408. The Chemistry of Boron. Part V.* New Methods for the Preparation of Ethyl- and n-Propyl-diboranes.

By L. H. Long and M. G. H. Wallbridge.

Alkyldiboranes $B_2H_{6-n}R_n$ have been prepared by reduction of alkylhalogenoborines. Di-n-propylchloroborine (but not the bromo- or iodo-compound) is reduced by sodium borohydride in the absence of a solvent to, mainly, tetra-n-propyldiborane; a similar reduction by lithium aluminium hydride gives lower yields in a more complex reaction. By the former method diethylchloroborine gives tetraethyldiborane, but only under pressure; and the latter method here fails. Preparation of the diethylchloroborine *in situ* from triethylborine and boron trichloride leads to side reactions and a reduced yield of ethyldiboranes. However, varying the R : B ratio of the reactants here provides a means of controlling the relative proportions of the various alkyldiboranes produced.

The properties of tetra-n-propyldiborane are described and its proton resonance spectrum is compared with the spectra of other compounds containing the BPr^n_2 grouping.

ALTHOUGH alternative syntheses are now known, the present investigation was begun when the only major study of alkyldiboranes $B_2H_{6-n}R_n$ (where $n = 1$—4 and R = Me, Et, Pr^n) was that of Schlesinger and his co-workers,[1] who equilibrated diborane with the appropriate trialkylboron: $2nBR_3 + (6-n)B_2H_6 \rightleftharpoons 6B_2H_{6-n}R_n$. They characterised all the methyl- and ethyl-diboranes except the 1,2-diethyl derivative, and mono- and 1,1-di-n-propyldiborane. The 1,2-diethyl isomer was later prepared by Solomon, Klein, and

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* Part IV, *J.*, 1954, 4457.

[1] (*a*) Schlesinger and Walker, *J. Amer. Chem. Soc.*, 1935, **57**, 621; (*b*) Schlesinger, Horvitz, and Burg, *ibid.*, 1936, **58**, 407; (*c*) Schlesinger, Flodin, and Burg, *ibid.*, 1939, **61**, 1078.

Hattori,[2] who in part contradict earlier work; and the tetra-n-propyl derivative was obtained by Mikhailov *et al.*[3] Diborane is converted directly into its propyl derivatives by reaction with propene [4] or, apparently (though in poor yield), cyclopropane.[5] Diethyl- and di-n-propyl-diborane are formed when vinyl and allyl bromide, respectively, are treated with sodium borohydride,[6] and trialkylborons are reduced by hydrogen under elevated [7] and reduced [8] pressure to alkyldiboranes, while methyldiboranes result [9] on reduction of mixtures of boron trichloride and methyl iodide by hydrogen and aluminium under pressure. n-Butyldiboranes have been obtained by controlled pyrolysis of tri-n-butylboron,[10] and by interaction of the compounds $Et{\cdot}CHCl{\cdot}CH_2{\cdot}BCl_2$ and $(Et{\cdot}CHCl{\cdot}CH_2)_2BCl$ severally with sodium borohydride in bis-2-methoxyethyl ether solvent.[11] More recently, alkyldiboranes have been prepared [12] by heating lithium borohydride with a trialkylaluminium (or alkylaluminium halide) plus a hydrogen halide or boron halide.

All except the last of these methods require diborane or hydrogen under pressure (which is inconvenient for large-scale preparations), or give poor yields or complex mixtures needing tedious separation. We here record a direct reduction of certain alkylboron halides R_2BX and RBX_2 to the hydrides, which appear as their dimers $(R_2BH)_2$ and $(RBH_2)_2$. It is analogous to the reduction, by Schlesinger and his co-workers,[13] of alkylhalogeno-derivatives of Group IV elements, ER_mX_{4-m} ($E = Si$, Ge, or Sn; $X =$ halogen; $m = 0$—3), to the corresponding hydrides ER_mH_{4-m} by means of lithium aluminium hydride in ether.

At the time of our preliminary report,[14] no reduction of alkylboron halides had been recorded, although other halogen-replacements were known.[15] Alkyldiboranes have since been produced [16] by reducing R_2BCl–$RBCl_2$ mixtures with sodium hydride, but other attempts to reduce alkylhalogenoborines gave products of different type.[17,18] However, $(Me_2N)_2BCl$ is reduced by lithium aluminium hydride in a straightforward manner.[19]

We find that, although the iodo- and bromo-compounds do not react with sodium borohydride, n-propyldiboranes are satisfactorily prepared [20] from di-n-propylchloroborine at its boiling point with this reagent in the absence of a solvent, or, in lower yield, at room temperature with lithium aluminium hydride in diethyl ether. The main product was the tetra-n-propyl derivative. The over-all reactions may be written:

$$2Pr^n_2BCl + 2NaBH_4 \longrightarrow 2NaCl + B_2H_2Pr^n_4 + B_2H_6$$

$$4Pr^n_2BCl + LiAlH_4 \longrightarrow LiCl + AlCl_3 + 2B_2H_2Pr^n_4$$

Other steps such as

$$Pr^n_2BCl + NaBH_4 \longrightarrow NaCl + B_2H_4Pr^n_2$$

which are not strictly comparable with the reaction of Schlesinger and his co-workers,[13] are equally feasible as it has not been possible to distinguish whether the less highly

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[2] Solomon, Klein, and Hattori, *J. Amer. Chem. Soc.*, 1958, **80**, 4520.

[3] Mikhailov, Akhnazaryan, and Vasil'ev, *Doklady Akad. Nauk S.S.S.R.*, 1961, **136**, 828.

[4] Zhigach, Siryatskaya, Antonov, and Makaeva, *Zhur. obshchei Khim.*, 1960, **30**, 227.

[5] Graham and Stone, *Chem. and Ind.*, 1957, 1096.

[6] Wartik and Pearson, *J. Inorg. Nuclear Chem.*, 1958, **5**, 250.

[7] Köster, *Angew. Chem.*, 1956, **68**, 383; Köster, Bruno, and Binger, *Annalen*, 1961, **644**, 1.

[8] Moe, Schultz, Shepherd, and Cromwell, U.S.P. 2,944,951/1960.

[9] Muetterties, *J. Amer. Chem. Soc.*, 1960, **82**, 4163; U.S.P. 2,925,439/1960.

[10] Rosenblum, *J. Amer. Chem. Soc.*, 1955, **77**, 5016.

[11] Gavlin and Maguire, U.S.P. 2,926,192/1960.

[12] Long and Sanhueza, *Chem. and Ind.*, 1961, 588.

[13] Finholt, Bond, Wilzach, and Schlesinger, *J. Amer. Chem. Soc.*, 1947, **69**, 2692.

[14] Long and Wallbridge, *Chem. and Ind.*, 1959, 295.

[15] Dollimore and Long, *J.*, 1953, 3906.

[16] Kali-Chemie A.-G., B.P. 823,327/1960.

[17] Auten and Kraus, *J. Amer. Chem. Soc.*, 1952, **74**, 3398.

[18] Booth and Kraus, *J. Amer. Chem. Soc.*, 1952, **74**, 1415.

[19] Coates, *J.*, 1950, 3481.

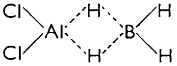
[20] Wallbridge and Long, B.P. 853,063/1960.

propylated diboranes also obtained arise directly or by disproportionation of the tetra-n-propyl derivative. It should be noted, however, that the latter alternative would be expected to give the 1,1-dialkyldiborane directly.

Experiments with diethylchloroborine were less successful. Little reaction could be obtained at temperatures up to its boiling point (77·5°) with sodium borohydride; although vigorous reaction occurred with lithium aluminium hydride at room temperature, the products were not ethyldiboranes; since the ethyl radicals appear quantitatively as triethylborine, the reaction here must be formulated:

$$3Et_2BCl + LiAlH_4 \longrightarrow LiCl + AlCl_2H,BH_3 + 2BEt_3$$

The solid aluminium compound, here written $AlCl_2H,BH_3$ as required by stoicheiometry, is probably dichloroaluminium borohydride:



This compound was characterized by Hoekstra and Katz [21] as a solid with a vapour pressure of ~1 mm. at 25°, which shows no tendency to disproportionate, and it was suggested (though not identified) by Olson and Sanderson [22] as an intermediate in the reaction between aluminium chloride and lithium borohydride. In the present experiments it was not separated from the lithium chloride, but it was observed to decompose at 150° liberating diborane and hydrogen. It is scarcely to be doubted that the same compound is initially formed from $Pr^n{}_2BCl$; but, since it decomposes just below the boiling point of tri-n-propylborine (156°), it could give rise to propyldiboranes by a secondary reaction such as $2BPr^n{}_3 + B_2H_6 \longrightarrow 2B_2H_3Pr^n{}_3$ (in which the diborane released may be assumed to be the intermediate). As triethylborine boils at 95°, this explains the apparent chemical difference (in their behaviour towards lithium aluminium hydride) between diethyl- and di-n-propyl-chloroborine.

Ethyldiboranes are, however, obtained on reducing diethylchloroborine by sodium borohydride under pressure at 145—165°. It was here convenient to prepare the diethylchloroborine *in situ* by the exchange reaction between triethylborine and boron trichloride at 165°: $BEt_3 + BCl_3 \rightleftharpoons BEt_2Cl + BEtCl_2$. If the reaction is carried out in an autoclave in the presence of sodium borohydride, ethyldiboranes are produced according to one or both of the over-all reactions:

$$2BEt_3 + xBCl_3 + 3xNaBH_4 \longrightarrow 3xNaCl + (4x - 4)B_2H_5Et + (5 - 2x)B_2H_4Et_2$$

$$2yBEt_3 + 2BCl_3 + 6NaBH_4 \longrightarrow 6NaCl + (16 - 2y)B_2H_3Et_3 + (3y - 12)B_2H_2Et_4$$

(where $1 < x < 2{\cdot}5$ and $8 < y < 12$), the relative proportions of the various ethyldiboranes depending on the $BEt_3 : BCl_3$ ratio. Formation of mono-, di-, and tetra-ethyl compounds has been established, though triethyldiborane was difficult to separate from unchanged ethylchloroborines and triethylborine. Yields were poor, partly because the reaction had not gone to completion even after 5 hours' heating with a small excess of sodium borohydride, and partly because of side reactions yielding ethane and hydrogen.

The ethyldiboranes have already been described.[1b] Tetra-n-propyldiborane is a colourless liquid which disproportionates at higher temperatures, as indicated by the absence of a sharp boiling point, the purest fraction boiling over the range 114—120°/100 mm. (cf. 91·2°/100 mm. for tri-n-propylborine). Disproportionation is also evident when the compound is refluxed under an atmosphere of nitrogen, the boron content of the liquid and the boiling point falling progressively to the values for tri-n-propylborine, while diborane is evolved: $3B_2H_2Pr^n{}_4 \longrightarrow 4BPr^n{}_3 + B_2H_6$. However, this compound appears (qualitatively) to disproportionate less readily than the corresponding ethyl derivative.

[21] Hoekstra and Katz, *J. Amer. Chem. Soc.*, 1949, **71**, 2488.

[22] Olson and Sanderson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 228.

The vapour density of tetra-n-propyldiborane accords with the formula $B_2H_2Pr_4$ after correction for slight disproportionation. Vapour-density measurements indicated that more volatile fractions obtained in the experiments were mixtures of the lower n-propyldiboranes and tri-n-propylborine.

Chemically tetra-n-propyldiborane shows certain resemblances to tri-n-propylborine. In air both are spontaneously inflammable, though with difficulty. Oxidation sets in initially without the appearance of a flame. That they have almost identical smells probably arises because one perceives the partly common oxidation products rather than the original compounds. However, tetra-n-propyldiborane liberates hydrogen with water: $B_2H_2Pr^n{}_4 + 2H_2O \longrightarrow 2Pr^n{}_2B{\cdot}OH + 2H_2$, and so has strong reducing powers. The reaction is smooth and easily controlled. In the presence of air, the oily di-n-propylborinic acid is rapidly hydrolysed and oxidized to n-propylboronic acid $Pr^n{\cdot}B(OH)_2$, a yellowish-white solid which is readily identified and estimated. The solid is contaminated with a little boric acid, but this does not hinder estimation of the boron, as both the boronic acid and boric acid titrate as monobasic acids in the presence of an excess of mannitol or glycerol. (In general, however, boron was estimated after distillation as trimethyl borate and subsequent hydrolysis.) The same ultimate hydrolysis products in the presence of air are obtained from mono-, di-, and tri-n-propyl-diborane, which are however readily distinguished since they give, respectively, 5, 4, and 3 mol. of hydrogen on contact with water. It is assumed that the isomer of the di-n-propyl derivative obtained was that found by Schlesinger *et al.*[15] The various ethyl derivatives were identified in the present study by methods similar to those used for the n-propyl compounds, together with vapour-pressure measurements whenever possible.

EXPERIMENTAL

Preparation of Trialkylborines.—Tri-n-propylborine. The method described by Long and Dollimore [23] was employed.

Triethylborine. The same method was used, but with ethyl bromide in place of n-propyl chloride, and di-n-butyl ether as solvent instead of diethyl ether. Boron trifluoride was passed into the reaction mixture until all the di-n-butyl ether was converted into the less volatile complex $Bu^n{}_2O,BF_3$, which remained in the flask when the triethylborine was distilled off (yield 65—70%). Triethylborine was also prepared in excellent yield by adding tri-n-butyl borate slowly to a slight excess of triethylaluminium and distilling off the product. The purified product boiled at 95°.

Preparation of Dialkylhalogenoborines.—Di-n-propyliodoborine. The preparation was from tri-n-propylborine and iodine by Long and Dollimore's method.[23] The yield was improved to 60% by distilling off the product from the reaction mixture under reduced pressure.

Di-n-propylbromoborine. (1) Di-n-propyliodoborine was refluxed with an excess of stannic bromide, according to a procedure described [15] for antimony tribromide, whereupon the yield was improved to 60%. (2) Tri-n-propylborine (47·6 g., 0·34 mole) was heated in a Kon flask at 135° while hydrogen bromide (42·0 g., 0·52 mole) was passed in during 4 hr.; propane (identified by v. p. and v. d. measurements) was liberated. The crude liquid product (32·2 g.) boiled at 137—150°. On fractionation it gave 26·2 g. of refined material, b. p. 143—146° (uncorr.). After allowance for unchanged borine recovered, the yield was 65%. This is the more convenient method.

Di-n-propylchloroborine. The method was analogous to method (2) above. Hydrogen chloride (55·0 g., 1·5 mole) was passed into tripropylborine (81·8 g., 0·77 mole) at 155°. The product (42·9 g., 55·5%), b. p. 124—128°, was distilled off as it was formed.

Diethylchloroborine. In attempts to prepare this in an autoclave at 150—210° from triethylborine and hydrogen chloride, as reported by Goubeau,[24] the compound was formed but was difficult to separate from starting materials, which also appeared to facilitate disproportionation. The preparation was effected by heating triethylborine and boron trichloride in a molecular

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[23] Long and Dollimore, *J.*, 1953, 3902.

[24] Goubeau, F.I.A.T. Review of German Science 1939—1946, Inorganic Chemistry, Part I, 1948, p. 215.

ratio of 2 : 1 at 340° for 2 hr. in an autoclave. Fractionation of the products gave diethylchloroborine, b. p. 76·5—79·5°, in 35% yield. Chlorine analysis was accomplished by hydrolysis of a weighed sample and titration against sodium hydroxide. The boron content was determined in the usual way after oxidation with concentrated nitric acid.

Reactions of the Dialkylhalogenoborines.—(*a*) *Di-n-propyl-bromo- and -iodo-borine with sodium borohydride.* No reaction occurred at the b. p. in the absence of a solvent or in cyclohexane or *m*-xylene.

(*b*) *Di-n-propylchloroborine with sodium borohydride.* Preliminary experiments showed that reaction became appreciable only above 100°. Sodium borohydride (15·3 g., 0·41 mole) was added slowly with stirring to refluxing dipropylchloroborine (33·4 g., 0·25 mole) contained in a nitrogen-filled 100-ml. 2-necked flask. Gases were evolved and collected in a trap at $-196°$. After 6—8 hours' heating, or when no more chlorine remained in the liquid phase, the condensed gases were separated by fractionation *in vacuo* and identified as a mixture of diborane (4·6 g.), hydrogen chloride (0·7 g.), and dipropylchloroborine (1·4 g.). After removal of the liquid products at 100 mm., a solid mixture of sodium chloride (13·4 g.) and borohydride (5·3 g.) remained in the flask.

The colourless liquid products (18·2 g.), b. p. 100—120°/100 mm., were separated into fractions (I), b. p. 100—110°/100 mm. (7·6 g.) and (II) b. p. 110—120°/100 mm. (10·6 g.); no sharp b. p. could be recorded. Attempts to distil them below 100 mm. were unsuccessful on account of frothing. Fraction II boiled mainly in the range 180—188° at 1 atm. Evidence for disproportionation during distillation is discussed below.

Fraction I was apparently mainly tri-n-propylborine contaminated with lower n-propyldiboranes formed by disproportionation, since boron analyses gave 8·8 and 8·6% (BPr^n_3 requires B, 7·7%), and only a very small proportion of the theoretically predicted volume of hydrogen for tetrapropyldiborane was obtained on hydrolysis. At atmospheric pressure the liquid boiled mainly in the range 160—165° (BPr^n_3, b. p. 156·1°).

Fraction II was split into fractions (A), b. p. 110—114°/100 mm. (2·9 g.), and (B), b. p. 114—120°/100 mm. (5·9 g.), a small higher-boiling residue remaining. Vapour-density measurements by Dumas's method gave molecular weights: (A), 181·3, 187·3; (B), 206·9, 204·5 (Calc. for $C_{12}H_{30}B_2$: *M*, 195·9). The method is known to give results several units % high: pure tri-n-propylborine gave *M* 152·0 and 155·9 (Calc. for $C_9H_{21}B$: *M*, 140·1). The boron contents of fractions (A) and (B) were 10·3% and 11·0%, respectively (Calc. for $C_{12}H_{30}B_2$: B, 11·0%). (Tripropylborine gave B, 7·8%, by this procedure.) The results indicate that fraction (B) was mainly tetra-n-propyldiborane, together with some of its disproportionation products.

Fractions (A) and (B) reduced aqueous silver nitrate, potassium permanganate, and bromine, as expected if n-propyldiboranes were present. Both reacted smoothly with water in the presence of air, evolving hydrogen and forming a white solid, m. p. 102—106°; but if air was excluded a colourless oil, believed to be di-n-propylborinic acid, floated on the surface. Boron estimations on the solid indicated n-propylboronic acid (m. p. 107°) contaminated with a little boric acid (Found: B, 13·3, 13·0. Calc. for $C_3H_9BO_2$: B, 12·3%).

Hydrolyses of two samples of fraction (B) gave the results in Table 1. They indicate disproportionation of the tetra-n-propyldiborane during distillation. When 3·80 g. of this liquid were refluxed, the reflux temperature fell slowly during 6 hr. from 168·2 to 164·0°, and then remained constant. A gas evolved was collected at $-196°$ and had the characteristics of diborane. A similar liquid mixture, consisting mainly of tetra-n-propyldiborane and its disproportionation products obtained by reduction with lithium aluminium hydride (see below), refluxed initially at 167·0°, after 2 hr. at 164·4°, and after 16 hr. at 162·5°, the boron content falling from 11·2% to 10·2% and 9·9%, respectively.

TABLE 1.

Hydrolysis of fraction (B), b. p. 114—120°/100 mm.

Wt. liquid (g.)	H_2 (ml.)	H_2 (ml.) calc. for $B_2H_2Pr^n_4$	$B_2H_2Pr^n_4$ (%)
0·9850	166·6	225·0	74·0
0·7080	118·9	161·8	73·5

Both liquids were pale yellow after heating, and it appears from the very small amount of gas collected that not all of the diborane formed is released from the solution. The residues consisted of lower n-propyldiboranes and tri-n-propylborine. Thus it seems that disproportionation to tri-n-propylborine and diborane is only partially effected by refluxing.

(*c*) *Chlorodi-n-propylborine with lithium aluminium hydride.* Lithium aluminium hydride (3·92 g., 0·1 mole), suspended in ether (30 ml.), was slowly added to di-n-propylchloroborine (30·6 g., 0·23 mole) in ether (20 ml.) at room temperature. The apparatus was similar to that used in the borohydride reduction, and similar precautions were taken. After the initial vigorous exothermic reaction, the mixture was gently warmed for ½ hr. A little hydrogen chloride (0·3 g.) was evolved. The liquid products were isolated by ether-extraction, and the grey solid remaining (13·4 g.) was shown by analysis for chlorine and lithium to be a mixture of lithium and aluminium chloride with unchanged hydride (1·5 g.). Of the 8·21 g. of chlorine originally used, 7·87 g. were recovered in the solid, so that, after allowance for the hydrogen chloride found, the agreement is nearly quantitative.

The ether extract yielded a colourless liquid (17·1 g.), b. p. 76°/21 mm., and a small amount of a fraction, b. p. 76—85°/21 mm. (BPr^n_3 has b. p. 53°/21 mm.). To the former was added a further 10·9 g. recovered from an identical run and the total (28·0 g.), when redistilled, gave fractions (C), b. p. 85—95°/80 mm. (9·0 g.), and (D), b. p. 95—108°/80 mm. (14·5 g.), plus a small liquid residue, b. p. >108°/80 mm. Fraction (C) (Found: B, 11·45%), d^{20} 0·72, gave little hydrogen on hydrolysis, showing it to be mainly tripropylborine (d^{20} 0·725) with only small amounts of n-propyldiboranes. Fraction (D) (Found: B, 11·2%) gave on hydrolysis hydrogen corresponding to 61% (two samples) of tetra-n-propyldiborane and n-propylboronic acid (Found: B, 13·3%), m. p. 106—107° (mostly), containing a little boric acid.

(*d*) *Diethylchloroborine with sodium borohydride.* Diethylchloroborine (8·8 g., 0·084 mole) was heated with sodium borohydride (4·1 g., 0·11 mole) in an evacuated Carius tube at 130° for 12 hr. After removal of the volatile products (7·8 g.), unchanged hydride (3·5 g.) and sodium chloride (0·70 g.) remained. The volatile products were fractionated *in vacuo* through a series of traps; ~2 ml. collected at −25°, 6·5 ml. at −78°, and only a very small fraction, shown to be hydrogen chloride (0·2 g.), at −196°. No diborane or ethyldiboranes were detected. The condensate in the −78° trap was diethylchloroborine (6·2 g.). The tail fraction (1·4 g.) was free from chlorine and spontaneously inflammable with difficulty in air. Vapour-pressure measurements (Table 2) correspond well with the volatility reported [1b] for tetraethyldiborane.

TABLE 2.

V. p. of fraction condensed at −25°.

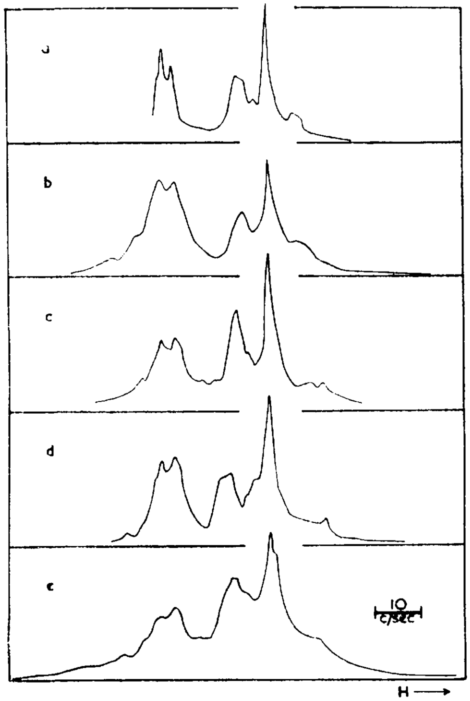
Temp.	−10·0°	−6·9°	−3·7°	−1·8°	0·0°	3·4°	7·2°	10·0°
Pressure (mm.)	0·0	0·1	0·2	0·3	0·5	0·8	1·0	1·2

However, the liquid melted over the range −59° to −35° ($Et_4B_2H_2$, m. p. = −56·5° to −56·0°), and hydrolysis of 0·3628 g. yielded only 26·0 ml. of hydrogen (Calc. for $B_2H_2Et_4$, 117·3 ml.). The boron content, determined on the residual solution after hydrolysis, was 18·5% (Calc. for $B_2H_2Et_4$, 15·5%), showing that other boron compounds were also present. Attempts to obtain more complete reaction by further experiments at higher temperatures (150° for 27 hr.) failed to improve the yield of ethyldiboranes.

(*e*) *Diethylchloroborine with lithium aluminium hydride.* Lithium aluminium hydride (2·39 g., 0·063 mole), suspended in ether (25 ml.), was slowly added to diethylchloroborine (21·8 g., 0·21 mole) with cooling in ice as required. No gas was obtained, but a colourless, spontaneously inflammable liquid (13·8 g.), d^{20} 0·704 (Found: B, 11·5%), was subsequently distilled off at 94—96° (BEt_3, b. p. 95·1°, d^{20} 0·696; B, 11·1%). The grey sludge remaining, when heated to about 150°, evolved hydrogen and diborane (1·4 g.); the residue (12·2 g.) was not investigated beyond estimating the chlorine (7·15 g.) and unchanged hydride (0·3 g.).

Action of Sodium Borohydride on a Mixture of Triethylborine and Boron Trichloride.—Sodium borohydride (31·0 g., 0·82 mole), triethylborine (43·4 g., 0·44 mole), and boron trichloride (26·2 g., 0·22 mole) were heated at 165° for 3 hr., then at 145° for 2 hr. in a high-pressure autoclave (625 ml.). The pressure rose from its initial value of about 1 atm. to a maximum of 77 atm., and remained at 43 atm. after cooling to room temperature. The gaseous products were released through a trap at −196°, all except hydrogen (17·4 l., 1·57 g.) condensing. The condensable gases (14·9 g.) were fractionated *in vacuo*; analysis (Bone–Wheeler, v. p., v. d.) showed them to consist predominantly of ethane (14·4 g.) with traces of diborane (0·3 g.) and hydrogen chloride (0·2 g.). No ethyldiboranes were detected.

The liquid products (26·0 g.) were distilled from the autoclave under reduced pressure, and fractionated *in vacuo* through traps at −20°, −78°, −196°. Most of the liquid collected at −78°. After further fractionation, the various fractions were analysed. This proved difficult in some cases because large amounts of unchanged ethylchloroborines were present, so that pure compounds were not obtained. The head trap (−196°) contained hydrogen chloride (0·4 g.), diborane (0·7 g.), and ethane (1·0 g.), with a mixture of ethylchloroborines, monoethyldiborane (0·4 g.), and a liquid ($\sim$4·0 g.) which could not be positively identified but was probably largely monoethyldiborane. This liquid was extremely unstable at higher temperatures (*e.g.*, at −11·9° the v. p. rose by 36 mm. in 3 min.), its molecular weight (v. d.); about 50 (Calc. for B_2H_5Et: *M*, 55·7), and its extrapolated b. p. about −8°. A small chlorine content (<10%) can be attributed to the presence of ethylchloroborines or boron trichloride. A peculiar feature was that on hydrolysis it evolved not only hydrogen but another gas in an almost equal volume (? propane). The middle trap (−78°) contained a liquid (8·2 g.) which, although it disproportionated slightly on further fractionation, was identified as containing ethyldichloroborine (4·0 g.), diethylchloroborine (2·5 g.), boron trichloride (0·5 g.), diborane (0·03 g.), and diethyldiborane (0·68 g.), but no triethyldiborane. The tail trap (−20°) retained 0·95 g. of liquid containing 0·26 g. of tetraethyldiborane (estimated by H_2 evolution upon hydrolysis). The tetraethyl compound was again contaminated. The white solid (62·9 g.) remaining in the autoclave contained unchanged hydride (5·2 g.) and sodium chloride (33·9 g.).



Proton nuclear magnetic resonance spectra of (a) BPr^n_2I, (b) BPr^n_2Br, (c) BPr^n_2Cl, (d) BPr^n_3, (e) $B_2H_2Pr^n_4$.

Nuclear Magnetic Resonance Spectra.—Proton resonance spectra, obtained with a Varian V4300-B spectrometer operating at 40 Mc./sec. are reproduced in the Figure.

DISCUSSION

The difficulties of isolating a particular alkyldiborane, as well as the appearance of trialkylborines and diborane, are ascribed to simultaneous disproportionation equilibria, the proportions of alkyldiboranes, $B_2H_{6-n}R_n$, that predominate varying according to the R : B ratio. Equilibria are established within a few hours at room temperature and more rapidly at elevated temperatures. Only by fractionation and storage much below 0° is it possible to isolate the individual members.

The nuclear magnetic resonance spectra reproduced show a strong genetic relationship, the main absorption system (over-all width ~1 chemical shift) being due to the BPr^n_2 group. The relative intensities of the individual peaks vary sufficiently for each compound to be identified, although the spectra for the bromo- and iodo-compound exhibit a particularly close resemblance. The spectrum for tetra-n-propyldiborane is most similar to those for tri-n-propyl- and di-n-propylchloro-borine (slightly more so to the latter in detailed relative intensities). At first sight surprising is the apparent absence of additional resonance attributable to bridge hydrogen atoms. In diborane the seven peaks arising from the bridge atoms have a spacing of ~40 c./sec. and are centred at a chemical shift of ~11 on the tetramethylsilane scale; that is, the centre falls well clear of the BPr^n_2 region with its chemical shift of ~8·5. However, the individual lines in the published [25] spectrum of the bridge hydrogen atoms in diborane are very broad; this might be due to instrumental factors, but alternatively might be caused by quadrupolar relaxation of the boron nuclei. If the latter is the case, the relatively much lower intensity to be expected for the two bridge hydrogen atoms in tetra-n-propyldiborane will be spread over a region of ~240 c./sec. (6 chemical shift units) and even the central maximum will be very weak indeed in relation to the main BPr^n_2 resonance. The necessary equipment was not at the time available to us for studying the ^{11}B resonance, but this has since been done [26] for some of the other alkyldiboranes and for certain trialkylborines including tri-n-propylborine. There appears to be no other reported study of hydrogen resonances of alkyldiboranes for comparison.

In a previous paper it was reported [15] that the reactivity of the di-n-propylhalogenoborines decreases in the order $BPr^n_2Cl > BPr^n_2Br > BPr^n_2I$, and the present work supports this, in that the chloro-compound reacts with sodium borohydride under conditions where the bromo- and the iodo-compound are inert. This order is the reverse of the surprising one observed for the relative acceptor properties of the boron trihalides,[27] for which no entirely satisfactory explanation has so far been forthcoming.

When triethylborine, boron trichloride, and sodium borohydride are heated under pressure the yield of ethyldiboranes is less than when pre-formed diethylchloroborine is reduced. The reduction in yield may be partly due to formation of ethyldichloroborine. However, as much as 38% of the ethyl groups appeared as ethane, and this probably did not arise by thermal decomposition of triethylborine or an ethyldiborane as the temperature did not exceed 165°. More probably, hydrogen chloride, a small quantity of which was isolated, was formed by reaction [28] of boron trichloride with the hydrogen also formed during the reaction: $2BCl_3 + 6H_2 \longrightarrow B_2H_6 + 6HCl$; this could then give ethane by reactions such as:

$$BEt_3 + HCl \longrightarrow BEt_2Cl + C_2H_6$$

$$NaBH_4 + BEt_3 + HCl \longrightarrow NaCl + B_2H_4Et_2 + C_2H_6$$

In addition, there is in this reaction evidence for the interaction of ethyl radicals among themselves, for the monoethyldiborane fraction was contaminated with an unidentified unstable substance of similar volatility which liberated (probably) propane on hydrolysis; although this accounts for at most a few per cent of the ethyl radicals, it emphasizes the complexity of the reaction. The main reaction may be expressed by the general equation:

$$(18\text{-}3n)NaBH_4 + (6\text{-}n)BCl_3 + 4nBR_3 \longrightarrow (18\text{-}3n)NaCl + 12B_2H_{6-n}R_n$$

In accordance with this, it is possible to exercise control over the R : B ratio of the alkyldiboranes produced by regulating the $BR_3 : BCl_3$ ratio in the reactants.

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