

## Reaction between Lithium Aluminium Hydride and Some Amino Alcohols studied by $^{27}\text{Al}$ and $^7\text{Li}$ Nuclear Magnetic Resonance

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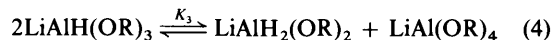
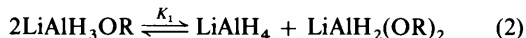
$\text{LiAlH}_4$  has been titrated with (-)-*N*-methylephedrine (1), (-)-quinine (2), and (-)-(*S*)-4-anilino-3-methylaminobutan-1-ol (3) in tetrahydrofuran and in bis-(2-methoxyethyl) ether. The titrations were followed by  $^{27}\text{Al}$  n.m.r. The establishment of equilibrium was verified from the results of back titrations. The ion  $\text{AlH}_4^-$  was found to be present in solution when 1.5 mol equiv. of (1) or 1.2 mol equiv. of (2) had been added. Computer fittings to experimental n.m.r. data indicated that disproportionation of monoalkoxyaluminates derived from (1) and (2) with re-formation of  $\text{LiAlH}_4$  takes place in both solvents. No sign of disproportionation was evident in the case of (3).  $^7\text{Li}$  N.m.r. showed that the compounds derived from  $\text{LiAlH}_4$  and the substrates (1)–(3) complex  $\text{Li}^+$  strongly enough to cause slow exchange on the n.m.r. timescale.

The asymmetric reduction of prochiral carbonyl compounds with a reagent prepared from  $\text{LiAlH}_4$  and various chiral alcohols has been the subject of many studies.<sup>1,2</sup> Such reducing agents are useful synthetic tools since they reduce several types of compounds, react fast, and enable high optical yields to be obtained with an appropriate choice of chiral alcohol. However, little is known about the structure of the actual reducing species. This is a considerable disadvantage since the optical yields are often irreproducible and the asymmetric induction may be very hard to predict. Some factors of importance are the extent of solvation of the  $\text{Li}^+$  and  $\text{AlH}_4^-$  ions and the formation of aggregates.<sup>3</sup> An important question is whether the initially formed alkoxyaluminates are stable or take part in disproportionation equilibria.

When an alcohol is added to a solution of  $\text{LiAlH}_4$ , alkoxyaluminates are formed and hydrogen gas is evolved [reaction (1)]. The alkoxyaluminates are formed in amounts determined



by the reactivity of the hydrides in the different species. If species with  $n > 1$  are formed, an excess of  $\text{AlH}_4^-$  ion is present in the solution even in a 1:1 molar mixture. It has been suggested<sup>4</sup> that the initially formed alkoxyaluminates are unstable and disproportionate as in reactions (2)–(4). If equilibrium accord-



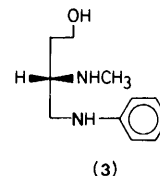
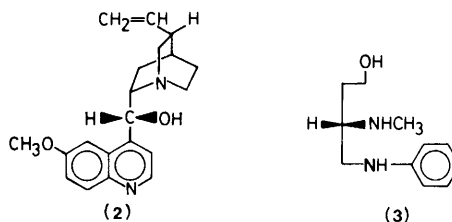
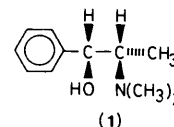
ing to these reactions is established, the concentration of 'free'  $\text{AlH}_4^-$  ions and of the alkoxyaluminates is determined by the equilibrium constants.

The capacity of discrete alkoxyaluminates to induce optical activity in reduction reactions is impossible to predict since their structures and concentrations are not known. However, if  $\text{AlH}_4^-$  ions are present in the solution, achiral reduction will proceed through this species which, of course, lowers the overall optical yield. This is one possible explanation for the low optical yields obtained when such monohydroxy alcohols as (-)-menthol or (+)-camphor were used.<sup>2a,5</sup> Červinka<sup>6</sup> suggested that the use of amino alcohols, e.g. cinchona

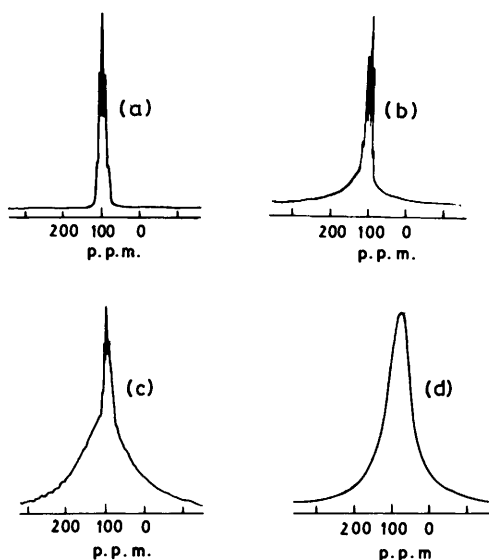
alkaloids, could be a remedy for this problem since their alkoxyaluminates should show less tendency to disproportionate in view of the possibility of chelation of the nitrogen lone pair with the aluminium or lithium atom.

Increased optical yields were, in fact, obtained. In their extensive study of the  $\text{LiAlH}_4$ -Darvon alcohol system, Mosher and his co-workers<sup>7,8</sup> obtained high optical yields, although  $\text{LiAlH}_4$  is present in the reducing mixture with this amino alcohol. This demonstrates the complexity of these systems.

In this work we used  $^{27}\text{Al}$  and  $^7\text{Li}$  n.m.r. to study the compounds formed by reaction between  $\text{LiAlH}_4$  and three different amino alcohols: (-)-*N*-methylephedrine (1), (-)-quinine (2), and (-)-(*S*)-4-anilino-3-methylaminobutan-1-ol (3). Our aim was to throw some light on the role of



disproportionation in predicting the stereochemical outcome of reductions of prochiral carbonyl compounds. (-)-*N*-Methylephedrine is a comparatively small and flexible molecule which possibly disproportionates rather easily since it can form a 1:2 ( $\text{LiAlH}_4$ :alcohol) compound without too much steric strain. The asymmetric induction reported in the literature with (-)-*N*-methylephedrine is low.<sup>9</sup> (-)-Quinine, used extensively by Červinka,<sup>6</sup> is bulky and rather rigid, and should have difficulty in forming a 1:2 compound; consequently it should have a smaller tendency to disproportionate. Optical yields are higher than for (-)-*N*-methylephedrine, but they vary considerably with reaction conditions. Both these alcohols have only one hydroxy group that can react to form an Al–O bond. The third



**Figure 1.**  $^{27}\text{Al}$  Spectra from solutions in THF: (a)  $\text{LiAlH}_4$ ; (b) molar ratio (1): $\text{LiAlH}_4$  1:1; (c) molar ratio (2): $\text{LiAlH}_4$  1:1; (d) molar ratio (3): $\text{LiAlH}_4$  1:1

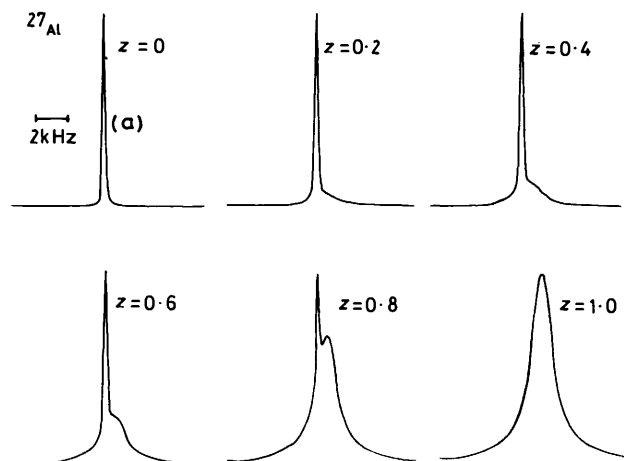
amino alcohol (3) has a hydroxy group as well as two secondary amino groups that can react with  $\text{LiAlH}_4$  to form one Al–O and two Al–N bonds. Sato *et al.*<sup>10</sup> obtained quite high optical yields when using this amino alcohol in asymmetric reductions.

### Experimental

**Chemicals.**—(–)-*N*-Methylephedrine (m.p. 87–88 °C) was prepared from (–)-ephedrine by the Eschweiler–Clarke method.<sup>11</sup> It was recrystallized from toluene and sublimed several times before use. (–)-Quinine (m.p. 177 °C; Merck p.a.) was used without further purification. It was dried at 70 °C and 0.1 mmHg for at least 12 h prior to use on each occasion. (–)-(*S*)-4-Anilino-3-methylaminobutan-1-ol was synthesized according to the procedure outlined by Sato *et al.*<sup>10</sup> with some modifications,<sup>12</sup> and distilled under vacuum (b.p. 164 °C at 0.3 mmHg). Tetrahydrofuran (TFH) (Merck p.a.) and diglyme [bis-(2-methoxyethyl) ether] (Fluka p.a.) were distilled over  $\text{LiAlH}_4$  and stored over 4 Å molecular sieves.

Stock solutions of  $\text{LiAlH}_4$  and  $\text{LiAlD}_4$  were prepared by refluxing for several hours, centrifuging the slurries, and transferring the clear solutions to storage bottles equipped with Teflon stopcocks and rubber septums. The solutions were always kept under dry nitrogen. Portions of liquid were removed by syringe as needed. Prior to use, the stock solutions were analysed by iodometric titration<sup>13</sup> and by measurements of the amount of hydrogen gas evolved when the  $\text{LiAlH}_4$  solution was hydrolysed by an acidic water–THF (diglyme) mixture at  $\pm 0$  °C in an ice-bath. The results of the two methods always agreed to within  $\pm 2\%$ .

**Titrations.**—In a typical experiment,  $\text{LiAlH}_4$  or  $\text{LiAlD}_4$  solution (2 ml) was injected into a 10 mm n.m.r. tube equipped with a Teflon-coated rubber septum, and the  $^{27}\text{Al}$  or  $^7\text{Li}$  spectrum was recorded. The titrations were performed by injecting samples of solutions of amino alcohols in the same solvent into the n.m.r. tube with vigorous shaking by a whirlmixer. The concentration of  $\text{AlH}_4^-$  in the solution reached its equilibrium value within 15–60 min after each addition, as proved by observing the  $^{27}\text{Al}$  spectrum for up to 24 h in some cases. The reproducibility of the determination of the  $\text{AlH}_4^-$



**Figure 2.** Some  $^{27}\text{Al}$  spectra from a titration of  $\text{LiAlD}_4$  with (3) in THF;  $z$  is the molar ratio [(3): $\text{LiAlD}_4$ ]

concentration from the  $^{27}\text{Al}$  spectra in different titrations was within  $\pm 5\%$ .

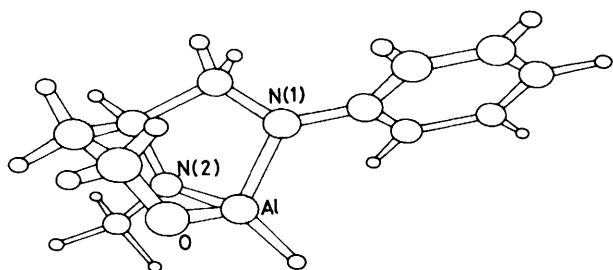
**N.m.r. Measurements.**—The  $^{27}\text{Al}$  spectra were recorded at 23.5 MHz and at the ambient probe temperature  $26.5 \pm 0.5$  °C with a Bruker CXP-100 spectrometer. The maximal sweep width (125 kHz) and band width (1 MHz) of the instrument were used. The pulse repetition rate was 50 ms. The  $^7\text{Li}$  spectra were recorded at 38.7 MHz with a JEOL FX-100 spectrometer. The pulse repetition rate was 11 s in this case.  $^{27}\text{Al}$  Chemical shifts are related to  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  (external standard).

### Results and Discussion

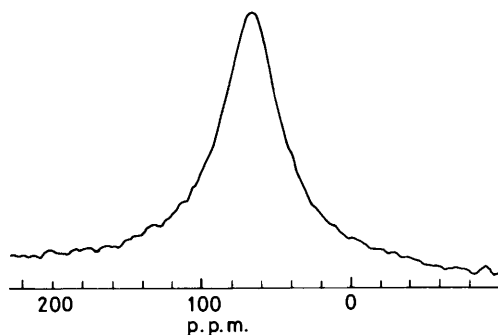
The stoichiometry of the reaction between  $\text{LiAlH}_4$  and the amino alcohols was studied by measurement of the amount of hydrogen gas evolved in reaction at room temperature. With the substrate (1) or (2) hydrogen gas was rapidly evolved in quantitative amount until all four hydrogen atoms had been displaced. With the amino alcohol (3) (1:1 molar ratio) hydrogen gas corresponding to three of the four available hydrogen atoms was immediately evolved. This shows that the two secondary amino groups and the hydroxy group react with  $\text{LiAlH}_4$  at similar rates.

**$^{27}\text{Al}$  N.m.r.**—The sensitivity of  $^{27}\text{Al}$  is quite high (20.7% of the sensitivity of  $^1\text{H}$ ) and  $\text{AlH}_4^-$  ions in solution can be studied conveniently by  $^{27}\text{Al}$  n.m.r. since the lines are fairly narrow.<sup>14a,b</sup> The spectrum from  $\text{AlH}_4^-$  is a well-resolved quintet ( $\delta$  98 p.p.m.;<sup>14b</sup>  $J_{\text{Al,H}}$  175 Hz;<sup>15</sup>  $\Delta\nu_{\frac{1}{2}}$  50 Hz) [Figure 1(a)]. The linewidth depends somewhat on the solvent.<sup>15</sup> As a result of a smaller spin–spin coupling constant, the  $\text{AlD}_4^-$  ion gives a broader  $^{27}\text{Al}$  spectrum ( $\delta$  97.8 p.p.m.;<sup>14b</sup>  $\Delta\nu_{\frac{1}{2}}$  110 Hz), without resolution of fine structure [Figure 2(a)]. The  $^{27}\text{Al}$  nucleus has a spin quantum number  $I = 5/2$  and a rather large electric quadrupole moment ( $0.149 \times 10^{-28}$  m<sup>2</sup>). Relaxation *via* the quadrupole mechanism can thus be very effective. A symmetrical environment (tetrahedral or octahedral) of the aluminium results in small quadrupole coupling constants and comparatively narrow lines as a result of less effective relaxation, while lower symmetry may give rise to lines that are too broad to be detected.

Figure 1 shows  $^{27}\text{Al}$  spectra from solutions in THF where one mole of  $\text{LiAlH}_4$  has reacted with one mole of amino alcohol. The products have lower symmetry than the  $\text{AlH}_4^-$  ion, and thus broader lines. As can be seen, the solutions with (1) and (2)



**Figure 3.** Plot from MNDO optimization<sup>16</sup> of a bicyclic structure for the reagent prepared from  $\text{LiAlH}_4$  and 1 mol equiv. of (3). A definite energy minimum is obtained with a calculated heat of formation of  $-90.0 \text{ kcal mol}^{-1}$ . The two rings are somewhat strained, as shown by the long Al-O (1.770 Å), Al-N(1) (1.879 Å), and Al-N(2) (1.845 Å) bonds

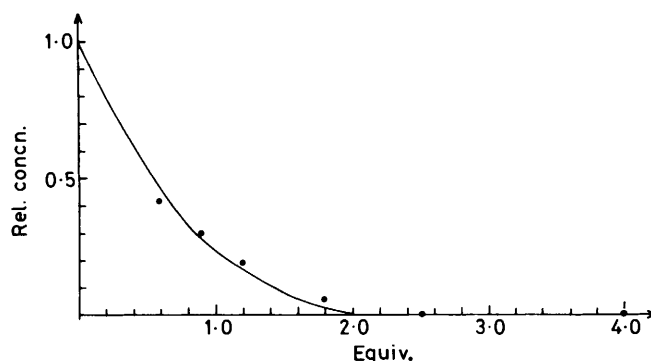


**Figure 4.**  $^{27}\text{Al}$  Spectrum of  $\text{LiAlH}_4$  + (2) in 0.25:1 molar mixture in THF

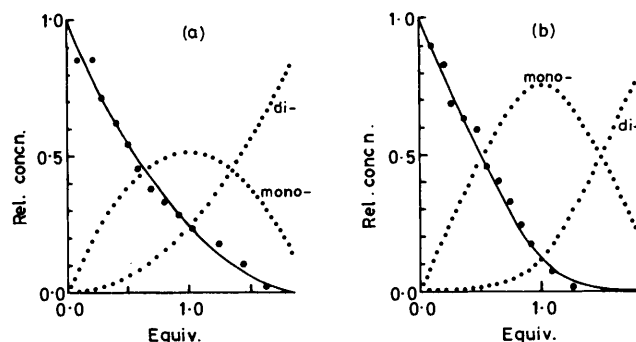
[Figure 1(b) and (c)] contain  $\text{AlH}_4^-$  ions as well as reaction products, whereas  $\text{AlH}_4^-$  has disappeared in the case of (3). For all three amino alcohols, the  $^{27}\text{Al}$  spectra showed one broad peak and the narrow peak from  $\text{AlH}_4^-$  ions. However, it was only for (3) that the total integral of the spectrum corresponded to all aluminium present. This shows that for the cases of (1) and (2) aluminium is present at least in three different forms:  $\text{AlH}_4^-$  ions, compounds giving rise to the broad peak, and compounds which have  $^{27}\text{Al}$  spectra that are too broad to be detected. To study this in more detail, we performed titrations of  $\text{LiAlH}_4$  solutions with the substrates (1)–(3). Figure 2 shows some spectra from such a titration of  $\text{LiAlD}_4$  with (3).

The concentration of  $\text{AlH}_4^-$  in solution decreases linearly as 1.0 in Figure 2). This shows that at equilibrium and in an excess of  $\text{LiAlH}_4$ , each molecule of (3) with its three reactive OH and NH groups has consumed one  $\text{AlH}_4^-$  ion. Compounds in which fewer than three hydrogen atoms of an  $\text{AlH}_4^-$  ion have reacted can be ruled out, since  $\text{AlH}_4^-$  would disappear more rapidly during the titration than observed experimentally. Sato<sup>10</sup> has suggested that (3) reacts with  $\text{LiAlH}_4$  to form a bicyclic compound with one five- and one six-membered ring. In order to investigate this point further we performed an MNDO<sup>16</sup> calculation which showed that this structure has a definite energy minimum (Figure 3).

For the substrates (1) and (2) it is difficult to integrate the broad signal because of base-line distortions in the spectra. Accordingly, we chose to follow the reactions by measuring the concentration of  $\text{AlH}_4^-$  ions in the solution from the height of the narrow signal of this species. First, it is important to determine whether equilibrium is established in solution or whether the concentrations of the different species are kinetically determined. This was tested by performing a reversed titration, i.e. a solution of (1) or (2) in THF was titrated with  $\text{LiAlH}_4$ . When 0.25 mol equiv. of  $\text{LiAlH}_4$  (1.0 mol equiv. of



**Figure 5.** Relative concentration of  $\text{AlH}_4^-$  as a function of ROH:  $\text{LiAlH}_4$  molar ratio for back titration of (1). The curve represents the best fit to experimental data for a forward titration of  $\text{LiAlH}_4$  with (1) with a calculated value  $K_1 = 0.22$  (see text)



**Figure 6.** Experimentally determined  $\text{AlH}_4^-$  concentrations (●) and calculated concentrations of  $\text{AlH}_4^-$  (—), mono- and di-alkoxyaluminates (---) obtained from computer fittings of reactions (1) and (2) to experimental data for titration of  $\text{LiAlH}_4$  with (a) (1) ( $K_1 = 0.22$ ) and (b) (2) ( $K_1 = 0.026$ )

corresponding to the quantitative reaction of all four hydrogen atoms was immediately evolved. The  $^{27}\text{Al}$  spectra consisted of one fairly narrow singlet ( $\Delta\nu_{\frac{1}{2}} 1000 \text{ Hz}$ ;  $\delta 65 \text{ p.p.m.}$ ), as seen in Figure 4, corresponding to about 80% of the total amount of aluminium added. A narrow signal is expected from a tetrahedral aluminium compound with four identical ligands. Thus, the formation of a tetra-alkoxy compound with (1) and (2) is indicated. Further additions of  $\text{LiAlH}_4$  caused no more gas evolution. The signal from  $\text{LiAlH}_4$  disappeared from the spectra within 60 min after each addition and the only peak visible was a very broad signal. This shows that  $\text{AlH}_4^-$  and the species giving the narrow singlet are transformed by some reaction into less symmetrical compounds. Below a ROH:  $\text{LiAlH}_4$  ratio of 1.2:1 for (1) and 1.5:1 for (2), the  $\text{AlH}_4^-$  concentration corresponds to the equilibrium value. Thus, equilibration of alkoxyaluminates involving  $\text{AlH}_4^-$  is evidenced in THF solution (Figure 5).

The next step was to check whether the proposed model for the disproportionation could be fitted to the experimentally derived  $\text{LiAlH}_4$  concentrations for the alcohols (1) and (2). The law of mass action was applied to reactions (2)–(4) and a system of equations was set up corresponding to the chemical equilibria and to the relations for the total concentrations of aluminium and alcohol, respectively.

The calculated  $\text{AlH}_4^-$  concentrations were fitted by a least-squares minimization method to the values measured by  $^{27}\text{Al}$  n.m.r., by varying the equilibrium constants. This procedure is

described in detail elsewhere.<sup>17</sup> In the case of (2), it was found that, for a good fit to experimental data, only reaction (2) needed to be taken into account [Figure 6(b)]. The estimated value of  $K_1$  was  $0.026 \pm 0.01$ . Inclusion of reactions (3) and (4) did not improve the fit. This shows that  $K_2$  and  $K_3$  do not affect the  $\text{LiAlH}_4$  concentration to any great extent. To obtain a measure of  $K_2$  and  $K_3$ , more information about the polyalkoxyaluminates appearing later in the titration is needed.

In the case of (1) the best fit to experimental  $\text{LiAlH}_4$  data yielded the value of  $0.22 \pm 0.1$  for  $K_1$ , i.e. reaction (2) is enough to explain the data in this case also [Figure 6(a)]. Even though the values of  $K_1$  for (1) and (2) are uncertain, the results of the computer fittings indicate that disproportionation of the monoalkoxyaluminates according to reaction (2) takes place in THF solution with these alcohols. The difference in  $K_1$  is significant and could always be reproduced.

The lower degree of disproportionation for the monoalkoxyaluminum of (–)-quinine is probably caused by difficulties in forming the dialkoxyaluminate with this bulky and rather rigid molecule. Figure 6 also shows the relative concentrations of mono- and di-alkoxyaluminates calculated from the equilibrium constants.

Titrations were performed with  $\text{LiAlH}_4$  concentrations in the range 0.01–0.5M in THF. For neither alcohol (1) nor (2) was any concentration dependence of the results of the titrations observed, showing that formation of aggregated species does not affect the equilibria under study. A change of solvent from THF to diglyme did not affect the equilibria to any measurable degree.

As seen in Figure 1, the differences in the  $^{27}\text{Al}$  chemical shift between the  $\text{AlH}_4^-$  signal and the broad peak are 15 p.p.m. for (1) and (2) and –25 p.p.m. for (3). These shifts all fall in the range for tetrahedrally co-ordinated aluminium, which is also the case for the peak in Figure 4 (–35 p.p.m.).<sup>14a</sup>

$^{7}\text{Li}$  N.m.r.—The  $^{7}\text{Li}$  nucleus has  $I = 3/2$  and a fairly small quadrupole moment, resulting in narrow lines in liquid systems. The sensitivity is high (27% of the sensitivity of  $^1\text{H}$ ) and the n.m.r. spectra are obtained quite easily. The  $^{7}\text{Li}$  spectrum of  $\text{LiAlH}_4$  in THF is a singlet with  $\delta$  0.27 p.p.m.,<sup>15</sup> and a linewidth  $< 1$  Hz at room temperature. The small linewidth indicates that the  $\text{Li}^+$  ions are solvated by THF and not too tightly bound to  $\text{AlH}_4^-$ .<sup>15</sup>

When a solution of  $\text{LiAlH}_4$  in THF was titrated with (2), a new peak 1.0 p.p.m. to lower frequency appeared in the spectrum. The total integral of the  $^{7}\text{Li}$  spectrum remained constant (corrected for the dilution). This spectrum clearly shows that the solution contains solvated  $\text{Li}^+$  ions and ions in a different environment. The lifetime of the bound  $\text{Li}^+$  ion can be estimated from the linewidths to be longer than 0.1 s at room temperature. It is evident that some product formed by reactions (1)–(4) is able to bind  $\text{Li}^+$  rather strongly. This unexpected behaviour indicates a special structure for the alkoxyaluminates formed by (2); it is tempting to make a comparison with the situation in crown ethers and cryptates<sup>18</sup> [Figure 7(a)].

In diglyme, the two  $^{7}\text{Li}$  signals were clearly visible but not totally separated at room temperature. When the temperature was increased, the two peaks broadened and at 80 °C started to coalesce.

When a solution of  $\text{LiAlH}_4$  in THF was titrated with (1) at room temperature, the  $^{7}\text{Li}$  signal gradually broadened to about 5 Hz at the equivalence point. When the temperature was lowered to –80 °C, the line was split into two peaks [Figure 7(b)] showing that the alkoxyaluminates formed by (1) can also bind  $\text{Li}^+$  ions. In diglyme, the chemical-shift difference was larger and at room temperature the  $^{7}\text{Li}$  signal exhibited a shoulder on the high-frequency side. When the temperature was

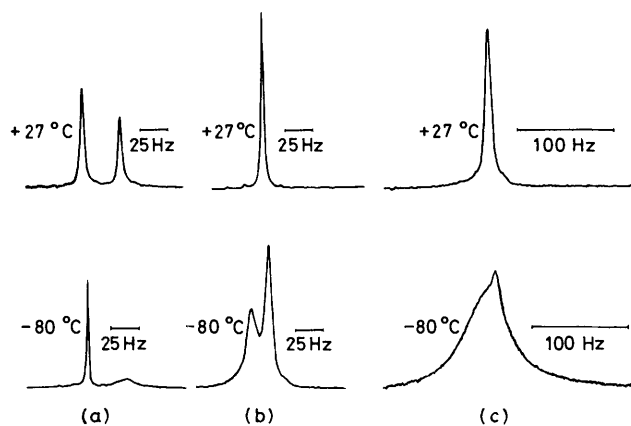


Figure 7.  $^{7}\text{Li}$  Spectra from solutions in THF with molar ratio [amino alcohol: $\text{LiAlH}_4$ ] 1:1 at 27 °C (upper row) and at –80 °C (lower row): (a) (2); (b) (1); (c) (3)

lowered to –20 °C, the signal became split; increasing the temperature to 40 °C caused coalescence of the two signals.

In the case of (3) [Figure 7(c)], a broad singlet (15 Hz) was observed in the  $^{7}\text{Li}$  spectrum at room temperature in THF. The signal developed a shoulder on the high-frequency side when the temperature was lowered to –80 °C in THF, while the shoulder was visible at –20 °C in diglyme.

We thus found that the alkoxyaluminates formed by all three amino alcohols studied can bind  $\text{Li}^+$  ions strongly enough to cause slow exchange with free solvated  $\text{Li}^+$  ions on a timescale defined by the chemical-shift difference. A common feature of these alkoxyaluminates is that they contain nitrogen and oxygen lone pairs. It is possible that some conformers have a suitable spatial arrangement for binding  $\text{Li}^+$  ions in a way similar to that in the 'cave' in a cryptand. Changing the solvent from THF to diglyme markedly alters the exchange rate of  $\text{Li}^+$  ions for all three amino alcohols. This ion-binding capacity may be of importance for the optical yield obtained in an asymmetric reduction. The  $\text{Li}^+$  ion might play an important role since it can associate with the carbonyl oxygen of the compound to be reduced during the hydride-transfer step. This association may lead to a more highly ordered transition state for reduction which may, in turn, increase the stereoselectivity. If the  $\text{Li}^+$  ion is strongly attached to the alkoxyaluminate this must influence its capacity to co-ordinate with the carbonyl oxygen, thus exerting a strong influence on the stereochemical course of the reaction.

## Conclusions

Our results show that, when  $\text{LiAlH}_4$  reacts with an amino alcohol in THF or diglyme, equilibration of alkoxyaluminates involving  $\text{LiAlH}_4$  takes place. The results of computer fittings support the disproportionation scheme represented by reactions (2)–(4). The values of the equilibrium constants thus obtained vary with the structure of the amino alcohol. The small and flexible (–)-*N*-methylephedrine molecule disproportionates to a significant degree, the bulkier and more rigid (–)-quinine less so; the tridentate amino alcohol (3) forms a bicyclic compound without production of any measurable amount of 'free'  $\text{LiAlH}_4$ . Although a number of other factors have to be considered when predicting the stereochemical outcome of an asymmetric reduction, these results agree with the order of effectiveness of (1), (2), and (3) as asymmetric reducing agents, as reported in the literature.<sup>1,9,10</sup> Thus, it may be concluded that disproportionation needs to be taken into

account when choosing the proper amino alcohol in an asymmetric reduction experiment.

### Acknowledgements

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