THE ACTION OF SODIUM HYDRIDE ON ETHYLALUMINUM DICHLORIDE AND DIBROMIDE

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In organoaluminum compounds, two types of alkylaluminum hydrides are possible: the dialkylaluminum hydrides R₂AlH and the alkylaluminum dihydrides RA₁H₂. The first compounds have been quite widely studied and used as reducing agents in organic chemistry. The second compounds have not so far been obtained. It is true that a paper of Schlesinger et al. [1] mentions the production of a complex of methylaluminum dihydride with lithium hydride CH₃AlLiH₃; however, this compound was not isolated and its individuality was not proved. We have found previously [2] that the reduction of ethylaluminum sesquibromide with sodium hydride leads to a mixture of diethylaluminum hydride and ethylaluminum dihydride containing the latter compound in smaller amount than was to be expected from the equation of the reaction.

In order to obtain ethylaluminum dihydride C₂H₅AlH₂, we have, in the present investigation, investigated the reduction of ethylaluminum dichloride and ethylaluminum dibromide with sodium and lithium hydrides. The reduction of ethylaluminum dichloride takes place smoothly under the action of a slight excess of sodium hydride in benzene solution in the presence of diethylaluminum hydride [2] as a catalyst at 25-30°. However, the reaction does not lead to the formation of ethylaluminum dihydride in individual form, and the reaction product consists of a mixture of diethylaluminum hydride and ethylaluminum dihydride, the relative amounts of which depend on the conditions of carrying out the reduction. In addition to these two compounds, sodium tetrahydroaluminate is also formed. We observed the formation of these three compounds in every case, in spite of variations in the reaction conditions. On carrying out the reaction with the calculated amount of sodium hydride (2 moles of NaH per 1 mole of C₂H₅AlCl₂), the reduction does not go to completion because of the formation of sodium tetrahydroaluminate. Thus, the reaction of sodium hydride with ethylaluminum dichloride takes place according to the following scheme

\[ C₂H₅AlCl₂ + NaH \rightarrow (C₂H₅)₂AlH + C₂H₅AlH₂ + NaAlH₄. \]

An analogous result is obtained in the reaction of sodium hydride with ethylaluminum dibromide

\[ C₂H₅AlBr₂ + NaH \rightarrow (C₂H₅)₂AlH + C₂H₅AlH₂ + NaAlH₄. \]

When the mixture of diethylaluminum hydride and ethylaluminum dihydride is treated with sodium hydride, the sole products of the reaction are sodium diethyldihydroaluminate and sodium tetrahydroaluminate. From this, it follows that ethylaluminum dihydride disproportionates under the action of sodium hydride with the formation of sodium diethyldihydroaluminate and sodium tetrahydroaluminate

\[ 2C₂H₅AlH₂ + 2NaH \rightarrow Na(C₂H₅)₂AlH₂ + NaAlH₄. \]

This explains the result of the reaction of ethylaluminum dichloride with sodium hydride. The ethylaluminum dihydride formed in the reduction partially reacts with the sodium hydride, giving sodium tetrahydroaluminate and sodium diethyldihydroaluminate, which, on reaction with ethylaluminum dichloride, is converted into diethylaluminum hydride. When an excess of sodium hydride reacts with ethylaluminum dichloride in benzene solution, a reaction takes place in accordance with the following scheme

\[ 2C₂H₅AlCl₂ + 6NaH \rightarrow Na(C₂H₅)₂AlH₂ + NaAlH₄ + 4NaCl. \]

The reaction of ethylaluminum dibromide with an excess of lithium hydride in ethereal solution takes place analogously

\[ 2C₂H₅AlBr₂ + 6LiH \rightarrow Li(C₂H₅)₂AlH₂ + LiAlH₄ + LiBr. \]
We have made an attempt to obtain sodium ethyltrihydroaluminate by disproportionation reactions of sodium tetraethylaluminate and sodium diethyldihydroaluminate with sodium tetrahydroaluminate. On heating sodium tetraethylaluminate with sodium tetrahydroaluminate at 180-190° for 10 hours, only sodium diethyldihydroaluminate and unchanged sodium tetrahydroaluminate were obtained.

\[
(C_2H_5)_4AlNa + NaAlH_4 \rightarrow 2(C_2H_5)_2AlNaH_2.
\]

No sodium ethyltrihydroaluminate was formed. In exactly the same way, heating sodium diethyldihydroaluminate with sodium tetrahydroaluminate at 180-190° for 10 hours gave no sodium ethyltrihydroaluminate, i.e., the disproportionation reaction does not proceed further than sodium diethyldihydroaluminate.

**EXPERIMENTAL**

The ethylaluminum dichloride was obtained by the reaction of ethylaluminum sesquichloride or triethylaluminum with the calculated amount of aluminum chloride at 150-180° with subsequent recrystallization of the solid reaction product from hexane; yield 90%; m.p. 32°. Found: C 18.52; H 3.91; Cl 55.54; Al 21.21%. \(C_2H_5AlCl_2\) Calculated: C 18.86; H 3.88; Cl 55.86; Al 21.25%. Literature data [3]: m.p. 32°.

The ethylaluminum dibromide was obtained by Grosse and Mavity's method [3], b.p. 120-122° (10 mm). Found: C 10.74; H 2.52; Br 73.70; Al 12.63%. \(C_2H_5AlBr_2\) Calculated: C 11.12; H 2.30; Br 74.04; Al 12.50%.

Reaction of ethylaluminum dichloride with sodium hydride. A mixture of 24.7 g (1.02 mole) of sodium hydride in 250 ml of benzene and 2.5 g of diethylaluminum hydride was heated at 70-80° and stirred for 30 minutes. Then a solution of 52 g (0.41 mole) of ethylaluminum dichloride in 50 ml of benzene was added to the reaction mixture at 25-30°. After completion of the addition, the reaction mixture was heated at 30-40° for 1 hour. The precipitate was filtered off under nitrogen and washed with 300 ml of benzene and then with 500 ml of tetrahydrofuran. After evaporation of the tetrahydrofuran filtrate, 6.5 g of sodium tetrahydroaluminate was obtained. Found: Al 49.80, 49.65%. \(NaAlH_4\) Calculated: Al 49.96%.

After evaporation of the benzene filtrate in vacuum, 20 g of a mixture of ethylaluminum dihydride and diethylaluminum hydride was obtained; analysis of the gases obtained from a sample of this after decomposition with butyl alcohol showed 50% of hydrogen and 50% of ethane. This mixture (19.5 g) was treated in 50 ml of benzene with 8 g of sodium hydride. The precipitate which formed was filtered off, washed with benzene, and dried. A yield of 3 g of sodium tetrahydroaluminate was obtained. The benzene solution was evaporated. After recrystallization from a mixture of hexane and benzene, the residue yielded 17 g of sodium diethyldihydroaluminate, m.p. 85-86°. Found: Al 24.65, 24.67%. \(NaAl(C_2H_5)_2H_2\) Calculated: Al 24.56%. Literature data [4]: m.p. 85-86°.

Reaction of ethylaluminum dibromide with sodium hydride. In a similar manner to the first experiment, 9.8 g (0.41 mole) of sodium hydride in 150 ml of benzene, 1 g of diethylaluminum hydride, and 36.5 g (0.17 mole) of ethylaluminum dibromide in 50 ml of benzene was heated at 70-80° and stirred for 30 minutes. Then a solution of 52 g (0.41 mole) of ethylaluminum dichloride in 50 ml of benzene was added to the reaction mixture at 25-30°. After completion of the addition, the reaction mixture was heated at 30-40° for 1 hour. The precipitate was filtered off under nitrogen and washed with 300 ml of benzene and then with 500 ml of tetrahydrofuran. After evaporation of the tetrahydrofuran filtrate, 6.5 g of sodium tetrahydroaluminate was obtained. Found: Al 49.80, 49.65%. \(NaAlH_4\) Calculated: Al 49.96%.

After evaporation of the benzene filtrate in vacuum, 20 g of a mixture of ethylaluminum dihydride and diethylaluminum hydride was obtained; analysis of the gases obtained from a sample of this after decomposition with butyl alcohol showed 50% of hydrogen and 50% of ethane. This mixture (19.5 g) was treated in 50 ml of benzene with 8 g of sodium hydride. The precipitate which formed was filtered off, washed with benzene, and dried. A yield of 3 g of sodium tetrahydroaluminate was obtained. The benzene solution was evaporated. After recrystallization from a mixture of hexane and benzene, the residue yielded 17 g of sodium diethyldihydroaluminate, m.p. 85-86°. Found: Al 24.65, 24.67%. \(NaAl(C_2H_5)_2H_2\) Calculated: Al 24.56%. Literature data [4]: m.p. 85-86°.

Reaction of ethylaluminum dichloride with sodium hydride. One gram of sodium diethyldihydroaluminate was added to 18 g (0.75 mole) of sodium hydride in 100 ml of benzene. After heating to 60°, 27.8 g (0.22 mole) of ethylaluminum dichloride and 20 ml of benzene were added in drops to the suspension obtained at 25-28°. Half an hour after the addition of the dichloride, the benzene was removed in vacuum. The white solid residue was treated with 500 ml of tetrahydrofuran. The green filtrate obtained after evaporation of the tetrahydrofuran in vacuum at 50° consisted of a liquid with crystals. The crystals were separated by filtration and washed twice with 10-ml portions of ether; 5.1 g of sodium tetrahydroaluminate was isolated. The clear filtrate was evaporated and heated in vacuum to 100° for 2 hours, after which the residue crystallized. After recrystallization from a mixture of benzene and hexane, 11.5 g of sodium diethyldihydroaluminate was obtained.

Reaction of ethylaluminum dibromide with lithium hydride. To a suspension of 3.2 g (0.40 mole) of finely ground lithium hydride in 120 ml of absolute ether, 24.5 g (0.113 mole) of ethylaluminum dibromide was added at such a rate that the ether boiled steadily. Then the mixture was heated at the same temperature for 5 hours. The precipitate was filtered off under nitrogen and washed with 200 ml of ether; after drying, 10.5 g of lithium bromide was obtained. The filtrate was evaporated in vacuum. The residual oil was treated with 100 ml of benzene with heating. The residue remaining was filtered off and dried in vacuum; 8.5 g of a mixture of lithium bromide and lithium tetrahydroaluminate with a content of the latter of 5% was obtained. The grease-like residue from the evapo-