SECTION 15

Aluminum

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Lithium Aluminum Hydride

$LiAlH_4$

I.

$$\underset{31.8}{4\,LiH} + \underset{133.4}{AlCl_3} = \underset{38.0}{LiAlH_4} + \underset{127.2}{3\,LiCl}$$

For the reaction between LiH and $AlCl_3$ to occur to a noticeable extent, the thick, hard lumps of lithium hydride must be ground to a very fine powder and then sieved. This treatment is performed under nitrogen. A very reactive ether suspension of LiH is obtained if the material is wet-ground with anhydrous ether in a special ball mill (K. Ziegler et al.) and used immediately.

A fresh suspension of 23.5 g. (2.96 moles) of LiH in 200 ml. of ether is introduced (with exclusion of moisture) into a three-neck flask provided with a dropping funnel, a reflux condenser and a stirrer. A solution of 71.2 g. (0.534 mole) of $AlCl_3$ in 300 ml. of ether is then added in drops with vigorous stirring. The reaction starts immediately, as shown by the boiling of the ether. The rate is kept uniform by adjustment of the addition rate. When all the $AlCl_3$ solution has been added, stirring is continued until the reaction has subsided, and the mixture is left to stand for some time. The contents of the flask are then filtered, using nitrogen pressure, through a fritted glass filter, and the clear filtrate is concentrated at atmospheric pressure until it has a syrupy consistency. The residual ether may be evaporated in vacuum at 70°C. The yield of $LiAlH_4$, based on $AlCl_3$, is about 85%.

Insufficient grinding of the LiH may prevent the reaction from starting spontaneously, or from going to completion, and lead to sudden, explosive bursts of renewed activity; in such cases the reaction is started by adding 200 ml. of ether, followed by a solution of 3 g. of $LiAlH_4$ in 30 ml. of ether, to the finely divided LiH. The subsequent procedure is the same as described above. According to Wiberg, a slight quantity of iodine may be used as an initiator instead of the $LiAlH_4$.

II.
$$\underset{31.8}{4\,LiH} + \underset{266.7}{AlBr_3} = \underset{38.0}{LiAlH_4} + \underset{260.5}{3\,LiBr}$$

According to Wiberg, the difficulties involved in the preparation of sufficiently reactive LiH are not encountered if $AlBr_3$ is used instead of $AlCl_3$. In this case, coarse LiH can be used:

An ether solution of $AlBr_3$ is prepared by adding small portions of the material (total 267 g. = 1 mole) to 750 ml. of extremely pure, dry ether in a flask cooled with ice-salt mixture. A 33-g. portion (4.1 moles) of coarsely ground LiH is placed in a three-neck flask with a reflux condenser, a stirrer and a dropping funnel. The hydride is covered with 250 ml. of ether, and the $AlBr_3$ solution is allowed to run in; the addition takes one to two hours. The stirred mixture is then heated to the boiling point of ether and kept at this temperature for a few hours. The LiBr and unreacted LiH precipitate on cooling. The solution is rapidly decanted through a layer of glass wool in a funnel. The filtrate obtained consists of an ether solution of $LiAlH_4$ saturated with LiBr. The solution may be stabilized by storing it over a small quantity of LiH.

PROPERTIES:

Colorless solid, stable in dry air at room temperature. The ether solution is used in inorganic and organic chemistry as a reducing and hydrogenating agent.

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K. Ziegler, H. G. Gellert, H. Martin and K. Nagel, Liebigs Ann. Chem. 589, 91 (1954).
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Calcium Aluminum Hydride

$Ca(AlH_4)_2$

$$\underset{168.4}{4\,CaH_2} + \underset{266.8}{2\,AlCl_3} = \underset{102.1}{Ca(AlH_4)_2} + \underset{333.0}{3\,CaCl_2}$$

A freshly prepared solution of $AlCl_3$ in tetrahydrofuran is added to a suspension of finely ground calcium hydride in the same