

SOLVATED LITHIUM TETRAHYDRIDOBORATE AND SODIUM TETRAHYDRIDOBORATE SOLUBLE IN BENZENE

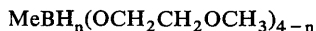
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Lithium tetrahydridoborate and lithium tetrakis(2-methoxyethoxy)borate yield conjugate solutions at a 1 : 1 ratio in benzene, the lower containing 42.8% and the upper 3.3% of LiBH_4 . $\text{LiB}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4$ at 23°C. The existence of solvated lithium tetrahydridoborate in a benzene solution was verified by ^{11}B -NMR and IR spectroscopy. X-ray diffraction of the solvate exhibited only the lines corresponding to lithium tetrakis(2-methoxyethoxy)borate and tetrahydridoborate. In its reducing properties the benzene solution of $\text{LiBH}_4 \cdot \text{LiB}(\text{OCH}_2\text{CH}_2\text{COH}_3)_4$ resembles lithium tetrahydridoborate in tetrahydrofurane or dioxane, with the difference that the reduction requires a longer reaction time. From the results of ^{11}B -NMR it can be assumed that the solubility of sodium tetrahydridoborate in a benzene solution of sodium monohydrido-tris(2-methoxyethoxy)borate or sodium tetrakis(2-methoxyethoxy)borate is caused by solvation of the sodium atom of tetrahydridoborate.

During the reaction of the 2-methoxyethyl ester of boric acid with lithium, sodium and potassium hydrides monohydridotrialkoxoborates, *II*, are formed; only sodium monohydridotris(2-methoxyethoxy)borate (*IIb*) is stable in a benzene solution¹. The lithium and potassium analogues (*IIa* and *IIc*, respectively) disproportionate to give a stoichiometric mixture of tetraalkoxo and tetrahydrido derivatives. Some literature sources^{2,3} state that disproportionation of simple lithium monohydrido-trialkoxoborates, $\text{LiBH}(\text{OR})_3$, $\text{R} = \text{CH}_3$, $i\text{-C}_3\text{H}_7$, $t\text{-C}_4\text{H}_9$, leads to the formation of relatively stable dihydridoalkoxoborates $\text{LiBH}_2(\text{OR})_2$,



I ($n = 0$), *II* ($n = 1$), *III* ($n = 2$), *IV* ($n = 4$);

a ($\text{Me} = \text{Li}$), *b* ($\text{Me} = \text{Na}$), *c* ($\text{Me} = \text{K}$),

and thus this alternative was also considered in the present paper, where $\text{R} = \text{CH}_3\text{O} \cdot \text{CH}_2\text{CH}_2$.

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TABLE I

The ^{11}B -NMR Spectrum of $\text{LiB}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4$ (*Ia*), LiBH_4 (*IVa*) and $\text{LiBH}_4 \cdot \text{LiB}(\text{OCH}_2 \cdot \text{CH}_2\text{OCH}_3)_4$ (*V*)

Compound ^a	BH_4 region	$\text{B}(\text{OR})_4$ region
<i>Ia</i> ^{b,c}	—	—2.2 (s)
<i>IVa</i> ^{d,e}	+38.2 (q, $J = 75$)	—
<i>V</i> ^{b,c}	+41.2 (q, $J = 83$)	—2.4 (s)
<i>V</i> ^{c,f}	+41.2 (q, $J = 83$)	—2.2 (s)
<i>V</i> ^{f,g}	+41.4 (q, $J = 83$)	—2.2 (s)

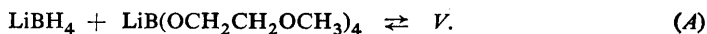
^a Chemical shift in p.p.m. (δ -scale), the coupling constant in Hz; s singlet, q quintet; ^b 6% solution in benzene; ^c 45°C; ^d solution in diethyl ether; ^e from the literature⁵; ^f 46% solution in benzene; ^g 37°C.

The reaction of lithium tetrakis(2-methoxyethoxy)borate (*Ia*) or the crystalline product, obtained by the reaction of 2-methoxyethyl ester of boric acid with lithium hydride¹, with lithium tetrahydridoborate (*IV*) was monitored and conjugate solutions were prepared from the two components which were poorly soluble in benzene, the lower containing 42.8% and the upper 3.3% of substance *V* at laboratory temperature the analysis of which indicated the presence of formal lithium dihydridobis(2-methoxyethoxy)borate (*IIIa*). The conjugate solutions of *V* in benzene are stable at laboratory temperature and the two phases are completely miscible above 60°C. The molecular weight of *V* determined cryoscopically is between 640–660 and ebullioscopically between 530–550 for a 1.5–2.5% benzene solution. These values correspond to a polymeration degree of 3.1–3.9 for the hypothetical dihydridodialkoxoborate, *IIIa*. With higher concentration of *V* in benzene solution the ebullioscopically determined molecular weight increases linearly and is approx. 1350 for a 10% concentration ($n = 8$).

Substance *V* completely free of the solvent is a viscous liquid at laboratory temperature and is completely miscible with tetrahydrofuran, 1,2-dimethoxyethane and dioxane. It yields a 2% solution in toluene at laboratory temperature; at higher temperatures conjugate solutions are formed similar to benzene solutions. Substance *V* is virtually insoluble in hexane, cyclohexane and diethyl ether, although lithium tetrahydridoborate alone yields a 4% solution in the latter at 25°C (ref.⁴).

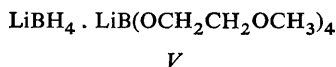
Substance *V* partially crystallized after standing for several weeks; both the solid and the liquid phase yield conjugate solutions in benzene with the same composition. The X-ray powder pattern of a mixture of the two phases is identical with the pattern for *Ia* and the weak lines not belonging to the spectrum of *Ia* can most probably be ascribed to substance *IVa*. This can then be explained by the existence of equilibrium

(A) between V and reactants Ia and IVa .



Separation of one or both components due to limited solubility in V shifts equilibrium (A) to the left.

In the next stage the ^{11}B -NMR spectra were measured for both conjugate solutions of V in benzene, where lithium cannot be solvated by oxygen atoms other than those from 2-methoxyethoxyl, and were compared with the spectra of compounds Ia and IVa (Table I). In both cases singlet $\delta = -2.2$ p.p.m. (vs $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$) corresponding to Ia and quintet $\delta = 41.2$ p.p.m. ($J = 83$ Hz) corresponding to IVa were found at an integral intensity ratio of 1 : 1. Therefore, the existence of a boron atom, to which two alkoxy and two hydride hydrogens are bonded, i.e. lithium dihydrido-bis(2-methoxyethoxy)borate ($IIIa$), can be excluded. The presence of a singlet and a quintet in the ^{11}B -NMR spectrum verifies the existence of BH_4 and $\text{B}(\text{OCH}_2\text{CH}_2\text{O} \cdot \text{CH}_3)_4$ configurations in compound V and thus justifies the assumption that compound V can be considered as IVa solvated by Ia .



This assumption is supported by the fact that in the BH valence vibration region bands at 2230 and 2280 cm^{-1} were found for substance V and a band at 2220 cm^{-1} and a small shoulder in the 2300 cm^{-1} region for the 3% benzene solution, which corresponds to the bands reported for IVa in 1,2-dimethoxyethane (2207, 2304 cm^{-1}) or in tetrahydrofuran⁵ (2217, 2305 cm^{-1}).

Further, the reducing properties of V and IVa alone in tetrahydrofuran and dioxane, respectively, were compared (Table II). Benzene solutions of V reduce aldehydes, ketones and carboxylic acid chlorides virtually quantitatively at laboratory temperature. At 80°C even esters of carboxylic acids are partially reduced, but generally with lower yields than obtained with lithium tetrahydridoborate alone. Carboxylic acid amides, aliphatic nitriles and halogens in molecules of the substances reduced are virtually unattacked by hydride V . *p*-Tolunitrile gave the corresponding amine in a yield of 28%. Nitrobenzene is also reduced only at 80°C to azoxybenzene and, to a lesser degree, as far as azobenzene. Aniline, which was isolated during the reduction of nitrobenzene by IVa in tetrahydrofuran^{6,7}, appears only in trace amounts.

Generally, the reducing power of V is lower than that of lithium tetrahydridoborate in tetrahydrofuran or dioxane⁷⁻¹², but higher than that of sodium tetrahydridoborate⁹ and approaches that of sodium hydridoalkoxoborates^{13,14}. Lithium hydridoalkoxoborates have so far been relatively rarely studied^{2,15}; the reducing properties

TABLE II

The Yields of Reductions with a $\text{LiBH}_4 \cdot \text{LiB}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4$ Solution in Benzene (V), and LiBH_4 in Tetrahydrofuran (VI)

2 hours, 25°C; the number in parentheses specifies the molar ratio of the hydride to the substance reduced.

Substance reduced	V	VI
Butanal	>98 (0.3) ^a	
Hexanal	>98 (0.3) ^a	83 (0.25) ^b
Benzaldehyde	>98 (0.3) ^a	91 (0.25) ^b
Cyclohexanone	>98 (0.3) ^a	c, d, e
Benzophenone	>98 (0.3) ^a	81 (0.25) ^b
Ethyl capronate	10 (0.6) ^a	
Ethyl capronate ^c	62 (0.6) ^a	
Ethyl capronate ^f	82 (0.6) ^a	
Butyl stearate		94 (0.7) ^g
Ethyl benzoate	1 (0.6) ^a	20 (0.7) ^g
Ethyl benzoate ^c	16 (0.6) ^a	83 (0.7) ^g
Benzoic acid	0 (0.9) ^a	0 ^c
Caproyl chloride	>98 (0.6) ^a	
Benzoyl chloride	84 (0.6) ^a	75–89 (1.0) ^h
Benzoyl chloride ^c	96 (0.6) ^a	
Butyramide ^{f, i}	3 (1.0)	0 ^j
Acetanilide ^k	2 (1.0) ^f	32 (1.2) ^l
ε-Caprolactam ^{f, m}	11 (1.0)	
p-Tolunitrile ⁿ	1 (1.0)	
p-Tolunitrile ^{c, n}	28 (1.0)	
Nitrobenzene	24 ^o , 9 ^p (1.5)	22 ^{b, r}
Bromobenzene	0 (0.5) ^s	
Bromobenzene ^c	3 (0.5) ^s	
Iodobenzene	1 (0.5) ^s	
Iodobenzene ^c	10 (0.5) ^s	

^a The yield of the corresponding alcohol determined by gas chromatography. ^b The yield of the corresponding alcohol according to the literature. ^c Reduction at the solvent boiling point.

^d Unreacted hydride and ketone present in the reaction mixture in addition to the products.

^e The yield of the corresponding alcohol according to the literature⁸. ^f Heating to the solvent boiling point for 10 hours. ^g The yield of the corresponding alcohol according to the literature¹², time, 24 hours. ^h Derivatives of the coumaroyl chloride, the yield of the corresponding alcohol according to the literature¹⁰.

ⁱ The product is n-butylamine. ^j According to the literature⁹.

^k The product is N-ethylaniline. ^l According to the literature¹¹, the reduction time is 20 hours at the solvent boiling point. ^m The product is hexamethylenamine. ⁿ The product is p-methylbenzylamine.

^o The product is azoxybenzene. ^p The product is azobenzene. ^r The product is aniline, the reduction time is 18 hours. ^s The product is benzene; the loss in the halogenobenzene was determined gas chromatographically. The reaction was carried out in toluene.

of these substances are, in contrast to sodium hydridoalkoxoborates, comparable with the reducing properties of the corresponding tetrahydridoborates. Under the conditions of reduction with hydride *V*, greater amounts of a compound with both a hydridic hydrogen and an alkoxy on a single boron atom are apparently not present and the decrease in the reducing power of the tetrahydridoborate configuration is probably caused by solvation of the lithium atom. Further solvation of a tetracoordinated boron atom is very improbable, but it is assumed^{6,16} that the ion pairs of lithium tetrahydridoborate, Li^+BH_4^- , are in close contact.

Analogously to the preparation of hydride *V*, sodium tetrahydridoborate was dissolved in a benzene solution of *Ib* or *Ib*, up to a ratio of $\text{B} : \text{H}^- = 1 : 1.68$ at laboratory temperature. A solid phase with a somewhat higher relative content of hydridic hydrogen gradually separates from this solution on prolonged standing. Even formal sodium dihydrido-bis(2-methoxyethoxy)borate (*IIIb*) is stable in tetrahydrofurane solution at 0°C . The ^{11}B -NMR spectra of the thus-prepared solutions are independent of the preparation procedure, but change considerably during aging of the substance. A 24 hour-old solution of *IVb* in a 12% solution of *Ib* in benzene exhibited a broad singlet, $\delta = -5.0$ p.p.m. (*vs* $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$), with a band-width of 300 Hz, in the region corresponding to the doublet of *Ib*, a sharp singlet of *Ib* ($\delta = -1.9$ p.p.m.) and a sharp quintet of *IVb* ($\delta = 43.3$ p.p.m., $J = 82$ Hz) at an integral intensity ratio of 37 : 33 : 30. The same solution five months old exhibited singlets $\delta = -7.4$ p.p.m., band-width, 300 Hz (corresponding to *Ib*), $\delta = -1.9$ p.p.m. (corresponding to *Ib*) and a quintet $\delta = 43.2$ p.p.m., $J = 81$ Hz (corresponding to *IVb*), at an integral intensity ratio of 70 : 11 : 19. Since the initial solution of sodium monohydrido-tris(2-methoxyethoxy)borate had an equilibrium composition, determined from ^{11}B -NMR, of 18% *Ib*, 78% *Ib* and 4% *IVb*, it seems that tetraalkoxoborate *IVb* plays a greater role during the first stage of dissolution and thus also of solvation of sodium tetrahydridoborate. During aging of a benzene solution, the per cent content of a broad singlet in the *Ib* signal region increases in the ^{11}B -NMR spectrum; in contrast to the original *Ib* spectrum, B—H coupling is completely suppressed.

As a model for solvation of sodium with 2-methoxyethoxyl bound to a boron atom can serve tridentate solvation of the sodium tetrahydridoborate cation with sodium tetramethoxoborate, by means of which the solubility of *IVb* in a tetrahydrofurane solution of sodium tetramethoxoborate at 0°C was explained by Brown and coworkers¹⁷; the oxygen atom in the β -position on the alkoxy may also take part in the solvation of sodium. Lithium in substance *IVa* in etheric solutions forms a close ion-pair, $\text{Li}^+\text{—BH}_4^-$, and is solvated only by two oxygen atoms of the donor solvent^{6,16}; this is probably one of the causes of different solubilities and stabilities of compound $\text{MeBH}_4 \cdot \text{MeB}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4$ for $\text{Me} = \text{Li}$ or Na .

EXPERIMENTAL

Chemicals used: All reactions with hydrides and alkoxoborates were carried out in an atmosphere of pure nitrogen. Crystalline substances *Ia* and *Ib* and a 50% benzene solution of *Iib* were prepared in the same manner as in the previous work¹. Commercial *IVa* had a purity of 98% and *IVb* a purity of 99%. Dried and distilled solvents were distilled with sodium dihydrido-bis(2-methoxyethoxy)aluminate immediately before use.

Spectroscopic measurements: ¹¹B-NMR spectra of benzene solutions were measured on a Varian XL-100-15 instrument at 30 MHz. B(OCH₃)₃ was employed as the external standard. IR spectra were obtained on a Beckman IR 20A spectrometer for 15% sample suspensions in perfluorokerosene, for the substances or for 3% benzene solutions. X-ray measurements were performed by the Debye-Scherrer method with a chamber diameter of 114.6 mm, employing CuK radiation filtered by a Ni filter, in Lindemann capillaries 0.3 mm in diameter. Substance *V* was drawn into the capillary *in vacuo* and partially crystallized after several months standing.

Determination of the molecular weights: Cryoscopic determinations of molecular weight *V* in 1.5–2.6% benzene solutions were carried out using the procedure described earlier¹⁸. For ebullioscopic determinations a Świętosławski ebulliometer was employed, the ebullioscopic constant used being 2.7. The molecular weight was measured in benzene in a concentration range of 1.5–10.5%. The dependence of molecular weight *V* on the solution concentration is summarized in Table III.

Preparation of a Benzene Solution of LiBH₄·LiB(OCH₂CH₂OCH₃)₄ (*V*)

0.5 mol (15 g) of *Ia*, 0.6 mol (13 g) of *IVa* and 500 ml of benzene were shaken for 12 hours at laboratory temperature. Most of the solid phase dissolved during this time. After filtering, two layers of benzene solution of *V* were obtained, with the following composition at 23°C: the upper layer — Li : B : H⁻ = 1.004 : 1 : 1.88 (the solution is 3.3% according to the boron determination; the lower layer — Li : B : H⁻ = 1.003 : 1 : 1.93 (the solution is 42.8% according to the boron determination). On evaporating the conjugate solutions to approx. one half of the initial volume, a homogeneous solution was obtained with a Li : B : H⁻ ratio of 1.004 : 1 : 1.93 (the solution is 64.9% according to the boron determination). This solution of *V* was used for the determination of the molecular weights, for reduction screening and for the preparation of solutions for spectroscopic studies. Substance *V* was prepared from this solution by evaporating benzene by heating for 1 hour at 0.1 Torr and 50°C. For LiBH₄·LiB(OCH₂CH₂OCH₃)₄ (339.9) calculated: 4.08% Li, 6.36% B, 1.186% H⁻; found: 4.07% Li, 6.32% B, 1.157% H⁻.

TABLE III

Dependence of the Molecular Weight of LiBH₄·LiB(OCH₂CH₂OCH₃)₄ (*V*) in Benzene Solution on the Concentration

Concentration, %	1.45	2.0	2.6	2.8	3.9	4.3	6.1	7.8	10.5
Ebullioscopy	550	550	—	530	660	690	920	1 070	1 370
Cryoscopy	640	660	650	—	—	—	—	—	—

Preparation of Solutions of $(\text{NaBH}_4)_x \cdot \text{NaB}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4$

The reaction between *Ib* and *IVb* in benzene was carried out under the same conditions as previously. After filtering off undissolved *IVb*, a transparent solution with a Na : B : H⁻ ratio of 1.005 : 1 : 1.68 was obtained (a 26.6% solution according to the B content). Crystals were isolated from the solution after 9 months' standing (a Na : B : H⁻ ratio of 1.01 : 1 : 1.74); the ratio in the remaining solution was 1.005 : 1 : 1.57 (a 22.6% solution according to the B content). By 12 hour stirring of *Ib* and *IVb* in tetrahydrofuran at 0°C a solution was prepared which was stable for several weeks at this temperature, while the solid phase separates after 12 hours at laboratory temperature.

Reduction with a Benzene Solution of *V*

The reductions were performed at 25°C and 80°C using the procedure described earlier^{19,20}. 6 ml of benzene and 0.01–0.1 mmol of an internal standard — dodecane, eicosane or docosane hydrocarbons, if the yield was monitored by gas chromatography — were added to 1 mmol of the hydride during the reduction. The molar ratio of *V* to the substance to be reduced and other conditions for the reductions are specified in the caption for Table II.

Reduction of Nitrobenzene by a Benzene Solution of *V*

To 3.81 g (7.1 mmol) of a 64.9% solution of *V* in benzene and 20 ml of benzene, 0.58 g (4.7 mmol) of nitrobenzene in 5 ml of benzene were added dropwise with cooling and stirring in a nitrogen atmosphere. The mixture was stirred for 2 hours at 80°C, decomposed by a saturated solution of ammonium chloride, the aqueous layer was shaken with ether and the joint non-aqueous fractions were dried using magnesium sulphate. Thin-layer chromatographic analysis on silica in a cyclohexane–benzene (3 : 1) solvent indicated that the reaction mixture contained azoxybenzene, azobenzene and tarlike substances remaining at the start, in addition to unreacted nitrobenzene. The solvent was evaporated and the residue was extracted with 50 ml of n-hexane. The hexane extract was evaporated and distilled with water vapour. Azobenzene was determined in the distillate colorimetrically (0.041 g, 9.5%) and azoxybenzene in the distillation residue titanometrically (0.090 g, 19.2%).

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