

THE CHEMISTRY OF SODIUM
ALKOXYALUMINIUM HYDRIDES. I.
SYNTHESIS OF SODIUM
BIS(2-METHOXYETHOXY)ALUMINIUM HYDRIDE*

B. ČÁSENSKÝ, J. MACHÁČEK and K. ABRHAM

*Institute of Inorganic Synthese,
Czechoslovak Academy of Sciences, Prague - Řež*

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Sodium bis(2-methoxyethoxy)aluminium hydride (*I*) was obtained by reaction of trisodium aluminium hexahydride with aluminium 2-methoxyethylate. Reactions of sodium aluminium hydride, followed by conductance measurements, with *a*) 2-methoxyethanol, *b*) sodium aluminium 2-methoxyethylate and *c*) methoxyethyl methoxyacetate gave rise to compound *I* and sodium tris(2-methoxyethoxy)aluminium hydride (*II*). Compounds *I* and *II* are well soluble in aromatic hydrocarbons.

In the last two decades the complex aluminium hydrides have become an indispensable tool of modern chemistry. The best-known of them, lithium aluminium hydride², has been the subject of a number of monographs³⁻⁵ and its use is described in thousands of papers. Much less attention has been paid to sodium aluminium hydride⁶, although it is more accessible and less expensive^{7,8}. Knowledge of the complex, substituted aluminium hydrides, especially of alkali alkoxyaluminium hydrides, is far from widespread. Out of these, alkali trialkoxyaluminium hydrides have been given most attention, owing to their ready accessibility and relative selectivity⁹⁻¹¹, compared to the parent, non-substituted hydride. More recently, some alkali dialkoxyaluminium hydrides¹²⁻¹⁴ and even sodium monoalkoxyaluminium hydrides^{14,15} have also been described. Two syntheses of sodium alkoxyaluminium hydrides, differing in the source of active hydrogen, have been reported. The earlier one, based on the reactions of sodium hydride with aluminium alcoholates¹⁶ or halo alcoholates¹³, leads to compounds $\text{NaAlH}_x(\text{OR})_{4-x}$, whereas the more recent high-pressure hydrogenation method¹⁷ starts from sodium alcoholate, aluminium and hydrogen, the general formulae of the products being $\text{NaAlH}_3(\text{OR})^{15}$ and $\text{Na}_3\text{AlH}_x(\text{OR})_{6-x}$. With the exception of trialkoxyaluminium hydrides, the reduction properties and stability of these substituted aluminium hydrides are known very little. In many cases even the individuality of some preparations has not been reliably identified.

A common property of all the aluminium hydrides hitherto described is that they dissolve only in solvents of a Lewis base nature, mainly in ethers, the most universal of them being tetrahydrofuran, dimethoxyethane and bis-2-methoxyethyl ether. None of the known aluminium hydrides

* Patented, ref.¹.

dissolves in aromatic hydrocarbons. From the technological point of view it is a serious disadvantage since the ethers employed are highly volatile and inflammable, readily oxidize to explosive peroxides, and easily absorb relatively great amounts of water. Another drawback of most of the complex hydrides is their self-ignition when finely dispersed or after evaporation of the solvent.

For the reasons described above we have attempted the synthesis of a new type of sodium alkoxyaluminium hydride, free of the drawbacks characteristic of these compounds, but retaining their reduction power. We started from the assumption that both the stability and the solubility in aromatic hydrocarbons would be substantially increased if the alkoxy, attached to the hydride, carried a group with free electron pairs at a suitable distance from the alkoxy oxygen, which would effect intramolecular solvation of the central atom. The compounds employed for this purpose were of the type $\text{—O—CH}_2\text{—CH}_2\text{—X—R}_n$, where $\text{X}=\text{O, S or N}$ and $n = 1-2$, depending on the binding capacity of the atom X. Our assumption has proved correct. The present paper describes the synthesis and properties of sodium bis(2-methoxyethoxy)aluminium hydride (I), as the most elementary compound complying with the requirements of stability and solubility. The preparation of tris(2-methoxyethoxy)aluminium hydride (II) is also described.

Of the general methods for the synthesis of substituted sodium aluminium hydrides the fundamental one for ascertaining the possible existence of a compound of the considered type is based on the reaction

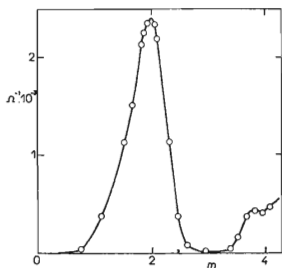


FIG. 1

Conductance as a Function of the Starting Molar Ratio $\text{CH}_3\text{OCH}_2\text{OH}_2\text{OH} : \text{NaAlH}_4$ (m) after the Reaction of the Two Components in Benzene

160 ml of benzene, 0.0827 mol of NaAlH_4 .

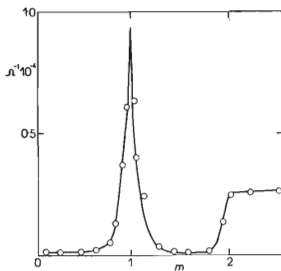
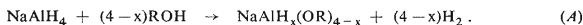


FIG. 2

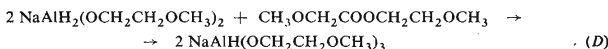
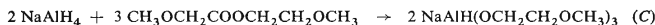
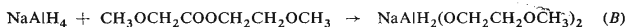
Conductance as a Function of the Starting Molar Ratio $\text{CH}_3\text{OCH}_2\text{COOCH}_2 \cdot \text{CH}_2\text{OCH}_3 : \text{NaAlH}_4$ (m) after the Reaction of the Two Components in Benzene

160 ml of benzene, 0.0499 mol of NaAlH_4 .



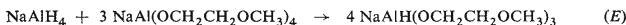
This reaction was employed in the present study. Its course was followed by measuring the conductance changes of the solution, benzene or diethyl ether being employed as solvent. It was expected that if the products were chemical individuals the courses of conductance would exhibit peaks or troughs. Fig. 1 represents alcoholysis of NaAlH_4 in benzene. This hydride is insoluble in benzene. Its reaction with 2-methoxyethanol produces an electrically conductive, benzene-soluble compound, so that the conductance of the solution increases. The first maximum of conductance corresponds to a molar ratio of two mol of 2-methoxyethanol to mol of sodium aluminium hydride, *i.e.* to bis(2-methoxyethoxy) aluminium hydride (*I*). Further additions of 2-methoxyethanol bring about a gradual decrease in the conductance to a minimum corresponding to a molar ratio of 2-methoxyethanol to $\text{NaAlH}_4 = 3 : 1$, *i.e.* to the formation of tris (2-methoxyethoxy)aluminium hydride (*II*). As a final product there is formed the alcoholate $\text{NaAl}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4$. Consequently, the conductance measurements revealed that alcoholysis of NaAlH_4 in benzene leads to two compounds with active hydrogen, *viz.* $\text{NaAlH}_2 \cdot (\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ and $\text{NaAlH}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$. The same conductance changes were observed in the alcoholysis in diethyl ether.

Compounds *I* and *II* are amorphous substances soluble in ethers and aromatic hydrocarbons. The compound originally supposed to be $\text{NaAlH}_3(\text{OCH}_2\text{CH}_2\text{OCH}_3)$ was identified by X-ray analysis and benzene extraction as a mixture of NaAlH_4 and compound *I*. Compounds *I* and *II* should also be intermediates in the reduction of methoxyethyl methoxyacetate:



This assumption has been substantiated by conductance measurements (Fig. 2) and synthetically.

The stabilities of compounds *I* and *II* and their solubility in aromatic hydrocarbons suggested another possibility of their formation, *viz.* the reactions of sodium aluminium 2-methoxyethylate with sodium aluminium hydride:



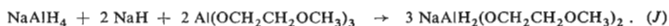
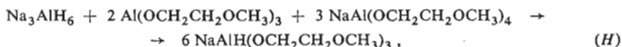
Both reactions proceed readily, as follows from conductance measurements and preparative experiments.

Synthesis of compound *I* starting from trisodium aluminium hexahydride proceeds quite smoothly also:



Since sodium aluminium hydride and trisodium aluminium hexahydride are easily accessible by direct synthesis^{7,8,18,19} the syntheses represented by reactions (*E*) to (*G*) are very rewarding methods. The synthesis from trisodium aluminium hexahydride is more economical.

Compounds *I* and *II* can also be obtained by other combinations of the fundamental reactions (*E*)–(*G*), for example:



The synthetic experiments are evaluated in Table I.

Compound *I* has been paid most attention since its prospective use in organic chemistry makes it very important. Its main asset is the fact that its hydride anion can be safely employed in non-polar solvents, such as aromatic hydrocarbons.

TABLE I

Syntheses of Sodium 2-Methoxyethoxyaluminium Hydrides By Reactions (*E*) to (*J*)

| Reaction | Solvent | Solution, analytical ratio | | |
|----------|-----------------|----------------------------|-------|----------------|
| | | Al | Na | H ⁻ |
| (E) | tetrahydrofuran | 1 | 0.99 | 0.95 |
| | diethyl ether | 1 | 0.98 | 0.96 |
| | benzene | 1 | 0.97 | 0.94 |
| (F) | tetrahydrofuran | 1 | 1.00 | 2.06 |
| | diethyl ether | 1 | 1.00 | 1.97 |
| | benzene | 1 | 0.97 | 1.98 |
| (G) | diethyl ether | 1 | 1.01 | 1.97 |
| | benzene | 1 | 1.01 | 1.95 |
| | toluene | 1 | 0.98 | 1.92 |
| (H) | dimethoxyethane | 1 | 1.03 | 0.96 |
| | diethyl ether | 1 | 0.99 | 0.94 |
| | toluene | 1 | 1.00 | 0.95 |
| (J) | toluene | 1 | 1.001 | 1.96 |

At 20°C compound *I* is a colourless to yellowish viscous liquid of a density d_{20} 1.122 g/cm³. By cooling to 0°C to -5°C it solidifies into a fragile vitriform substance; its melting point is not sharp. The difference thermic analysis in a range from -20 to +20°C revealed no change produced by variation of temperature and X-ray analysis at -50°C has proved that this compound does not have a crystalline structure. It seems that the pure compound *I* is a coordination polymer. The inflammation point, measured by Abel-Penský's method, is 150°C and the combustion heat is 5.333 kcal/kg. Fig. 3 shows that work with this compound is quite safe up to 170°C. At this temperature a slight decomposition was observed, which turned self-sustaining at 214°C.

Compound *I* is excellently soluble in aromatic hydrocarbons (indefinitely in benzene; it forms two conjugated solutions with toluene, concentrations 6% and 42%, and two conjugated solutions with xylene, 6% and 60%) and ethers (two conjugated solutions with diethyl ether, 5% and 60%, infinite solubility in dimethoxyethane and tetrahydrofuran). In aliphatic hydrocarbons (heptane) and alicyclical ones (cyclohexane) it is insoluble. Ebullioscopic measurements of molecular weight in a benzene solution have revealed that in a wide concentration range the compound is monomeric in this solvent. The benzene solutions were also investigated for the relations of viscosity and density to temperature and concentration (Figs 4 - 6). Of special interest is the viscosity break at a concentration of approx. 55%. At this concentration the composition of the solution corresponds to the formula $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$.

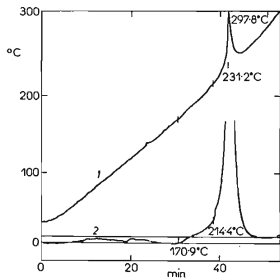


FIG. 3

Records of Thermic Analysis (1) and Difference Thermic Analysis (2) of Sodium Bis-(2-methoxyethoxy)aluminium Hydride

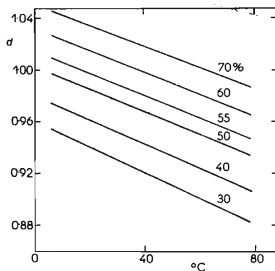


FIG. 4

Density (g/cm³) in Relation to Temperature at Different Concentrations of Sodium Bis-(2-methoxyethoxy)aluminium Hydride in Benzene

.2 C₆H₆ (theoretical concentration is 56.4%). In this connexion the formation of the conjugated solutions should also be given some attention; the theoretical concentrations corresponding to substances NaAlH₂(OCH₂CH₂OCH₂)₂-3 CH₃.C₆H₅, NaAlH₂(OCH₂CH₂OCH₃)₂.C₆H₄(CH₃)₂ and NaAlH₂(OCH₂CH₂OCH₃)₂.2(C₂H₅)₂O are 42.24%, 65.56% and 57.62%, respectively. In electrolysis of a benzene solution of compound I sodium is deposited on the cathode (tree-like crystals) and hydrogen is evolved on the anode. The concentration of bis(2-methoxyethoxy)aluminium hydride increases. At an alternating current of 100 V and 300 H the values of conductivity, κ , and equivalent conductivity, k , were $\kappa = 3.2780 \cdot 10^{-4} \Omega^{-1} \text{ cm}^{-1}$, $k = 1.4319 \cdot 10^{-1} \Omega^{-1} \text{ equiv.}^{-1} \text{ cm}^{-2}$ (measured in a 2.29M solution in benzene).

Since sodium bis(2-methoxyethoxy)aluminium hydride (compound I) is derived from NaAlH₄, much of the chemical behaviour of this compound resembles the elementary aluminium hydrides (NaAlH₄, LiAlH₄). The main difference from these consists in the fact that compound I is not self-igniting in the air or water; hydrolysis manifests itself by the evolution of hydrogen only. Solutions of compound I behave similarly. Fig. 7 shows the rate of the decrease in the content of the hydride anions (active hydrogen) in a 70% benzene solution of compound I in contact with the air. Compound I reacts with water with the evolution of hydrogen. If an excess of water is employed for the hydrolysis it is possible to determine quantitatively the hydride hydrogen in a given complex. With an equivalent amount of dilute water (*e.g.* 3M-H₂O in dimethoxyethane) the reaction of compound I (Fig. 8) is described by the equation.

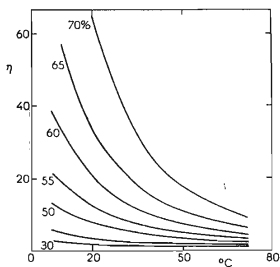


FIG. 5

Viscosity (cP) of a Benzene Solution of Sodium Bis(2-methoxyethoxy)aluminium Hydride in Relation to Temperature and Concentration

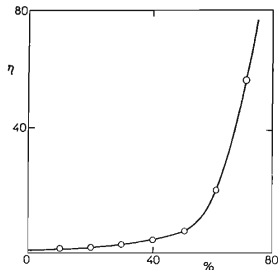


FIG. 6

Viscosity (cP) of a Benzene Solution of Sodium Bis(2-methoxyethoxy)aluminium Hydride in Relation to Concentration (%) at 20°C



The compound $\text{NaAlO}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ is soluble in benzene and in dimethoxyethane. This explains why solutions of $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ when handled in the air do not go turbid, in contrast to the solutions of sodium and lithium aluminium hydrides.

The reaction of compound *I* with alcohols is accompanied by the evolution of hydrogen.



The reaction with NH_3 yields hydrogen and a mixture of compounds $\text{NaAl}(\text{NH}_2)_2 \cdot (\text{OR})_2$ and $\text{NaAl}(\text{NH})(\text{OR})_2$. Analogous reactions occur in the case of primary amines. Reaction of compound *I* with carbon dioxide gives methanol.

Boron halides react with solutions of compound *I* with the evolution of B_2H_6 . Similarly, reaction of silicon chloride with alkylhalosilicon compounds produces SiH_4 and alkylsilanes^{1,20}. Reaction with aluminium halides yields alkoxyaluminium

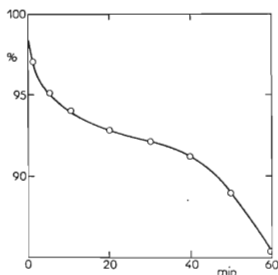


FIG. 7

Time Decrease in the Content of the Active Hydrogen in a 70% Solution of Sodium Bis(2-methoxyethoxy)aluminium Hydride in Benzene when in Contact with the Air

Temperature 26°C, rel. humidity 36%, area in contact with the air 1.77 cm², layer 7 mm.

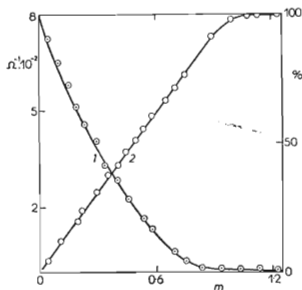


FIG. 8

Conductance (1) and Amount of Liberated Hydrogen as Functions of the Starting Molar Ratio $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2:\text{H}_2\text{O}$ (*m*) (2) after the Reaction of this Hydride with Water in Dimethoxyethane

160 ml of dimethoxyethane, 0.0567 mol of sodium bis(2-methoxyethoxy)aluminium hydride. Titrated with 2.78M- H_2O in dimethoxyethane.

hydrides. With LiBr or LiI compound *I* is partially converted into its lithium analogue. A similar reaction proceeds with MgBr₂. The reaction with *J*₂ is used analytically for the determination of active hydrogen; the summary equation is



At room temperature or mildly elevated temperature compound *I* reduces the same functional groups and with approximately the same efficiency as lithium aluminium hydride, but in contrast to the latter agent the reduction proceeds as readily in ethers as in aromatic hydrocarbons^{1,21-25}. Owing to its higher heat-stability compound *I* can be employed to reduce groups which cannot be reduced by lithium aluminium hydride. An example is hydrogenolysis of aliphatic and aromatic halo derivatives²⁶, especially hydrogenolysis of a number of esters of aromatic hydroxy and amino acids, in which the carboxyl group can be reduced up to the final degree, *i.e.* to the methyl group²⁷. The fact that compound *I* forms stable, low-viscosity solutions even at 70% concentrations in benzene and toluene facilitates the work. The solutions can be poured from one vessel to another in contact with the air with practically no decomposition and without any risk, so that the quantity to be added to the reaction mixture can be simply measured out by means of a graduated cylinder. Whether the agent is added to the compound to be reduced or *vice versa* is immaterial. If the reaction product is little soluble in water, but well soluble in aromatic hydrocarbons (the most frequent case) the final isolation of the product is much easier than after reductions conducted in ethers. Methoxyethanol, formed as a by-product in the use of compound *I*, is excellently soluble in aqueous media, so that it can be removed from the aromatic hydrocarbon by washing it with water. Some problems are encountered only with compounds which are approximately as water-soluble and volatile as methoxyethanol. In such cases the use of lithium aluminium hydride is preferable.

From the studies hitherto published it appears that compound *I* may be as important for organic chemistry as lithium aluminium hydride has been in the last decades.

EXPERIMENTAL

Chemicals

Benzene, diethyl ether, tetrahydrofuran and dimethoxyethane were dried with a sodium wire. The last traces of water were removed by distillation from a mixture with lithium aluminium hydride. 2-Methoxyethanol was absolutised and distilled. Methoxyethyl methoxyacetate²⁸ was prepared from methoxyacetic acid and 2-methoxyethanol and distilled (b.p. 95°C at 15 Torr). Sodium aluminium hydride was obtained by direct synthesis from sodium, aluminium and hydrogen and recrystallized from tetrahydrofuran, purity 98.5%. Trisodium aluminium hexahydride was also obtained by direct synthesis¹⁸, purity 88.1%.

Conductivity Measurement

The measuring cell was equipped with three concentric platinum cylinders (diameters d_1 18 mm, d_2 14 mm, d_3 10 mm), the first and the third cylinders being the same electrode. The height of the cylinders, fixed in place by glass, was 20 mm. The conductivity constant of the cell was 0.0173 cm^{-1} ; the measuring apparatus was an impedance bridge, Tesla BM 394. The conductivity was measured with alternating voltage. The temperature of the reaction mixture was 25°C .

Alcoholysis was effected in the measuring cell containing NaAlH_4 in a given solvent, to which 2-methoxyethanol was brought from a burette. After each addition of 2-methoxyethanol the ohmic resistance of the reaction mixture was allowed to equilibrate and measured. Aluminium sodium 2-methoxyethylate was added to the dissolved NaAlH_4 in the solid state.

Synthesis of $\text{NaAl}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4$

Sodium (31.64 g) and shavings of aluminium (37.25 g, 99.9%) were mixed under nitrogen with 2-methoxyethanol (1200 ml). The mixture was refluxed till the metals had completely dissolved. The excess of 2-methoxyethanol was distilled off and the white product was dried at 130°C and 1 Torr, yield 480 g, melting temperature $110\text{--}120^\circ\text{C}$. For $\text{C}_{12}\text{H}_{28}\text{AlNaO}_8$ (350.3) calculated: 41.14% C, 8.05% H, 7.70% Al, 6.56% Na; found: 41.05% C, 8.11% H, 7.75% Al, 6.62% Na.

Synthesis of $\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$

To shavings of Al (48.5 g, 99.99%) and HgCl_2 (0.1 g) under nitrogen was added 2-methoxyethanol (70 ml) and the mixture was heated. When the reaction had started the heating was discontinued and 1000 ml of 2-methoxyethanol was gradually added. The reaction mixture was refluxed until all aluminium had dissolved. The excess of 2-methoxyethanol was distilled off and the product, a yellow viscous liquid, was dried at 130°C and 1 Torr; yield 450 g. For $\text{C}_9\text{H}_{21}\text{AlO}_6$ (242.2) calculated: 42.86% C, 8.39% H, 10.69% Al; found: 42.78% C, 8.47% H, 10.73% Al.

Synthesis of $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$

To Na_3AlH_6 (5.9 g, 88.1%) in 30 ml of benzene was added in the course of 15 min aluminium 2-methoxyethylate (25.2 g) in 30 ml of benzene. The reaction mixture was refluxed for 0.5 h, cooled down and filtered to remove the impurities. Benzene was distilled off and the residue dried at 130°C and 1 Torr. There was obtained 29.5 g of a yellow syrupy product. For $\text{C}_6\text{H}_{16}\text{AlNaO}_4$ (202.2) calculated: 35.65% C, 7.98% H, 0.99% H^- , 13.34% Al, 11.37% Na; found: 35.21% C, 7.95% H, 0.95% H^- , 13.31% Al, 11.30% Na.

Synthesis of $\text{NaAlH}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$

To NaAlH_4 (1.37 g, 98.4%) and 20 ml of benzene was added under nitrogen in the course of 15 min aluminium sodium 2-methoxyethylate (26, 25 g) in 40 ml of benzene. The reaction mixture was refluxed for 0.5 h. The clear solution was then distilled to remove the benzene and the product, a yellow syrupy liquid, was dried at 1 Torr and 130°C . For $\text{C}_9\text{H}_{22}\text{AlNaO}_6$ (276.2) calculated: 39.13% C, 8.02% H, 0.36% H^- , 9.76% Al, 8.32% Na; found: 38.86% C, 7.95% H, 0.34% H^- , 9.81% Al, 8.34% Na.

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