

ON THE BEHAVIOUR AND REACTIVITY
OF SOLUTIONS OF COMPLEX HYDRIDES. III.*

REDUCTION AND DEHALOGENATION BY SODIUM
HYDRIDO-TRIS(2-DIMETHYLAMINOETHOXY)ALUMINATE

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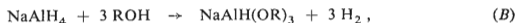
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Crystalline sodium hydrido-tris(2-dimethylaminoethoxy)aluminate, soluble in ethers and aromatic and aliphatic hydrocarbons, has been prepared. The hydride has been employed to reduce the ketone, ester, nitrile and nitro groups, and to dehalogenate aliphatic and aromatic halogen derivatives.

Lithium and sodium hydridoalkoxyaluminates are well known as specific reducing agents¹. Most attention has been given to reductions by lithium hydridoalkoxyaluminates; the main representative of these agents is lithium hydrido-tris(tert-butoxy)aluminate, which has proved to be very selective. These compounds, however, are soluble in ethers only. Within the framework of a wider research of sodium hydridoalkoxyaluminates we prepared^{2,3} sodium dihydrido-bis(2-methoxyethoxy)aluminate, whose high solubility in aromatic hydrocarbons will make it possible to study the properties and reactivity of hydridoalkoxyaluminates in solvents of this type. The solubility can be ascribed to the free electron pairs on the oxygen of the methoxyl group, which can participate in intramolecular solvation of the sodium cation. We were interested in how the replacement of the alkoxyl oxygen in the β position by the more basic nitrogen atom would affect the properties of the hydride.

The present paper describes the preparation and reduction properties of one representative of sodium hydrido-dialkylaminoethoxyaluminates, *viz.* sodium hydrido-tris(2-dimethylaminoethoxy)aluminate, $\text{NaAlH}[\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_3$. This compound, like the 2-methoxyethoxy derivatives, is soluble not only in ethers and aromatic hydrocarbons, but in aliphatic hydrocarbons as well. (The solubility in 100 g of a solvent is 22.5 g in diethyl ether, 19.5 g in benzene and 7 g in heptane at 25°C).

Syntheses³⁻⁵ of sodium hydridotrialkoxyaluminates starting from hydrides can be described by the following reactions



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The hydride employed in the present work was obtained by reaction (C) from sodium tetrahydroaluminate and sodium tetrakis(2-dimethylaminoethoxy)aluminate in benzene.

The results of the experiments are summarized in Tables I–III. Table I shows that the ketone group of 2-methylcyclohexanone, though sterically hindered, is reduced by sodium hydrido-tris(2-dimethylaminoethoxy)aluminate in high yields, like in the reduction⁶ by sodium dihydrido-bis(2-methoxyethoxy)aluminate. Unlike the latter hydride⁷, however, sodium hydrido-tris(dimethylaminoethoxy)aluminate is a weaker reducing agent for esters, whose reaction is incomplete. In the reduction of ethyl caproate it was only in the use of a 50% excess of the hydride (Table I, experiment 4) that no unchanged ester was left in the reaction mixture. For this reason the mixture was investigated for the presence of the corresponding aldehyde.

The literature contains reports on the reduction of nitriles to aldehydes^{4,8} by $\text{NaAlH}(\text{OC}_2\text{H}_5)_3$ and of amides to aldehydes⁹ by NaAlH_4 at room temperature. At 75°C acyl chlorides¹⁰ can be reduced to aldehydes by $\text{LiAlH}(\text{O}-t\text{-C}_4\text{H}_9)_3$ and recently even esters of carboxylic acids by various non-substituted hydridoaluminates¹¹, and in high yields¹² by $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$.

In the reduction of esters of saturated acids by the dimethylaminoethoxy hydride no aldehyde was detected even in the use of insufficient amounts of the hydride. However, in the case of ethyl cinnamate the corresponding aldehyde was formed in yields up to 3% in the direct reduction and up to 12% in the inverse reduction (Table II). The reduction of ethyl cinnamate has therefore been paid more attention.

TABLE I
Reductions by Sodium Hydrido-tris(2-dimethylaminoethoxy)aluminate in Benzene

Exp.	Compound	Proce- dure	Hydride mol %	°C	Time h	Product	Yield %
1	2-methylcyclohexanone	A	110	25–80	2	2-methylcyclohexanol	98
2	2-methylcyclohexanone	A	110	0–25	2	2-methylcyclohexanol	94
3	ethyl caproate	A	220	25–80	2	1-hexanol	85
4	ethyl caproate	A	300	0–80	2	1-hexanol	95
5	ethyl caproate	A	220	0–25	2	1-hexanol	76
6	ethyl benzoate	B	65	0–25	1.5	benzyl alcohol ^a	17
7	ethyl benzoate	B	80	0–25	1.5	benzyl alcohol	23
8	<i>p</i> -tolunitrile	B	120	0–25	2	<i>p</i> -tolualdehyde	75 ^b
9	butyronitrile	B	120	0–25	10	butyraldehyde	2
10	benzyl cyanide	A	120	20–80	1	oily products ^c	
11	nitrobenzene	C	600	0–30	0.5	azobenzene	46

^aBenzaldehyde was not detected by gas chromatography; ^bisolated as an adduct with sodium bisulphite; ^cneither aldehyde nor amine was isolated.

The mechanism of the reduction is obscured by polymerization of the intermediates; prior to gas-chromatographic analysis the reaction mixture had to be distilled. The distillation residue amounted to as much as 50% of the product in some cases. In the chromatographic analysis we followed only changes in the yields of 3-phenyl-2-propene-1-ol (*I*), 3-phenyl-1-propanol (*II*) and 3-phenyl-2-propenal (*III*). The other products, formed to a minor scale only, were not identified. 3-Phenyl-2-propenal was isolated in some experiments in the form of 2,4-dinitrophenylhydrazone because isolation with the aid of sodium bisulphite was not successful.

Table II shows that under the conditions reported for the reduction of esters by $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ to aldehydes¹² the dimethylaminoethoxy hydride failed to react (experiment 1). In the inverse procedure the addition of the hydride at 0°C gave rise to the unsaturated alcohol *I*, which soon polymerized under the conditions of the reduction. The arising aldehyde proved relatively stable under these conditions and was detected in the reaction mixture even when a 220% excess of the hydride was employed (experiment 6). Comparison of experiments 6 and 7 suggests that 3-phenyl-2-propene-1-ol (*I*) is also resistant to further reduction to 3-phenyl-1-pro-

TABLE II

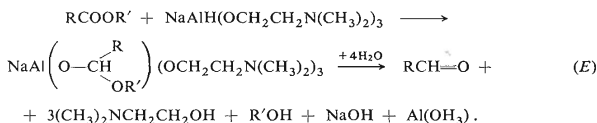
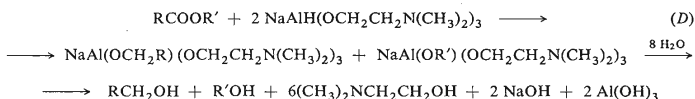
Reduction of Ethyl Cinnamate by Sodium Hydrido-tris(2-dimethylaminoethoxy)aluminat in Benzene

Exp.	Proce- dure	°C ^a	Time, h	Hydride mol %	Unchan- ged esters %	Products, %		
						<i>I</i>	<i>II</i>	<i>III</i>
1	<i>B</i>	-75 ^b	8	100	100	—	—	—
2	<i>B</i>	20	1.5	100	78	16	—	3
3	<i>B</i>	20	3	150	59	8	—	9 ^c
4	<i>B</i>	20	3	200	41	3	1	12 ^d
5	<i>B</i>	20	3	250	13	13	12	12
6	<i>B</i>	20	3	320	—	28	26	2
7	<i>B</i>	20	3	420	—	30	26	—
8	<i>A</i>	20	2	110	56	16	—	3
9	<i>A</i>	20	2	210	1	31	11	3
10	<i>A</i>	20	2	300	—	4	51	—
11	<i>A</i>	0	2	150 ^e	43	5	—	6
12	<i>A</i>	25	18	150 ^e	42	6	—	3
13	<i>A</i>	60	2	150 ^e	49	3	2	2

^aDuring addition of the agent the temperature was kept at 0°C; ^bthe temp. -75°C was maintained even during addition of the hydride; ^c5% of the aldehyde isolated in the form of 2,4-dinitrophenylhydrazone; ^d8% of the aldehyde isolated in the form of 2,4-dinitrophenylhydrazone; ^ea quarter-hydrolysed hydride was employed.

panol (II). The distilled reaction mixture contained nearly pure alcohol (II) only in the normal reduction of ethyl cinnamate (experiment 10). Experiments 11–13 show the lower reducing efficacy of the partially hydrolysed hydride.

Judging by the results of the reduction of esters of carboxylic acids and by analogies from the literature^{7,11,12} the total reduction of an ester to alcohol can be described by reactions (D) and the partial reduction to aldehydes by reactions (E):

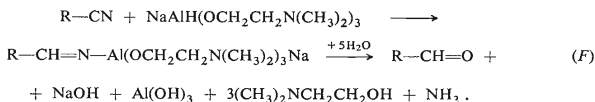


p-Tolunitrile was reduced at room temperature to the corresponding aldehyde (Table I), which was isolated as a sodium-bisulphite adduct in a yield of 75%. Butyronitrile and benzyl cyanide afforded practically no aldehyde. At elevated temperatures, however, hydrogen was evolved, which is in agreement with the published data on the reduction of nitriles to aldehydes by the action of sodium hydridoalkoxyaluminates^{4,13}. The reduction of aromatic nitriles is expressed by reaction (F). Aliphatic nitriles at room temperature did not react, at higher temperatures side reactions occurred, caused by the acidity of the α -hydrogen.

TABLE III

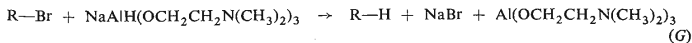
Dehalogenation by a 50% Solution of Sodium Hydrido-tris(2-dimethylaminoethoxy)aluminate

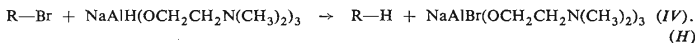
Exp.	Compound	Solvent	°C	Time h	Product	Yield %
1	1-bromoheptane	benzene	80	1	heptane	99
2	1-bromoheptane	tetrahydrofuran	60	1	heptane	99
3	chlorocyclohexane	benzene	80	20	cyclohexane	1
4	chlorocyclohexane	tetrahydrofuran	60	20	cyclohexane	0
5	chlorocyclohexane	xylene	140	16	cyclohexane	6
6	bromobenzene	toluene	110	1	benzene	56
7	<i>o</i> -chlorotoluene	benzene	80	20	toluene	6



The reduction of nitrobenzene by an excess of sodium hydrido-bis(2-methoxyethoxy)-aluminate was originally reported¹⁴ to be a non-specific reaction leading to a mixture of compounds, azobenzene and hydrazobenzene being the main products. Other authors¹⁵, however, isolated pure azobenzene in good yields. In the reduction by sodium hydrido-tris(2-dimethylaminoethoxy)aluminate nitrobenzene afforded azobenzene and small amounts of hydrazobenzene, phenylhydroxylamine and aniline. From the reaction mixture was isolated 46% of azobenzene, which contained only 0.7%, based on hydrazobenzene, of the reducing compounds. The yield of azobenzene and the percentual content of hydrazobenzene are somewhat lower than in the reduction by hydrides^{15,16} $\text{NaAlH}(\text{OCH}_2\text{CH}_2\text{OR})_3$ and $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OR})_2$; it is evident that even in these cases the hydrogen anion in sodium hydrido-tris(2-dimethylaminoethoxy)aluminate is less active. The data on the dehalogenation efficacy of the studied hydride (Table III) are essentially in keeping with those obtained with analogous alkoxy hydrides. The dehalogenation effect of lithium aluminium hydride on aromatic halogen derivatives is known to be weak, but it considerably increases by a partial decomposition of the hydride with methanol¹⁷.

Yields higher still were obtained⁴ with $\text{NaAlH}(\text{OC}_2\text{H}_5)_3$, and the best dehalogenation agent for aromatic derivatives appears to be $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$, especially when modified by the addition of an equimolar amount of methanol⁹. The approximate equality of yields of dehalogenated products, in the use of the hydride studied, suggests that 2-dimethylaminoethoxyl behaves like a non-substituted alkoxy or 2-alkoxyethoxyl in enhancing the Lewis acid character of aluminium hydride, so that the carbon-halogen linkage is split more efficiently than by the action of a non-alkoxylated hydride¹⁷, the nitrogen atom having no significant effect on the course of the reaction. In the dehalogenation of 1-bromoheptane it was observed that from the onset of the reaction insoluble sodium bromide separated from the reaction mixture. When the reaction had ended analysis of the mixture demonstrated the absence of bromine, and all aluminium was found in the solution. These facts indicate that the dehalogenation proceeds by reaction (G) and sodium chloro-tris(2-dimethylaminoethoxy)aluminate (IV), which would be produced by reaction (H), is either not formed at all or rapidly disproportionates, in contrast to the reaction reported^{18,19} to occur in the dehalogenation by sodium hydrido-bis(2-methoxyethoxy)aluminate.





Owing to its dehalogenation effects, particularly with aliphatic compounds, its power to reduce aromatic nitriles to aldehydes, and in view of the easy removal of 2-dimethylaminoethanol from the hydrolysed mixture in the form of a salt, sodium hydrido-tris(2-dimethylaminoethoxy)aluminate proves to be a useful arrival to the class of selective reducing complex hydrides.

EXPERIMENTAL

Sodium Tetrakis(2-dimethylaminoethoxy)aluminate

To 27 g of aluminium shavings under nitrogen was added 0.1 g of mercury chloride and 50 ml of 2-dimethylaminoethanol. A brief heating started the reaction, then 500 ml of 2-dimethylaminoethanol was added dropwise. When all the aluminium had dissolved there was added 23 g of sodium and another 800 ml of 2-dimethylaminoethanol and the reaction mixture was heated till all the sodium had gone into the solution. The excess of the alcohol was distilled off under reduced pressure and the product was dried 8 h at 140°C and 0.1 Torr. There was obtained 403 g (100%) of a white crystalline compound, well soluble in warm benzene: For $\text{C}_{16}\text{H}_{40}\text{AlN}_4\text{NaO}_4$ (402.5) calculated: 6.70% Al, 13.92% N, 5.71% Na; found: 6.71% Al, 14.01% N, 5.71% Na.

Sodium Hydrido-tris(2-dimethylaminoethoxy)aluminate

To 350 g of $\text{NaAl}[\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_3$ under nitrogen was added 16 g of NaAlH_4 (98.5%) and 1500 ml of benzene. The mixture was refluxed for 3 h, then cooled down to 30°C and filtered. After a day's standing there had separated crystals which were collected on a filter under nitrogen, washed with 100 ml of cold benzene and dried 8 h at 25°C and 0.1 Torr. There was obtained 256 g (70%) of a white compound, melting at 95–96°C. After the crystallization the solution was concentrated and another 100 g (27.5%) of the product was obtained. For $\text{C}_{12}\text{H}_{31}\text{AlN}_3\text{NaO}_3$ (315.4) calculated: 0.319% H^- , 8.55% Al, 13.32% N, 7.29% Na; found: 0.318% H^- , 8.57% Al, 13.10% N, 7.25% Na.

Reduction and Dehalogenation

All the handling with, and reactions of the hydride were carried out under nitrogen, care being taken to exclude contact with humidity. The reaction mixtures were analysed in a gas chromatograph Griffin and George, London, type IIB, the reduction products of ethyl cinnamate in a gas chromatograph LP Chrom III. The identity of bands of the starting compounds and the final products was verified by comparison with the bands of authentic standards, for which calibration curves were constructed. The average error of four determinations of the individual compounds was lower than 2%. Data on the gas-chromatographic analysis after the reduction of the individual compounds: 2-methylcyclohexanone — 20% carbowax 1500 on chromosorb, 100°C; ethyl capronate — 15% silicone elastomer on celloite, 99°C; ethyl benzoate and *p*-tolunitrile — the same system, 125°C; butyronitrile — 20% carbowax on chromosorb, 80°C; ethyl cinnamate — 15% silicone elastomer on chromosorb, 180°C; aliphatic halogenated hydrocarbons — the same system, 110°C; aromatic halogenated hydrocarbons — 20% carbowax 1500 on chromosorb, 110°C.

"Normal" reduction (procedure A). To a 15% solution of the hydride (6 to 30 mmol) in benzene a 5% benzene solution of the compound to be reduced was added dropwise under stirring in the course of 15 min, the reaction mixture being cooled in an ice-water bath. Stirring was continued for 1 to 2 h at room temperature after which time the reaction mixture was decomposed by the addition of 15 ml of dilute (1 : 1) hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with two 3-ml portions of ether. The organic layer, combined with the ethereal extracts, was dried with magnesium sulphate. The dry solution was analysed directly by gas chromatography. All exceptions are given in Tables I—III.

"Inverse" reduction (procedure B). To 8 mmol of an ester in 2 ml of benzene or 50 ml of n-hexane a 14% solution of the hydride in benzene was added dropwise under stirring during 15 min at 0°C. After 2 hours' stirring at room temperature the reaction mixture was decomposed by the addition of 15 ml of dilute (1 : 1) hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with two 3-ml portions of ether. The extracts and the organic layer were combined and dried with magnesium sulphate. The solvent was removed by distillation and the reduction products were distilled at 12 Torr up to 200°C. The amount of polymeric products formed in the reaction was determined from the weight of the distillation residue.

Reduction of nitrobenzene (procedure C). To 15.4 g (48.4 mmol) of the hydride in 30 ml of benzene 1 g (8.12 mmol) of nitrobenzene in 2 ml of benzene was added dropwise in the course of 15 min under stirring and cooling with ice. The mixture was stirred for 30 min at room temperature, then decomposed by the addition of 30 ml of a concentrated solution of ammonium chloride. The aqueous layer was twice extracted with 5-ml portions of ether, the organic layer and the extracts were combined, dried with magnesium sulphate and analysed chromatographically in a thin layer of silica gel employing a system cyclohexane-benzene (3 : 1); the spots were detected in UV light. On the basis of known R_F values¹⁴ it was ascertained that besides azobenzene the reaction mixture contained hydrazobenzene, aniline and phenylhydroxylamine. The reaction mixture was taken to dryness *in vacuo*, the residue was dissolved in 2 ml of methanol and 50 ml of water was added. The separated crystals of azobenzene were collected on a filter and dried; yield 0.36 g (46%), m.p. 65°C (reported^{20,21} m.p. 66—67.5°C). The content of reducing compounds in this product was determined iodometrically²² to be 0.7% (based on hydrazobenzene).

Isolation of Aldehydes

a) After the reduction (procedure B) the organic layer, combined with the ethereal extracts, was diluted with 10 ml of ether and stirred for 8 h with a solution of 2 g of sodium bisulphite in 3 ml of water. The separated crystalline adduct was collected on a filter, washed with a few drops of water and 30 ml of ether. The aldehyde was released by decomposition of the adduct with a 15% solution of sodium carbonate; its purity was tested by gas chromatography. b) 3-Phenyl-2-propenal was precipitated from an ethereal solution by the addition of a saturated solution of 2,4-dinitrophenylhydrazine in 2M-HCl; the separated hydrazone was collected on a filter and recrystallized from benzene; m.p. 256°C (reported²⁰ m.p. 255°C).

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