

ON THE BEHAVIOUR AND REACTIVITY OF SOLUTIONS  
OF COMPLEX HYDRIDES. VII.\*

REDUCTION BY SODIUM  
TRIS(2-DIMETHYLAMINOETHOXY)TETRAHYDRIDODIALUMINATE

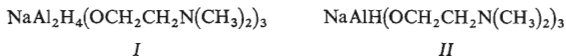
O. KŘÍŽ, J. MACHÁČEK and O. ŠTROUF

*Institute of Inorganic Chemistry,  
Academy of Sciences, 250 68 Řež-Prague*

Received July 14th, 1972

Reductive properties and dehalogenation ability of a new hydride, sodium tris(2-dimethylaminoethoxy)tetrahydridodialuminate, have been studied and compared with the properties of similar reagents.

In connection with a more extensive study of sodium alkoxyhydridoaluminates containing a donor atom on the  $\beta$ -carbon of the alkoxy group, *i.e.* nitrogen or oxygen<sup>1-3</sup>, we prepared sodium tris(2-dimethylaminoethoxy)tetrahydridodialuminate<sup>4</sup> (*I*) soluble in ether and aromatic hydrocarbons. Hydride *I* can also be prepared



in addition to other methods, by addition of an equimolar amount of aluminum hydride or of its complex with trimethylamine to sodium tris(2-dimethylaminoethoxy)hydridoaluminate<sup>4</sup> (*II*). Hydride *II* functions in this reaction as a strong Lewis base capable of expelling even trimethylamine from the stable complex  $\text{AlH}_3 \cdot 2(\text{CH}_3)_3\text{N}$ . In this paper reductive properties of hydride *I* are investigated and compared with the properties of the reaction components, *i.e.* hydride *II* and aluminum hydride, or its adduct with trimethylamine.

Reductive properties of hydride *I* are summarized in Table I. The carbonyl group of cyclohexanone is reduced quantitatively and that of benzophenone to 95% to the corresponding carbinol even at room temperature. The reduction of an ester group should be carried out at an elevated temperature. When  $\alpha,\beta$ -unsaturated aldehydes and esters are reduced the corresponding saturated alcohol is formed along with an appreciable amount of polymeric products and a very small amount of the  $\alpha,\beta$ -unsaturated alcohol. Even when the reduction was carried out at 0°C poly-

\* Part VI: This Journal 38, 842 (1973).

meration could not be prevented and the reaction mixture did not contain a larger proportion of  $\alpha,\beta$ -unsaturated alcohol. In the case of cinnamaldehyde the ratio of the formed 3-phenyl-1-propanol and polymeric products depends distinctly on the excess of hydride used for the reduction, while on reduction of ethyl cinnamate the yield of the saturated alcohol is affected only negligibly. Benzoic acid chloride may be reduced with hydride *I* to benzyl alcohol in good yield. Under milder conditions (25°C) 11% of benzaldehyde was isolated from the reaction mixture. However,

TABLE I

Reduction with a Toluene Solution of Sodium Tris(2-dimethylaminoethoxy)tetrahydridodialuminate

Reduced substance	$R^a$	Conc. of hydride	Temperature °C	Time h	Product <sup>b</sup> (yield, %)
Cyclohexanone	0.27	10	25	2	cyclohexanol (99)
Cyclohexanone	0.39	10	25	2	cyclohexanol (>99)
Benzophenone	0.75	25	25	4	diphenylmethanol (95) diphenylmethane (<1)
Benzophenone <sup>d</sup>	0.75	25	80	2	diphenylmethanol (25) diphenylmethane (2)
3-Phenyl-2-propenal <sup>c,d</sup>	0.27	10	25	1	3-phenyl-1-propanol (15)
3-Phenyl-2-propenal <sup>c</sup>	0.75	10	25	1	3-phenyl-1-propanol (85)
Ethyl caproate	0.52	15	25	2	1-hexanol (75)
Ethyl caproate	0.62	15	80	1	1-hexanol (99)
Ethyl cinnamate <sup>c,d</sup>	0.55	10	25	2	3-phenyl-1-propanol (15) 3-phenyl-1-propen-2-ol (2)
Ethyl cinnamate <sup>c,d</sup>	1.0	10	0	1	3-phenyl-1-propanol (20) 3-phenyl-1-propen-2-ol (2)
Ethyl cinnamate <sup>d</sup>	1.0	10	25	2	3-phenyl-1-propanol (20)
Ethyl cinnamate <sup>d</sup>	1.0	10	80	1	3-phenyl-1-propanol (21)
Benzoyl chloride <sup>c</sup>	0.75	15	80	1	benzyl alcohol (97)
<i>p</i> -Tolunitrile <sup>c</sup>	0.30	10	25	1	<i>p</i> -tolualdehyde (73) <sup>e</sup>
Nitrobenzene	2.25	15	25	2	azoxybenzene (~50) <sup>f</sup> , (43) <sup>g</sup> azobenzene (~5) <sup>f</sup>
Nitrobenzene	2.25	15	80	1	azoxybenzene (~40) <sup>f</sup> , (33) <sup>g</sup> azobenzene (<5) <sup>f</sup>

<sup>a</sup>  $R$  molar ratio of hydride and reduced substance; <sup>b</sup> the yields were determined gas chromatographically; <sup>c</sup> the reduction was carried out inversely; <sup>d</sup> the part of the polymeric products (70 to 85%) was determined as the residue of distillation at 200°C/12 Torr; <sup>e</sup> the aldehyde was isolated as an adduct with sodium hydrogen sulfite; <sup>f</sup> the part of azoxybenzene and azobenzene was determined semiquantitatively from the intensity of spots on thin-layer chromatograms; <sup>g</sup> the yield of azoxybenzene isolated by crystallisation from *n*-hexane.

TABLE II

Dehalogenation with a 15% Toluene Solution of Sodium Tris(2-dimethylaminoethoxy)tetrahydridodialuminate (reaction time 2 h)

$R^a$	Temperature, °C	Heptane, % <sup>b</sup>	$R^a$	Temperature, °C	Benzene, % <sup>b</sup>
	1-chloroheptane			chlorobenzene	
0.3	25	< 1	0.5	25	< 1
0.3	80	21	0.5	80 <sup>c</sup>	4
0.5	25	3		bromobenzene	
0.5	80	47	0.5	25	22
1.0	25	6	0.5	80	47
1.0	80	76		iodobenzene	
	1-bromoheptane		0.3	25	20
0.5	25	49	0.3	80	27
0.5	80	>99	0.5	25	40
			0.5	80	52
			1.0	25	78
			1.0	80	91

<sup>a</sup>  $R$  is the molar ratio of hydride and the reduced substance; <sup>b</sup> the yield was determined by gas chromatography; <sup>c</sup> 10 h.

aldehyde was isolated in a good yield from the reduction products of *p*-tolunitrile. Reduction of nitrobenzene gave azoxybenzene as the main product even when the excess of hydride *I* was appreciable (350%, per azobenzene). The product contained only a small amount of azobenzene. An attempt at hydroalumination of the olefinic double bond in (+)-camphene was unsuccessful even when the mixture was allowed to react at 100°C for several days.

From the results it follows that the reductive properties of hydride *I* and aluminum hydride or sodium tris(dimethylaminoethoxy)hydridoaluminate (*II*) are different. For example, in contrast to hydride *I* aluminum hydride (either in the form of ethate<sup>5</sup> or an adduct with trimethylamine<sup>6</sup>) reduces saturated carboxylic acid esters at a greater rate than ketones, it reduces benzophenone up to diphenylmethane<sup>7</sup>, it does not attack the double bond in  $\alpha,\beta$ -unsaturated carbonyl and carboxyl compounds<sup>8</sup>, and during hydroalumination it adds to the olefinic double bond<sup>9</sup>. The most striking difference between hydride *I* and hydride *II* is manifest in the reduction of nitrobenzene to azoxybenzene in the first case, and a reduction up to azobenzene<sup>1</sup> in the second.

The results of dehalogenation are presented in Table II. From the course of the reaction it is evident that the reaction depends strongly on the molar excess of the hydride. With the exception of the dehalogenation of 1-bromoheptane, it is evident

that maximally a quarter of the hydride hydrogen takes part in the reaction in all cases; this means that in halogenation the hydride hydrogen from the complex hydride *II* is utilised, and that the hydrogen atoms originating from aluminum hydride do not participate in the reaction. The results of dehalogenation with a 300% excess of hydride *I* are practically identical with those<sup>1</sup> obtained when dehalogenation was carried out with hydride *II*. In the dehalogenation of 1-bromoheptane other hydride hydrogens of the reagent are also utilised and therefore the excess of hydride must not be as high as above. This is in agreement with the dehalogenation of alkyl bromide with aluminum hydride<sup>10</sup>.

### EXPERIMENTAL

The starting compounds for the reduction and the chromatographic standards were of analytical grade. Crystalline sodium tris(2-dimethylaminoethoxy)tetrahydridodialuminate (*I*) was prepared on reaction of sodium tetrahydridoaluminate and aluminum tris(2-dimethylamino)ethoxylate in toluene<sup>4</sup>. The manipulations and the reactions with hydride *I* were carried out under exclusion of moisture in a nitrogen atmosphere, using a method described earlier<sup>1-3</sup>. The conditions are given in Tables I and II.

### REFERENCES

1. Kříž O., Macháček J.: *This Journal* 37, 2175 (1972).
2. Kříž O., Čásenský B., Štrouf O.: *This Journal* 38, 842 (1973).
3. Kříž O., Čásenský B., Štrouf O.: *This Journal* 38, 2076 (1973).
4. Macháček J., Čásenský B., Abrham K.: *This Journal* 38, 343 (1973).
5. Brown H. C., Yoon N. M.: *J. Am. Chem. Soc.* 88, 1464 (1966).
6. Hanslík T., Mareš F.: Unpublished results.
7. Blackwell J., Hickinbottom W. J.: *J. Chem. Soc.* 1961, 1405.
8. Jorgenson M. J.: *Tetrahedron Letters* 1962, 559.
9. Ziegler K., Krupp F., Zosel K.: *Ann.* 629, 241 (1960).
10. Yoon N. M., Brown H. C.: *J. Am. Chem. Soc.* 90, 2927 (1968).

Translated by Ž. Procházka.