Alkoxohydridoaluminates. Part 2.[1] The Influence of Alkyl Substituents, Solvent, and Temperature on the Molar Fractions of Components, Equilibrium Constants, and ^{27}Al N.M.R. Data for Equilibrium Mixtures Containing $Bu_4N^+AlH_{4-n}(OR)_n^-$

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Molar fractions, equilibrium constants of mutual exchange, and ^{27}Al n.m.r. data of compounds $Bu_4N^+AlH_{4-n}(OR)_n^-$ and the dependence of these on n (0–4); R (Me, Et, Nonyl, Pr^i, cyclo-C_6H_{11}, Ph, and Bu^t); solvent (benzene, tetrahydrofuran, 1,2-dimethoxyethane, diglyme); and temperature (23 and 70 °C) are presented. Predominant separation of cation from anion and, consequently, the slowest exchange, is found with $Bu_4N^+AlH(OR)_3^-$ and bulky R, in 1,2-dimethoxyethane at 70 °C. Such compounds, free of tetra-, tri- and di-hydrido components are expected to exhibit a very high reduction stereoselectivity proportional to the steric strain resulting from the presence of all three bulky alkoxy groups.

This series of contributions on alkoxohydridoaluminates (AHA) is focused on the analysis of the main factors (and their interplay) governing the selective reductions carried out using these species. In Part 1 we showed[1] that the alkoxohydridoaluminates $Bu_4N^+AlH_{4-n}(OR)_n^-$ of given analytical formulae are not distinct compounds, but represent a living system, consisting of all species $AlH_{4-n}(OR)_n^-$ [(1; n = 0), (2; n = 1), (3; n = 2), (4; n = 3), and (5; n = 4)]. Of these, only the species (1)–(4) show reducing power which decreases significantly from (1) to (4). On the other hand, the reduction stereoselectivity for uncomplexed anions (1)–(5) increases in the opposite order: (1) < (2) < (3) < (4).[2] An important property of the system (1)–(5) is the existence of mutual exchange of H and OR ligands.[3] If sufficiently fast, this exchange can significantly influence the results of a reduction reaction due to a continuous replenishment of the fastest reducing AlH_4^- anion at the expense of the slower, but more selective, reducing alkoxohydridoaluminates (2)–(4). In spite of the great number of articles dealing with species (2)–(4),[4,5] detailed information on the actual composition of the equilibrium systems (1)–(5) was not available. The first quantitative contribution was presented in 1984 by our group for solutions of $Bu_4N^+AlH_{4-n}(OR)_n^-$ where R = Me, Et, Pr^i, Nonyl, Bu^t, and cyclohexyl.[6] Data for the system $Li^+AlH_{4-n}(OR)_n^-$ (R = Bu, Bu^s, Bu^t) have appeared recently and show similar results.[7] We present here a ^{27}Al n.m.r. study of the influence of alkyl groups, solvent, and temperature on the n.m.r. data of individual components (1)–(5) and on their overall stoicheiometric ratios in equilibrium mixtures.

$Bu_4N^+AlH_{4-n}(OR)_n^-$

	n		R
(1)	0	(a)	Me
(2)	1	(b)	Et
(3)	2	(c)	Nonyl
(4)	3	(d)	Pr^i
(5)	4	(e)	cyclo-C_6H_{11}
		(f)	Ph
		(g)	Bu^t

Results and Discussion

System Studied.—The behaviour of the alkoxohydridoaluminates (1)–(5) and, consequently, their ^{27}Al n.m.r. data depend on several variables (nature of R, cation, solvent, and temperature). The ion-pairs $Bu_4N^+AlH_{4-n}(OR)_n^-$, which show relatively narrow ^{27}Al n.m.r. signals, were used to study the effect of changing these variables.

Attempts to prepare uniform solutions of tetrabutylammonium salts of (2) or (3) always resulted in a mixture of all species (1)–(5); consequently the equilibrium mixtures (1)–(5) were studied. Most of these equilibrium mixtures were prepared according to equation (1):[3]

$$AlH_4^- + Al(OR)_4^- \rightleftharpoons AlH_3OR^- + AlH(OR)_3^- \rightleftharpoons 2\,AlH_2(OR)_2^- \quad (1)$$

The starting compounds were mixed in the given ratios in pure solvents, namely in benzene (B), tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), and diglyme (DG), respectively, and the reaction mixture was then heated to 80 °C for 24 h to reach equilibrium (Method A). This process was monitored by ^{27}Al n.m.r. spectroscopy. The preparation confirmed our expectations:[1] a low H/OR exchange rate due to the absence of a catalytic effect of the Na^+ or Li^+ cations, as has been found for alkyl exchange with tetra-alkylaluminates[8] and for H/D exchange between $LiAlH_4$ and $LiAlD_4$.[9] In the absence of such promotion, *i.e.* with the Bu_4N^+ salts, the equilibrium was practically complete in a few minutes with (5a), in several hours with (5b) and (5c) in benzene, and after 18 h with (5d), (5e) in DME and DG. On the other hand, no observable exchange was achieved after 30 days with (5g) at ambient temperature. For comparison, similar equilibration with the Na^+ salts was faster by at least two orders of magnitude,[10] and still shorter times can be expected with equivalent Li^+ compounds for which intermolecular catalysis promoted by the metal bonding sphere was considered.[8]

The very slow exchange between (1) and (5g), even at 80 °C, meant that the (1)–(5g) mixtures had to be prepared by a different method, namely by the alcoholysis of $Bu_4N^+AlH_4^-$ with various equivalents of t-butyl alcohol in appropriate solvents. This method can also be achieved with other alcohols ROH (R = a–f) according to equation (2). With less strain-inducing alkyl groups, the equilibrium was attained in <24 h when heated to 80 °C (Method B), as demonstrated by the

$$Bu_4NAlH_4 + nROH \longrightarrow Bu_4NAlH_{4-n}(OR)_n^- + nH_2 \quad (2)$$

Table 1. The composition (mol %) of mixtures $[Bu_4N^+][(1)-(5d)]$ obtained by methods A and B (see text).

Method of preparation	mol % (1)	(2)	(3)	(4)	(5)
A	16.5	3	8	40.5	32
B	13	4	11	42	30

species **(1)**–**(5d)**, showing only insignificant differences in composition (Table 1).

^{27}Al N.M.R. Measurements.—The solutions of the mixtures **(1)**–**(5)**, **(a)**–**(g)** obtained in equations (1) and (2) were measured with and without ^1H decoupling at 52.1 MHz in 10 mm tubes (sealed under argon) at 23 and 70 °C. The chemical shift and the line widths at half height ($w_{\frac{1}{2}}$) of the ^{27}Al signals of individual species $[Bu_4N^+]$[**(1)**–**(5)**, **(a)**–**(g)**] and their dependence on solvent and temperature are given in Table 2. On inspection of these results, it can be seen that in any mixture, irrespective of alkyl group or solvent, as well as in the non-equilibrium mixture **(1)**–**(5g)** formed by alcoholysis, all five signals present are due to anions **(1)**–**(5)**. This shows that the exchange rate is slow on the n.m.r. time-scale not only at ambient temperature but also at 70 °C, and there is no coalescence of signals. For a discussion of the dependence of $\delta(^{27}Al)$ on the number of OR groups and the character of R, see Part 1.[1]

Minimal differences in the ^{27}Al chemical shifts of individual aluminium nuclei in anions **(1)**–**(5)**, **(a)**–**(g)** are caused by changes of solvent and temperature and indicate that these species interact negligibly not only with aromatic hydrocarbons but also with mono-, di-, or tri-dentate ethers, represented by THF, DME, and DG, respectively (see below).

The coupling constants $J(^{27}Al-^1H)$ of all compounds **(1)**–**(5)**, **(a)**–**(f)** are only slightly influenced by solvent and exhibit the following values (Hz): **(1)** 174, **(2)** 181–192, **(3)** 197–217, and **(4)** 230–241. The t-butoxy derivatives **(2g)**–**(5g)** are somewhat exceptional and show lower values, namely **(2g)** 165–167, **(3g)** 175–190, and **(4g)** 217–222.

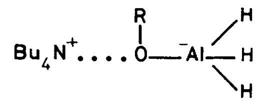
The line widths ($w_{\frac{1}{2}}$) of the ^{27}Al n.m.r. signals of the individual species **(1)**–**(5)** **(a)**–**(g)** are significantly influenced by temperature, solvent, number of alkoxy groups, and bulk of the alkyl R group (Table 3). The observed differences in the values of $w_{\frac{1}{2}}$ can be explained by the existence of ion–ion (I) or ion–multipole (II)–(V) associations and their separation by molecules of solvent according to equation (3). The interactions

$$Bu_4N^+AlH_{4-n}(OR)_n^- + S \rightleftharpoons Bu_4N^+S + SAlH_{4-n}(OR)_n^- \quad (3)$$

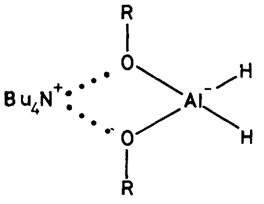
(I)–(V) are generally weak with tetrabutylammonium salts (as follows from the small changes in their ^{27}Al n.m.r. shifts caused by changes in temperature and solvent) but they are sufficient to influence significantly the $w_{\frac{1}{2}}$ values. The stronger these relatively weak interactions, the less symmetrical the electric field around the observed ^{27}Al nuclei and the faster the rate of substituent exchange. Both effects contribute to the broadening of a given signal. The strength of these interactions can be expected to decrease with: (*i*) increasing bulk of the alkyl group R, which becomes operative only at a certain number of OR groups; (*ii*) decreasing number of OR groups in a given molecule; (*iii*) increasing polarity of the solvent; (*iv*) increasing temperature; and (*v*) decreasing concentration of the solution (Table 4). Based on these considerations, the strongest association (and therefore the greatest $w_{\frac{1}{2}}$ values) can be expected with $Al(OMe)_4^-$ in benzene at 23 °C, while the weakest association, *i.e.* practically solvent separated ion pairs, are expected with t-butoxy derivatives in polar solvents at elevated temperatures. The data in Table 3 confirm these expectations.

$Bu_4N^+ \cdots AlH_4^-$

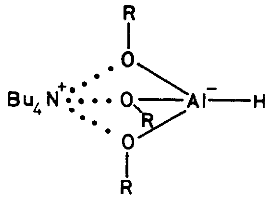
(I)



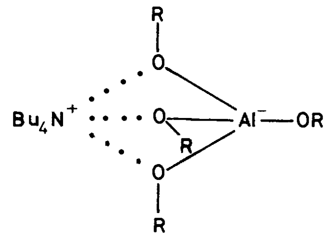
(II)



(III)



(IV)



(V)

Support for a slight association of Bu_4N^+ with the individual anions **(1)**–**(5)** can be found in the small differences in the chemical shift of their central ^{27}Al atoms caused by changes in concentration, temperature (Table 4), and solvent separation of ion-pairs according to equation (3). The interaction of the positively charged Bu_4N^+ ion with the oxygen atom bound to the aluminium atom in (II)–(V) can cause a decrease in oxygen electron density and, consequently, a decrease in the negative charge on the central aluminium atom. Taking the $w_{\frac{1}{2}}$ values as a rough criterion of the strength of the $Bu_4N^+ \cdots$ **(1)**–**(5)** association, we see that the ^{27}Al n.m.r. signal moves slightly to lower magnetic field with increasing $w_{\frac{1}{2}}$ values (increasing interactions) (*cf.* Tables 1 and 4). The differences amount only to about 2 ppm when comparing the 'strongest' and the 'weakest' association with **(5)** and only up to 1 ppm with **(2)**. Despite these very small differences, the expected trend is detectable, which confirms the presence of weak associations (I)–(V) and shows the ^{27}Al n.m.r. chemical shifts to be relatively reliable evidence.

These associations (I)–(V) are too weak to influence the stereoselectivity in reductions of cycloketones.[2] When present as salts of Bu_4N^+ cations, the alkoxohydridoaluminate anions **(2)**–**(4)** behave during reduction reactions, therefore, as separate particles, and the access to a group to be reduced is given predominantly by their own bulk.

$Bu_4NAlH_{4-n}(OR)_n$ Equilibrium Mixtures.—In contrast with equilibrium mixtures of Li^+ or Na^+ alkoxohydridoaluminates which showed very broad superimposed signals, and which could be analysed only with difficulty,[7] the signals of Bu_4N^+ analogues were narrow and well resolved, so that we could determine their molar fractions with an accuracy of ±2%. The $Bu_4NAlH_{4-n}(OR)_n$ system allowed, however, a study only of

Table 2. ^{27}Al N.m.r. data (δ at 23 °C and $w_{\frac{1}{2}}$) for the compounds $Bu_4NAlH_{4-n}(OR)_4$ in B, THF, DME, and DG.[a]

		(1)		**(2)**		**(3)**		**(4)**		**(5)**	
Solvent	R	δ	$w_{\frac{1}{2}}$	δ	$w_{\frac{1}{2}}$	δ	$w_{\frac{1}{2}}$	δ	$w_{\frac{1}{2}}$	δ	$w_{\frac{1}{2}}$
B	**(a)**	101.6	30	121.1	130	111.5	220	90.6	420	72.6	700
		(100.9)	20	(120.9)	50	(111.5)	90	(90.6)	150	(72.0)	250
	(b)	101.5	35	118.2	90	108.3	140	87.8	365	68.3	700
		(100.8)	20	(117.9)	60	(107.7)	100	(87.3)	135	(69.5)	220
	(c)	101.6	50	118.5	200	107.1	200	87.0	900	70.4	1 100
		(100.9)	25	(118.2)	70	(108.0)	115	(87.1)	230	(69.3)	400
	(d)	101.6	30	118.7	90	108.2	150	87.8	280	70.7	600
		(101.0)	25	(118.2)	55	(107.7)	60	(87.1)	100	(69.1)	180
	(e)	101.6	50	115.0	140	103.0	210	85.1	380	66.8	260
		(100.9)	30	(114.7)	70	(103.3)	75	(84.2)	105	(65.8)	130
	(f)	101.7	30	116	1 000	101	900	77.6	700	52.6	120
		(101.1)	35	(115.5)	300	(103.1)	400	(76.1)	300	(52.6)	60
	(g)	101.6	30	108.6	65	94.2	45	75.5	35	51.6	70
		(100.6)	20	(108.3)	50	(93.8)	35	(74.4)	25	(51.8)	35
THF	**(a)**	100.0	20	120.8	130	111.8	145	90.4	180	71.8	220
		(99.3)	10	(120.6)	55	(111.6)	50	(90.1)	65	(71.2)	90
	(b)	99.9	25	118.0	60	108.3	65	87.8	80	69.4	130
		(99.5)	25	(117.7)	45	(107.9)	50	(87.3)	40	(68.8)	80
	(c)[b]	—	—	—	—	—	—	—	—	—	—
	(d)	100.0	25	118.3	70	108.6	70	87.8	80	68.6	160
		(99.5)	15	(118.0)	50	(108.3)	50	(87.4)	40	(68.1)	80
	(e)	100.1	20	114.8	85	104.0	100	84.7	90	66.3	130
		(99.5)	20	(114.3)	55	(103.5)	60	(83.7)	50	(65.3)	75
	(f)	100.1	25	115.9	320	102	400	75.7	380	52.8	35
		(99.7)	15	(115.6)	240	(102.2)	280	(75.4)	220	(52.1)	25
	(g)	100.3	25	108.2	55	94.0	40	74.8	35	55.7	40
		(99.7)	15	(107.9)	40	(93.3)	30	(74.5)	35	(52.2)	20
DME	**(a)**	101.0	25	120.8	60	111.8	65	90.6	85	71.9	120
		(100.3)	15	(121.1)	40	(111.9)	40	(90.3)	50	(71.4)	80
	(b)	101.0	20	118.2	75	108.4	75	87.8	75	69.7	135
		(100.3)	15	(117.9)	45	(108.0)	45	(87.3)	45	(68.9)	60
	(c)	101.1	20	118.6	95	108.6	120	88.0	165	69.4	305
		(100.4)	15	(118.3)	70	(108.3)	70	(87.5)	75	(68.7)	120
	(d)	101.1	20	118.7	80	108.8	70	87.8	90	69.1	130
		(100.4)	15	(118.4)	50	(108.5)	50	(87.2)	45	(68.4)	75
	(e)	101.9	25	114.8	100	104.0	90	85.2	95	66.6	145
		(100.4)	20	(114.4)	50	(103.7)	50	(84.1)	45	(65.7)	65
	(f)	101.1	20	115.0	—	101.3	800	76.2	420	53.2	45
		(100.5)	20	(116.0)	500	(101.4)	320	(75.6)	210	(52.5)	20
	(g)	101.3	15	108.5	40	94.3	30	74.3	20	56.1	20
		(100.5)	15	(108.1)	30	(93.6)	25	(73.2)	15	(54.9)	15
DG	**(a)**	101.0	12	121.1	60	111.9	85	90.5	120	71.9	220
		(100.4)	10	(120.8)	35	(111.5)	40	(90.0)	55	(71.3)	115
	(b)	101.1	15	118.2	65	108.3	95	87.7	100	68.6	210
		(100.5)	10	(117.8)	40	(107.9)	45	(87.2)	45	(68.9)	90
	(c)	101.2	20	118.9	130	108.7	180	88.2	180	69.6	400
		(100.5)	10	(118.3)	65	(108.2)	80	(87.2)	75	(68.7)	100
	(d)	101.2	20	118.4	70	108.6	90	87.8	90	69.1	160
		(100.5)	12	(118.2)	40	(108.1)	55	(87.2)	50	(68.3)	90
	(e)[e]	—	—	—	—	—	—	—	—	—	—
	(f)	101.2	25	115.7	450	102	600	75.8	500	53.1	50
		(100.5)	15	(116.0)	300	(101.0)	300	(75.5)	250	(52.4)	30
	(g)	101.3	30	108.5	80	94.1	80	74.5	60	56.0	30
		(100.6)	16	(108.1)	45	(93.6)	40	73.4	40	(54.8)	16

[a] Values of δ at 70 °C are given in parentheses. [b] Values not recorded.

those equilibrium mixtures with alkyl groups R which offer low steric hindrance, *e.g.* **(a)**–**(f)**. Systems with R = Bu^t or even bulkier alkyl groups, exchanged so slowly that no equilibrium was reached, even at 80 °C, in a reasonable time.

To determine the main factors influencing the abundance of the species **(1)**–**(5)**, the ^{27}Al n.m.r. proton decoupled spectra of the systems analysed as $Bu_4NAlH_{4-n}(OR)_n$, prepared in at least two experiments, were measured at ambient and elevated temperatures for different R [**(a)**–**(f)**]; *n* (usually six values in the range *n* = 0–4), and solvents (always B, THF, DME, or DG;

Table 3. The influence of temperature, selected solvents, and the number and bulk of alkyl groups R on the line width ($w_{\frac{1}{2}}$/Hz) of the ^{27}Al n.m.r. signals of (**2**)–(**5**).

			$w_{\frac{1}{2}}$			
R	Solvent	Temperature	(**2**)	(**3**)	(**4**)	(**5**)
(**a**)	B	22	130	220	420	700
		70	50	90	150	250
	DME	70	40	40	50	80
(**b**)	B	22	90	140	365	700
		70	60	140	125	230
	DME	70	45	45	45	60
(**d**)	B	22	90	150	280	600
		70	55	60	100	180
	DME	70	50	50	45	75
(**g**)	B	22	65	45	35	70
		70	50	35	25	35
	DME	70	30	25	15	15

Table 4. Concentration (c) and temperature (T) dependence of ^{27}Al n.m.r. shift (δ) and line width ($w_{\frac{1}{2}}$) for $Bu_4NAl(OMe)_4$ in benzene.

c/mol dm^{-3}	T/°C	δ/ppm	$w_{\frac{1}{2}}$/Hz
0.42	22	73.46	718
	80	71.94	279
0.21	22	73.35	685
	80	72.03	267
0.10	22	73.30	646
	80	71.97	232
0.02	22	73.24	528
	80	71.82	169

sometimes toluene, diethyl ether, or dioxane). This database, amounting almost to 1 500 ^{27}Al n.m.r. spectra, has shown that the main principles affecting the composition of such systems can be illustrated graphically using as an example three equilibrium mixtures with R = Me, Pr^{i}, and Ph in solvents at the extremes of solvating ability, *e.g.* benzene (○) and diglyme (□), at 23 °C and at 70 °C Figures 1(*a*)–(*d*). The present data are a complete and revised version of those presented in 1984,[6] because repeated experiments have proved that previous equilibration times were insufficient with some systems.

Inspection of Figures 1(*a*)–(*d*) demonstrates (*i*) the presence of all five species (**1**)–(**5**) in the equilibrium mixtures of analytical composition $Bu_4NAlH_{4-n}(OR)_n$, irrespective of R, solvent used, or temperature; the same holds for the systems with R = (**b**,**c**,**e**); (*ii*) negligible differences in molar fractions of the individual species (**1**)–(**5**) caused by changes in the character of aliphatic alkyl groups but distinct differences brought about by the phenyl group (**f**); (*iii*) a dominance of monohydrido species (**4**) not only with alkyl (Me, Et, and nonyl) but also with branched s-alkyl derivatives (Pr^{i} and cyclohexyl); analogous behaviour was deduced with $LiAlH_{4-n}(OR)_n$ (R = Bu, Bu^{s}, and Bu^{t}),[7] which has corrected an earlier presumption of the absence and, consequently, low stability of the components (**4**) with s-alkyl groups in reaction equilibria; and (*iv*) a low abundance (< 12%) of the trihydrido (**2**) and dihydrido (**3**) species, of which the latter is usually present in a greater amount.

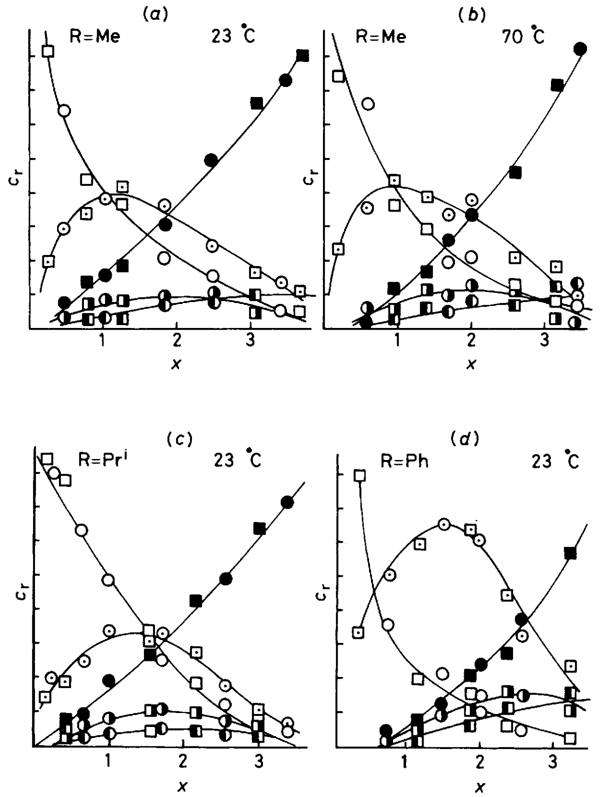


Figure 1. Relative concentrations (c_r) of compounds (**1**)–(**5**) determined by ^{27}Al n.m.r. analysis at the given temperatures in equilibrium mixtures obtained by mixing (4-x)Bu_4NAlH_4 with $x$$Bu_4NAl(OR)_4$ in B(○) or DG(□) with subsequent heating to 80 °C for 24 h. AlH_4^- = ●, ■; $AlH_3(OR)^-$ = ◐, ◧; $AlH_2(OR)_2^-$ = ◑, ◨; $AlH(OR)_3^-$ = ⊙, ⊡; $Al(OR)_4^-$ = ○, □.

The equilibrium mixtures composed of the [Bu_4N^+][(**1**)–(**5**); (**a**)–(**f**)] members can be described by twelve bimolecular reactions, represented by the six equilibrium reactions (4)–(9), of which only three are linearly independent. To describe a given system, equations (5)–(7) were selected and the equilibrium constants K_2–K_4 for $Bu_4N^+AlH_2(OR)_2^-$ were calculated from the composition of individual equilibrium mixtures (Table 5). In all systems measured a sufficient equilibrium and, consequently, thermodynamic control of the metathesis was ensured.

$$AlH_4^- + Al(OR)_4^- \underset{}{\overset{K_1}{\rightleftarrows}} AlH_3OR^- + AlH(OR)_3^- \qquad (4)$$

$$2\,AlH_3OR^- \overset{K_2}{\rightleftarrows} AlH_2(OR)_2^- + AlH_4^- \qquad (5)$$

$$2\,AlH_2(OR)_2^- \overset{K_3}{\rightleftarrows} AlH_3OR^- + AlH(OR)_3^- \qquad (6)$$

$$2\,AlH(OR)_3^- \overset{K_4}{\rightleftarrows} AlH_2(OR)_2^- + Al(OR)_4^- \qquad (7)$$

$$AlH_4^- + AlH(OR)_3^- \overset{K_5}{\rightleftarrows} AlH_3OR^- + AlH_2(OR)_2^- \qquad (8)$$

$$Al(OR)_4^- + AlH_3OR^- \overset{K_6}{\rightleftarrows} AlH(OR)_3^- + AlH_2(OR)_2^- \qquad (9)$$

If the equilibrium composition is given by entropic factors, the ratio of the components (**1**)–(**5**) for a system showing the stoicheiometry $Bu_4NAlH_2(OR)_2$ will be 1:4:6:4:1 and K_2 = K_4 = 0.8K_3. The ratios found for the systems (**1**)–(**5**); (**a**)–(**f**) were, however, entirely different which indicated a dissimilarity (bonding, steric) between H^- and OR^- ligands bound to the central aluminium atom,[1] *i.e.* the importance of an enthalpic factor.

The dissociation constants K_4 (K_2, K_3) of individual alkoxy derivatives (R = Me, Et, Pr^{i}, and Ph) were found to vary only slightly with solvent, temperature, and, surprisingly, also with aliphatic alkyl group (*cf.* K_4 = 0.16, 0.23, and 0.14 for Me, Et, and Pr^{i}, respectively). Great differences in individual K values and, consequently, a reversed equilibrium direction were, however, observed between alkoxy and phenoxy derivatives. This diverse behaviour is evident when comparing the constants K_7 for the overall metathetic reaction [equation (10)] involving all

Table 5. Disproportionation constants K_2, K_3, and K_4, the constant K_7 for the overall exchange reaction for the system $Bu_4NAlH_{4-n}(OR)_n$, and their estimated standard deviation σ_{n-1} values showing the dependence on the alkyl R group, solvent, and temperature.

R	T/°C	Solvent	K_4	σ_{n-1}	K_3	σ_{n-1}	K_2	σ_{n-1}	K_7	σ_{n-1}
(a)	23	B	0.16	0.02	2.3	0.3	10.5	2.0	0.041	0.010
		DME	0.135	0.013	3.0	0.7	9	5	0.039	0.010
	70	B	0.145	0.015	2.3	0.7	10	2	0.039	0.010
		DME	0.137	0.007	3.0	1.2	7	4	0.040	0.005
(b)	23	B	0.23	0.09	1.6	0.3	20	3	0.017	0.004
		DME	0.13	0.02	2.1	0.5	20	10	0.021	0.009
	70	B	0.25	0.07	1.35	0.09	15	2	0.029	0.008
		DME	0.19	0.03	6.0	0.2	14	5	0.040	0.009
(d)	23	B	0.14	0.04	2.0	0.6	12.5	3.5	0.080	0.030
		DME	0.16	0.04	2.3	0.5	22	7	0.005	0.002
	70	B	0.20	0.05	1.75	0.70	13.5	8.0	0.070	0.030
		DME	0.24	0.05	1.9	0.4	9.2	3.0	0.012	0.050
(f)	23	B[a]	—	—	—	—	—	—	—	—
		DME	0.023	0.006	4.2	1.3	3.3	0.2	2.0	1.0
	70	B	0.037	0.010	2.7	0.4	3.0	1.0	4.0	0.5
		DME	0.021	0.007	4.6	1.3	3.3	0.3	2.6	1.0

[a] Could not be determined.

$$2\,AlH_4^- + 2\,Al(OR)_4^- \overset{K_7}{\rightleftharpoons} AlH_3OR^- + 2\,AlH_2(OR)_2^- + AlH(OR)_3^- \quad (10)$$

five members (**1**)–(**5**). While the K_7 values for the aliphatic alkyl groups show a distinct shift to the starting compounds (**1**) and (**5**), the value for phenoxy derivatives give evidence to support a shift to the mixed phenoxyhydrido species (**2f**)–(**4f**). The cause of this diversity is under investigation. Mutually different directions were also observed for reaction (6) in the case of the Bu_4N^+ and Li^+ salts. While the former counter-ion prefers disproportionation, the Li^+ cation[7] favours the opposite tendency.

Kinetic Aspects.—The result of a stereospecific reduction of a carbonyl compound is significantly dependent on the equilibration rates within the system (**1**)–(**5**), (**a**)–(**g**). To get sufficient stereospecifity, reduction rates are needed which are several orders faster than those of the undesired metathetic reactions. Our preliminary experiments have indicated that the rate of the metathesis can be strongly reduced by substituting the Li^+ or Na^+ cations by the Bu_4N^+ cation and, especially, by increasing the bulk of the alkyl group in an alkoxy group. Only with the t-butoxy group, and with even larger alkyl groups, is the exchange rate so slow that disproportionation does not interfere with the reduction. This knowledge provides the possibility of finding the optimum stereospecifically reducing alkoxohydridoaluminates for a given case.

Conclusions

Tetrabutylammonium alkoxohydridoaluminates are reducing agents in which the catalysis of the ligand exchange and consequent disproportionation is strongly suppressed when compared with the Li^+ and Na^+ salts. The metal cation to anion co-ordination bonds are absent but weak electrostatic interactions still operate. These interactions can be reduced and, consequently, the exchange ratios can be further lowered with increasing bulk of the alkyl R group, with the polarity of solvent, and with increasing temperature. Under these conditions, the disproportionation of the prepared compound (**4**) is practically absent during the reduction reaction.

The maximum stereoselectivity in the reduction can be thus expected to occur when using tetrabutylammonium trialkoxohydridoaluminates (**4**) with R = Bu^t (or an even bulkier alkyl group), free of (**1**)–(**3**), dissolved in a polar ether (*e.g.* DME), and working at elevated temperatures. In such a system, the stereoselectivity of reduction will be dominated by the steric demands of the three bulky OR groups in (**4**). Preliminary results are in accord with this idea.[10]

For the above reason, the alkoxohydridoaluminates with R_4N^+ counter-cations and bulky alkyl groups can serve as a model for systems approximating this boundary type. Similar reducing behaviour can be therefore expected with Li^+ or Na^+ alkoxohydridoaluminates in the presence of strongly complexing molecules such as aprotic amines, crown ethers or multidentate ethers (DG, DME).

Experimental

N.M.R. Measurements.—The ^{27}Al n.m.r. spectra were recorded at 52.128 MHz using a Varian XL-200 spectrometer with and without ^1H decoupling. The samples, dissolved in pure non-deuteriated solvents given in Table 2, were measured in sealed 10 mm tubes provided with a capillary containing the standard: an aqueous solution of $[Al(OH_2)_6]Cl_3$ = 0 ppm. The intensity ratio of narrow signals (**1**)–(**5**) (<80 Hz) was determined by spectrometer integration. That of wider signals (>80 Hz) was determined by manual curve resolution carried out directly on the spectrometer using our own program.

Materials.—All reactions and manipulations were carried out in dry argon. The solvents and alcohols used were dried over CaH_2 and distilled immediately before use. The starting compounds Bu_4NAlH_4 and $Bu_4NAl(OR)_4$ were prepared as described in Part 1.[1]

The equilibrium mixtures were prepared by mixing appropriate amounts of 0.2 mol dm^{-3} solutions of (**1**) and (**5a**–**f**) in given solvents (B, THF, DME, and DG) in a reaction flask and an aliquot was transferred to an n.m.r. tube, which was sealed and heated for 24 h at 80 °C to attain equilibrium. Measurements were performed after 1–3 days, and with less reactive species (**d**, **e**) were repeated after 1 month or later. No further changes in ratios were found after that time.

$Bu_4N^+AlH_{4-n}(OR)_n^-$ *Mixtures.*—To a solution of Bu_4N^+-AlH_4^- in a given solvent was slowly added an appropriate quantity of Bu^tOH in the form of very small drops from a syringe needle. The resulting solution was heated for several hours to 80 °C till hydrogen evolution had ceased. An aliquot was transferred to an n.m.r. tube which was then sealed.

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Received 12*th July* 1988; *Paper* 8/02796J