

REACTIONS OF ALKALI HYDRIDES WITH 2-METHOXYETHYL BORATE.  
SYNTHESIS OF SODIUM  
MONOHYDRIDO-TRIS(2-METHOXYETHOXY)BORATE

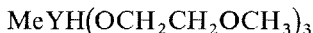
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Alkali monohydrido-tris(2-methoxyethoxy)borates are formed by reaction of the corresponding alkali hydride (LiH, NaH, KH) with an equimolar amount of 2-methoxyethyl borate. However, under the conditions of the reaction they disproportionate to tetrakis(2-methoxyethoxy)borate and tetrahydridoborate; the lithium and the potassium salts disproportionate completely, the sodium one to an extent of 16 mol % only. The properties of the prepared sodium monohydrido-tris(2-methoxyethoxy)borate (84% purity) were comparable with those of the analogous sodium monohydrido-tris(2-methoxyethoxy)aluminate.

In a connexion with our research of sodium monohydridoalkoxyalkoxyaluminates we have prepared sodium monohydrido-tris(2-methoxyethoxy)borate (*Ib*),  $\text{NaBH} \cdot (\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$ , which is the boron analogue of the previously described<sup>1</sup> sodium monohydrido-tris(2-methoxyethoxy)aluminate (*Ia*),  $\text{NaAlH}(\text{OCH}_2\text{CH}_2 \cdot \text{OCH}_3)_3$ . The reason for it was the fact that with the full coordinative saturation of the central atom in *Ib* the association and the solvation phenomena, affecting the behaviour of the hydride in a solution, can occur only on the sodium atom, having free coordination centres, whereas in *Ia* these phenomena can also involve the remaining two coordination centres of the aluminium atom. Comparison of the properties of the two analogous hydrides, *Ia* and *Ib*, was expected to indicate rough similarity of their structural fundamentals.



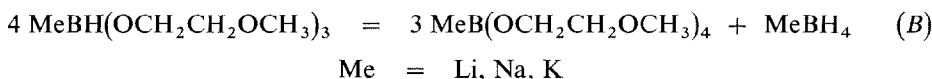
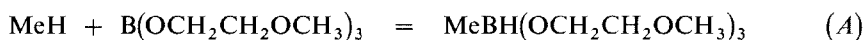
*Ia*; Me = Na, Y = Al   *Ib*; Me = Na, Y = B   *Ie*;  $\text{NaBH}(\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2)_3$

*Ic*; Me = Li, Y = B   *Id*; Me = K, Y = B

In the first place we investigated, by <sup>11</sup>B-NMR spectroscopy and/or polarography, the extents of disproportionation of compounds *Ib*–*Id*, arising from the reaction<sup>2–7</sup>

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of an alkali hydride with 2-methoxyethyl borate (equation (A)), to tetrakis(2-methoxyethoxy)borate and tetrahydridoborate of the alkali metal (equation (B)).



The effect of replacement of the oxygen atom at the  $\beta$  position of the ethoxy group by a nitrogen atom was investigated by comparing the reaction courses of the transient intermediate *Ie* and the compound *Ib*.

## EXPERIMENTAL

### Chemicals

2-Methoxyethyl borate, prepared by reaction of boric acid with 2-methoxyethanol<sup>8,9</sup> (yield 75%), boiled at 126–128°C/8 Torr; 2-dimethylaminoethyl borate<sup>10</sup>, b.p. 165–168°C/8 Torr, was prepared by an analogous esterification of 2-dimethylaminoethanol (yield 80%). Both esters proved to have the expected compositions and were chromatographically pure. Prior to use they were dried by distillation from NaH *in vacuo*. Crystalline lithium and sodium tetrakis(2-methoxyethoxy)borates were obtained in 100% yields by reactions<sup>11</sup> of 2-methoxyethyl borate with equimolar amounts of LiOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub> and NaOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub> in benzene. The prepared sodium hydride<sup>12,13</sup> had a purity of 95% (specific surface of 2.5 m<sup>2</sup>/g); the purity of lithium hydride<sup>14</sup> and potassium hydride was 94% and 97%, respectively. Pre-dried and distilled tetrahydrofuran, diethyl ether and benzene were re-distilled just before use from NaAlH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>. Unless otherwise stated, all operations in the syntheses were carried out under nitrogen.

### Methods

Polarographic analyses were carried out with an apparatus LP-60 (Laboratorní přístroje, Prague), recorders EZ 2 (sensitivity 3.6 · 10<sup>-9</sup> A/cm), Radelkis OH 102 and Radelkis OH 993 being employed. pH was measured with a pH-meter Radelkis OP-206 connected to a glass electrode (Radiometer, type G 202 B) and a reference saturated calomel electrode (s.c.e.), prepared according to Hanzlík<sup>15</sup>. For polarography a dropping mercury electrode was employed; the time of a drop was 2.94 s at a mercury head of 70 cm and the potential of s.c.e. in 0.1M-KCl. The flow rate of mercury was  $m_h = 1.82$  mg/s. A universal, unit-built measuring cell, with a jacket, was used<sup>16</sup>. A constant temperature was maintained with an ultrathermostat U 10 with a precision of ±0.02°C. The measuring cell was separated from the reference electrode by a liquid bridge with a carbon junction. Prior to starting a series of experiments the pH-meter was set with 0.01M sodium tetraborate. pH was measured before and after hydrolysis. The differences between the measured pH values in the individual measurements did not exceed 0.08. The accuracy of a measurement was ±0.02 pH units. Britton–Robinson's buffers<sup>17</sup> were used; their ionic strengths were brought to  $\mu = 0.15$  by additions of sodium perchlorate. The chemicals were of A. G. purity. The initial concentration of borohydride ions was 0.001M. The inert gas was argon. Infrared spectra were measured in the region 3800–700 cm<sup>-1</sup> with a double-beam spectrophotometer UR 10 Zeiss, Jena in cells of NaCl, 0.04 to 0.15 mm thick, with 5 to 10% solutions in CCl<sub>4</sub> or with a 14% solution in benzene.

<sup>11</sup>B-NMR spectra were measured in a Czechoslovak prototype spectrograph at 32.0 MHz with B(OCH<sub>3</sub>)<sub>3</sub> as internal standard. Radiographs were obtained by the Debye-Scherrer method, the chamber diameter being 114.6 mm. Radiation Cu<sub>Kα</sub> was filtered through a nickel filter in Lindemann's capillaries, 0.5 or 0.3 mm thick. Molecular weights were determined cryoscopically in an apparatus described previously<sup>18</sup>. Alkali metals were determined by titration after hydrolysis. Boron was determined after an addition of mannitol by titration<sup>19</sup> with a volumetric solution of NaOH. The hydride hydrogen was determined volumetrically after decomposition with 20% sulphuric acid.

#### Sodium Monohydrido-tris(2-methoxyethoxy)borate (*Ib*)

To NaH (1.1 mol) in benzene or tetrahydrofuran (300 ml) was added dropwise the ester (1 mol) at such a rate as to keep the mixture boiling. After 3 h the mixture was cooled to room temperature, the unreacted NaH was filtered off, the solvent removed by distillation and the residue was dried at 60°C/0.1 Torr for 3 h. *Ib* was obtained in a practically quantitative yield as a yellowish viscous liquid. The ratio Na : B : H<sup>-</sup> determined by analysis was 1.08 : 1.08 : 1.0. *Ib* was infinitely soluble in benzene, diethyl ether and tetrahydrofuran.

#### Reaction of Lithium Hydride with 2-Methoxyethyl Borate

The reaction was conducted in benzene as in the reaction of sodium hydride. After cooling the filtrate to room temperature crystals of the product separated (80% yield); these were washed with diethyl ether and dried at 50°C/10 Torr for 5 h. Analyses determined a ratio of Li : B : H<sup>-</sup> = 1.01 : 1.11 : 1.00. Identity of the Debye-Scherrer radiograph of the product with that of lithium tetrakis(2-methoxyethoxy)borate, and the presence of an only anodic wave with a half-wave potential  $E_{1/2} = -0.18$  V vs s.c.e., corresponding to  $E_{1/2}$  of tetrahydridoborate ions, proved the product to be a mixture of LiBH<sub>4</sub> and lithium tetrakis(2-methoxyethoxy)borate. Hydrolysis of this product (followed polarographically) proceeded as a pseudomonomolecular reaction in buffered aqueous solutions of pH 7.50 to 10.15. The activation energy of the hydrolysis was  $E_a = 19 \pm 0.5$  kcal/mol, which is approximately a double of that found<sup>20</sup> for the reaction of BH<sub>4</sub><sup>-</sup> with H<sub>3</sub>O<sup>+</sup>.

#### Reaction of Potassium Hydride with 2-Methoxyethyl Borate

The reaction was conducted in benzene, like in the foregoing case. After cooling, filtration, distilling-off the solvent and drying (5 h, 80°C/0.1 Torr) there was obtained a product (90%) with the ratio K : B : H<sup>-</sup> = 1.00 : 1.13 : 1.01. According to its radiograph it was not crystalline. Polarography in 0.1M-NaOH revealed only one anodic wave,  $E_{1/2} = -0.19$  V, corresponding to BH<sub>4</sub><sup>-</sup>.

#### Reaction of Sodium Hydride with 2-Dimethylaminoethyl Borate

The reaction was conducted with equimolar amounts of NaH and the ester in boiling tetrahydrofuran. In the course of the reaction a sediment separated, which according to chemical and Debye-Scherrer analyses was sodium tetrakis(2-dimethylaminoethoxy)borate. The filtrate contained Na, B and hydride hydrogen in a non-stoichiometric ratio.

#### Reduction of 3,3,5-Trimethylcyclohexanone by Hydride *Ib*

The reduction was accomplished in tetrahydrofuran at 25°C as previously described<sup>21</sup>. In 0.5 h the reaction was complete. Gas chromatography of stereoisomeric 3,3,5-trimethylcyclohexanols

detected 79% of the *trans* isomer, which figure was not changed even after 3 more hours. In the reduction of 3,3,5-trimethylcyclohexanone by the hydride *Ia* in tetrahydrofuran under similar conditions we had obtained<sup>22</sup> 77% of *trans*-3,3,5-trimethylcyclohexanol.

## RESULTS AND DISCUSSION

Esters of boric acid react with alkali hydrides and form monohydrido-tris(alkoxy)-borates<sup>2-7</sup>, where the valency saturation of the boron atom is full. Stability of these alkoxy hydrides depends on both the alkali metal and the nature of the substituent.

We chose an alkoxy substituted in its  $\beta$ -position with a group having a donor atom, since substituents of this type had proved to have an essential effect on the properties of hydridoalkoxy aluminates. This effect is ascribed to intramolecular solvation by the donor at the  $\beta$ -position, giving rise to the thermodynamically favoured five-membered ring. In our study we chose the most frequently used  $\beta$ -alkoxyalkoxy group, *viz.* 2-methoxyethoxyl, having an oxygen donor atom, and, for comparison, 2-dimethylaminoethoxyl, with nitrogen as the donor atom. In the latter case, however, there formed, instead of the expected hydride *Ie*, a mixture of compounds, whose composition did not conform to the simple disproportionation of *Ie* to tetrakis(2-dimethylaminoethoxy)borate and  $\text{BH}_4^-$  (equation (B)) and which was not further investigated. The more complex course of the reaction, compared to the reaction of  $\beta$ -methoxyethoxy derivatives, is evidently due to greater steric demands of the 2-dimethylamino group.

The stability of  $\beta$ -methoxyethoxy derivatives depends on the alkali metal, which functions as an acceptor in intramolecular solvation. The best acceptor of the series lithium, sodium and potassium is sodium, since with this alkali metal the disproportionation proceeds to about 16 mol %, whereas with the lithium and potassium analogues, *Ic* and *Id*, the disproportionation is complete. The result of the disproportionation is a stoichiometric mixture of the tetraalkoxy and the tetrahydrido derivatives (equation (B)).

The formation of *Ib* was corroborated by <sup>11</sup>B-NMR and IR spectra. The <sup>11</sup>B-NMR spectra (32.0 MHz) of 30% solutions of *Ib* in benzene, diethyl ether and tetrahydrofuran at room temperature exhibited a doublet with an interaction constant  $J = 125$  c.p.s. and a chemical shift  $\delta = -5.4$  p.p.m. (*vs*  $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ ). The stretching B—H vibrations in the IR spectra of *Ib* were at 2135 and 2300  $\text{cm}^{-1}$ , with an inflexion on the lower side of the wave numbers. The positions of the bands agree with the expected ones<sup>23</sup>. The deformation B—H vibrations (1000–1200  $\text{cm}^{-1}$ ) were overlapped by either the B—O—C valence bands or the C—O stretching vibration. Completely absent in *Ib* was the stretching vibration of the pseudomultiple bond  $\text{B} \div$  (1300–1400  $\text{cm}^{-1}$ ) on the trigonally  $sp^2$  hybridized boron atom, present in esters of boric acid. However, the spectrum contained the B—O—C vibration at 960  $\text{cm}^{-1}$  with an  $sp^3$  hybridized boron atom.

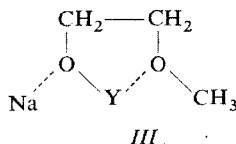
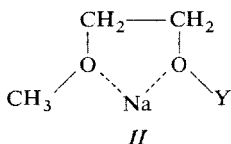
The extent of disproportionation of *Ib*, according to equation B, was determined

from the  $^{11}\text{B}$ -NMR spectra and polarographically. The symmetry of the doublet in the NMR spectra on the higher-field side was upset by superimposition of a singlet at  $\delta = -1.3$  p.p.m. (*vs*  $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ ). The location of this singlet agreed with the experimental value of the chemical shift of sodium tetrakis(2-methoxyethoxy)-borate in benzene ( $\delta = -1.7$  p.p.m. *vs*  $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ ). From the areas of the doublet and the singlet we estimated the contents of the individual compounds: 84 mol% of *Ib*, 12 mol% of sodium tetrakis(2-methoxyethoxy)borate and, from stoichiometry, 4 mol% of  $\text{NaBH}_4$ . This equilibrium composition was not affected by the solvent, not even by water.

In polarography in 0.1M-NaOH containing gelatine (0.02%) *Ib* gave two irreversible anodic waves, one of which, having a half-wave potential  $E_{1/2} = -0.18$  V *vs* S.C.E., was identical with that observed with  $\text{NaBH}_4$ . The remaining anodic wave, of  $E_{1/2} = -0.67$  V *vs* S.C.E., belonged to the compound *Ib*, in accordance with the above-mentioned  $^{11}\text{B}$ -NMR spectrum. The heights of the diffusion waves were used to calculate the contents of  $\text{NaBH}_4$  and *Ib*, which were found identical with those estimated from the  $^{11}\text{B}$ -NMR spectra in organic solvents. The diffusion character of the second wave is evident from the linear dependence of the limit current,  $i_d$ , on concentration and on  $\sqrt{h}$ . On an AC polarographic record the top of the peak occurred at  $E_p = -0.62$  V *vs* S.C.E.. The difference between  $E_{1/2}$  and  $E_p$  also confirms the irreversibility of the electrode process. *Ib* was relatively stable in alkaline aqueous solutions, as was observed by polarography of this hydride dissolved in 0.4M-NaOH. Only a half of the hydride was hydrolysed after 24 h.

Alkoxy-substitution in sodium tetrahydridoborate is known to increase the reducing power. The same has been found to be true of *Ib*, which was shown by preliminary experiments to be a stronger reducing agent than  $\text{NaBH}_4$ . In this aspect it resembles sodium monohydrido-tris(methoxy)borate,  $\text{NaBH}(\text{OCH}_3)_3$ , which also exhibits similar wave numbers<sup>24</sup> for the B—H bond (2135 and 2300  $\text{cm}^{-1}$ ). Unlike  $\text{NaBH} \cdot (\text{OCH}_3)_3$ , however, the anodic wave half-wave potential of *Ib* ( $E_{1/2} = -0.67$  V) was shifted to the negative side from that of  $\text{NaBH}_4$  ( $E_{1/2} = -0.18$  V); this shift accords with the higher reducing power.

We compared the properties of compounds *Ib* and *Ia*, which are analogues but differ in the electron shells on the central atom. In *Ib* the central atom (boron) is fully coordination-saturated, so that it cannot function as an acceptor in solvation, whereas the free 3d orbitals of the central (aluminium) atom in *Ia* make solvation possible. Consequently, in the former compound solvation can occur on sodium only (*II*), whereas in the latter the central atom *Y*(*III*) may also be involved.



All the compared properties of the amorphous *Ib* and *Ia*, soluble in ethers as well as in aromatic solvents, were found to be similar. Thus the association degree determined cryoscopically in benzene was  $n = 2$  to 3 for either hydride, and, which is more important, was independent of concentration in both cases<sup>18</sup>. The stretching vibration of the  $\beta$ -methoxyethoxyl ligands in the IR spectra were comparable (except the band at  $960\text{ cm}^{-1}$ , associated with B—O—C). The similarity of the two hydrides manifested itself even in the stereochemical course of reduction of 3,3,5-trimethylcyclohexanone; the ratios of the formed stereoisomeric alcohols were practically identical<sup>22</sup>. Consequently, the molecules of the two hydrides are likely to share some structural features.

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