

REDUCTION OF ORGANIC SUBSTANCES  
BY SODIUM MONOHYDRIDO-TRIS  
(2-METHOXYETHOXO)BORATE\*

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Sodium monohydrido-tris(2-methoxyethoxo)borate, readily soluble in aromatic hydrocarbons and ethers, reduces aldehydes and ketones and at an elevated temperature also esters of carboxylic acids to the corresponding alcohols with a satisfactory yield.

We recently prepared<sup>1</sup> sodium monohydrido-tris(2-methoxyethoxo)borate,  $\text{NaBH} \cdot (\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$  (*I*), a new hydride in the series of complex alkoxyhydrides with two donor atoms in the alkoxy group. Hydride *I* disproportionates in various solvents at laboratory temperature to c. 20%, giving sodium tetrahydridoborate,  $\text{NaBH}_4$  (*II*), and sodium tetrakis(2-methoxyethoxo)borate,  $\text{NaB}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4$  (*III*). This disproportionation is complete with the lithium and potassium analogues<sup>1</sup>. The lithium analogue has been studied in greater detail<sup>2</sup>, showing that this is not a simple mixture of lithium tetrahydridoborate,  $\text{LiBH}_4$  (*IV*), and lithium tetrakis(2-methoxyethoxo)borate,  $\text{LiB}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4$  (*V*), but a molecular compound  $\text{LiBH}_4 \cdot \text{LiB}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4$  (*VI*). Compound *VI* exhibits decreased reactivity with compound *IV* alone in hydrolysis<sup>1</sup> and reduction of organic compounds<sup>2</sup>. An analogous molecular compound,  $\text{NaBH}_4 \cdot \text{NaB}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4$  (*VII*), is formed from hydrides *II* or *I* and *III* (ref.<sup>2</sup>).

In the present paper, reduction of some organic substances by an equilibrium mixture of hydride *I* and compound *VII* in benzene, *i.e.* at a molar ratio of the two substances of 20 : 1 (refs<sup>1,2</sup>) is studied. At this ratio, both forms of hydride hydrogen, *i.e.* hydrogen bound in alkoxyhydride *I* and that present in molecular compound *VII*, are present in the reaction mixture, at least at the beginning of the reaction. However, considering that hydridoalkoxoborates are generally stronger reductants than the corresponding tetrahydridoborates<sup>3,4</sup> and that compound *VII* should be a weaker reductant than *II* by analogy with *VI*, the results of the reductions can be interpreted as resulting from reduction by hydride *I*.

\* Part XIV in the series On the Behavior and Reactivity of Solutions of Complex Hydrides; Part XIII: This Journal *41*, 193 (1976).

It follows from Table I that saturated aldehydes and ketones are reduced virtually quantitatively to the corresponding alcohols within 2 hours at 25°C, even if only a 30% excess of the reductant is present. The reduction of aromatic aldehydes and ketones is c. 50% complete under these conditions; the yield can be increased by increasing the hydride-to-carbonyl compound ratio or by considerable prolonging of the reaction time. An increase in the reaction temperature does not improve the alcohol yield, as side products are formed. With  $\alpha,\beta$ -unsaturated aldehydes and ketones only the carbonyl group is reduced with formation of the corresponding unsaturated alcohols; their yield is, however, decreased by formation of polymeric substances. In the reduction of 1-phenyl-1-butene-3-one, the expected alcohol does not appear at all in the reaction mixture, as it is apparently dehydrated under the reaction conditions and converted into 1-phenyl-1,3-butadiene. The reduction of acyl chlorides by a 150–200% excess of hydride *I* at 25°C gives 70 to 90% alcohol yields. If the reduction is carried out with the stoichiometric hydride amount at 5°C, using the inversion method, the appropriate aldehyde is formed; c. 25% n-hexanal is formed from hexanoyl chloride and over 50% benzaldehyde from benzoyl chloride (Table I), but always in a mixture with the corresponding alcohol. Up to 50% n-hexanal was obtained from hexanoyl chloride by the reaction at -78°C (tetrahydrofuran, 6 h). As could be expected, carboxylic acids are not reduced at all by hydride *I*, as was verified on benzoic acid. The reduction of carboxylic acid esters as far as to the alcohol is rather slow; for example, 76% n-hexanol is formed after 2 h-reduction of ethyl hexanoate by a 200% excess of hydride *I* at 80°C (Table I) and the alcohol yield is virtually quantitative only when a 300% hydride excess is used and the reaction time is increased to 15 h. The reaction rate of the ester reduction is increased when benzene is replaced by tetrahydrofuran or 1,2-dimethoxyethane (Table II). Nitrogen-containing acid derivatives – amides, lactams and nitriles – are reduced only slightly by hydride *I* in benzene or in etheric solvents (Tables I and II); nitriles of aromatic acids are exceptional, yielding about 30% of the corresponding amides at the solvent boiling point. Nitrobenzene yields azoxybenzene and azobenzene as the main products; a 3 : 1 mixture of these substances (16% conversion) is formed at laboratory temperature, while a 1 : 1 mixture (50% conversion) is formed at the benzene boiling point. Aryl halide hydrogenolysis does not proceed to a very high extent under the conditions studied. It follows from the comparison of the reducing properties of *I* with the reducing efficiency of sodium monohydrido-trimethoxyborate,  $\text{NaBH}(\text{OCH}_3)_3$  (*VIII*) (ref.<sup>3</sup>), that, similar to the series of sodium hydridoalkoxo-aluminates<sup>5</sup>, the hydridoborate *I* with the second donor atom in the alkoxy, is a somewhat stronger reductant.

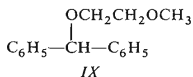
It should be mentioned that, during the reduction of benzophenone, 1-(diphenylmethoxy)-2-methoxyethane (*IX*) appears among the reaction products in addition to the expected diphenylmethanol. The content of *IX* is somewhat higher if the reduction is performed at an elevated temperature and approaches 20% in the reaction

TABLE I

Reduction by a 10% Benzene Solution of Sodium Monohydridotris(2-methoxyethoxy)borate (I) for 2 h at 25°C

Substance reduced	Product	Yield, %	R <sup>a</sup>
n-Hexanal	n-hexanol	98 <sup>b</sup>	1.3
Benzaldehyde	benzyl alcohol	51 <sup>b</sup>	1.3
Benzaldehyde <sup>c</sup>	benzyl alcohol	92 <sup>b</sup>	1.3
Benzaldehyde	benzyl alcohol	93 <sup>b</sup>	2
3-Phenyl-2-propenal	3-phenyl-2-propene-1-ol	68 <sup>b</sup>	2
3-Phenyl-2-propenal <sup>d</sup>	3-phenyl-2-propene-1-ol	49 <sup>b</sup>	2
Cyclohexanone	cyclohexanol	98 <sup>b</sup>	1.3
1-Phenyl-3-butanone	1-phenyl-3-butanol	98 <sup>b</sup>	1.3
Benzophenone	diphenylmethanol	46 <sup>b</sup>	1.3
Benzophenone	diphenylmethanol	84 <sup>b</sup>	2
1-Phenyl-1-butene-3-one	1-phenyl-1,3-butadiene	33 <sup>b</sup>	1.5
Hexanoyl chloride <sup>e</sup>	n-hexanal	26 <sup>b</sup>	1
Hexanoyl chloride	n-hexanol	72 <sup>b</sup>	2.5
Benzoyl chloride <sup>e</sup>	benzaldehyde	54 <sup>b</sup>	1
Benzoyl chloride	benzyl alcohol	90 <sup>b</sup>	3
Benzoic acid <sup>d</sup>	benzyl alcohol	0 <sup>b</sup>	3
Ethyl hexanoate <sup>d</sup>	n-hexanol	76 <sup>b</sup>	3
Ethyl benzoate <sup>d</sup>	benzyl alcohol	79 <sup>b</sup>	3
Phenylacetone <sup>d,f</sup>	2-phenylethylamine	2 <sup>g</sup>	4
Benzonitrile <sup>d,f</sup>	benzylamine	28 <sup>h</sup>	3
Butyramide <sup>d,f</sup>	n-butylamine	0 <sup>h</sup>	4
Acetanilide <sup>d,f</sup>	n-ethylaniline	2 <sup>h</sup>	4
$\epsilon$ -Caprolactam <sup>d,f</sup>	hexamethyleneimine	2 <sup>h</sup>	4
Nitrobenzene <sup>f</sup>	azoxybenzene	12	6
	- azobenzene	4	6
Nitrobenzene <sup>d,f</sup>	azoxybenzene	26	6
	+ azobenzene	25	6
Bromobenzene	benzene	0 <sup>i</sup>	2
Bromobenzene <sup>d,f</sup>	benzene	4 <sup>i</sup>	2
Iodobenzene	benzene	0 <sup>i</sup>	2
Iodobenzene <sup>d,f</sup>	benzene	11 <sup>i</sup>	2

<sup>a</sup> The ratio of hydride mol to the mol of the substance reduced. <sup>b</sup> Product yield determined gas chromatographically. <sup>c</sup> Reduction time 60 h. <sup>d</sup> Reduction at the solvent boiling point. <sup>e</sup> Reduction carried out at 5°C. <sup>f</sup> Reduction time 4 h. <sup>g</sup> Yield determined from the loss in benzyl cyanide. <sup>h</sup> Yield of amine obtained by distillation with water vapour. <sup>i</sup> Yield determined gas chromatographically from the loss of halogeno benzene.



in benzene at 80°C. The content of *IX* in the reaction mixture does not further increase when the reaction time is prolonged. As we encountered an analogous phenomenon earlier<sup>6</sup>, in the reduction of benzophenone with *VI*, it can be assumed that this reaction, in addition to alkylation of aromatic hydrocarbons by sodium dihydro-bis(2-alkoxyethoxy)aluminates<sup>7,8</sup>, is another reaction made possible by the presence of the second oxygen atom in the β-position of the hydride alkoxy.

### EXPERIMENTAL

Sodium monohydrido-tris(2-methoxyethoxy)borate (*I*) was prepared by the same procedure as previously<sup>1</sup>. The analysis of a 50% benzene solution of *I* gave a ratio of Na : B : H<sup>-</sup> = 1.005 : 1 : 1.016. The organic substances to be reduced were distilled or crystallized from a suitable solvent before the reaction; the solvents used for the reduction were first dried and then distilled from a NaAlH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub> solution.

#### Reduction of Organic Compounds by Hydride *I*

The reactions were carried out in a dry nitrogen atmosphere at 25°C or at the solvent boiling point, with stirring, in the same way as in an earlier work<sup>2</sup>. In the reduction of benzophenone, 1-(diphenylmethoxy)-2-methoxyethane (*IX*) formed as a side product was isolated by preparative gas chromatography on 3% polyethylene glycol 20M deposited on silanized Chromosorb W. The substance yields a mass spectrum with a molecular ion at *m/e* 242 (9%) and the most pronounced fragments at *m/e* 183 (64%) and 167 (100%), corresponding to dissociation of <sup>1</sup>CH<sub>2</sub>CH<sub>2</sub>.OCH<sub>3</sub> and <sup>1</sup>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, respectively, from the molecular ion of the original molecule

TABLE II

Reduction by a 10% Sodium Monohydrido-tris-(2-methoxyethoxy)borate (*I*) in Various Solvents for 1 h at 25°C

Substance reduced	Product	Yield, %			R <sup>a</sup>
		benzene	THF <sup>b</sup>	MG <sup>c</sup>	
Cyclohexanone	cyclohexanol	84	96	96	1.1
Ethyl hexanoate	n-hexanol	12 <sup>d</sup>	28	23	3.2
Phenylacetonitrile	2-phenylethylamine	2	3	3	5
ε-Caprolactam	hexamethyleneimine	traces	traces	traces	5
p-Tolunitrile	p-methylbenzylamine	30	21	20	4

<sup>a</sup> Ratio of mol of hydride *I* to mol of the substance reduced. <sup>b</sup> Tetrahydrofuran. <sup>c</sup> 1,2-Dimethoxyethane. <sup>d</sup> The yield is 29% after 4 h.

of IX. The  $^1\text{H-NMR}$  spectrum of the substance at 100 MHz contains singlets at  $\delta = 3.30$  ppm (integral intensity 3), 3.50 ppm (4), 5.27 ppm (1) and a broad split singlet at  $\delta = 7.18$  ppm (11) (vs tetramethylsilane), corresponding to  $\text{CH}_3\text{O}-$ ,  $-\text{CH}_2\text{CH}_2\text{O}-$ ,  $-\text{CH}-$  and  $\text{C}_6\text{H}_5-$  groups of compound IX, respectively.

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#### REFERENCES

1. Sochor P., Kadlecová H., Štrouf O.: *This Journal* 40, 3177 (1975).
2. Kříž O., Sochor P.: *This Journal* 41, 193 (1976).
3. Brown H. C., Mead E. J.: *J. Amer. Chem. Soc.* 75, 6263 (1953).
4. Brown H. C., Mead E. J., Shoaf C. J.: *J. Amer. Chem. Soc.* 78, 3616 (1956).
5. Kříž O., Čásenský B., Štrouf O.: *This Journal* 38, 2076 (1973).
6. Kříž O.: Unpublished results.
7. Černý M., Málek J.: *This Journal* 39, 842 (1974).
8. Málek J., Černý M.: *J. Organometal. Chem.* 84, 139 (1975).

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