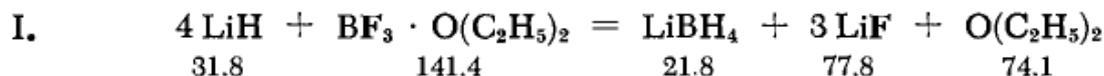
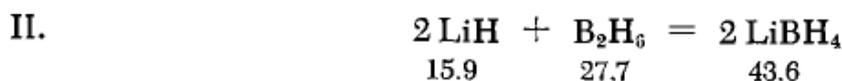


Lithium Borohydride



A steel autoclave, provided with a threaded, removable head, is filled with finely powdered LiH, and sufficient absolute ether is added to cover the LiH with a thick layer. Then about 2/3 of the stoichiometric amount of BF₃ ether is added. The autoclave is closed at once, since the reaction starts immediately. The reactants are heated at 120-130°C for several hours. After the autoclave has cooled, it is opened, and its contents are diluted with liberal amounts of ether and transferred to a flask. The ether solution is then decanted and the residual solvent distilled off. The LiBH₄ product is recrystallized from absolute ether, taking care to exclude moisture. The LiBH₄ crystallizes with one mole of ether of crystallization; this can be removed in vacuum at 33°C.



The apparatus shown in Fig. 240 is used. The required amount of B₂H₆ is condensed in trap *f*₁ at -196°C under an N₂ blanket. Then the trap is connected to the apparatus and the dry reaction vessel is filled with 10 g. of finely divided LiH and 400 ml. of absolute ether. Stopcock *h*₄ is opened to allow N₂ to enter. The latter can initially escape via *v*₂ and later, after the stopcocks at trap *f*₁ and *h*₂ have been opened, via *v*₁. The apparatus is thoroughly flushed with N₂; then *h*₄ and *h*₃ are closed. The Dewar flask *f*₁ is removed from trap *f*₁, and trap *f*₂ is then immersed in a Dewar flask at -196°C. As a result, B₂H₆ will slowly evaporate from *f*₁ to *f*₂. Any

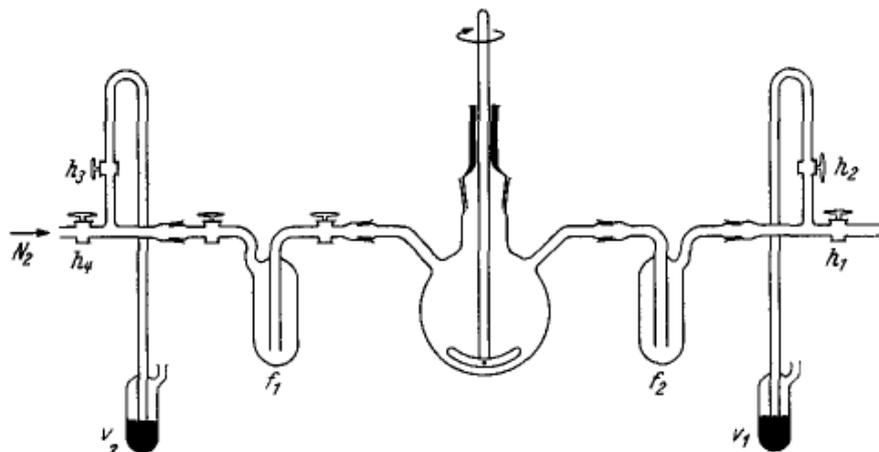


Fig. 240. Preparation of LiBH₄ from LiH and B₂H₆.

*f*₁, *f*₂ —traps; *h*₁ to *h*₄—stopcocks; *v*₁, *v*₂—pressure release valves.

entrained N_2 can escape via v_1 . The reaction vessel is well stirred while B_2H_6 passes through it. Any unreacted B_2H_6 will condense in f_2 . When f_1 is empty, the last traces of B_2H_6 are flushed out from f_1 into f_2 (use N_2). Close h_2 , open h_3 and, by placing the Dewar flask at f_1 and removing it from f_2 , allow B_2H_6 to evaporate in the opposite direction. If the LiH is sufficiently reactive, two such passes of B_2H_6 through the reaction vessel, i.e., once in each direction, will suffice. Nitrogen is allowed to enter via h_1 ; this will flush the remainder of the B_2H_6 into f_1 , where it will freeze out. The trap is then closed and the apparatus may be disassembled. The reaction vessel is rinsed with ether, the combined ether phase is decanted off, and the $LiBH_4$ is isolated by evaporating the solvent.

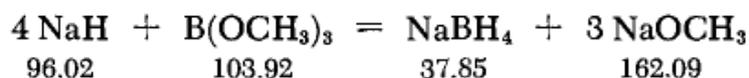
PROPERTIES:

Loose white powder. Hydrolyzes in the presence of atmospheric moisture. In the presence of H_2O , gives off H_2 in a violent reaction. Approximately 2.5 g. of $LiBH_4$ will dissolve in 100 ml. of ether at $19^\circ C$. Used as a reducing agent in the same manner as $LiAlH_4$.

REFERENCES:

- H. I. Schlesinger. and H. C. Brown. *J. Amer. Chem. Soc.* 62, 3429 (1940).
 G. Wittig and P. Hornberger. *Z. Naturforsch.* 6b, 225 (1951).
 H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp. *J. Amer. Chem. Soc.* 75, 199 (1953).

Sodium Borohydride



The reaction is carried out in a round-bottom, three-neck cylindrical flask. A mercury-seal Monel stirrer is placed in the central neck. The stirrer is equipped with five blades, arranged one over the other. The blade dimensions should be such that the stirrer can fit through the neck, but still fit the wall of the flask as closely as possible. A thermometer is placed in the second neck and a condenser on the third. The top of the condenser is equipped with a wye-tube adapter, one side of which connects to a dropping funnel and the other to a soda-lime drying tube. The flask is placed in an electric furnace, the top of which is covered with glass wool and an asbestos lid. The thermometer is removed, and the flask flushed with N_2 through this neck. Then 50 g. of NaH is rapidly added and 50 g. of $B(OCH_3)_3$ is placed in the dropping funnel. The stirrer and the furnace are then turned on. As soon as the thermometer indicates

a temperature of 200°C in the flask, the ether is added dropwise at a uniform rate. The addition should require 20–40 minutes, during which the temperature is kept at 230–270°C. The stirring is continued at this temperature for another hour. The flask is then allowed to cool and thoroughly dried isopropylamine or liquid NH₃ is used to extract the NaBH₄ from the now solid mixture, which, however, should have become well pulverized as a result of the constant stirring. The extraction with isopropylamine is carried out by refluxing for a few minutes; the extraction with NH₃ is done by stirring the reaction product for a few minutes. In either case the extract is filtered through a fritted glass filter and the solvent is evaporated. The NaBH₄ remains as a fine white powder, with a purity of 90–96%. The yield is 86–94%. The NaBH₄ is purified by recrystallization from either isopropylamine or water (it forms a dihydrate).

For unknown reasons the nature of the NaH used exerts a great influence on the yield and purity of the final product. Therefore, it is best to check the suitability of the starting material by making a small-scale preparation first. If the product is unsatisfactory, the NaH is preheated to 250°C and a small quantity of impure NaBH₄ from a preceding run is added to start the reaction. The yield can also be improved by a more uniform rate of addition of the B(OCH₃)₃.

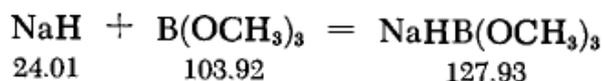
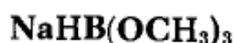
PROPERTIES:

Fine, white crystals (cubic system). Decomposes slightly in neutral aqueous solutions, from which it can be partially recrystallized as a dihydrate. Rapidly hydrolyzes in acid solution. Stable up to 400°C.

REFERENCES:

- H. I. Schlesinger, H. C. Brown and A. E. Finholt. *J. Amer. Chem. Soc.* 77, 205 (1953).

Sodium Trimethoxyborohydride



A one-liter, round-bottom flask equipped with a reflux condenser is well dried and flushed with N₂. Finely powdered NaH (43 g.) is added, followed by 230 g. of B(OCH₃)₃, slowly added from a dropping funnel on top of the condenser. The reaction, which begins at once, liberates a considerable amount of heat. After the addition of the ester, the contents are refluxed at 70°C for several hours. This causes a fivefold increase in the volume of the product, which

simultaneously becomes pure white. When the volume no longer increases, the reflux condenser is replaced by a downward condenser and the excess $B(OCH_3)_3$ is distilled off. The yield is nearly quantitative. It is best, however, to pretest the available NaH in a small experimental run and, if necessary, modify the reaction

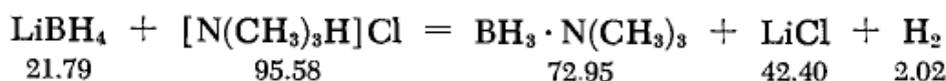
PROPERTIES:

Loose white powder. Stable in dry air; hydrolyzes slowly in moist air. Decomposes when heated to 230°C . Rapidly reacts with B_2H_6 to form $NaBH_4$ and $B(OCH_3)_3$. Decomposed by alcohol, forming H_2 .

REFERENCE:

H. C. Brown, H. I. Schlesinger, I. Sheft and D. M. Ritter. *J. Amer. Chem. Soc.* 77, 192 (1953).

Borine Trimethylaminate



A 100-ml. three-neck flask, equipped with a stirrer, a reflux condenser and a dropping funnel, is used and 1.68 g. of $[N(CH_3)_3H]Cl$ is added to it. A solution consisting of 0.42 g. of $LiBH_4$ in diethyl ether is slowly introduced from the dropping funnel. If vigorously stirred, the reaction proceeds at room temperature. When the generation of H_2 diminishes, the contents are refluxed for another hour. All solvent is then distilled and the solid residue is transferred to a vacuum sublimation apparatus, where the $BH_3 \cdot N(CH_3)_3$ is sublimed in vacuum at 40°C and collected in a cooled receiver. The yield is 85%.

PROPERTIES:

White hexagonal crystals. Stable. M.p. 94°C .

REFERENCES:

- G. W. Schaeffer and E. R. Anderson. *J. Amer. Chem. Soc.* 71, 2143 (1949).
 A. B. Burg and H. I. Schlesinger. *J. Amer. Chem. Soc.* 59, 780 (1937).