

**ON THE BEHAVIOUR AND REACTIVITY OF SOLUTIONS
OF COMPLEX HYDRIDES. VIII.*****THE REDUCTION PROPERTIES
OF NEW SODIUM (ALKOXYALKOXY)HYDRIDOALUMINATES****

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Benzene solutions of sodium bis(1-methyl-2-methoxyethoxy)-, bis(1,1-dimethyl-2-methoxyethoxy)-, bis(2-propoxyethoxy)-, bis(2-isopropoxyethoxy)- and bis(2-butoxyethoxy)dihydridoaluminates and of sodium tris(1,1-dimethyl-2-methoxyethoxy)-, tris(3-methoxypropoxy)-, tris(3-methyl-3-methoxypropoxy)- and tris(4-methoxybutoxy)hydridoaluminates have been investigated for their reducing powers on compounds containing a ketonic, ester, amide, nitrile, carbonyl-chloride and a nitro group. The effect of structural changes of the alkoxyalkoxy groups of the hydrides on their reduction properties is discussed.

The useful properties of sodium bis(2-methoxyethoxy)dihydridoaluminate^{1,2} have become the reason of its industrial production*** and practical use. The structure of this reducing agent is not yet quite clear. Its high solubility in aromatic hydrocarbons (which renders it so distinct from sodium alkoxyhydridoaluminates) and other properties suggest an intramolecular solvation, utilizing the free electron pair on the methoxyl oxygen. In an attempt to elucidate the relation between its state in a solution and its reactivity, reduction³, physico-chemical⁴⁻⁶ and stereochemical⁷⁻⁹ studies have been performed in our laboratories.

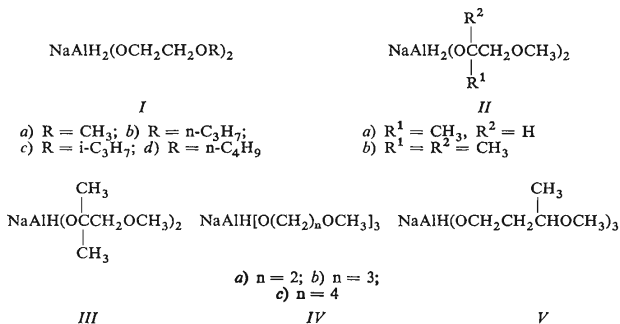
The present paper treats the effect of modifications of the alkoxyalkoxy groups in the compounds *Ia* and *IVa* on the selectivity of reductions of organic compounds. The structural alterations consist in: 1) the replacement of 2-methoxyl by a higher alkoxy, 2) substitution of methyl(s) for the hydrogen atom(s) at position 1 of the 2-methoxyethoxyl group, 3) prolongation of the hydrocarbon chain between the oxygen atoms, 4) substitution of a methyl group for this prolonged chain. We have investigated five sodium bis(alkoxyalkoxy)dihydridoaluminates derived by the structural alterations 1 and 2 from the hydride *Ia* (*Ib-d*, *IIa*, *IIb*) and four sodium tris(alkoxyalkoxy)hydridoaluminates derived by the alterations 2, 3 and 4 from the hydride *IVa* (*III*, *IVb-c*, *V*).

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*** VCHZ Synthesia, Kolín (ČSSR) and Realco (U.S.A.)

The hydrides *I–V* have been characterized by analytical determination of the ratios Na : Al : H⁻ in their benzene solutions; to calculate the stoichiometry of the reductions the determined concentrations of the hydride anions were employed. Some typical examples of the reductions are compiled in Table I, in comparison with the reductions accomplished with the hydride *Ia*.



The reductions of the ketone group of cyclohexanone in benzene solutions of all the hydrides studied have proved virtually quantitative. The differences among the reducing powers of hydrides with different alkoxyalkoxy substituents manifested themselves in the reductions of esters, ethyl caproate and ethyl cinnamate. In the reduction of ethyl caproate at room temperature significantly lower yields of 1-hexanol were observed with the hydrides *Ila*, *I Ib* and *III*; the reducing power decreased in the order *I Ia*, *I Ib*, *III*, i.e. with the increasing degree of alkylation of the alkoxyalkoxy group and with the decreasing number of hydride anions in the molecule. Hexanal was never detected in the reaction mixture. It was not formed even under milder conditions (lower temperatures, a smaller excess of the reducing agent). The reducing powers of the other hydrides are very similar to those of the hydride¹⁰ *Ia*. After the reductions of ethyl cinnamate by the α -substituted hydrides *I Ia*, *I Ib*, *III* and by the monohydridoaluminates *IVc* and *V* at room temperature 3-phenyl-1-propanol was never present in the reaction mixtures (it is a sole product of the reduction by the hydride¹⁰ *Ia*), the identified compounds were 3-phenyl-2-propen-1-ol and 3-phenyl-2-propenal only. The highest yields of the former were obtained in the reductions by the hydride *I Ia* and *V*, the lowest with the hydride *III*. The rest of the hydrides studied gave rise to 3-phenyl-1-propanol as the main product. The reductions of ethyl cinnamate were accompanied by the formation of polymeric substances in considerable quantities. For this reason the reaction products were distilled prior to gas chromatography. This accounts for the worse reproducibility

TABLE I
Reductions with 15% Solutions of the Hydrides I to V in Benzene

| Compound reduced | Product | Yield in the use of the hydride | | | | | | | | | |
|--------------------------------|--|---------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| | | Ia | Ib | Ic | Id | Ila | Ilb | III | IVa | IVb | V |
| Cyclohexanone ^a | cyclohexanol ^j | >97 ^k | >99 | >99 | >99 | >99 | >99 | 99 | 99 | 99 | >99 |
| Ethyl caproate ^b | 1-hexanol ^j | >98 ^{l,m} | 98 | >99 | 99 | 92 | 50 | 8 | >99 | 99 | >99 |
| Ethyl cinnamate ^c | total yield | 45 | 51 | 56 | 60 | 44 | 7 | 3 | 50 | 21 | 44 |
| | 3-phenyl-1-propanol ^j | 45 ^{m,n} | 39 | 54 | 52 | 0 | 0 | 0 | 50 | 0 | 0 |
| | 3-phenyl-2-propen-1-ol ^j | 0 | 6 | 2 | 6 | 40 | 4 | 2 | 0 | 10 | 40 |
| | 3-phenyl-2-propenal ^j | 0 | 6 | 0 | 2 | 4 | 3 | 1 | 0 | 11 | 4 |
| Benzoyl chloride ^d | benzylalcohol ^j | 79 | 77 | 80 | 77 | 80 | 72 | 61 | — | 61 | — |
| Butyramide ^e | n-butyramine | 89 | 88 | — | 94 | 92 | 90 | 62 | 87 | 87 | — |
| N-phenylacetamide ^f | N-phenylethylamine | 85 ^o | 81 | 83 | 71 | 70 | — | 66 | 69 | — | — |
| Caprolactam ^g | hexamethylenimine | 82 ^o | — | — | 89 | 88 | 67 | — | — | — | — |
| Benzyl cyanide ^h | basic compounds distil- ling with steam | 48 | 52 | 53 | 47 | 36 | 29 | — | 29 | — | — |
| | 2-phenylethylamine ^j | 12 | 15 | 15 | 12 | 6 | 5 | — | 6 | — | — |
| Nitrobenzene ⁱ | total yield | 79 | 76 | 85 | 75 | 70 | <10 | 0 | 90 | 75 | 62 |
| | hydrazobenzene | 48 | 45 | 47 | 34 | 19 | 0 | 0 | 33 | 12 | 3 |
| | azobenzene | 31 | 31 | 38 | 41 | 51 | <10 | 0 | 57 | 63 | 59 |

^a Temperature 25°C, reaction time 2 h, molar ratio of the hydride to the compound reduced R = 1:1; ^b 25°C, 2 h, R = 2:2; ^c 25°C, 2 h, R = 2:2; ^d 25°C, 5 h, R = 2; ^e 80°C, 4 h, R = 5; ^f 80°C, 4 h, R = 4; ^g 80°C, 4 h, R = 4; ^h 25°C, 4 h, R = 4; ⁱ 25°C, 0.5 h, R = 6; ^j the yields were determined by gas chromatography; ^k taken from ¹⁸; ^l the value for ethyl dodecanoate; ^m taken from ¹⁰; ⁿ R = 4:8; ^o taken from ¹¹.

of determination of the reaction products than in the other cases. To minimize the formation of the polymers only a 10% excess of the hydride was employed, as in the reduction of ethyl caproate. Apart from the formation of polymers, another difference between the reductions of ethyl caproate and ethyl cinnamate is the frequent formation of aldehyde in the reductions of cinnamate. Reduction of benzoyl chloride with the hydride *Ia* at room temperature gave benzyl alcohol as a sole product (Table I). About 2% of benzaldehyde was isolated from the reaction mixture after reductions with an equimolar amount of this hydride at 0°C; similarly the hydrides *Ib–Id* and *IVc* gave about 1% of the aldehyde, but the alcohol was never detected. No reductions were effected under these conditions with the hydrides *IIa* and *IIB*.

The hydride *Ia* is known¹¹ to reduce primary and substituted amides and lactams to amines in very good yields, although amides (especially the primary ones) were reported¹² to resist the action of complex hydrides. The studied sodium (alkoxyalkoxy)hydridoaluminates also reduced butyramide, N-phenylacetamide and ϵ -caprolactam. A lower reactivity was observed only with those hydrides which proved less efficacious in the reduction of esters; this phenomenon is evidently dependent on the type of the amide reduced (Table I). The lowest reducing power was observed again with the hydride *III*. The yield of an amine depends on the reaction temperature; this was demonstrated on the reductions of butyramide by the hydrides *IIa* and *IIB* at 25°C (4 h, 10% excess of hydride), which gave merely 13% and 5% of n-butylamine, respectively. Aromatic nitriles are reduced by the hydride *Ia* to amines in good yields, whereas aliphatic nitriles are practically non-reactive¹¹. The reductions of benzyl cyanide at 25°C by the hydrides studied gave only low yields of 2-phenylethylamine (determined by gas chromatography), at higher temperatures there were formed considerable quantities of polymeric substances. Comparison of the yields of 2-phenylethylamine suggests only slight differences among the hydrides of type *I* and indicates a weaker reducing power of the hydrides *II* and *IVb*. In addition to the unreacted benzyl cyanide, the neutral products of the reduction contained 2-phenylmethanol (gas chromatography); the aldehyde was never detected.

Depending on the reaction conditions, the hydride *Ia* reduced nitrobenzene to azobenzene¹³ (92%) or hydrazobenzene¹⁴ (37%). The hydrides *I* to *V* afforded a mixture of azobenzene and hydrazobenzene in an overall conversion up to 90% (Table I). In the case of the hydride *IIB* only azobenzene was formed in a low yield (thin-layer chromatography). Judging by the proportion of the reduction products, the hydrides *Ib–d* are comparable in reactivity with the hydride *Ia*, whereas the α -substituted hydride, *IIa*, and those with longer carbon chains between the two oxygen atoms of the alkoxyalkoxyls, *IVb*, *IVc* and *V*, are markedly weaker (Table I).

The results compiled in Table I demonstrate that different alkoxyalkoxy groups have unequal effects on the reducing power of sodium (alkoxyalkoxy)hydridoaluminates. Replacement of 2-methoxyl by a larger alkoxyl in the hydride *Ia* (modification 1) practically did not affect the reducing power. By contrast, replacement of the

α -hydrogen in the 2-methoxyethoxy group of the hydride *Ia* by a methyl group (modification 2) had a strong effect indeed. With the α,α -disubstituted hydride, *Ib*, the decrease in the reducing power is so great as to make this hydride markedly different from the other sodium bis(2-alkoxyalkoxy)dihydridoaluminates studied. The effect of a double substitution is even more marked with the hydride *III* (analogue of *IVa*), whose reducing power was the lowest in all cases and was comparable with that of lithium tris(tert-butoxy)hydridoaluminate¹². The reducing power of the monohydridoaluminates, *IVc* and *V*, decreases with extending the carbon chain between the oxygen atoms (modifications 3); this decrease is especially marked in the reductions of C=C bonds (ethyl cinnamate) and N=N bonds (azobenzene). In this aspect the hydride *IVc* resembles sodium triethoxyhydridoaluminate¹⁵. It can be concluded that the reducing power of sodium alkoxyalkoxyhydridoaluminates is suppressed by substitutions on the alkoxyalkoxyl near to its linkage to the aluminium atom, by the increasing number of alkoxy groups in the molecule, and, to some extent, by prolongation of the hydrocarbon chain between the two oxygen atoms. The dependence of the reducing power on the structural factor is analogous to the relation between the stability of the individual types of sodium alkoxyalkoxyhydridoaluminate and this factor¹⁶.

EXPERIMENTAL

Chemicals. Benzene solutions of the hydrides were prepared earlier¹⁶. The relative contents of sodium, aluminium and hydride hydrogen (Na : Al : H⁻) were: *Ia* 0.99, 1, 1.90; *Ib* 0.95, 1, 2.00; *Ic* 1.09, 1, 1.85; *Id* 1.01, 1, 1.98; *Ila* 1.00, 1, 1.95; *Ilb* 1.04, 1, 1.70; *III* 1.04, 1, 0.83; *IVb* —, 1, 1.20; *IVc* 0.96, 1, 0.86; *V* 1.00, 1, 1.07.

Reductions. The reductions of cyclohexanone, ethyl caproate, ethyl cinnamate and nitrobenzene and analysis of the reaction mixtures were described previously¹⁷. As examples, the reductions of butyramide and benzoyl chloride are described below.

Reduction of Butyramide by Sodium Bis(2-butoxyethoxy)dihydridoaluminate (*Id*)

To a 15% solution of *Id* (28.2 mmol), cooled in an ice bath and under a nitrogen atmosphere, butyramide (0.98 g, 11.3 mmol) was added in the course of 10 min. After it had gone into the solution the mixture was heated to 80°C under stirring for 4 h. It was then decomposed with hydrochloric acid (1 : 1) and extracted with ether. The ethereal layer was alkalified and the basic products were distilled out with a jet of steam and titrated with 0.2M-HCl. The aqueous solutions, containing 10.6 mmol (94%) of the crude amine hydrochloride, was taken to dryness, the liberated base extracted into ether, and analysed in a gas chromatograph LP Chrom III (packed with 20% QF₁ on Chromosorb W). Yield 9.8 mmol (87%) of n-butylamine.

Reduction of Benzoyl Chloride by Sodium Bis(2-propoxyethoxy)dihydridoaluminate (*Ib*)

To a 20% solution of *Ib* (11.6 mmol) in an ice bath was added dropwise during 10 min a solution of benzoylchloride (1.48 g, 5.27 mmol) in 5 ml of benzene. The solution was stirred at 25°C for 5 h, then decomposed with hydrochloric acid (1 : 1). The organic substances were extracted

into ether and the quantity of benzyl alcohol was determined as in the preceding case by gas chromatography, n-hexadecane being used as the internal standard. Yield 4.05 mmol (77%) of benzyl alcohol; less than 1% of benzaldehyde was formed.

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