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Reaction of Lithium Aluminum Hydride with Hindered Phenols. Formation of Tricoordinate Aluminum Species

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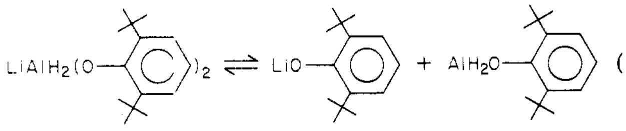
Lithium aluminum hydride reacts readily with 3 molar equiv of 2,4,6-tri-*tert*-butylphenol in refluxing ether. It has been demonstrated that the products resulting from this reaction cause the conversion of axial to equatorial cyclohexanols in the presence of a ketone. This behavior is attributed to the formation of tricoordinate aluminum species. An ether solution of bis(2,4,6-tri-*tert*-butylphenoxy)aluminum hydride was prepared, and infrared spectra provide evidence for the existence of this species in solution resulting from the reaction of $LiAlH_4$ with 3 molar equiv of 2,4,6-tri-*tert*-butylphenol.

The chemistry of compounds containing Al–H bonds is of considerable interest due to the utility of many of these hydrides as reducing agents.[1] The chemical behavior of alkoxy- or (aryloxy)aluminum hydride species[2] is of particular interest since many of them occur as intermediates in the metal hydride reduction of ketones and other compounds, and some of these hydrides have found use as readily prepared, selective reducing agents. The behavior of these species such as their possible disproportionation[3] is relevant to an understanding of mechanism[4] and stereochemistry[5] in metal hydride reductions.

Recently we have reported the decomposition of the hindered tetracoordinate compound lithium bis(2,6-di-*tert*-butylphenoxy)aluminum hydride (1) in refluxing tetrahydrofuran (THF) to a tricoordinate species.[6] A possible mode of decomposition resulting in the formation of the tricoordinate species 2 is shown in eq 1. It was observed that refluxing a solution of 1 in THF resulted in loss of active hydride and ring opening of THF to 1-butanol, and this was attributed to coordination of a tricoordinate aluminum species such as 2 with THF and subsequent reduction of the THF. Tetrahydrofuran is an efficient base toward complexation of tricoordinate aluminum compounds, more so for example than diethyl ether.[7] Solutions of aluminum hydride in THF have been observed to slowly lose hydride with the formation of 1-butanol.[8] Recently the facile ring opening of THF and other cyclic ethers by the combination of lithium tri-*tert*-butoxyaluminum hydride–triethylborane has been reported.[9]



1 2 (1)

We have carried out further studies of the behavior of hindered tetracoordinate lithium (aryloxy)aluminum hydrides in diethyl ether and now report further evidence for the formation of tricoordinate aluminum compounds in the reaction of $LiAlH_4$ with hindered phenols in ether.

Results and Discussion

Attempted Preparation of $LiAlH(OAr)_3$ in Diethyl Ether. While $LiAlH_4$ in diethyl ether reacts readily with 2 equiv of 2,4,6-tri-*tert*-butylphenol, 3 (or 2,6-di-*tert*-butylphenol), at room temperature (ca. 20 °C), substitution of hydride by a third molar equivalent of 3 is very slow because of steric hindrance to formation of the lithium tris(aryloxy)aluminum hydride.[10] The third equivalent of hydrogen is evolved at a convenient rate in refluxing ether, however. The extent of reaction is readily followed by measurement of hydrogen evolution. While this would appear to correspond to formation of 4 in accordance with eq 2, the reducing properties of the resulting solution in

$$LiAlH_4 + \underset{3}{3ArOH} \xrightarrow[\text{reflux}]{Et_2O} \underset{4}{LiAlH(OAr)_3} + 3H_2 \quad (2)$$

Ar = 2,4,6-tri-*tert*-butylphenyl

reactions with 3,3,5-trimethylcyclohexanone (dihydroisophorone, DHI) suggest that 4 cannot be the major reducing species present.

Scheme I

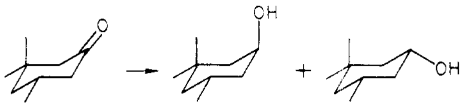
$$LiAlH_4 + 3ArOH \xrightarrow[\text{ether}]{25\ ^\circ C} LiAlH_2(OAr)_2 + 2H_2 + ArOH$$

$$LiAlH_2(OAr)_2 \xrightarrow[\text{heat}]{\text{path a}} LiOAr + AlH_2(OAr) \xrightarrow{ArOH} \underset{5}{AlH(OAr)_2} + H_2$$

$$LiAlH_2(OAr)_2 \xrightarrow[\text{ArOH, heat}]{\text{path b}} \underset{4}{LiAlH(OAr)_3} + H_2$$

$$4 \longrightarrow LiOAr + \underset{5}{AlH(OAr)_2}$$

In entries 3 and 4 of Table I, 2 molar equiv of 3 was reacted with $LiAlH_4$ without heating to give lithium bis(aryloxy)aluminum hydride. Reduction of DHI with this reagent gave 70% of the trans (axial) alcohol (eq 3).



(3)

DHI trans (axial) cis (equatorial)

[†] This article is taken in part from work toward a Ph.D. thesis by T.A.M., Jr.

(1) (a) W. G. Brown, *Org. React.*, **6**, 469 (1951); (b) N,. G. Gaylord, "Reductions with Complex Metal Hydrides", Interscience, New York, 1956; (c) H. C. Brown and S. Krishnamurthy, *Tetrahedron*, **35**, 567 (1979).

(2) For a review, see J. Malek and M. Cerny, *Synthesis*, 217 (1972).

(3) H. C. Brown and C. J. Shoaf, *J. Am. Chem. Soc.*, **86**, 1079 (1964).

(4) K. E. Wiegers and S. G. Smith, *J. Am. Chem. Soc.*, **99**, 1480 (1977); K. E. Wiegers and S. G. Smith, *J. Org. Chem.*, **43**, 1126 (1978); E. C. Ashby and J. R. Boone, *J. Am. Chem. Soc.*, **98**, 5524 (1976).

(5) (a) H,. Haubenstock and E. L. Eliel, *J. Am. Chem. Soc.*, **84**, 2363 (1962); (b) H. Haubenstock, *J. Org. Chem.*, **38**, 1765 (1973).

(6) H. Haubenstock and N.-L. Yang, *J. Org. Chem.*, **43**, 1463 (1978).

(7) E. Bonitz, *Chem. Ber.*, **88**, 742 (1955); S. Searles, Jr., and M. Tamres in "The Chemistry of the Ether Linkage", S. Patai, Ed., Interscience, 1967, p 278.

(8) H. C. Brown and N. M. Yoon, *J. Am. Chem. Soc.*, **88**, 1464 (1966).

(9) S. Krishnamurthy and H. C. Brown, *J. Org. Chem.*, **44**, 3678 (1979); H. C. Brown and S. Krishnamurthy, *J. Chem. Soc., Chem. Commun.*, 868 (1972).

(10) J. S. Meek and C. Bouboulis, *J. Org. Chem.*, **26**, 1302 (1961).

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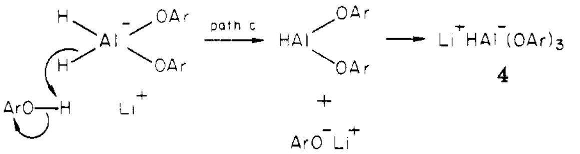
Table I. Reaction of $LiAlH_4$ with ArOH[a] in Diethyl Ether. Reduction of DHI

entry	amt $LiAlH_4$, mmol	amt ArOH, mmol	reflux t, h	H_2 evolved, mmol	amt DHI, mmol	product analysis,[b] %		
						DHI	trans alc[c]	cis alc[c]
1	10	30	1	29	10	11	47	53
2	10	30	1.75	30	10	16	36	64
3	10	20	0[d]	21	18	4	70	30
4	10	20	0[d]	22	18	3	69	31
5	10.4	20.8	0[d]	22.2	18.7	7	62	38
6	10.4	20.8	1	23.5	18.7	7	63	37
7	10.4	31.2[e]	0[d]	34.0	9.4	0	67	33
8	10.4	31.2[e]	1	28.9	9.4	0	65	35

[a] Ar = 2,4,6-tri-*tert*-butylphenyl except where noted. [b] Analysis by gas chromatography. [c] Alcohols are normalized to 100%. [d] No reflux period. [e] Ar = p-tolyl.

Reduction of DHI with $LiAlH_4$ gave 55% trans alcohol,[5a] and it is reasonable that a more sterically hindered reducing agent should give a greater proportion of trans alcohol. On this basis it might be expected that the bulky reagent **4** would give more than 70% trans alcohol, yet in entries 1 and 2 of Table I, where 3 molar equiv of **3** were reacted with $LiAlH_4$ followed by reduction of DHI, the proportion of trans alcohol formed was even lower than that produced with $LiAlH_4$.

An explanation for this unexpected result involves the decomposition on heating of hindered tetracoordinate aluminum species to tricoordinate species, as proposed previously in tetrahydrofuran.[6] Two such possible pathways, a and b, are shown in Scheme I. If path a were followed the hindered tetracoordinate species, **4** might not be formed at all. Depending on the mechanism of the reaction of $LiAlH_4$ derivatives with phenols, **4** might not be formed for a different reason, as outlined in path c (eq 4). According to this scheme, the formation of **4** would require combination of the tricoordinate aluminum species with LiOAr, and this might not occur due to steric hindrance to formation of the tetracoordinate species **4** containing bulky groups.



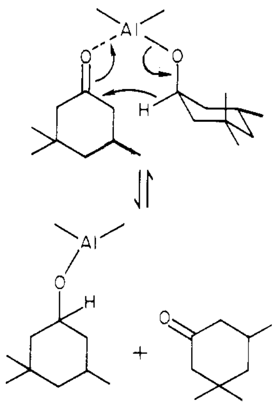
(4)

4

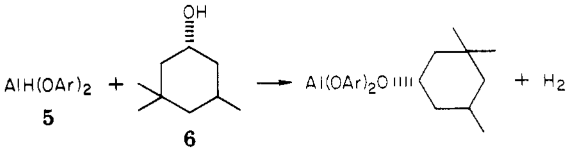
Entries 5 and 6 in Table I show the results of two experiments carried out simultaneously in which lithium bis(aryloxy)aluminum hydride was prepared, in one case heated under reflux for 1 h and in the other case not heated. In each case DHI was then added at room temperature, and the reaction mixture was hydrolyzed after 30 min. The stereoselectivity and extent of reduction in both cases were identical within experimental error. This suggests that the bis(aryloxy) hydride does not substantially break down in refluxing ether, but path a of Scheme I is not ruled out as a possibility. Formation of **4** via path b seems unlikely due to the severe steric hindrance involved in **4** as shown by attempted construction with space-filling models.

The observation of equilibration or the demonstration of conversion of axial to the more stable equatorial cyclohexanols in the presence of a cyclohexanone (in excess) would provide evidence for the intervention of tricoordinate aluminum species such as **5**. This would be expected to involve a Meerwein–Ponndorf–Verley–Oppenauer type[11] of oxidation–reduction mechanism as illustrated in Scheme II for 3,3,5-trimethylcyclohexanols and DHI. This has been observed with various types of tricoordinate aluminum species.[11,12] On the other hand, tetracoordinate aluminum species are not known to cause equilibration in the reduction of ketones. The possible occurrence of such partial equilibration is suggested by the relatively large proportion of the cis (equatorial) alcohol formed in entries 1 and 2 of Table I. In contrast to these results the reduction of DHI by $LiAlH(OC_6H_4\text{-}CH_3\text{-}p)_3$ gave predominantly the trans (axial) alcohol as shown in entry 7 of Table I. Heating of the reaction mixture gave the same result within experimental error (entry 8). The less hindered p-cresol behaved markedly differently in its reaction with $LiAlH_4$ (in a 3:1 molar ratio) than the more highly hindered phenol **3**.

Scheme II



Equilibration Studies.[13] A test for equilibration was planned in the following manner. After reaction of $LiAlH_4$ with 3 molar equiv of ArOH, the residual Al–H bonds were reacted with 1 molar equiv of pure (axial) *trans*-3,3,5-trimethylcyclohexanol (**6**, eq 5). This procedure was thought to offer an advantage in that DHI added after reaction of **5** with **6** would not be reduced by Al–H bonds, and therefore any conversion of axial to equatorial alcohol could readily be detected.



(5)

5

6

The amount of hydrogen evolved on addition of trans alcohol **6** to the "$LiAlH_4$ + 3ArOH" system in several experiments is shown in Table II. In each case approximately half of the added alcohol **6** reacted with Al–H

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[11] A. L. Wilds, *Org. React.*, 2, 178 (1944); C. Djerassi, *ibid.*, 6, 207 (1951).

[12] (a) E. L. Eliel and M. N. Rerick, *J. Am. Chem. Soc.*, **82**, 1367 (1960); (b) E. L. Eliel, *Rec. Chem. Prog.*, **22**, 129 (1961); (c) H. Haubenstock and E. B. Davidson, *J. Org. Chem.*, **28**, 2772 (1963).

[13] The term "equilibration" is used here to refer to a net conversion of axial to equatorial alcohol, regardless of whether complete equilibration has actually been attained.

Table II. $LiAlH_4$ and 3ArOH.[a] Subsequent Addition of Trans Alcohol 6[b]

entry	run	amt $LiAlH_4$, mmol	amt ArOH, mmol	H_2 evol,[c] mmol	amt 6, mmol	H_2 evol, mmol
1	TC-6	18.7	56.1	*d*	18.7	9.7
2	TB-98	20.7	62.4	60.2	20.8	12.4
3	TB-46	20.6	61.8	65.0	20.6	10.8
4	TB-48	10.3	30.9	29.2	10.3	4.6[e]
5	TB-60	10.3	30.9	28.2	10.3	3.5
6	TB-68	41.2	123.6	125.5	41.2[b]	20.7
					41.4[b,f]	12.1

[a] Solvent is diethyl ether. Ar = 2,4,6-tri-*tert*-butylphenyl. [b] Alcohol in entry 6 is cyclohexanol. [c] Following reflux period. [d] Not measured accurately. [e] This represents a control experiment in which hydrolysis after addition of 6 resulted in the evolution of 5.9 mmol of H_2. [f] This represents a second addition of alcohol to the reaction mixture.

Table III. Gas Chromatographic Analyses. Experiments TC-6 and TB-98

TC-6[a]			TB-98[b]		
t, h	% DHI[c]	% *trans*-6[d]	*t*, h	% DHI[c]	% *trans*-6[d]
0[e]	14	70	0[e]	17	60
0.5	10	57	0.3	14	53
12.1	11	51	1.1	13	52
36.4	11	46	18.0	14	51
71.3	11	39	25.2	14	48
94.5	11	35	41.3	14	49
141.6	11	30	67.2	14	40
166.4	10	30	89.3	13	37
284.4	11	27	95.4	13	36
			118.3	14	34
			145.3	13	31

[a] 9.4 mmol of DHI added. This experiment corresponds with entry 1 of Table II. The experiment was conducted at room temperature (ca. 25 °C) for 0.2 h, at which point the reaction mixture was heated under reflux. [b] 10.4 mmol of DHI added. The reaction mixture was heated under reflux at 40.7 h. This experiment corresponds with entry 2 of Table II. [c] Percent of total amount alcohols and ketone. [d] *trans*- and *cis*-3,3,5-trimethylcyclohexanols normalized to 100%. [e] Zero time corresponds to completion of DHI addition.

bonds, as indicated by the quantity of hydrogen evolved. That this is not simply due to an insufficient amount of Al–H present is shown by the reproducibility of the effect and also by the results of a control experiment shown in entry 4 of Table II. In this control, no DHI was added, and the reaction mixture was hydrolyzed after the addition of 6. Additional hydrogen was evolved in the amount shown (footnote *e*, Table II), demonstrating that active hydride, Al–H, was present after the addition of 6. The total hydrogen evolution in entry 4 (Table II) represents 97% of the total hydride content originally present. In the experiments where DHI was added (Table III) there was a net reduction of DHI, again showing the presence of active Al–H bonds.

Two possible explanations for incomplete reaction of the alcohol 6 are considered: (1) there are at least two "Al–H species" present, not all of which can react with 6; (2) about half of the alcohol 6 is consumed in one or more processes which do not generate hydrogen. The first possibility cannot itself explain the result due to the data shown in entry 6 of Table II. In this experiment cyclohexanol was added in two consecutive portions, and in each addition only about half of the available hydride was consumed (note that in the second addition only about 20 mmol of cyclohexanol could have reacted). Possible explanations for the incomplete reaction of 6 are discussed later (vide infra).

The first three entries in Table II represent experiments that are similar in that DHI was added to the reaction mixture subsequent to the addition of 6. Aliquots were analyzed by gas chromatography, with the results for experiments TC-6 and TB-98 shown in Table III[14] and in Figure 1. In experiment TC-6 there was a very rapid drop in the percent of trans alcohol 6 on addition of DHI. Within 0.5 h the composition of the reaction mixture changed to 57% 6 and 43% cis alcohol. Part of this is due to a net reduction of DHI by residual Al–H bonds. From the data in Table II, entry 1, it is seen that 9.0 mmol of 6 did not react with Al–H, and it is assumed that on hydrolysis this "diverted" alcohol was regenerated. The gas chromatographic analysis indicates that 6.3 mmol of DHI was reduced by residual Al–H and that 3.1 mmol of DHI was unreduced. If half of the reduced DHI afforded equatorial alcohol and this is the only source of this alcohol, then it is readily calculated that the product would consist of 87% trans alcohol 6 and 13% cis (equatorial) alcohol. Inspection of Table III shows that even at zero time, only 70% trans alcohol 6 was present and that this further decreased. Thus it is evident that axial alcohol was converted to equatorial alcohol. This isomerization constitutes evidence for the existence of tricoordinate aluminum species. The rapid conversion of axial to equatorial alcohol was followed by a further slow change to 27% 6, while the proportion of DHI remained constant over a long period. The results for experiment TB-98 were similar.

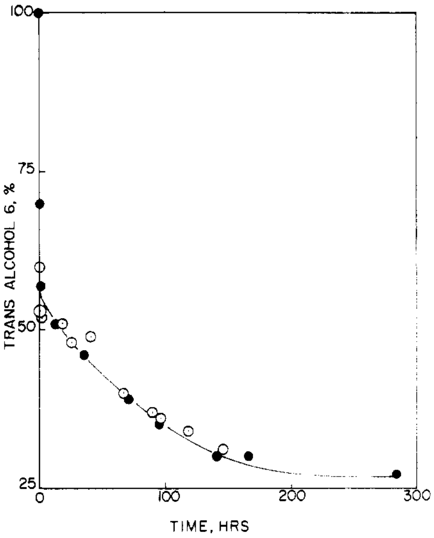

Figure 1. Conversion of axial alcohol 6 to the equatorial compound in the presence of DHI: ⊙, experiment TC-6; ●, experiment TB-98.

In a modification of the equilibration experiment, a different ketone than DHI was employed as the oxidizing agent. Lithium aluminum hydride was reacted with 3

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(14) Experiment TB-46 showed similar results, but fewer aliquots were taken.

Table IV. Equilibration of 6 with 4-*tert*-Butylcyclohexanone[a]

t, h	% C_9 ketone[b]	% trans (axial) C_9 alc[c]	% C_{10} ketone[d]	% cis (equatorial) C_{10} alc[c]	C_9/C_{10} area[e]
0[f]	29	46	22	35	0.98
1	26	42	27	34	0.99
24	27	42	25	32	0.99
48	27	41	25	32	0.98
72	27	40	24	31	1.02
96	26	40	23	31	0.98
228	29	39	21	29	1.04

[a] 10.3 mmol of 4-*tert*-butylcyclohexanone (C_{10} ketone) added. This experiment corresponds to entry 5 of Table II. [b] DHI, percent of C_9 ketone and C_9 cis and trans alcohols. [c] Cis and trans alcohols normalized to 100%. [d] 4-*tert*-Butylcyclohexanone, percent of C_{10} ketone and alcohols. [e] Area ratio of all C_9 species and C_{10} species. [f] Zero time was taken to be immediately after addition of the C_{10} ketone. The reaction mixture was kept at room temperature (ca. 20 °C).

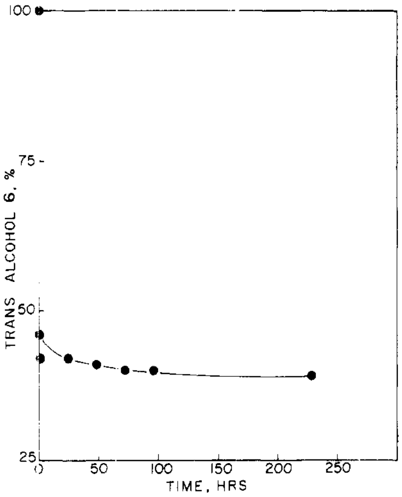
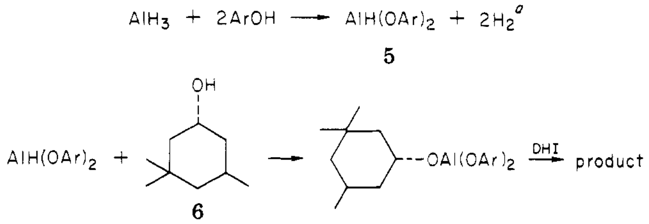


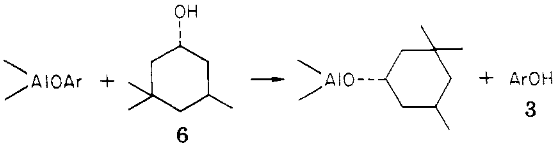
Figure 2. Conversion of axial alcohol 6 to the equatorial compound in the presence of 4-*tert*-butylcyclohexanone (experiment TB-60).

molar equiv of 3, and 1 molar equiv of pure 6 was added to the resulting reaction mixture. This was followed by addition of 4-*tert*-butylcyclohexanone (experiment TB-60). Aliquots were quenched in aqueous acid and analyzed by gas chromatography. The results obtained are shown in Table IV and Figure 2. It is seen that a remarkably rapid oxidation–reduction occurred, and immediately following addition of the C_{10} ketone, 29% of the C_9 alcoholate was oxidized to DHI with a simultaneous conversion of residual trans (axial) C_9 alcoholate to cis (equatorial) alcoholate. In a duplicate experiment where an aliquot of the reaction mixture was analyzed prior to addition of the C_{10} ketone, it was shown that no conversion of axial to equatorial C_9 alcohol occurred, and therefore the presence of a ketone is required. After the initial fast reaction very little change occurred over a long time period. The area ratio of C_9 to C_{10} species (ketone plus alcohols) remained constant over this period, showing the absence of any side reaction consuming one or more of the products. While 27% net oxidation of C_9 alcoholate occurred, 76% net reduction of the C_{10} ketone occurred, corresponding to about 5 mmol of C_{10} ketone reduced by residual Al–H bonds from the incomplete reaction of 6. If, in fact, the diverted portion of 6 which failed to react with Al–H bonds (vide supra) is assumed to be incapable of conversion to equatorial alcohol, then it can be calculated that the proportion of 6 in the product should be considerably higher (91% trans). Yet the observed result is 40% 6. It therefore may be concluded that at least a portion of the diverted alcohol 6 is in a form which can be converted to cis alcohol. A likely possibility is displacement of the phenol by 6 as shown in eq 6. In this process hydrogen is not evolved, yet the trans alcoholate is capable of conversion to the cis compound on addition of ketone. Infrared evidence for this process has been obtained (vide infra).

Scheme III



[a] 6.6 mmol measured.



(6)

In a further modification of the equilibration experiment the system "$LiAlH_4$ + 3ArOH" was reacted with cyclohexanol in two portions (experiment TB-68, Table II, entry 6). It was found that subsequent addition of DHI (41.2 mmol) resulted in very little oxidation of cyclohexanol, and gas chromatographic analysis of the resulting reaction mixture showed only 4% cyclohexanone and 96% cyclohexanol. The small extent of oxidation of cyclohexanol appears to be related to the more hindered structure of DHI and its corresponding alcohols.

Preparation of $AlH(OAr)_2$ (5). Equilibration of 6. The preparation of 5 from AlH_3 in ether was carried out in order to compare its chemical properties and infrared spectrum with those of the solution derived from the reaction of $LiAlH_4$ with ArOH (vide supra). A solution of aluminum hydride in diethyl ether was prepared by the reaction of $LiAlH_4$ with anhydrous $ZnCl_2$ according to the procedure of Ashby et al.[15] The aluminum hydride solution was standardized by the method of Felkin[16] and further characterized by its infrared spectrum (see Table VI). Aluminum hydride (3.4 mmol) was reacted with 2 molar equiv of ArOH (6.8 mmol) in ether to give 5 in a manner analogous to the preparation of simple alkoxy- and dialkoxyalanes.[17,18] The tricoordinate species 5 was reacted with a slight excess of trans alcohol 6 (4.8 mmol), and equilibration was initiated by the addition of DHI (1.7 mmol). These processes are shown in Scheme III. The gas chromatographic analysis of aliquots from the reaction mixture is shown in Table V and Figure 3. There is again a rapid conversion of axial to equatorial alcohol upon introduction of the DHI, and this is followed by a slower change. The conversion of axial alcohol 6 to the equatorial alcohol is greater than can be accounted for on the basis

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[15] E. C. Ashby, J. R. Sanders, P. Claudy, and R. Schwartz, *J. Am. Chem. Soc.*, **95**, 6485 (1973).

[16] H. Felkin, *Bull. Soc. Chim. Fr.*, 347 (1951). A solution of iodine in toluene was used instead of benzene.

[17] W. W. Zajac, Jr., and K. J. Byrne, *J. Org. Chem.*, **38**, 384 (1973).

[18] H. Nöth and H. Suchy, *Z. Anorg. Allg. Chem.*, **358**, 44 (1968).

Table V. Gas Chromatographic Analysis. Equilibration of 6 by Tricoordinate Aluminum[a]

t, h	% DHI[b]	% *trans*-6[c] (axial)
0[d]	16	28
1.4	11	17
9.6	8	12
24.0	8	11
35.6	6	10
50.9	7	10
71.9	6	9
107.5	6	7
119.6	6	7
173.3	6	6
192.3	6	6

[a] See Scheme III for the expected structure of reagent. The concentration of the reagent prior to addition of DHI was 0.06 M. [b] Percent of ketone and alcohols. [c] Alcohols normalized to 100%. [d] Zero time was taken to be immediately after the addition of DHI.

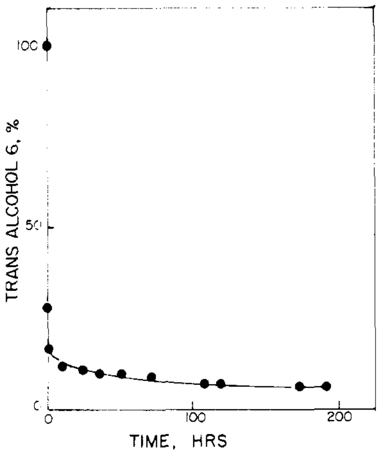


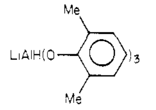
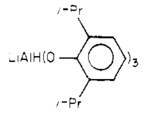
Figure 3. Equilibration of 6 with $AlH(OAr)_2$ in the presence of DHI.

of having added excess **6**, and this can be attributed to the process shown in eq 6. However, the 6% ketone found (Table V) is also low since 26% is calculated on the basis of no net reduction of added DHI. Because of the small quantities being used in this experiment, the difference between the 6% DHI found and the 26% DHI calculated represents only 1.3 mmol.

In a duplicate experiment 3.8 mmol of AlH_3 was reacted with 7.6 mmol of **3** (H_2 evolution 7.0 mmol) followed by 3.8 mmol of **6** (H_2 evolution 2.2 mmol). Immediately following the addition of 3.8 mmol of DHI, analysis showed 39% DHI and only 15% trans alcohol **6** (the alcohols are normalized to 100%). After 12.3 h, there was 27% DHI and 5% **6** (normalized). Thus, efficient equilibration of alcohols by the tricoordinate aluminum species **5** was demonstrated.

Disproportionation of **5** to (aryloxy)- and tris(aryloxy)aluminum hydride species is unlikely since the tris(aryloxy)aluminum compound could not be prepared by the addition of 3 molar equiv of ArOH (**3**) to AlH_3 in ether. When the reaction mixture was refluxed for 19 h almost 2 molar equiv of H_2 was evolved.

Table VI. Infrared Al-H Stretching Frequencies for $LiAlH_4$, AlH_3, and Aryloxy Derivatives

aluminum compd	ν_{Al-H}, cm^{-1}	solvent (concn, M)
$LiAlH_4$	1705	Et_2O (1)
	1655	THF (1)
$LiAlH_2(OAr)_2$[a]	1690	THF (0.07)
$LiAlH(OPh)_3$	1780	Et_2O (1)
	1826	Et_2O (0.1)
	1844	Et_2O (1)
AlH_3	1791	Et_2O (0.1)
$HAl(OAr)_2$[a]	1887	Et_2O (0.09)

[a] Ar = 2,4,6-tri-*tert*-butylphenyl.

Infrared Spectra. The infrared Al-H stretching frequencies (ν_{Al-H}) for solutions of tetracoordinate and tricoordinate aluminum compounds prepared in this work are listed in Table VI. Literature values[19-21] of ν_{Al-H} for $LiAlH_4$ in ether vary considerably over a range of about 1700-1760 cm^{-1}. The frequency varies with hydride concentration due to different extents of association.[19,22] The ν_{Al-H} for AlH_3 which we have found (Table VI) is very close to that reported by Ashby et al.[15] for approximately the same concentration. Substitution of hydrogen by aryloxy groups to give **5** resulted in a marked increase in ν_{Al-H} to 1880 cm^{-1} (Table VI). Reported values for $AlH(O\text{-}t\text{-}Bu)_2$ in THF are 1860,[23] 1850,[24] and 1859 cm^{-1} (Nujol)[18] and for $AlH(O\text{-}i\text{-}Pr)_2$ are 1845 (THF)[24] and 1848 cm^{-1} (Nujol mull).[25]

Lithium aluminum hydride (9.5 mmol in ether) was reacted with ArOH (28.5 mmol) with heating under reflux as in the experiments described above. The hydrogen evolution measured was 29.4 mmol. After filtration under nitrogen, the clear colorless filtrate's infrared spectrum was examined and found to be almost identical with that of **5**, showing a ν_{Al-H} of 1890 cm^{-1}. A minor difference consisted of the presence of two medium-intensity bands at ca. 828 and 537 cm^{-1} in the filtrate spectrum which were absent in the spectrum of **5**. However, similar bands were found in the spectrum of the lithium salt of **5** (in THF) which was prepared by the reaction of butyllithium with the phenol **3**. The close identity of the spectra of **5** and the filtrate constitute strong evidence for the formation of **5** in the reaction of $LiAlH_4$ with 3 molar equiv of phenol **3**. In an experiment where **5** was reacted with 1 molar equiv of the trans alcohol **6** in accordance with eq 5, an infrared spectrum of the resulting solution showed that the Al-H stretching absorption almost disappeared, but a small peak at 3650 cm^{-1} increased in intensity. The intensity further increased on addition of a further small excess of **6**. This band is characteristic for the O-H stretching frequency of the phenol and suggests that the phenol is being liberated in agreement with the process shown in eq 6. This band is not due to alcohol **6** since a spectrum of **6** in ether at about the same concentration showed an O-H stretching band at 3490 cm^{-1} and no absorption at 3650 cm^{-1}. This reaction of **6** to liberate phenol (eq 6) is probably not the only pathway diverting **6** from

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reacting with Al–H bonds in the equilibration studies (vide supra) and other processes; possibly reaction of **6** with a lithium salt may occur.

Summary

The reducing properties of species derived from the reaction of $LiAlH_4$ with the hindered phenol **3** and the demonstration of conversion of axial to equatorial cyclohexanols point to the formation of tricoordinate aluminum species as reactive intermediates. Further evidence for their formation has been obtained from infrared spectral comparisons with tricoordinate aluminum species prepared from aluminum hydride.

In the absence of measurements of the degree of association of these tricoordinate species, it is tentatively assumed that they react in the monomeric form. However, information regarding the oligomeric nature of these species is important to a complete understanding of their behavior.

Experimental Section

Reagents and Solvents. The substituted phenols were obtained from Aldrich Chemical Co. 2,4,6-Tri-*tert*-butylphenol was recrystallized from aqueous ethanol; mp 131.5–132 °C (lit.[26] mp 130–131 °C). 2,6-Diisopropylphenol was distilled; bp 83–85 °C (2 mm). Phenol was analytical reagent grade as obtained from Mallinckrodt Chemical Co. and was sublimed prior to use; mp 38.5–39 °C. Dihydroisophorone was prepared by oxidation of the corresponding alcohols.[27] 4-*tert*-Butylcyclohexanone was obtained from the Aldrich Chemical Co. and was distilled. *trans*-3,3,5-Trimethylcyclohexanol was prepared by reduction of the ketone with lithium tri-*sec*-butylborohydride (L-selectride)[28] and was distilled: bp 50 °C (0.5 mm); mp 56–56.5 °C (lit. mp 58.5,[27] 57.3,[29] 56 °C[30]). Gas chromatographic analysis showed no impurities. Diethyl ether (anhydrous grade) was further dried over KOH pellets and then distilled from CaH_2 under dry nitrogen.[31]

Gas chromatographic analyses were performed on a Hewlett-Packard 5750B instrument using either thermal-conductivity or flame-ionization detectors. DHI and its corresponding alcohols as well as the 4-*tert*-butylcyclohexanols were readily separated on a 12 ft × $^1/_8$ in., 5% Carbowax 20-M column at a 131 °C column temperature. Infrared spectra were recorded on a Beckman 4260 spectrometer. Spectra of hydride solutions were taken by using 0.1-mm NaCl solution cells fitted with septa, purged with N_2, and filled by syringe.

$LiAlH_4$ solutions were prepared by refluxing the solid reagent (Alfa-Ventron) with dry ether under N_2. After the residue was allowed to settle, the solution was filtered by syringe technique under positive nitrogen pressure.[32,33] The resulting solutions were standardized by titration[16] and checked by H_2 evolution on addition of known quantities of phenols or alcohols.

Reaction of LiAH$_4$ with 3. Reduction of DHI.[34] To 10.0 mL of $LiAlH_4$ in ether (10 mmol of $LiAlH_4$) in a 100 mL, three-necked, round-bottomed flask fitted with a dry ice condenser, magnetic stirrer, equilibrated addition funnel, and septum was added **3** (30 mmol in 40 mL of ether) under N_2. The reaction mixture was then heated under reflux for 1 h and 45 min and allowed to cool, and the 29.5 mmol of H_2 that evolved was measured with a wet-test meter connected to a dry ice/heptane trap. An additional 15 mL of dry ether was added, and this was followed by the dropwise addition of DHI (10 mmol in 10 mL of ether). The reaction mixture turned yellow on addition of DHI, and 30 min after the addition the solution was clear and colorless and was then hydrolyzed by the addition of 10% H_2SO_4. The aqueous layer was extracted with ether, and the combined ether solution was washed with saturated $NaHCO_3$ and saturated NaCl and dried over anhydrous $MgSO_4$. After concentration by distillation through an 18-in., helix-packed fractionation column the solution was analyzed by gas chromatography.

During the addition of **3** to $LiAlH_4$, a thick white precipitate was formed after 2 equiv of **3** had been added. After the reflux period, during which the third equivalent of **3** reacted, most of the solid had dissolved, leaving a small quantity of solid residue. This completely dissolved on subsequent addition of DHI.

Equilibration Experiment TC-6. To 20.0 mL of 0.94 M $LiAlH_4$ in ether (18.7 mmol of $LiAlH_4$) was added **3** (56.1 mmol in 80 mL of ether) under N_2. The reaction mixture was heated under reflux for 1 h and 45 min and allowed to cool to room temperature. The trans alcohol **6** (18.7 mmol in 20 mL of ether) was added, and 9.7 mmol of H_2 evolved. After 10 min, DHI was added (9.4 mmol in 10 mL of ether). On completion of the addition a 2-mL aliquot was withdrawn by syringe and quenched in 2 mL of 10% H_2SO_4. Subsequently, additional aliquots were removed (see Table III). The reaction mixture was heated under reflux which started 10 min after the completion of addition of the DHI. After being dried with anhydrous Na_2SO_4, the aliquots were analyzed by gas chromatography.

Preparation of 5. A solution of aluminum hydride in ether was prepared by the reaction of $LiAlH_4$ with anhydrous $ZnCl_2$.[15] To 3.4 mmol of AlH_3 in 30 mL of ether was added **3** (6.8 mmol in 15 mL of ether) without heating, and 6.6 mmol of H_2 was evolved. No precipitation occurred. This solution was subsequently used for equilibration experiments and infrared measurement.

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Registry No. 3 (Ar = 2,4,6-tri-*tert*-butylphenyl), 732-26-3; **3** (Ar = *p*-tolyl), 106-44-5; **4** (Ar = 2,4,6-tri-*tert*-butylphenyl), 74063-05-1; **4** (Ar = *p*-tolyl), 74063-06-2; **4** (Ar = Ph), 59034-16-1; **4** (Ar = 2,6-dimethylphenyl), 54081-36-6; **4** (Ar = 2,6-diisopropylphenyl), 54003-97-3; **5** (Ar = 2,4,6-tri-*tert*-butylphenyl), 74063-10-8; *cis*-**6**, 933-48-2; *trans*-**6**, 767-54-4; $LiAlH_4$, 16853-85-3; DHI, 873-94-9; $LiAlH_2(O\text{-}2,4,6\text{-tri-}tert\text{-butylphenyl})_2$, 74063-07-3; AlH_3, 7784-21-6; 4-*tert*-butylcyclohexanone, 98-53-3; *cis*-4-*tert*-butylcyclohexanol, 937-05-3.

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