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

REDUCTION OF ALUMINIUM SESQUI(2-METHOXYETHOXY)HYDRIDE

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Substances containing a carbonyl, carboxyl, amide, nitrile, and nitro group or halogen atom were reduced with a benzene solution of aluminium sesqui(2-methoxyethoxy)hydride. The reducing properties of the investigated compound are compared with those of similar reagents.

It was found that reducing properties of sodium alkoxyhydridoaluminates are affected by the presence of a donor atom in the alkoxy group and that this effect is dependent mainly on the possibility of forming intramolecular solvated structures with energetically advantageous five- and six-membered rings[1,2]. In this paper we describe the reducing properties of aluminium sesqui(2-methoxyethoxy)hydride[3] (*I*) where only the aluminium atom may function as an acceptor during intramolecular solvatation. We were mainly interested in the difference of reduction properties of hydride *I* and aluminium hydride itself[4,5] on one hand, and aluminium alkoxyhydrides with a simple alkoxyl group in the molecule on the other[6]. The results of the reduction and dehalogenation of some representative functional groups by aluminium sesqui(2-methoxyethoxy)hydride are listed in Tables I—III.
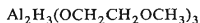
$$Al_2H_3(OCH_2CH_2OCH_3)_3$$
$$I$$

Aliphatic and cyclic saturated ketones are reduced in high yield to corresponding alcohols (Table I, exp. 1, 2). Benzophenone (exp. 9) is reduced in 96% yield to diphenylcarbinol. The reaction products contained only 3% of diphenylmethane. In this way *I* differs distinctly from aluminium hydride itself and aluminium chlorohydrides ("mixed hydrides") prepared from lithium tetrahydridoaluminate by reaction with aluminium chloride, which on reduction of benzophenone afford diphenylmethane in a yield[7] up to 92%. Carboxylic acids and their esters are reduced with hydride *I* less easily. Attempts at isolation of intermediates of aldehydes were un-

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TABLE I

Reductions with Hydride *I* in Benzene (concentration 10%)

No	Reduced compound R^a	Time h/°C	Product, %
1	cyclohexanone	2	cyclohexanol (94^c)
	0·35	25	
2	4-phenyl-2-butanone	2	4-phenyl-2-butanol (97^c)
	0·5	25	
3	4-phenyl-3-buten-2-one[b]	2	4-phenyl-2-butanol (3^c)
	1	25	4-phenyl-3-buten-2-ol (79^c)
			polymeric products[d] (16)
4	3-phenyl-2-propenal[b]	2	3-phenyl-1-propanol (7^c)
	1	25	3-phenyl-2-propen-1-ol (84^c)
			polymeric products[d] (7)
5	3-phenyl-2-propenal	2	3-phenyl-1-propanol (6^c)
	1	25	3-phenyl-2-propen-1-ol (52^c)
			polymeric products[d] (37)
6	3-phenyl-2-propenal	1	3-phenyl-1-propanol (52^c)
	1	80	3-phenyl-2-propen-1-ol (4^c)
			polymeric products[d] (38)
7	3-phenyl-2-propen-1-ol	2	3-phenyl-1-propanol (11^c)
	1	25	3-phenyl-2-propen-1-ol (73^c)
			polymeric products[d] (15)
8	3-phenyl-2-propen-1-ol	1	3-phenyl-1-propanol (42^c)
	1	80	3-phenyl-2-propen-1-ol (19^c)
			polymeric products[d] (37)
9	benzophenone	2	diphenylcarbinol (96^c)
	1[e]	80	diphenylmethane (3^c)
10	ethyl caproate	2	n-hexanol (7^c)
	0·35	0	
11	ethyl caproate	2	n-hexanol (98^c)
	0·9[f]	80	
12	ethyl cinnamate	2	3-phenyl-2-propen-1-ol (3^c)
	0·7	25	3-phenyl-2-propenal (2^c)
			polymeric products[d] (30)
13	ethyl cinnamate	1	3-phenyl-1-propanol (20^c)
	1·35[f]	80	3-phenyl-2-propen-1-ol (4^c)
			polymeric products[d] (70)
14	benzoic acid	2	benzyl alcohol (75^c)
	1·35[e]	80	

[a] *R* is the molar ratio of hydride and the reduced compound; [b] reduction was carried out in the inverted manner; [c] the yield was determined by GC; [d] the fraction of the polymeric products was determined from the distillation residue at 200°C/12 Torr; [e] concentration of hydride 20%; [f] concentration of hydride 15%.

successful. When hydride *I* was used for the reduction of cinnamic aldehyde, ethyl cinnamate, and 4-phenyl-3-buten-2-one the corresponding saturated and unsaturated alcohols were formed the ratio of which was affected appreciably by the reduction conditions. In a normal procedure the saturated alcohol predominates (exp. 5, 6, 13), while in an inverse one (exp. 3, 4) unsaturated alcohol prevails. The yields are decreased by the formation of polymeric products (up to 70% in experiment 13). A similar polymerization of α,β-unsaturated carbonyl and carboxyl compounds was also observed during the reduction with complex sodium dimethylaminoethoxy- and alkoxyalkoxyhydridoaluminates[1,2,8]. On reduction of cinnamic alcohol 3-phenyl-1-propanol (exp. 8) may be prepared. Hence, it is probable that on reduction of α,β-unsaturated carbonyl compounds an intermediate is involved in which

TABLE II

Reduction of Carboxylic Acid Derivatives with Hydride *I* in Benzene

No	Reduced compound	R^a conc. of hydride, %	Time, h temp., °C	Product, %
1	caproyl chloride	0·4 5	2 0	hexanal (12)
2	benzoyl chloride	0·45 5	2 25	benzaldehyde (29)
3	cinnamoyl chloride	0·5 10	2 25	3-phenyl-2-propen-1-al (20)
4	butyramide	1·7 25	2 80	n-butylamine (75)
5	caprolactam	1·4 20	2 80	hexamethyleneamine (97)
6	*p*-tolunitrile	1·4 25	2 80	*p*-toluidine (97)
7	*p*-tolunitrile	0·4 15	3 25	*p*-toluidine (23) *p*-toluialdehyde (12)
8	benzyl cyanide	1·4 20	2 80	2-phenyl-1-ethylamine (88, 66[b])
9	benzyl cyanide	1·4 15	3 25	2-phenyl-1-ethylamine (29)
10	butyronitrile	1·4 20	2 80	n-butylamine (86, 61[b])
11	butyronitrile	0·4 15	3 25	n-butylamine (24)

[a] R is the molar ratio of hydride and the reduced compound; [b] the amine was isolated as base.

aluminium is bound in a five-membered ring. The existence of an analogous intermediate is also supposed in the reaction of cinnamic aldehyde with excess lithium tetrahydridoaluminate[9]. Neither the oxo nor the ester group in ethyl acetoacetate can be reduced with hydride I. Acyl chlorides were reduced with an equivalent amount of hydride I in order to isolate an aldehyde as a reaction product. In Table II experiments are listed with maximum yield of aldehyde isolated in the form of sodium bisulfite compound (exp. 1—3). The yields are relatively low and the reaction mixture contains both the corresponding alcohol and the unreacted acyl chloride. In the case of cinnamoyl chloride the reduction is accompanied by polymerization. As expected, amide and lactams are reduced with hydride I to the corresponding amine at a higher temperature (Table II, exp. 4,5); the same effect is obtained with aluminium hydride or sodium bis(2-alkoxyethoxy)dihydridoaluminates[1].

Aromatic nitriles — and in contrast to complex sodium alkoxyalkoxyhydridoaluminates also aliphatic ones — are reduced with excess hydride I at 80°C to corresponding amines in good yields (Table II, exp. 6, 8, 10). When nitriles are reduced with an equimolar amount of hydride at room temperature an amine is again formed in all instances, but the yield is substantially lower (exp. 7, 9, 11). Under these conditions the corresponding aldehyde was isolated from the reduction products of p-tolunitrile in 12% yield in the form of a sodium bisulfite compound while in the case of benzyl cyanide reduction only 1% of aldehyde was isolated. Hydride I does not reduce the nitro group; nitrobenzene could not be reduced appreciably even at 80°C. Dehalogenation of aromatic and aliphatic halogenoderivatives takes place in very low yields (Table III).

The reductive reagent I prepared by us displays in some instances reducing prop-

TABLE III
Dehalogenation with Aluminium Sesqui(2-methoxyethoxy)hydride[a]

Dehalogenated compound	h	°C	Product, %[b]
n-Heptyl bromide[c]	2	25	n-heptane (3)
n-Heptyl bromide[c]	3	80	n-heptane (61)
Cyclohexyl chloride[c]	10	80	cyclohexane (1)
Cyclohexyl chloride[d]	30	65	cyclohexane (1)
Benzyl chloride[c]	2	25	toluene (3)
o-Chlorotoluene[c]	2	25	toluene (1)
o-Chlorotoluene[c]	30	80	toluene (9)
Jodobenzene[e]	2	25	benzene (1)

[a] The molar ratio of hydride and the reduced compound is 0·7; [b] the yield was determined by GC; [c] dehalogenation was carried out in benzene; [d] tetrahydrofuran; [e] toluene.

erties which are different from those of aluminium hydride[4,5], aluminium alkoxy-
hydrides[6], and sodium bis(2-methoxyethoxy)dihydridoaluminate and its analogues[1].
According to its composition hydride I should be most similar to simple aluminium
alkoxyhydrides in its physical and reductive properties. Among simple aluminium
mono- and dialkoxyhydrides only aluminium isopropoxy, isobutoxy, and tert-butoxy-
hydrides[6,10] are non-polymeric (dimeric and trimeric) and therefore soluble in aro-
matic hydrocarbons. Aluminium methoxy- or ethoxyhydrides are associated to such an
extent that they are practically insoluble in common hydrocarbon solvents and even
ethers. Aluminium di-n-butoxyhydride and higher dialkoxyhydrides are soluble
only in tetrahydrofuran in which they are used as reducing reagents[6]. High solubility
of hydride I in ethers, but also in aromatic hydrocarbons, and low viscosity of even
very concentrated solutions indicates a low degree of association. According to a cryo-
scopic determination of the molecular weight compound I is dimeric in benzene solu-
tions in a wide concentration range[11] ($0.1 - 0.7$ m). Aluminium mono- and dialkoxy-
hydrides in which alkoxyl is isopropoxyl, n-butoxyl, and isobutoxyl are selective
reagents reducing aldehydes, ketones, and acyl chlorides to corresponding alcohols,
which, however, do not attack either the nitro group or the ester, amide, and nitrile
group[6], while hydride I does reduce the ester, amide and nitrile groups. In its reactivity
toward amides and nitriles it is similar to a freshly prepared solutions of aluminium
hydride. However, in contrast to it hydride I is also able to reduce a double bond
conjugated with a carbonyl or carboxyl group, and does not practically attack, at 0°C,
either the ketonic or the ester group of β-ketoesters (while aluminium hydride affords
corresponding diols in $70 - 80\%$ yield)[4]. When reductions with I were followed no posi-
tive results could be obtained even with terminal olefins at 100°C in benzene and
heptane, which contrasts with the results achieved with aluminium hydride and its
etherate which under such conditions add to the terminal double bond in good
yield[12]. From the above said it can be judged that hydride I is not a molecular com-
pound of aluminium hydride and aluminium 2-methoxyethanolate, i.e. $AlH_3.Al.$
$(OCH_2CH_2OCH_3)_3$.

EXPERIMENTAL

The starting compounds for reduction and standards for chromatographic analysis were of analytic-
al grade. The benzene solution of aluminium sesqui(2-methoxyethoxy)hydride (I) used for reduction
was prepared by reaction of commercial sodium bis(2-methoxyethoxy)dihydridoaluminate with
aluminium chloride[3]; its content of aluminium, hydride hydrogen, sodium, and chlorine was
determined analytically. For $C_9H_{24}Al_2O_6$ (282.2) calculated Al : H^- = 1 : 1.5; found Al : H^- =
= 1 : 1.44. The sample did not contain sodium. The chlorine content was less than 4% (alumi-
nium as basis of calculation).

Reduction and Dehalogenation

Manipulation and reactions with the hydride were carried out under exclusion of moisture,
in nitrogen atmosphere, and under stirring. The analyses of the reaction mixture were carried

out as in the preceding communications[1,2]. The conditions for the performance of single reactions are given in Tables I—III. As an example the reduction of benzyl cyanide is described here:

To a 25% benzene solution of 68·5 mmol of aluminium sesqui(2-methoxyethoxy)hydride (*I*) (calculated as hydride ion) 6·02 g (51·3 mmol) of benzyl cyanide in 6 ml of benzene were added over 10 minutes at 0°C under stirring and in a nitrogen atmosphere. The reaction mixture was heated under stirring at 80°C for 2 hours and decomposed with HCl (1 : 1). After extraction with ether and alkalization the basic products were eliminated by steam distillation and titrated. The aqueous solution which contained 45·1 mmol (87%) of amine hydrochloride was evaporated to dryness and the liberated amine extracted with ether, which was then dried and distilled off through a column. The distillation residue gave on chromatography 4·1 g (66%) of chromatographically pure 2-phenylethylamine, b.p. 195—198°C.

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