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THE REACTION OF DIBORANE WITH BORON TRICHLORIDE IN THE PRESENCE OF ETHERS—THE CHLOROBORANE ETHERATES*†

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Abstract—Diborane does not react to any significant extent with boron trichloride in the absence of ethers. In the presence of ethers (dimethyl ether, diethyl ether, diglyme, tetrahydrofuran and tetrahydropyran) reaction readily occurs at room temperatures to form chloroborane etherates, as indicated by the equations:

$$B_2H_6 + BCl_3 + 3R_2O \rightarrow 3H_2ClB{\cdot}OR_2$$
$$B_2H_6 + 4BCl_3 + 6R_2O \rightarrow 6HCl_2B{\cdot}OR_2$$

These chloroborane etherates may also be synthesized from the alkali metal borohydrides in accordance with the reactions:

$$MBH_4 + BCl_3 + 2R_2O \rightarrow 2H_2ClB{\cdot}OR_2 + NaCl$$
$$MBH_4 + 3BCl_3 + 4R_2O \rightarrow 4HCl_2B{\cdot}OR_2 + NaCl$$

Their formation accounts for the low yield of diborane realized in treating the alkali metal borohydrides with an excess of boron trichloride in ether solutions. A number of the chloroborane etherates have been isolated and characterized. They react with olefins to form organoborane derivatives and to reduce the carbonyl groups in typical ketones, but not in esters.

IN examining the formation of diborane by treatment of sodium borohydride with boron trifluoride and boron trichloride, we observed an interesting difference in the behaviour of these two compounds.(1) An excess of boron trifluoride did not affect the essentially quantitative yield of diborane, whereas an excess of boron trichloride resulted in marked decreases in the amount of diborane evolved from the reaction mixture. Only by the use of the precise stoicheiometric quantity of boron trichloride was it possible to realize the maximum yield of diborane.

It was apparent that the results could be accounted for if the diborane and excess boron trichloride reacted to form non-volatile products, chloro derivatives of diborane. Indeed, in the electric discharge procedure for the synthesis of diborane, the reaction product obtained by passing hydrogen and boron chloride through the discharge apparently consists of a mixture of boron trichloride and partially hydrogenated material.(2) However, these materials are unstable, and readily disproportionate into boron trichloride and diborane. It was only by applying great experimental skill, that BURG was able to isolate and characterize monochlorodiborane,

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* Molecular Addition Compounds. II.

† Based upon a thesis submitted by P. A. TIERNEY in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

‡ Standard Oil Research Foundation Fellow, 1955–1956. Parke, Davis and Company Fellow, 1956–1957.

(1) H. C. BROWN and P. A. TIERNEY, *J. Amer. Chem. Soc.* **80**, 1552 (1958).

(2) H. I. SCHLESINGER and A. B. BURG, *J. Amer. Chem. Soc.* **53**, 4321 (1931).

B_2H_5Cl, as one of the disproportionation products. Within a short time at room temperature this material was transformed into diborane and boron trichloride.⁽³⁾

In spite of the reported instability of the chloroboranes, it appeared that they might be stabilized by the ethers used as reaction media. Accordingly, a study was undertaken of the reaction of diborane with boron trichloride in the presence of several representative ethers.

RESULTS

Equimolar mixtures of diborane with boron trichloride or with boron trifluoride at room temperature exhibited pressures which were additive for the two components, and these pressures exhibited no significant change over 24 hr. No evidence of any reaction was observed. Diborane was no more soluble in a dilute solution of boron trifluoride in diglyme than in the solvent itself. On the other hand, diborane was rapidly absorbed by a dilute solution of boron trichloride in diglyme (diethyleneglycol dimethyl ether). One mole of diborane reacted per mole of boron trichloride present.

Solutions of boron trichloride in diglyme are relatively unstable—the ether is split with the formation of methyl chloride.⁽¹⁾ However, such solutions saturated with diborane appeared to be stable over long periods of time.

Because the low volatility and polyfunctionality of diglyme introduced experimental and interpretive difficulties, the phenomenon was examined with other simpler ethers, such as dimethyl ether, diethyl ether, tetrahydrofuran and tetrahydropyran. Diethyl ether and tetrahydropyran were the preferred reactants because of their demonstrated stability toward splitting by boron trichloride.⁽¹⁾

An equimolar mixture of boron trichloride and diborane was treated with an excess of diethyl ether at 0°. Small increments of the ether were removed at 0° until the pressure dropped sharply to 3 mm and remained sensibly constant at this value. The molar ratio of ether to boron trichloride was 3·0. The product was a liquid which melted over a wide range, —85 to —105°.

In the case of tetrahydropyran, the corresponding reaction product, formed by mixing equimolar amounts of diborane and boron trichloride with three molar equivalents of the ether, appeared to be more stable, melting sharply at 19–20°. Tetrahydrofuran formed a similar derivative, m.p. —36° to —38°.

An experiment was carried out in a sealed tube with a 3 : 1 molar mixture of dimethyl ether and boron trichloride and an excess of diborane. After 36 hr at room temperature, the excess diborane was recovered by distillation from the reaction mixture at —78°. The results indicated that precisely one mole of diborane had reacted per mole of boron trichloride present. The melting point of the product was —20 to —21°.

These results clearly indicate that boron trichloride and diborane do not react significantly in the absence of ethers, but in their presence undergo reaction to form liquid products of low volatility, containing boron, active hydrogen, chloride, and ether in the ratio 1 : 2 : 1 : 1. On this basis the reactions can be written:

$$B_2H_6 + BCl_3 + 3(CH_3)_2O \rightarrow 3BH_2Cl{\cdot}O(CH_3)_2$$
$$B_2H_6 + BCl_3 + 3(C_2H_5)_2O \rightarrow 3BH_2Cl{\cdot}O(C_2H_5)_2$$
$$B_2H_6 + BCl_3 + 3(CH_2)_4O \rightarrow 3BH_2Cl{\cdot}O(CH_2)_4$$
$$B_2H_6 + BCl_3 + 3(CH_2)_5O \rightarrow 3BH_2Cl{\cdot}O(CH_2)_5$$

⁽³⁾ A. B. BURG, *J. Amer. Chem. Soc.* **56**, 499 (1934).

It was also observed that boron trichloride and diborane in a 4 : 1 molar ratio reacted with ethyl ether to form relatively stable, non-volatile products. Ether was removed at 0° from a reaction product of this composition in excess ether until the pressure dropped suddenly to a value near zero. At this point the ratio of ether to boron trichloride was 1·5. A similar experiment was carried out with tetrahydropyran. The observed ratios of reactants corresponds to the possible formation of a dichloroborane etherate and tetrahydropyranate:

$$B_2H_6 + 4BCl_3 + 6(C_2H_5)_2O \rightarrow 6BHCl_2{\cdot}O(C_2H_5)_2$$

$$B_2H_6 + 4BCl_3 + 6(CH_2)_5O \rightarrow 6BHCl_2{\cdot}O(CH_2)_5$$

The ethyl ether product exhibited a melting point of −25 to −30°, whereas the tetrahydropyran derivative melted at 10–15°.

In the case of the monochloroborane etherates, the stoicheiometry of the reaction clearly establishes the formation of the product with the composition, $BH_2Cl{\cdot}OR_2$. In the case of the dichloroborane etherates, the stoicheiometry alone cannot eliminate the possibility that the reaction product consists of a mixture of the known boron trichloride etherates[(4–6)] and the corresponding monochloroborane etherates.

$$B_2H_6 + 4BCl_3 + 6R_2O \rightarrow BH_2Cl{\cdot}OR_2 + BCl_3{\cdot}OR_2$$

Diethyl ether–boron trichloride melts at 56°. The low melting point, −25 to −30°, of the "dichloroborane etherate" suggests that large quantities of the trichloride addition compound, required by the above equation (50 mole per cent), cannot be present in the reaction product. It is possible that the reaction product consists primarily of the $BHCl_2{\cdot}OR_2$ product with minor equilibrium quantities of the $BH_2Cl{\cdot}OR_2$ and $BCl_3{\cdot}OR_2$ derivatives present. This would account for the relatively wide range observed for the melting points. A more detailed study of these products has been undertaken to resolve these questions.*

A solution of sodium borohydride in diglyme was treated with an equimolar quantity of boron trichloride. No diborane was evolved. The supernatant solution was separated from the precipitate, presumably sodium chloride, and analysed for boron, chloride and active hydrogen. The analysis corresponded to the formation of the monochloroborane etherate. The chemical behaviour of the solution corresponded precisely to the product obtained by the reaction of diborane with boron chloride in diglyme. Consequently, the reaction may be written:

$$NaBH_4 + BCl_3{\cdot}OR_2 + OR_2 \rightarrow NaCl\downarrow + 2BH_2Cl{\cdot}OR_2$$

The utility of the chloroborane etherates as hydrogenation and hydroboration reagents was briefly examined. At room temperature chloroborane ethyl etherate rapidly reduced acetone and related ketones, but did not affect esters, such as ethyl acetate. Ethylene reacted with dichloroborane pyranate at room temperature to form an organoborane, presumably triethylboron, and tetrahydropyran–boron trichloride.

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* Research in progress with Mr. G. Klender.

(4) E. Wiberg and W. Sutterlin, *Z. Anorg. Chem.* **202,** 22 (1931) report the melting point of dimethyl ether–boron trichloride to be 76°.

(5) W. Nespital, *Z. Phys. Chem.* **B 16,** 153 (1932) reports the melting point of diethyl ether–boron trichloride to be 56°.

(6) J. Grimley and A. K. Holliday, *J Chem. Soc.* 1212 (1954) report the melting points of tetrahydrofuran-boron trichloride as 38–52°, and tetrahydropyran–boron trichloride as 49–52°.

DISCUSSION

It is quite evident from the results that there is a remarkable difference in the behaviour of boron trifluoride and boron trichloride toward diborane in the presence of ethers. The rapid reaction of boron trichloride with diborane in the presence of ethers to form the relatively stable, non-volatile products, the monochloroborane and dichloroborane etherates, accounts for the deletorious effect of excess boron trichloride in the generation of diborane from alkali metal borohydrides.(1)

The marked difference in the behaviour of boron trichloride and boron trifluoride in these reactions may be attributed to the greater effect of chlorine over fluorine on the acid strength of boron acids.(7) On this basis both $BHCl_2$ and BH_2Cl would be sufficiently strong acids to form stable addition compounds with ethers, whereas the corresponding fluorine derivatives, BHF_2 and BH_2F, would be less strong acids and would result in less stable derivatives. Consequently the driving force for the reaction would come primarily from the replacement of one stable co-ordination bond by three, individually weaker, but collectively stronger, co-ordination bonds.

$$B_2H_6 + Cl_3B{\cdot}OR_2 + 2R_2O \rightarrow 3BH_2Cl{\cdot}OR_2$$

The chloroborane etherates exhibit many of the hydrogenation and hydroboration reactions of diborane itself. Moreover, the complexes are liquids which can be handled more readily than gaseous diborane. Consequently, they may prove to be useful reagents for organic syntheses and we are currently examining their potentialities for this purpose.*

EXPERIMENTAL

Apparatus. Except where otherwise stated, all experiments were conducted in the usual all-glass high vacuum system in which the materials came in contact only with glass and mercury.(8)

Analyses. Active hydrogen was measured by hydrolysing samples in a water-filled inverted burette. Chloride was determined as hydrochloric acid by titration with standard sodium hydroxide using methyl red as indicator, following hydrolysis in a closed system. Boron was determined as boric acid by adding mannitol and titrating with standard sodium hydroxide using phenolphthalein as indicator.

Materials. Boron trichloride (Matheson), v.p. 481 mm at 0°, was purified through the formation and dissociation of its nitrobenzene addition compound.(7) Diborane was prepared from sodium borohydride.(1)

Diglyme (Ansul Chemical Company) was twice distilled from lithium aluminium hydride under reduced pressure: b.p. 64° at 16 mm, n_D^{20} 1·4087. Tetrahydropyran (Dupont), after 24 hr over calcium hydride, was twice distilled from lithium aluminium hydride under nitrogen: b.p. 86–87° at 742 mm: n_D^{20} 1·4203; v.p. 75 mm at 28°, 20 mm at 0°. Tetrahydrofuran was treated with sodium hydroxide pellets and then twice distilled from lithium aluminium hydride under dry nitrogen:(9) b.p., 65° at 742 mm, v.p. 147 mm at 29°, 70 mm at 0°. Ethyl ether (Mallinckrodt) was treated with calcium hydride for 24 hr, and distilled from the hydride directly into the line: v.p. 189 mm at 0°. Dimethyl ether (Matheson) was purified by distillation in the vacuum apparatus: v.p. 35 mm at −78°.

Acetone was dried over anhydrous calcium sulphate, distilled through a 50 plate column: b.p., 56° at 748 mm, n_D^{20} 1·3590. Ethylene was obtained from a commercial cylinder and used directly.

Reaction of diborane with boron trichloride in diglyme. Into the reaction vessel was placed 2·5 ml of diglyme and 0·500 mmole of diborane. The pressure in the flask at 25° was 71 mm. Boron

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* Research with Dr. B. C. Subba Rao.

(7) H. C. Brown and R. R. Holmes, *J. Amer. Chem. Soc.* **78**, 2173 (1956).
(8) R. T. Sanderson, *Vacuum Manipulations of Volatile Compounds.* Wiley, New York (1947).
(9) T. Higuchi, *Analyt. Chem.* **22**, 534 (1950); *J. Amer. Chem. Soc.* **73**, 2676 (1951).

trichloride was condensed into the flask. The pressure dropped rapidly. After 24 hr, the pressure was 4 mm at room temperature.

Preparation of monochloroborane etherate from sodium borohydride and boron trichloride in diglyme. In a 50 ml round-bottom flask was placed 4·00 ml of a 1·01 M solution of sodium borohydride in diglyme, followed by 4·00 ml of a 1·00 M solution of boron trichloride in tetrahydropyran. A white precipitate formed, along with traces of a gas. The precipitate was allowed to settle for 1 hr, then a 2·00 ml sample of the clear solution was removed and analysed for boron, chloride and active hydrogen. The results, 1·93 mmoles of boron, 1·96 mmoles of chloride and 3·90 mmoles of hydrogen, correspond to the formation of the monochloroborane derivative.

Preparation of monochloroborane–tetrahydropyran. In a reaction flask of 15 ml capacity were introduced 0·552 mmole of tetrahydropyran, 0·184 mmole of diborane and 0·184 mmole of boron trichloride. The liquid nitrogen bath was removed and the materials permitted to warm up. Near room temperature a vigorous reaction occurred with the formation of a white solid, and the pressure decreased to almost zero. The product melted at 19–20°.

Preparation of monochloroborane–tetrahydrofuran. The procedure and quantities were identical with the above experiment. The product consisted of large, triangular shaped crystals, m.p. −38 to −36°.

Preparation of monochloroborane–ethyl ether. In the flask were condensed 1·00 mmole of diborane, 1·00 mmole of boron trichloride and 3·00 mmoles of ethyl ether. After 40 hr, the pressure was 14 mm. Traces of volatile impurities were removed, with the flask cooled to −78°. The residue melted over a wide range, −85 to −105°.

Preparation of monochloroborane–methyl ether. In a 4 ml tube fitted with a break-tip were condensed 2·00 mmoles of dimethyl ether, 0·67 mmole of boron trichloride and 1·34 mmoles of diborane. The sealed tube was allowed to stand at room temperature for 36 hr. The tube was opened and gases volatile at −80° removed. There was collected 0·67 mmole of diborane. Thus, the reactants had interacted in the ratio, 1·00 B_2H_6 : 1·00 BCl_3 : 3·00 $(CH_3)_2O$, to form the product, m.p. −20 to −21°.

Preparation of dichloroborane–tetrahydropyran. Boron trichloride, 0·270 mmole, diborane, 0·093 mmole were placed in the reaction tube with 0·555 mmole of tetrahydropyran. The materials reacted to produce a white solid, m.p. 10–15°.

Preparation of dichloroborane–ethyl ether. Into the reaction vessel were condensed 0·67 mmole of boron trichloride, 1·72 mmoles of ethyl ether and 0·17 mmole of diborane. The reaction was permitted to proceed at room temperature for 1 hr, following which the excess ether was removed at low temperature. There was obtained 0·71 mmole. The material in the flask was a white solid, m.p. −25 to −30°.

Reaction of monochloroborane–tetrahydropyran with acetone and ethyl acetate. The following experiments are typical of those carried out to explore the reducing action of these reagents towards typical organic derivatives. A sample of monochloroborane–tetrahydropyran, 0·555 mmole, was prepared from the components. On treatment with water in the reaction vessel the pressure of hydrogen developed was 280 mm. An identical sample, 0·555 mmole, was treated with approximately 1 ml of acetone (excess). After 30 min, the reaction mixture was hydrolysed. No hydrogen was formed.

In a similar experiment, 0·555 mmole of the complex was treated with 1 ml of ethyl acetate (excess). After 1 hr, the reaction mixture was hydrolysed. The hydrogen evolved developed a pressure of 277 mm.

Reaction of dichloroborane–tetrahydropyran with ethylene. Into an ampoule fitted with two break-tips were condensed 0·185 mmole of diborane, 0·740 mmole of boron trichloride and 1·11 mmole of tetrahydropyran. The tube was sealed. After 24 hr at room temperature, it was opened to the line. The pressure was less than 1 mm. Ethylene, 5·57 mmoles, was introduced and the reaction sealed and allowed to stand at room temperature for 2 weeks.* The tube was opened and the products distilled. There was obtained 4·44 mmoles of ethylene. The material volatile at 40° was exposed to oxygen. It ignited instantly, indicating the formation of boron–carbon bonds. The residue in the tube which was not volatile was hydrolysed and analysed for boron and chloride. There were found 0·67 mmole boron and 2·07 mmoles chloride.

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* The long reaction time is not essential. In later work we have observed rapid reactions with a number of olefins. Work in progress with Dr. B. C. SUBBA RAO. With shorter reaction times the alkyl chloroboranes can be isolated. The disproportionation which was here observed was apparently a consequence of the long reaction time.