

THE CHEMISTRY OF SODIUM ALKOXYALUMINIUM HYDRIDES. IV.*
SYNTHESIS OF SODIUM
HYDRIDO(2-DIMETHYLAMINOETHOXY)ALUMINATES
AND DIALUMINATES

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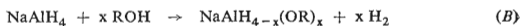
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The main products of the reaction of sodium tetrahydridoaluminate with 2-dimethylaminoethanol, followed by conductance measurements, were sodium hydrido-tris(2-dimethylaminoethoxy)aluminate (*I*) and sodium dihydrido-bis(2-dimethylaminoethoxy)aluminate (*II*). Sodium trihydrido(2-dimethylaminoethoxy)aluminate (*III*) was unstable and disproportionated to trisodium hexahydridoaluminate and sodium tetrahydrido-tris(2-dimethylaminoethoxy)dialuminate (*IV*). The latter compound was also obtained by the reaction of sodium tetrahydridoaluminate with aluminium 2-dimethylaminoethylate and by the reaction of compound *I* with AlH_3 .

Hydrido-alkoxyaluminates can be divided into two classes, with a non-substituted alkoxy group¹⁻⁵ and with substituted alkoxy groups⁶⁻⁸. The β position of the substituted alkoxy is bound to ethereal oxygen. The free electron pairs of this oxygen participate in the coordination of the deficient orbitals of the metallic atoms of the complex hydrides and are responsible for their solubility in aromatic hydrocarbons. An example of such a soluble hydride is $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$. Similar properties would be expected of compounds with the more basic tertiary nitrogen at the β -position of the alkoxy group. The simplest representative of such an alkoxy group is 2-dimethylaminoethoxyl. Its influence, compared to that of 2-methoxyethoxyl, on the properties of the complex hydrides is the subject of the present paper.

We have studied the syntheses of sodium hydrido- and dihydrido-(2-dimethylaminoethoxy)aluminates starting from compounds with anionic hydrogens, such as NaH , NaAlH_4 and Na_3AlH_6 , according to the described¹⁻⁵ reactions (*A*) and (*B*) and reactions (*C*) to (*E*), which we previously employed for the synthesis of the 2-methoxyethoxy derivative^{6,7}. The formation of hydrido-alkoxyaluminates according to the reactions (*C*) to (*E*) proceeds in aromatic hydrocarbons and in ethers. Reaction (*A*) has been investigated in diethyl ether, tetrahydrofuran, benzene and toluene at the temperatures of their boiling points.

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As can be seen from Table I the reaction failed to occur in ether. In tetrahydrofuran it proceeded to a small extent, but in benzene and toluene the yields were quantitative.

Aluminium 2-dimethylaminoethylate exists as a trimer at 4°C and a dimer at 80°C. Since aromatic compounds enhance the conversion of the trimer to the dimer⁹, it is evident that only the dimer reacted with NaH. The course of the reaction was dependent on the specific surface of sodium hydride. If the hydride employed had a small specific surface (beads of fused NaH) the reaction did not occur at all.

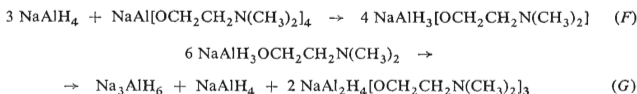
The progressive replacement of the hydride anions in NaAlH₄ by 2-dimethylaminoethoxy groups (reaction (B)) has been studied in detail in order to detect the individual intermediates. The reaction course was followed by conductance measurements in ethers and aromatic hydrocarbons. As can be seen from Fig. 1 the di-, tri- and tetraalkoxy compounds were detected, but not the monoalkoxy compound, in accordance with the results obtained with the 2-methoxyethoxy derivatives⁷. In contrast to these results⁷, however, there appeared an additional conductance peak at the ratio NaAlH₄ : (CH₃)₂NCH₂CH₂OH = 1 : 3.5. This phenomenon might be due to the presence of a compound formed by replacement of an anionic hydrogen in the dimer of sodium hydrido-tris(2-dimethylaminoethoxy)aluminate by another alkoxy group.

The failure of our attempts at the detection of sodium trihydrido-(2-dimethylaminoethoxy)aluminate, in the conductometric titration of NaAlH₄ with 2-dimethylaminoethanol, stimulated our interest in its stability. This vitric labile compound was prepared by the reaction of NaAlH₄ with sodium tetrakis(2-dimethylaminoethoxy)aluminate in tetrahydrofuran (reaction (F)). By heating in benzene it disproportionated to Na₃AlH₆, NaAlH₄ and sodium tetrahydrido-tris(2-dimethylaminoethoxy)dialuminate (reaction (G))

TABLE I

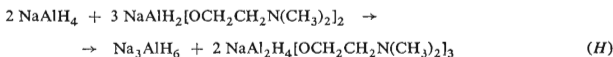
Analytical Ratios Al : Na : H⁻ in the Synthesis of NaAlH[OCH₂CH₂N(CH₃)₂]₃ by Reaction (A)

Solvent	Ratio	Solvent	Ratio
Diethyl ether	1 : 0.02 : 0.00	Benzene	1 : 1.036 : 0.99
Tetrahydrofuran	1 : 0.11 : 0.09	Toluene	1 : 1.034 : 0.98



In contrast to the disproportionation of sodium trihydrido-(2-methoxyethoxy)aluminate, producing NaAlH_4 and sodium dihydrido-bis(2-methoxyethoxy)aluminate⁷, there were formed not only compounds in which the coordination number of aluminium was 4, but even compounds with the coordination number 6.

On the basis of the finding that the reaction of NaAlH_4 with $\text{NaAlH}_2[\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_2$ produces the unstable $\text{NaAlH}_3[\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_2$ reaction (G) can be simplified in such a way that Na_3AlH_6 and sodium tetrahydrido-tris(2-dimethylaminoethoxy)dialuminate are the sole products. This simplified reaction (H) can be employed for the synthesis of these compounds.



In contrast to other methods^{10,11}, very pure Na_3AlH_6 was prepared in this way. At the same time the first hydrido-alkoxy dialuminate was obtained. This stable compound (IV), whose molecule binds AlH_3 , is the actual driving force for the formation of Na_3AlH_6 from NaAlH_4 , expressed by reaction (I).

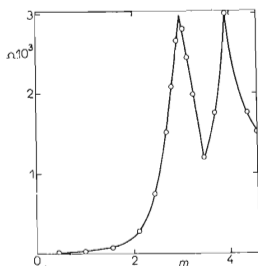


FIG. 1

Electric Resistance in Relation to the Molar Ratio, m , of $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}:\text{NaAlH}_4$
160 ml of 1,2-dimethoxyethane, 0.0444 mol of NaAlH_4 .

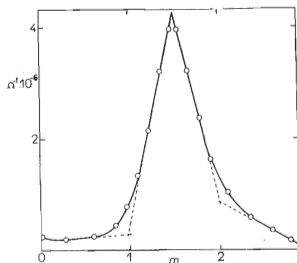
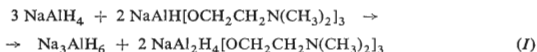
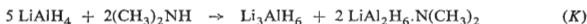
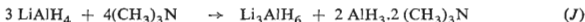


FIG. 2

Electric Conductance in Relation to the Molar Ratio, m , of $\text{AlH}_3 \cdot 2(\text{CH}_3)_3\text{N}:\text{NaAlH}_3 \cdot [\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_3$
25 ml toluene, 0.00466 mol of $\text{NaAlH}_3 \cdot [\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_3$.



Sodium hydrido-tris(2-dimethylaminoethoxy)aluminate, binding AlH_3 with the formation of compound *IV*, acts as a strong Lewis base, capable of displacing even $(\text{CH}_3)_3\text{N}$ from the stable complex $\text{AlH}_3 \cdot 2(\text{CH}_3)_3\text{N}$. Trisodium hexahydrido aluminate probably arises from the reaction of NaH (formed by dissociation of NaAlH_4 to NaH and AlH_3) with another NaAlH_4 . An analogous mechanism is assumed^{12,13} for the formation of Li_3AlH_6 , described by the summary Eqs (*J*) and (*K*).

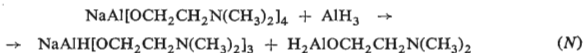


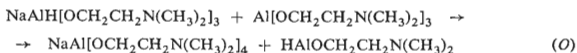
In addition to the reactions (*G*) to (*I*), reactions (*L*) and (*M*) have also been proposed for the synthesis of sodium tetrahydrido-tris(2-dimethylaminoethoxy)dialuminate.



Reaction (*L*) proceeds smoothly in boiling toluene or benzene. Conductance measurements revealed a peak at a ratio of NaAlH_4 to aluminium 2-dimethylaminoethylate = 1 : 1, which corresponds to compound *IV*. The preparation of this compound by reaction *N* is quite easy as well. In this case AlH_3 reacts in the form of etherate, if the reaction is conducted in diethyl ether, or in the form of bis(trimethylamine) in toluene as solvent. This reaction (*M*) is noteworthy for the course of conductance in the titration of a toluene solution of sodium hydrido-tris(2-dimethylaminoethoxy)aluminate with a toluene solution of bis(trimethylamine) of AlH_3 . Fig. 2 shows conductance changes at molar ratios of the reagents 1 : 1, 1 : 1,5 and 1 : 2. These results suggest the formation of more hydrido-alkoxypolyaluminates by the addition reactions between compound *I* and AlH_3 . We have succeeded in isolating the compounds corresponding to the molar ratios 1 : 1 and 1 : 1,5, i.e. $\text{NaAl}_2\text{H}_4[\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_3$ and $\text{Na}_2\text{Al}_5\text{H}_{11}[\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_6$. The polyanions are analogous to those known with sodium halogeno- and alkylaluminates.

In an attempt to synthesize more alkoxy derivatives derived from sodium hydrido-dialuminate, further reactions have been investigated. The formation of sodium trihydrido-tetrakis(2-dimethylaminoethoxy)dialuminate was expected from the reaction of AlH_3 with the corresponding sodium tetraalkoxyaluminate. Sodium hydrido-hexakis(2-dimethylaminoethoxy)dialuminate was expected to result from the reaction of compound *I* with aluminium 2-dimethylaminoethylate. Attempts at isolation of these dialuminates have ended in failure. Conductance measurements and isolated compounds revealed that instead of the formation of the substituted hydrido dialuminates the exchange reactions (*N*) and (*O*) had occurred:





As expected, the synthesized compounds *I* and *II* proved soluble in aromatic hydrocarbons like their analogues derived from 2-methoxyethanol. In addition, they were soluble even in aliphatic hydrocarbons (heptane)⁸. Cryoscopic measurements of the molecular weight of sodium hydrido-tris(2-dimethylaminoethoxy)aluminate in benzene showed the compound to be a dimer. The wide bands of the Al-H vibrations at 1733 and 1759 cm⁻¹, observed with a 10% solution in benzene, also indicated an oligomeric character of this compound. Records of differential thermic analysis and gravimetric analysis show the compound to be stable up to 170°C, at which temperature it begins to decompose. Sodium dihydrido-bis(2-dimethylaminoethoxy)aluminate at 20°C is a viscous liquid; on cooling to 0°C it solidifies to a vitric substance, soluble in aromatic hydrocarbons, ethers and heptane. Its pyrolysis starts at 170°C. The wide bands of the Al-H vibrations at 1600, 1713 and 1760 cm⁻¹ indicate an oligomeric character. Sodium tetrahydrido-tris(2-dimethylaminoethoxy)dialuminate is a white crystalline substance, well soluble in 1,2-dimethoxyethane and tetrahydrofuran. In benzene or diethyl ether it dissolves to about a 10% solution. Pyrolysis starts at 170°C.

EXPERIMENTAL

Chemicals. Dry benzene and toluene were obtained by distillation from sodium dihydrido-bis(2-methoxyethoxy)aluminate. Diethyl ether, tetrahydrofuran and 1,2-dimethoxyethane were pre-dried with a sodium wire and distilled from LiAlH₄. 2-Dimethylaminoethanol was distilled from calcium hydride. NaAlH₄ was synthesized from sodium, aluminium and hydrogen and crystallized from tetrahydrofuran, purity 98.5%. Na₃AlH₆ was also obtained by direct synthesis^{11,14}, purity 88.1%. Bis-(trimethylamine) of aluminium hydride was prepared according to Wiberg¹⁵, purity 99.2%. Pulverized sodium hydride was supplied from the Synthetic Department of the Institute and NaH in the bead form (99.8%) was a product of the firm Dynamit-Nobel.

Conductance measurements. The procedure and apparatus were described previously⁷. In following reactions (*B*) and (*L*), 2-dimethylaminoethanol or a solution of Al[OCH₂CH₂N(CH₃)₂]₃ was added from a burette to NaAlH₄ in a chosen solvent. In reactions (*M*) and (*O*) solutions of AlH₃.2(CH₃)₃N and Al[OCH₂CH₂N(CH₃)₂]₃, respectively, were added from a burette to a solution of compound *I*. In reaction (*N*) a solution of AlH₃.2(CH₃)₃N was added to sodium tetrakis(2-dimethylaminoethoxy)aluminate. In all cases the ohmic resistance was measured after each addition of a reagent when it had reached a stable value.

Synthesis of Al[OCH₂CH₂N(CH₃)₂]₃. To 27 g of aluminium shavings (99.99%) and 0.1 g of HgCl₂ was added 50 ml of 2-dimethylaminoethanol. The reaction was started by a brief heating and 500 ml of 2-dimethylaminoethanol was added dropwise. To effect complete dissolution of aluminium the reaction mixture was finally heated to 135°C. The mixture was distilled, a fraction boiling at 156–160°C/0.4 Torr being collected. There was obtained 250 g of a colourless liquid, which solidified into white crystals, well soluble in ethers and aromatic hydrocarbons. For C₁₂H₃₀AlN₃O₃ (291.5) calculated: 9.27% Al, 14.41% N; found: 9.21% Al, 14.30% N.

Synthesis of NaAlH[OCH₂CH₂N(CH₃)₂]₃

This compound was prepared by reaction of NaAl[OCH₂CH₂N(CH₃)₂]₄ with NaAlH₄ in benzene⁸. For C₁₂H₃₁AlN₃NaO₃ (315.4) calculated: 0.391% H⁻, 8.55% Al; found: 0.320% H⁻, 8.53% Al.

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

a) *Reaction C.* To 40.3 g of 99.5% $\text{NaAl}[\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_4$ under nitrogen was added 5.5 g of 98.5% NaAlH_4 and 100 ml of toluene. The reaction mixture was boiled under a reflux condenser for 2 h. Toluene was distilled off and the viscous colourless liquid was dried at 0.5 Torr and 100°C for 4 h, yield 45.5 g. For $\text{C}_8\text{H}_{22}\text{AlN}_2\text{NaO}_2$ (228.2) calculated: 0.88% H^- , 11.82% Al, 12.27% N, 10.06% Na; found: 0.86% H^- , 11.77% Al, 12.20% N, 10.11% Na. b) *Reaction E.* To 6.5 g of 88.1% Na_3AlH_6 and 30.0 g of $\text{Al}[\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_3$ under nitrogen was added 100 ml of tetrahydrofuran and the mixture was refluxed for 2 h and filtered. Tetrahydrofuran was distilled off from the filtrate and the product was dried for 4 h at 100°C and 0.5 Torr; yield 32.5 g. For $\text{C}_8\text{H}_{22}\text{AlN}_2\text{NaO}_2$ (228.2) calculated: 0.88% H^- , 11.82% Al, 10.06% Na; found: 0.84% H^- , 11.57% Al, 9.96% Na.

Disproportionation of $\text{NaAlH}_3[\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]$

To 8.3 g of 98.5% NaAlH_4 and 20.2 g of $\text{NaAl}[\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_4$ under nitrogen was added 100 ml of tetrahydrofuran and the mixture was refluxed for 1 h. After removing the solvent and 2 hours' drying at 80°C and 0.5 Torr there was obtained a transparent vitric substance, which was dissolved in 100 ml of benzene. The mixture was refluxed for 5 h, filtered, and the solid substance was washed with two 30-ml portions of benzene. X-ray analysis of this substance demonstrated the presence of Na_3AlH_6 and NaAlH_4 . The filtrate was distilled to remove the solvent and the residue was dried 2 h at 80°C and 0.5 Torr. The white compound contained 1.12% H^- , 15.52% Al, 12.21% N, 6.75% Na, which corresponds to a ratio H : Al : N : Na = 3.87 : 2.0 : 3.02 : 1.02.

Reaction of $\text{NaAlH}_2[\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]$ with NaAlH_4

To 15.5 g of 98.5% NaAlH_4 and 203 g of a 47.6% benzene solution of $\text{NaAlH}_2[\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_2$ was added 250 ml of benzene. The reaction mixture was refluxed for 8 h and filtered through a sintered glass. The collected solid was washed with five 70-ml portions of benzene and dried at 80°C and 0.5 Torr for 5 h; yield 14.0 g (white powder). For Na_3AlH_6 (102.0) calculated: 67.66% Na, 26.45% Al, 5.95% H; found 67.50% Na, 26.24% Al, 5.94% H. The filtrate and the benzene washings were combined and distilled to remove the solvent. The white solid residue was dried 5 h at 80°C and 0.5 Torr; yield 94.5 g. For $\text{C}_{12}\text{H}_{33}\text{Al}_2\text{N}_3\text{NaO}_3$ (345.4) calculated: 1.17% H^- , 15.65% Al, 12.18% N, 6.66% Na; found: 1.14% H^- , 15.56% Al, 12.10% N, 6.73% Na.

Synthesis of $\text{NaAl}_2\text{H}_4[\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_3$

a) *Reaction of NaAlH_4 with $\text{Al}[\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_3$.* To 12.5 g of 98.5% NaAlH_4 and 66.4 g of $\text{Al}[\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_3$ was added 300 ml of toluene and the mixture was refluxed for 2 h. Then 220 ml of toluene was distilled off, 100 ml of heptane was added, and the mixture was left standing overnight. The white crystalline substance that had separated was collected on a filter, washed with 100 ml of cold heptane and dried 5 h at 60°C and 0.5 Torr; yield 69 g. For $\text{C}_{12}\text{H}_{33}\text{Al}_2\text{N}_3\text{NaO}_3$ (345.4) calculated: 1.17% H^- , 15.65% Al, 12.18% N, 6.66% Na; found: 1.20% H^- , 15.68% Al, 11.95% N, 6.53% Na.

b) *Reaction of $\text{NaAlH}[\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_3$ with AlH_3 .* To 42.0 g of $\text{NaAlH}[\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_3$ in 300 ml of diethyl ether was added 0.133 mol of AlH_3 in 130 ml of the same solvent. After an hour's boiling under a reflux condenser 300 ml of ether was distilled off. The separated white crystals were collected on a filter, washed with two 50-ml portions of diethyl ether and dried

4 h at 50°C and 0.5 Torr; yield 35 g. For $C_{12}H_{33}Al_2N_3NaO_3$ (345.4) calculated: 1.17% H^- , 15.68% Al, 6.66% Na; found: 1.19% H^- , 15.81% Al, 6.60% Na.

Reaction of $NaAlH[OCH_2CH_2N(CH_3)_2]_3$ with $Al[OCH_2CH_2N(CH_3)_2]_3$

To 20.2 g (0.063 mol) of $NaAlH[OCH_2CH_2N(CH_3)_2]_3$ in 100 ml of toluene was added, at 60°C, 18.5 g (0.063 mol) of $Al[OCH_2CH_2N(CH_3)_2]_3$ in 25 ml of toluene. A white substance separated. After cooling down the mixture it was collected on a filter, washed with two 30-ml portions of cold toluene and dried at 50°C and 0.5 Torr; yield 25.0 g $NaAl[OCH_2CH_2N(CH_3)_2]_4$. For $C_{16}H_{40}AlN_4NaO_4$ (402.5) calculated: 6.70% Al, 13.92% N, 5.71% Na; found: 6.82% Al, 13.74% N, 5.61% Na.

Reaction of $NaAl[OCH_2CH_2N(CH_3)_2]_4$ with AlH_3

To 13.4 g (0.033 mol) of $NaAl[OCH_2CH_2N(CH_3)_2]_4$ was added 100 ml of an ethereal solution of AlH_3 (0.033 mol) and the mixture was heated until the complex alcoholate had dissolved. After reducing the volume of the mixture, by distillation, to 35 ml and cooling down there separated white crystals, which were collected on a filter, washed with 15 ml of cold ether and dried; yield 5.8 g of $NaAlH[OCH_2CH_2N(CH_3)_2]_3$. For $C_{12}H_{31}AlN_3NaO_3$ (315.4) calculated: 0.319% H^- , 8.55% Al, 7.29% Na; found: 0.315% H^- , 8.72% Al, 7.26% Na.

Synthesis of $Na_2Al_5H_{11}[OCH_2CH_2N(CH_3)_2]_6$

To 15.77 g of $NaAlH[OCH_2CH_2N(CH_3)_2]_3$ in 150 ml of diethyl ether was added 0.075 mol of AlH_3 in 75 ml of the same solvent. After keeping the mixture refluxing for an hour 190 ml of ether was distilled off, 30 ml of heptane was added, and the mixture was allowed to crystallize. The separated white crystals were washed with two 20-ml portions of cold heptane and dried at room temperature for 6 h at 0.5 Torr; yield 13.6 g. For $C_{24}H_{71}Al_5N_6Na_2O_6$ (720.8) calculated: 1.53% H^- , 18.71% Al, 11.66% N, 6.38% Na; found: 1.46% H^- , 18.65% Al, 11.53% N, 6.14% Na.

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