

THE CHEMISTRY OF SODIUM ALKOXYALUMINUM HYDRIDES. II.*
DIRECT SYNTHESIS OF SODIUM
BIS(2-METHOXYETHOXY)ALUMINUM HYDRIDE

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Sodium bis(2-methoxyethoxy)aluminum hydride (*I*) was prepared from sodium, aluminum, and 2-methoxyethanol in benzene, under hydrogen gas pressure. In the first reaction stage sodium tetrakis(2-methoxyethoxy)aluminum and sodium 2-methoxyethylate are formed. Then hydrogenation begins under formation of sodium hydride as the first component which contains a hydride hydrogen, and only afterwards sodium tris(2-methoxyethoxy)aluminum hydride (*II*) appears, from which compound *I* is formed. The formation of sodium hydride is explained by the reactions of sodium 2-methoxyethylate with compounds *I*, *II*, and aluminum hydride.

In paper^{1,2} we described the procedures leading to sodium bis(2-methoxyethoxy)-aluminum hydride (*I*) and sodium tris(2-methoxyethoxy)aluminum hydride (*II*). The common feature of all these methods is that hydrogen was used as one of the starting components in the form of hydrides. As a second general, route for the preparation of sodium alkoxyaluminum hydrides the direct synthesis of these substances is utilised, during which the hydride ion is formed directly during the reaction.

In the field of substituted sodium aluminum hydrides a direct synthesis is known from the preparation of sodium aluminum hydride^{3,4}, trisodium aluminum hexahydride⁵, and also from the preparation of sodium alkoxyaluminum hydrides^{6,7}.

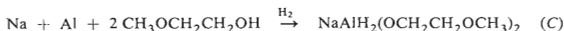
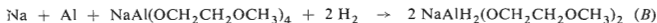
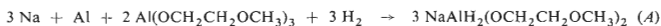
In this paper we describe a new method of synthesis of sodium alkoxyaluminum hydrides, which by its simplicity and ease of performance simplifies substantially the known procedures and which enables the preparation of pure derivatives capable of existence. This paper deals mainly with the preparation of compound *I*.

Instead of sodium alcoholate which is easily oxidised and manipulation of which is more difficult (it is substantially less soluble than aluminum alcoholate) we used sodium. We made use of the greater solubility of aluminum 2-methoxyethylate and aluminum sodium 2-methoxyethylate, and we expected that these substances would have a similar effect as alkylaluminum compounds or alkylaluminum hydrides, taking into account that they represented one of the reacting components and that,

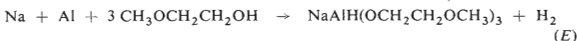
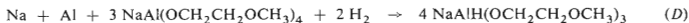
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therefore, their concentration would be higher by an order of magnitude. This assumption was found to be correct. Hydrogenation took place with both alcoholates¹ and thus it was possible to obtain the required hydrides from these substances stoichiometrically. The knowledge acquired led us to the performance of a direct synthesis, taking sodium, aluminum, and 2-methoxyethanol as the starting components. The success of this method was dependent on the question of whether all alcohol would react to alcoholates under the reaction conditions in a reasonably short time. It was found that the reaction again took place satisfactorily. The advantage of this method consists mainly in the fact that instead of ground aluminum the commonly accessible granulated aluminum powder may be used and that the reaction takes place without the addition of catalysts.

The formation of compound *I* may be expressed by the following overall equations:



In a similar way compound *II* was also prepared, according to equations:



Similarly as in the preceding paper² we were unable to prepare $\text{NaAlH}_3 \cdot (\text{OCH}_2\text{CH}_2\text{OCH}_3)$. In benzene a mixture of compound *I* and NaAlH_4 or Na_3AlH_6 is formed. In reaction carried out in dimethoxyethane in which NaAlH_4 is soluble, the solution has a composition corresponding to $\text{NaAlH}_3(\text{OCH}_2\text{CH}_2\text{OCH}_3)$. All this corroborates the results from the preceding work. The knowledge that during a direct synthesis carried out in aromatic hydrocarbons NaAlH_4 and Na_3AlH_6 is formed in addition to compound *I* may be utilised for the preparation of these sodium aluminum hydrides.

The most important of the proposed procedures was the preparation of sodium-bis(2-methoxyethoxy)aluminum hydride from sodium, aluminum, and 2-methoxyethanol, and therefore this reaction was submitted to further study. It was important to identify the intermediates of the reaction and to find optimum reaction conditions. The reaction course was followed both by subtraction of samples during the reaction (*a*), and by interrupting the reaction at its certain stage (*b*).

a) During the reaction six samples were withdrawn from the reaction mixture, the compositions of which are given in Table I. In the cakes of samples 1–5 X-ray analysis has demonstrated only sodium hydride and aluminum. In the cake of sample 6 traces of Na_3AlH_6 were found

in addition to sodium hydride and aluminum. The cake did not in any sample contain more than 2% of carbon. These results show that total —OR residue is continuously present in the solution. Sodium is in solution at the start of hydrogenation, on hydrogenation 50% of it passes into the cake in the form of sodium hydride, and on further hydrogenation it returns into solution. Aluminum passes continually into solution. The consumption of hydrogen was in this case more difficult owing to an error caused by the loss of hydrogen and by the change in the volume of the reaction mixture during the withdrawal of samples, and therefore it could not correspond accurately to the determined active hydrogen. Nor could it be excluded that a part of the previous sample was not present in the sampling tube.

b) After the consumption attained the value indicated in Fig. 1 the reaction was interrupted and the mixture obtained was analysed. The compositions of the reaction mixtures obtained are listed in Table II.

TABLE I
Composition of the Samples Withdrawn

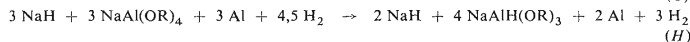
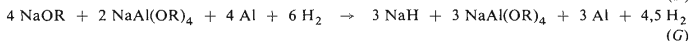
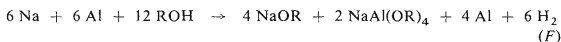
Sample	Hydrogen consumption, %	Solution		Cake % Na	Ratio in the solution		
		% Na	% Al		Na	Al	H ⁻
1	8	6.2	2.16	0.31	3.36	1	0
2	25	5.42	2.98	1.3	2.13	1	0
3	40	3.18	3.62	3.21	1.03	1	0
4	55	3.35	4.32	2.64	0.99	1	0.59
5	65	4.21	4.84	1.88	1.02	1	0.81
6	90	4.86	5.41	0.99	1.05	1	1.8

TABLE II
Composition of the Reaction Mixtures in Dependence on the Hydrogen Consumption

Hydrogen consumption, %	Solution				Cake Na
	Na	: Al	: H ⁻	: OR	
0	3.000	1.000	0.000	6.000	0.000
15	1.605	1.000	0.000	4.687	0.880
25	1.011	1.000	0.000	4.000	1.061
30	0.991	1.000	0.228	3.838	0.941
50	0.993	1.000	0.985	2.903	0.539
80	1.026	1.000	1.643	2.268	0.208
88	1.022	1.000	1.825	2.182	0.116
100	1.001	1.000	2.050	2.010	0.002

Sodium in the cake was present in the form of sodium hydride which was demonstrated by X-ray analysis. Only in the sample after the consumption of 80% of hydrogen, traces of Na_3AlH_6 were also found in addition to NaH . In no case was more than 0.5% of carbon found in the cake (relatively to the amount of carbon in the utilised 2-methoxyethanol).

The results obtained permit us to suppose the following reaction course:



The formation of alcoholates according to equation (F) takes place during the reaction of 2-methoxyethanol with sodium and aluminum. In the terminal phase of the reaction (G) the mixture is shortly before the start of the hydrogenation (Table II – zero consumption). During this reaction all hydrogen it set free which is then reconsumed during the hydrogenation. This should be born in mind when the sample is weighed: the autoclave may be filled maximally up to 60% of its actual hydrogenation space.

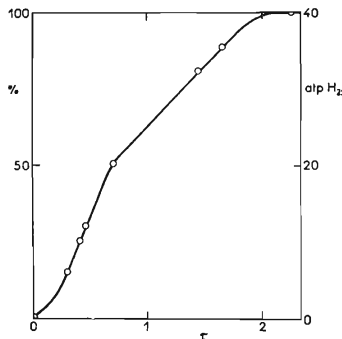
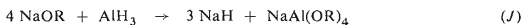


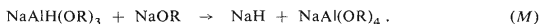
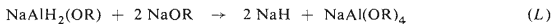
FIG. 1

Dependence of the Hydrogen Consumption on Time (h) During the Synthesis of Sodium Bis(2-methoxyethoxy)aluminum Hydride, with Indication of Interrupted Experiments

The reaction course according to equation (G) is of special interest. In this stage only Al can be hydrogenated in the reaction mixture, under formation of AlH_3 on its surface. The present NaOR can react with the formed AlH_3 according to equations (J) and (K):



It was proved experimentally that aluminum hydride reacts with sodium alcoholate under formation of sodium hydride (equation (J)). On the supposition that the reaction takes place under a transitory formation of the instable $\text{NaAlH}_3(\text{OR})$ according to equation (K) and that excess NaAl(OR)_4 is present in the reaction mixture, the final product must be NaAlH(OR)_3 which is formed *via* $\text{NaAlH}_2(\text{OR})_2$. Compounds *I* and *II* are soluble in benzene, but in spite of this no active hydrogen was found in the solution up to 25% of hydrogen consumption. The composition of the reaction mixture is given in Table II at a 25% hydrogen consumption. What remained to be determined was whether compounds *I* and *II* also react with sodium 2-methoxyethylate according to equations (L) and (M).



It was proved experimentally that these reactions also take place, so that it is impossible to determine unambiguously whether aluminum hydride reacts with sodium 2-methoxyethylate under formation of sodium hydride directly or *via* intermediates *I* and *II*. The course of these reactions is very interesting in comparison with lithium compounds⁸, in which reactions of lithium alkoxyaluminum hydrides with lithium hydride are considered up to the formation of lithium aluminum hydride. The formation of compounds *II* and *I* according to equation (H) and (I) when the hydrogen consumption was above 25%, may be explained by the reaction of sodium aluminum hydride with sodium tetrakis(2-methoxyethoxy)aluminum or with compound *II*. Sodium aluminum hydride is formed here on reaction of aluminum hydride with sodium hydride after all sodium 2-methoxyethylate had been reacted. The knowledge obtained shows that the reaction under formation of *II* and *I* takes place at a higher rate than the formation of trisodium aluminum hexahydride from sodium aluminum hydride and sodium hydride.

Next we investigated the effect of concentration, temperature, hydrogen pressure, surface, and excess of aluminum. From the observed dependences it is evident that the reaction is affected by all parameters measured. For the determination of optimum conditions, however, it is necessary to choose those which are most suitable for the accessible technical equipment, raw material produced, safety measures, thermal stability of substances, and the properties of the solution.

With increasing temperature the reaction takes place more rapidly; at a temperature over 170°C a slow thermal decomposition of the substance takes place. At 214°C this decomposition takes place spontaneously. The reaction may be performed at 170–175°C without danger, but

the product obtained contains the decomposition products which devalue it by precipitating gradually from clear solutions even after several months of storing. When the precipitate is filtered off the equilibrium is disturbed again, which has a new formation of precipitate as a consequence. This precipitate also greatly impairs filtration. The precipitate contains mainly $\text{NaAlH}_2(\text{OCH}_3)(\text{OCH}_2\text{CH}_2\text{OCH}_3)$ and $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2 \cdot \text{Al}(\text{OCH}_3)_3$. Optimum temperature is 150°C . The increase in pressure also enhances the reaction. The final pressure should not drop below 50 atp. The increasing concentration of the reaction components increases the reaction rate. Obviously, efforts are made to prepare solutions of as high a concentration as possible, both to obtain a faster reaction course and also better utilisation of the autoclave. With highly concentrated solutions the overheating of the reaction mixture by the heat of reaction may take place, or else an overheating of the reaction mixture on the autoclave walls may be observed, leading thus to the devaluation of the product. With solutions where the concentration is over 55% a great increase in viscosity² is observed and hence the filtration of the product is impaired. We recommend working with solutions of up to 55% concentration. The reaction has a greater rate when surface of aluminum increases. However, preparations with a large surface area cause trouble during filtration and the finely dispersed aluminum passes into the product. For these reasons it is best to use fine granulated aluminum powder.

From the given dependences the following optimum conditions follow for the synthesis of sodium bis(2-methoxyethoxy)aluminum hydride: Temperature $150^\circ\text{C} \pm 5^\circ\text{C}$, maximum pressure given by autoclave parameters and minimum pressure 50 atp., final concentration of the product 50–55%, and a 50% excess of a superfine granulated aluminum powder.

EXPERIMENTAL

Chemicals Used

Benzene, 1,2-dimethoxyethane predried with a sodium wire and distilled over lithium aluminum hydride, 2-methoxyethanol absolutised and distilled. Sodium was of 99.9% purity. The granulated aluminum powder used had a $0.180 \text{ m}^2/\text{g}$ surface area unless stated otherwise, ground material $1.372 \text{ m}^2/\text{g}$. Sodium 2-methoxyethylate was prepared from sodium and excess 2-methoxyethanol. The product was dried at 130°C and 1 Torr until its weight was constant. The product obtained was dissolved in benzene and dried again at 130°C and 1 Torr to a constant weight. The solution of aluminum hydride in diethyl ether was prepared from lithium aluminum hydride and aluminum chloride⁹.

Preparation of Sodium Bis(2-methoxyethoxy)aluminum Hydride

A 2 litre autoclave provided with an anchor stirrer (130 r.p.m.) was filled with 65 g of Na (2.8 mol), 113 g of 98% aluminum (powder; 4.1 mol), 514 g of benzene, and 418 g of 2-methoxyethanol (5.5 mol), then closed and pumped to 85 atp. The stirring and heating was switched on and the reaction mixture allowed to warm up to 40°C , while the pressure increased to 130 atp. An exothermic reaction took place at 115°C under liberation of hydrogen. After 20 minutes the temperature rose to 140°C and the pressure to 218 atp (144 atp at 0°C). After this hydrogenation took place. The temperature was kept at 150°C and the mixture stirred until the hydrogen consumption ceased (3.5 hours). The total consumption of hydrogen was 69 atp when recalculated to 0°C . After cooling and de-aeration of the autoclave the reaction mixture was filtered to remove aluminum and impurities. The filtration cake was washed with 60 ml of benzene and the filtrates were

combined. Yield: 1048 g of a yellowish solution, *i.e.* 98.1% relative to 2-methoxyethanol. When the solution of $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ was analysed the following values were found: 6.04% Na, 6.94% Al, 0.537% H^- , Na : Al : $\text{H}^- = 1.02 : 1 : 2.07$.

Investigation of the reaction course by sample withdrawal: The experiments were carried out at 70–80 atp and 150°C in a 2 liter hydrogenation autoclave fitted with an anchor-stirrer (130 r.p.m.). After each sample withdrawal the pressure in the autoclave was restored. The sample weight was 30–50 g. For our experiments 66 g of Na (2.86 mol; 10% excess), 107 g of a 98% aluminum (powder 3.88 mol; 50% excess), 395 g of 2-methoxyethanol (5.2 mol), and 600 ml of benzene were used.

Investigation of the reaction course by stopping the reaction: The experiments were carried out in a 200 ml shaking autoclave. The reaction mixture was stirred by means of three iron balls. Temperature and pressure were measured during the experiment. In single experiments the temperature 140–150°C and the pressure 120–200 atp was chosen, because it was convenient for the monitoring of the reaction. After the determination of the true volume of the consumed hydrogen three experiments were carried out where the consumption was complete, and the sodium bis(2-methoxyethoxy)aluminum hydride obtained was analysed. The average hydrogen consumption was taken as 100%. In single experiments the autoclave was rapidly cooled after the required consumption was attained. After cooling and control reading of the cold pressure the reaction mixture was taken off from the autoclave. Solid material was filtered off and the cake was washed and the filtrates combined. Both the obtained solution and the filtration cake were analysed. For our work 4.5 g of Na (0.2 mol), 8.2 g of a 98% aluminum (powder; 0.3 mol, 50% excess), 30.4 g of 2-methoxyethanol (0.4 mol), and 50 ml of benzene were employed.

Reaction of Sodium Tris(2-methoxyethoxy)aluminum Hydride with Sodium 2-Methoxyethylate

To a boiling mixture of sodium 2-methoxyethylate (0.1158 mol) in 100 ml of toluene a solution of sodium tris(2-methoxyethoxy)aluminum hydride (0.0965 mol) in 40 ml of toluene was added dropwise over 5 minutes. The mixture (weight 165.5 g) became turbid and the milky suspension formed was allowed to settle. In the suspension X-ray analysis has shown sodium hydride, but the solution did not contain hydride hydrogen. Analysis of solution, calculated: 1.57% Al, 1.61% Na; found: 1.57% Al, 1.64% Na.

Reaction of Aluminum Hydride with Sodium 2-Methoxyethylate

To a solution of sodium 2-methoxyethylate (0.226 mol) in 60 ml of dimethoxyethane a solution (25 ml) of aluminum hydride (0.037 mol) in diethyl ether was added dropwise at 40°C over 10 minutes. The mixture (weight 84.1 g) became turbid. After addition of aluminum hydride it was boiled for 25 minutes and then allowed to sediment. X-ray analysis has shown the presence of sodium hydride in the suspension, but the solution did not contain hydride hydrogen. Analysis of solution, calculated: 1.12% Al, 2.97% Na; found: 1.13% Al, 3.02% Na.

Following of the Reaction Conditions

Final concentration of the product, temperature, and hydrogen pressure: The experiments were carried out in a 2 l hydrogenation autoclave with a stirrer. The autoclave was connected with a pressure container of hydrogen of 2 l volume, provided with an accurate manometer. Hydrogen pressure was kept within ± 3 atp by periodic pumping in of hydrogen from the reservoir. The consumption of hydrogen was determined from the pressure drop in the reservoir. The final consumption was taken as 100%.

Surface area and excess of aluminum: The experiments were carried out in a 200 ml shaking autoclave. The reaction mixture was stirred by means of three iron balls at 140°C. The starting hydrogen pressure was 205 atp, and the final concentration of the product was 50%. When the dependence on the surface area of aluminum was measured a 50% excess of aluminum was taken. Granulated aluminum powder of the following surface areas was tested: 0.115 m²/g and 0.180 m²/g. The ground aluminum had 1.372 m²/g surface area. When the effect of excess of aluminum was measured ground aluminum of 1.372 m²/g surface area was employed.

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