloride [14]

$$2LiBH_4 + 2HCl \longrightarrow 2LiCl + B_2H_6 + 2H_2 \qquad (5)$$

which would also explain the small quantity of chlorine compounds remaining in the gas phase, since the hydrogen chloride will have reacted at a temperature below that at which reaction (1) becomes appreciable. The diborane formed according to reaction (5) will then react further

$$(6\text{-}n)B_2H_6 + 2nBMe_3 \rightleftharpoons 6B_2H_{6-n}Me_n \qquad (6)$$

and the over-all equation becomes that given earlier. Yields are near quantitative, and the methyldiborane to be favoured in the reaction products can be predetermined by

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[13] H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.*, 1955, **77**, 3164.

[14] H. C. Brown, H. I. Schlesinger, I. Sheft, and D. M. Ritter, *J. Amer. Chem. Soc.*, 1953, **75**, 192.

varying the Me : B ratio in the reactants. Although aluminium chloride was added, subsequent experiments indicated it to be unnecessary in this instance.

The substitution of hydrogen chloride by boron trichloride is disadvantageous with sodium borohydride, but hardly affects the yield with the lithium compound. With sodium borohydride the reaction is clearly complex. Although, unlike the lithium compound, it does not react appreciably with boron trichloride [15] in the presence of aluminium chloride, it appears that diborane is slowly released, possibly according to the equation:

$$3NaBH_4 + 3AlCl_3 + BCl_3 \longrightarrow 3NaAlCl_4 + 2B_2H_6$$

However, much of this appears to react according to equation (4), since hydrogen is released and the concentration of boron in the solid phase increases considerably. Alternatively the two reactions may occur in a single step without the release of diborane as an intermediate:

$$5NaBH_4 + 3AlCl_3 + BCl_3 \longrightarrow 2NaB_3H_8 + 3NaAlCl_4 + 2H_2$$

Investigation of the boron balance reveals that the final proportion of boron in the solid phase is considerably higher, even, than is revealed by analysis, in harmony with the supposition that sodium triborohydride is formed, as this substance is more difficult to hydrolyse [10] than the simple borohydride. However, it must be emphasised that sodium triborohydride was not positively identified, and that no attempt was made to isolate it from the mixture that constituted the solid residue. The hydrogen released will account for the hydrogen chloride, which was found in moderate amounts, according to the known [16] reaction: $2BCl_3 + 6H_2 \longrightarrow B_2H_6 + 6HCl$. The total amount will have been much larger, since large quantities of methane were formed according to equation (1), and the simultaneous production of dimethylchloroborane will then account for the formation of methyldiboranes by reactions (2) and (3) as before. To explain the formation of methyldichloroborane observed in this instance it appears to be necessary to invoke the competing reaction

$$BMe_3 + BCl_3 \longrightarrow BMe_2Cl + BMeCl_2$$

This is reported to occur at 380—390° (Wiberg and Bolz [17]), or 350—400° (Becher [18]), but it may have occurred in our system at 155°, particularly if catalysed by aluminium chloride. The net result of these complexities is that, in the combination of boron trichloride and sodium borohydride with trimethylborane, only a relatively small proportion of the boron becomes converted to methylboranes, so that as a method of preparation this combination is greatly inferior to the others investigated.

With lithium borohydride, however, these complications do not occur, and the yield of methyldiboranes is almost quantitative. No methane is produced, and little or no hydrogen, so that wastage of material is minimised. As it was shown in a separate experiment that boron trichloride reacts below 140° with lithium borohydride to produce diborane quantitatively, the mechanism seems to be:

$$3LiBH_4 + BCl_3 \longrightarrow 3LiCl + 2B_2H_6 \qquad (7)$$

Reaction (7) actually sets in at room temperature and will be simultaneously accompanied by the equilibration reaction (6) to produce methyldiboranes according to the over-all equation already given, in this case without complications from side-reactions. Here, as with the other reactions discussed, the maximum concentration of any desired diborane derivative in the equilibrium mixture of alkyldiboranes may be realised by controlling the alkyl : boron ratio in the reactants.

[15] L. H. Long and A. C. Sanhueza, unpublished results.

[16] British Thomson-Houston Co. Ltd., B.P. 623,760/1949.

[17] As reported by J. Goubeau, F.I.A.T. Review of German Science 1939—1946, Inorg. Chem., Part I, p. 238.

[18] H. J. Becher, *Z. anorg. Chem.*, 1953, **271**, 243.

Studies of the partial disproportionation of tetramethyldiborane reveal that whereas equilibration is complete in about 30 min. at 40°, the time required at 0° is 24 hr. or more, which explains why the methyldiboranes can be isolated at low temperatures.

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