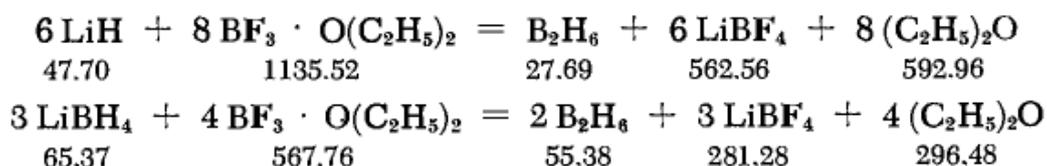


Diborane



Diborane was first obtained from the mixture of boron hydrides resulting from the hydrolysis of magnesium boride; later it was produced by spark discharge in mixtures of BCl_3 or BBr_3 with H_2 [1, 2, 3]. It now can be produced more easily and in larger quantities by the reaction of LiH , NaH or alkali borohydrides with BF_3 diethyl etherate [4]. To obtain good yields, the alkali hydrides must be very finely powdered. Since alkali hydrides are hygroscopic and difficult to grind, the use of alkali borohydrides, which are fine powders to start with, has certain advantages for laboratory-scale synthesis. On the other hand, LiH is a particularly economical starting material for the production of larger quantities of B_2H_6 .

The procedure to follow can be applied regardless of whether an alkali hydride or alkali borohydride is used. The reaction vessel *a* (Fig. 239), which can have a capacity of 0.5 to 2 liters, depending on need, is used. The cold finger *b* acts as a reflux condenser. From *b*, the product B_2H_6 is passed through four successive cold traps f_1 to f_4 . Ground joints and stopcocks should be greased with silicone lubricant, but in quantitative work it is best to use mercury seals. The four traps are connected to a storage flask which in turn

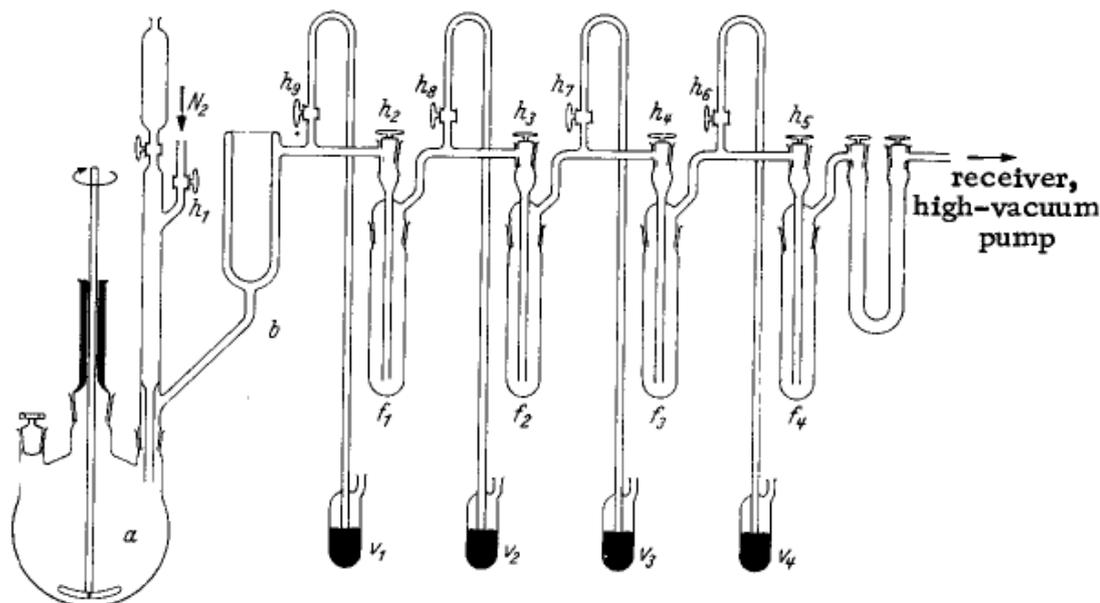


Fig. 239. Preparation of B_2H_6 .

a—reaction vessel; *b*—cold finger; f_1 to f_4 —traps; h_1 to h_6 —stopcocks; v_1 to v_4 —mercury-filled pressure release valves.

is connected to a high-vacuum pump. All the equipment must be thoroughly dried prior to the run. The finely divided hydride or borohydride is placed in the reaction vessel and suspended in some anhydrous ether, and the required quantity of BF_3 etherate is placed in the dropping funnel. Use double the stoichiometric quantity of BF_3 etherate. The entire apparatus is thoroughly flushed with dry, purified N_2 ; the cold finger b and trap f_1 are cooled to -78°C and traps f_2 and f_3 to the temperature of liquid N_2 . When all the equipment is properly flushed with N_2 , stopcocks h_1, h_5, h_7, h_8 and h_9 are closed and the BF_3 etherate is added slowly in drops to the hydride, using constant, vigorous stirring. At the same time the reaction vessel is heated to 60°C . When gas generation ends the B_2H_6 is flushed into the traps (using N_2), where it freezes out at -196°C . After the reaction, some ether and a trace of B_2H_6 will be found in f_1 . The product will be largely in f_2 , with a smaller amount in f_3 . Now stopcocks h_2 and h_3 are closed and the cooling bath under trap f_1 is replaced by a Dewar flask filled with liquid N_2 . This trap is used to collect the residues forming when B_2H_6 is purified by fractional condensation. To purify, traps f_2 to f_4 are evacuated and the B_2H_6 condensed in f_2 . Then trap f_3 is cooled to -100°C and trap f_4 to -196°C , and by slow heating the contents of f_2 are transferred into f_3 and f_4 . After a single fractionation, f_4 will contain pure diborane. The fractionation can be repeated with f_3 cooled to -140°C .

To prevent ignition on disassembly of the apparatus, the flask is flushed again with N_2 , which can escape via v_2 if stopcocks h_2 and h_3 are left open. Some methanol is added dropwise to the reaction flask and the contents of trap f_1 are allowed to thaw. The N_2 will then contain enough methanol vapor to render harmless all B_2H_6 residues in f_1 .

PROPERTIES:

Spontaneously igniting gas with strong, characteristic odor. M.p. -165.7°C , b.p. -92.5°C . Reacts quickly with water to form H_3BO_3 and H_2 .

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