The Composition of "Mixed Hydride" Reagents. A Study of the Schlesinger Reaction

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Abstract: The composition in diethyl ether solution of what is commonly called "mixed hydride" reagents has been studied. The products of the reactions of lithium aluminum hydride and aluminum chloride, aluminum bromide, and aluminum iodide in the stoichiometric ratios 3:1, 1:1, 1:3, and 1:4 have been determined. The reduction of aluminum halide to aluminum hydride by lithium aluminum hydride has been shown to be stepwise proceeding through the intermediate hydridoaluminum halides. All of the hydridoaluminum halides were prepared by this reaction and characterized as the triethylamine adducts. An explanation is provided for the anomalous solubility behavior of lithium chloride in the "mixed hydride" reaction mixture which has a direct bearing on the nature of the reducing species in solution. The relevance of the determined "mixed hydride" composition to the mechanism of "mixed hydride" reduction is discussed.

The use of lithium aluminum hydride as a reducing agent in both organic and inorganic synthesis is well known.[2] Several years after the introduction of $LiAlH_4$ as a reducing agent, a number of reports[3] appeared using lithium aluminum hydride in combination with aluminum chloride as a more selective reducing agent. Mixture of these two compounds has become known as the "mixed hydride" reagent. Although the mixture most commonly used has a $LiAlH_4/AlCl_3$ ratio of 1:4, other ratios have been used, such as 3:1, 1:1, and 1:3.

The stereochemical course of lithium aluminum hydride reduction was shown by Trevoy and Brown[4] to proceed by an SN2 pathway as evidenced by the reduction of 1,2-dimethyl-1,2-epoxycyclopentane to *trans*-1,2-dimethyl-1-cyclopentanol. Further evidence of a backside nucleophilic attack was provided by Eliel[5] who found that optically active 1-chloroethylbenzene is reduced with $LiAlD_4$ to ethylbenzene-1-*d* resulting in inversion of configuration. Although initial reaction involving $LiAlH_4$ proceeds by nucleophilic attack of $[AlH_4]^-$, there seems to be some question as to the nature of subsequent reducing species. Specifically there is evidence to indicate that in the reduction of epoxides by $LiAlH_4$, the steric nature of the reducing species increases from $[AlH_4]^-$ to $[AlH_3OR]^-$ ... $[AlH(OR)_3]^-$, etc., resulting in slower reaction and higher selectivity.[6] On the other hand there is evidence that disproportionation of the intermediate $LiAlOR_nH_{4-n}$ compounds to $LiAlH_4$ and $LiAl(OR)_4$ is rapid when R is a secondary alkyl group such that $[AlH_4]^-$ is the reducing species throughout the reaction.[7-9] It appears that the nature of the reducing species depends on whether reduction is faster than disproportionation or *vice versa.* Eliel and co-workers[8] have shown that $LiAl(OCH_3)_3H$ reduces 3,3,5-trimethylcyclohexanone with more stereoselectivity than $LiAl(O\text{-}i\text{-}C_3H_7)_3H$ because the latter disproportionates rapidly to $LiAlH_4$ and $LiAl(O\text{-}i\text{-}C_3H_7)_4$ and the $LiAlH_4$ performs the reduction. Thus reduction of 3,3,5-trimethylcyclohexanone is faster than disproportionation when $LiAl(OCH_3)_3H$ is the reducing agent whereas the opposite is true when $LiAl(O\text{-}i\text{-}C_3H_7)_3H$ is used. Although ketones and monosubstituted epoxides lead to secondary lithium alkoxyaluminohydrides, it might be an oversimplification to make a general statement that $LiAlH_4$ is the reducing species in these systems. It appears that more work is needed before the nature of the attacking species in $LiAlH_4$ reductions is understood fully.

A study of the literature reveals that the mechanism of "mixed hydride" reduction is even more involved than that of just $LiAlH_4$ although an amazing amount of order has evolved in this area due to the elegant and painstaking work of Eliel and co-workers. Through the use of $LiAlD_4$ these workers labeled the positions of attack in epoxide systems and thereby were able to postulate reasonable mechanisms of reduction. For example they showed that reduction of styrene oxide by $LiAlD_4$-$4AlCl_3$ produced 2-phenylethanol-1-*d* whereas reduction with $LiAlD_4$ alone produced the expected 1-phenylethanol-2-*d*.[10] This was interpreted to mean that the "mixed hydride" reduction proceeded through phenylacetaldehyde formed by a hydride shift of the ring-opened epoxide. On the other hand $LiAlD_4$-$^1/_3AlCl_3$ reduced styrene oxide to 2-phenylethanol-2-*d* which precludes the intermediate formation of phenylacetaldehyde.

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[1] J. Prather, Summer National Science Foundation Undergraduate Fellow from Mississippi State University, 1964.

[2] N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956.

[3] (a) R. F. Nystrom, *J. Am. Chem. Soc.*, 77, 2544 (1955); (b) R. F. Nystrom, *ibid.*, 81, 610 (1959); (c) E. L. Eliel and T. J. Prosser, *ibid.*, 78, 4045 (1956); (d) E. L. Eliel and M. Rerick, *J. Org. Chem.*, 23, 1088 (1958).

[4] L. W. Trevoy and W. G. Brown, *J. Am. Chem. Soc.*, 71, 1675 (1949).

[5] E. L. Eliel, *ibid.*, 71, 3970 (1949).

[6] R. Fuchs and C. A. Vander Werf, *ibid.*, 74, 5917 (1952).

[7] D. J. Cram and F. D. Greene, *ibid.*, 75, 6005 (1953).

[8] H. Haubenstock and E. L. Eliel, *ibid.*, 84, 2363 (1962).

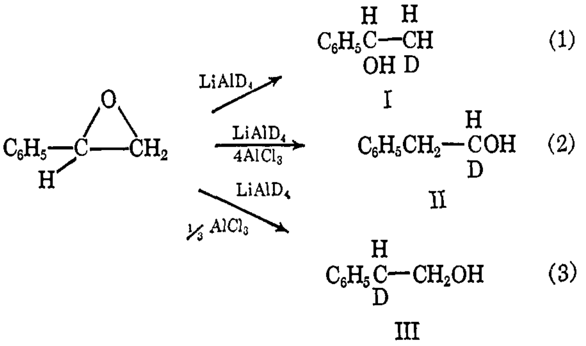
[9] H. C. Brown and C. J. Shoaf, *ibid.*, 86, 1079 (1964).

[10] E. L. Eliel and D. W. Delmonte, *ibid.*, 80, 1744 (1958).

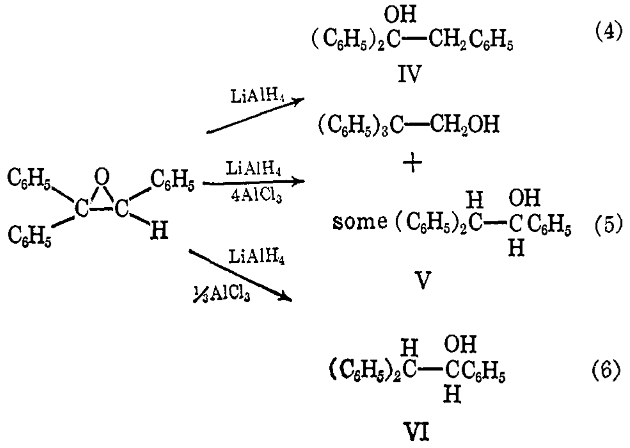
Table I. Aluminum Halides and Hydridoaluminum Halides[a]

Compound	Yield, %	Mp, °C	Calcd, % Al	Calcd, % X	Calcd, % N	Found, % Al	Found, % X	Found, % N
$AlCl_3$-$N(C_2H_5)_3$	92.2	113–114.5	11.5	45.4	5.8	11.6	44.1	5.6
$HAlCl_2$-$N(C_2H_5)_3$	88.5	44.4–44.9	13.5	35.5	7.0	14.1	35.7	6.8
H_2AlCl-$N(C_2H_5)_3$	96.2	−4 to −6	16.3	21.4	8.4	16.2	20.7	8.3
$AlBr_3$-$N(C_2H_5)_3$	96.7	138–140	7.4	65.2	3.8	7.7	64.5	3.8
$HAlBr_2$-$N(C_2H_5)_3$	93.1	34–35	9.4	55.4	4.9	8.9	54.4	4.6
H_2AlBr-$N(C_2H_5)_3$	94.0	−5 to −10	12.9	38.2	6.7	12.6	38.1	6.4
AlI_3-$N(C_2H_5)_3$	84.5	240 dec	5.5	74.9	2.8	5.9	73.6	3.2
$HAlI_2$-$N(C_2H_5)_3$	92.4	. . .	7.1	66.3	3.7	6.7	65.1	3.8
H_2AlI-$N(C_2H_5)_3$	94.3	. . .	10.5	49.4	5.5	10.2	47.8	5.7
AlH_3-$N(C_2H_5)_3$	99.5	12.5–15.0	20.6	. . .	10.7	20.1	. . .	11.6

[a] The hydridoaluminum halides both as the etherates and trimethylaminates have been prepared previously by E. Wiberg, K. Modritzer, and R. Uson Local, *Rev. Acad. Cienc. Exact. Fis. Quim. Nat. Zaragoza*, [1] **9**, 91 (1954). These compounds were not prepared, however, from $LiAlH_4$ and the corresponding aluminum halide, but by the redistribution of aluminum hydride and aluminum halide in ether solution.



The fact that all three reagent combinations reduce epoxides by a different mechanism was demonstrated further by Eliel and co-workers[11] through reduction studies involving triphenylethylene oxide. The results are summarized as follows.



The fact that VI is not a result of a hydride shift followed by reduction of the corresponding ketone was demonstrated by reduction of triphenylethylene oxide by $LiAlD_4$–$^1/_3AlCl_3$ to 1,2,2-triphenylethanol-2-*d*. Mechanisms describing these reductions have been postulated on the basis of AlH_3 as the reducing species produced from $LiAlH_4$–$^1/_3AlCl_3$ and $HAlCl_2$ from $LiAlH_4$–$4AlCl_3$ although this has never been proved. In a review article covering the entire area of "mixed hydride" reductions Eliel[12] suggested that "further work on the nature of the mixed hydride reagent is clearly required." In an attempt to remove all doubt as to the nature of the "mixed hydride" reagent, we have undertaken a study of the reaction of $LiAlH_4$ and $AlCl_3$ in 3:1, 1:1, 1:3, and 1:4 ratio.

Experimental Section

All reactions and manipulations were carried out in a dry nitrogen atmosphere. Diethyl ether (Fisher) was purified by distillation over lithium aluminum hydride. Triethylamine (Fisher) was purified by distillation over sodium aluminum hydride. Aluminum chloride and aluminum bromide were obtained pure (assay 99%) from Fisher Scientific and used without further purification. Aluminum iodide was obtained from City Chemical Corp., New York, N. Y., and was purified by high-vacuum distillation at approximately 200°.

Preparation of Triethylamine Adducts of the Aluminum Halides. $AlCl_3 \cdot N(C_2H_5)_3$, $AlBr_3 \cdot N(C_2H_5)_3$, and $AlI_3 \cdot N(C_2H_5)_3$ were prepared by adding approximately 50 g of the appropriate aluminum halide to 300 ml of diethyl ether at −10°. After solution, triethylamine was added in a mole ratio of 2:1 with respect to the aluminum halide. The product then was isolated by removing the ether solvent and excess triethylamine under reduced pressure and recovering the solid product. The product yields and analyses are reported in Table I.

Preparation of the Hydridoaluminum Halides Complexed to Triethylamine. $HAlCl_2 \cdot N(C_2H_5)_3$, $H_2AlCl \cdot N(C_2H_5)_3$, $HAlBr_2 \cdot N(C_2H_5)_3$, $H_2AlBr \cdot N(C_2H_5)_3$, $HAlI_2 \cdot N(C_2H_5)_3$, and $H_2AlI \cdot N(C_2H_5)_3$ were prepared by the same general method.

A. $HAlX_2 \cdot N(C_2H_5)_3$. For preparation of the $HAlX_2 \cdot N(C_2H_5)_3$ compounds 0.2 mole of $LiAlH_4$ in 100 ml of diethyl ether was added to 0.6 mole of AlX_3 in 500 ml of diethyl ether at −10°. The AlX_3 solution in diethyl ether was prepared by adding AlX_3 to diethyl ether at −10° in order to minimize ether cleavage. After addition of the $LiAlH_4$ was completed, 1.6 moles of triethylamine was added to the clear reaction mixture. In the case of reactions of $LiAlH_4$ and $AlCl_3$, a precipitate formed almost immediately which was filtered, weighed, and analyzed. The weight of solid corresponded closely to the weight of lithium chloride expected from the reaction, and halogen analysis of the precipitate was consistent with relatively pure lithium chloride. The reaction filtrate then was concentrated at reduced pressure and the solid–liquid product extracted with benzene in order to remove the $HAlX_2 \cdot N(C_2H_5)_3$ product from any lithium halide present. In the case of the chloride product only a trace of LiCl was separated at this stage, however, in the case of the bromide and iodide, major amounts of lithium bromide and lithium iodide were separated from the hydride product at this point. The benzene solutions of hydride product then were concentrated at reduced pressure in order to remove the benzene and leave behind the relatively pure $HAlX_2 \cdot N(C_2H_5)_3$ compound. The isolated LiBr and LiI corresponded closely in weight to that expected and had the proper composition.

Melting points of the hydride products were obtained by adding about 1–2 g of the sensitive hydrides to a small test tube and varying the temperature of a water bath back and forth until melting and freezing could be observed easily over a 2° change in temperature.

Infrared spectra of the hydrides were obtained on a Perkin-Elmer Model-21 in benzene solution. The Al–H stretching band for the $HAlX_2 \cdot N(C_2H_5)_3$ compounds appeared at 5.27 μ for the chloride, bromide, and iodide. For the $H_2AlX \cdot N(C_2H_5)_3$ com-

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(11) M. N. Rerick and E. L. Eliel, *J. Am. Chem. Soc.*, **84**, 2356 (1962).

(12) E. L. Eliel, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **22**, 129 (1961).

pounds the Al–H band was observed at 5.40 μ. The Al–H band for $LiAlH_4$ and $AlH_3 \cdot N(C_2H_5)_3$ were observed at 5.75 and 5.60 μ, respectively. The Al–H band for $HAlCl_2 \cdot O(C_2H_5)_2$ in benzene appeared at 5.22 μ, indicating little difference in Al–H stretching frequency between the diethyl ether and triethylamine adduct of $HAlCl_2$.

B. $H_2AlX \cdot N(C_2H_5)_3$. The preparation of $H_2AlX \cdot N(C_2H_5)_3$ compounds was similar to that described above for the $HAlX_2 \cdot (C_2H_5)_3$ compounds except that the ratio of $LiAlH_4/AlX_3/N(C_2H_5)_3$ was 1:1:4 instead of 1:3:8.

Preparation of $AlH_3 \cdot N(C_2H_5)_3$. To 500 ml of diethyl ether at −10° was added 22.7 g (0.17 mole) of aluminum chloride. To this solution at −10° was added 250 ml of a 2.036 *M* solution (0.51 mole) of $LiAlH_4$ in diethyl ether rapidly (30 sec). Immediately 125 ml of triethylamine was added. A white precipitate appeared which was filtered and shown to be lithium chloride. The ether solvent then was removed at reduced pressure and the product was isolated as a white solid. The solid was dissolved in benzene which caused a small amount of white solid to separate. The solid was filtered and discarded, the benzene was removed at reduced pressure, and the resulting white solid was analyzed. The analyses are reported in Table I.

Reaction of $LiAlH_4$ and $AlCl_3$ in 1:3 and 1:4 Ratio. Lithium aluminum hydride and aluminum chloride were allowed to react in 1:3 and 1:4 ratio as described above except that no triethylamine was added after the reaction. The hydride product was separated from the by-product LiCl, after distillation of the ether solvent at reduced pressure, by benzene extraction followed by distillation of the benzene at reduced pressure.

Results and Discussion

Apparently the only stoichiometric ratio in which the reaction of lithium aluminum hydride and aluminum chloride has been studied is 3:1. This reaction is generally referred to as the Schlesinger reaction and has been used mainly for the preparation of aluminum hydride.[13] In this reaction, aluminum chloride is

$$3LiAlH_4 + AlCl_3 \longrightarrow 4AlH_3 + LiCl \qquad (7)$$

added rapidly to a diethyl ether solution of lithium aluminum hydride. The lithium chloride precipitates from solution and is filtered within minutes of the reactant addition. Fast filtration of the lithium chloride is necessary in order to effect separation of the aluminum hydride which polymerizes in solution and also precipitates shortly after the reactant addition.

We have studied the reaction of lithium aluminum hydride and aluminum halides in diethyl ether in several stoichiometric ratios and have found the reduction of aluminum halide to aluminum hydride to proceed stepwise by way of the intermediate hydridoaluminum halides. The hydridoaluminum halides were detected by infrared analysis and identified by isolation followed by elemental analysis.

$$LiAlH_4 + 3AlX_3 \longrightarrow 4HAlX_2 + LiX \qquad (8)$$

$$LiAlH_4 + AlX_3 \longrightarrow 2H_2AlX + LiX \qquad (9)$$

$$3LiAlH_4 + AlX_3 \longrightarrow 4H_3Al + 3LiX \qquad (10)$$

An unusual aspect of these reactions is that lithium chloride, although insoluble in diethyl ether, does not precipitate from the reaction mixture when the stoichiometry is such as to produce $HAlCl_2$ or H_2AlCl. However, the lithium chloride can be made to precipitate by adding triethylamine to the reaction mixture in an equimolar quantity corresponding to the hydridoaluminum halide produced after the reaction is completed. In this case the hydridoaluminum halides are isolated as the amine complexes by simply removing the solvent under vacuum after filtering the precipitated lithium chloride. Alternatively, the lithium chloride by-product from this reaction also can be separated from the hydridoaluminum halide by complete removal of the diethyl ether solvent from the reaction mixture followed by extraction of the hydride product with benzene. The lithium chloride once crystallized in its stable crystalline lattice is easily separable from the hydridoaluminum halides which are very soluble in benzene. These results indicate that lithium chloride forms a complex with the hydridoaluminum halide which is soluble in diethyl ether. When triethylamine is added the lithium chloride precipitates because the aluminum orbital is now occupied by the electrons from the amine. When triethylamine was not added to the

$$\begin{tikzcd} \mathrm{LiAlH_4 + 3AlCl_3} \arrow[r] & \mathrm{4HAlCl_2 + LiCl} \arrow[dl] \\ \mathrm{3HAlCl_2 + LiAlCl_3H} \arrow[r, "\mathrm{4Et_3N}"] & \mathrm{LiCl + 4HAlCl_2 \cdot Et_3N} \qquad (11) \end{tikzcd}$$

reaction mixture and all of the diethyl ether solvent was removed, it appeared that $LiAlCl_3H$ dissociated to lithium chloride and hydridoaluminum dichloride because of the high lattice energy of lithium chloride.

When preparing aluminum hydride by the Schlesinger method, lithium chloride precipitates minutes after the reactants are mixed. The lithium chloride does not precipitate immediately probably due to the formation of $LiAlH_3Cl$, however, the heat of polymerization of AlH_3 to $(AlH_3)_x$ is the driving force for the dissociation of the complex and the precipitation of lithium chloride. Thus the solubility of lithium chloride in these reactions is now understood and successful methods for separating the lithium chloride from the hydridoaluminum halides are now available.

The reactions of lithium aluminum hydride and aluminum bromide as well as aluminum iodide were also studied in the same manner as described for $AlCl_3$. Similar results were obtained. In these reactions lithium bromide and lithium iodide are produced as by-products; however, these alkali metal halides are soluble in diethyl ether. For this reason isolation of the desired hydride product from the lithium halide was effected by benzene extraction of the reaction product after solvent evaporation.

Evans and co-workers,[14] who studied the reaction of $LiAlH_4$ and $AlCl_3$ (and AlI_3) conductometrically, interpreted the first step of the reaction of $LiAlH_4$ and aluminum halide differently. They suggest the following stoichiometry for the initial step.

$$LiAlH_4 + 2AlCl_3 \longrightarrow LiCl + Al_2Cl_5^+ + AlH_4^- \qquad (12)$$

$$LiAlH_4 + 3AlI_3 \longrightarrow Li^+ + Al_2I_7^- + H_2AlI \qquad (13)$$

Our results cannot be interpreted in terms of the sequence suggested by Evans, *et al.* Neither eq 12 nor 13 proposes the intermediate formation of $HAlX_2$; yet the infrared spectra of the resulting reaction mixture (hydride/halide, 1:3) has a strong Al–H absorption band at 5.27 μ. The Al–H bands we observed for $HAlCl_2$, H_2AlCl, and H_3Al are at 5.27, 5.40, and 5.60 μ, respectively. In the first step of the reaction the disappearance of the Al–H band of $LiAlH_4$ (5.75 μ) coincides with the appearance of the Al–H band for $HAlCl_2$ at 5.27 μ and the disappearance of the Al–H band

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(13) A. E. Finholt, A. C. Bond, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).

(14) G. G. Evans, J. K. Kennedy, and F. P. Del Greco, *J. Inorg. Nucl. Chem.*, **4**, 40 (1957).

for $HAlCl_2$ in the second step coincides with the appearance of the Al–H band for H_2AlCl (5.60 μ), etc. Thus the appearance of the Al–H band, characteristic of $HAlCl_2$, at the hydride/halide ratio of 1:3 is indicative of a stepwise reduction as described by eq 8–10.

Although the final product of the reaction of lithium aluminum hydride and aluminum chloride in 1:3 ratio has been established as a mixture of $4HAlCl_2 + LiCl$, one is tempted to conclude that the lithium chloride is complexed to 1 mole of the 4 moles of $HAlCl_2$ present in order to explain the lithium chloride solubility. Thus in solution the product of this reaction is probably $3HAlCl_2 + LiAlCl_3H$. Since $HAlCl_2$ is the product of least reduction of aluminum chloride, one might conclude that reaction of lithium aluminum hydride and aluminum chloride in 1:4 ratio (most often used "mixed hydride" reagent) merely produces the same product as from the reaction in 1:3 ratio, but with 1 mole of aluminum chloride remaining in solution unreacted. Since the lithium chloride does not precipitate in this reaction either, it could be complexed with either the $HAlCl_2$ or $AlCl_3$. Thus the actual reaction product in solution could be represented by either eq 15 or 16 or a mixture of both.

$$\mathrm{LiAlH_4 + 4AlCl_3 \longrightarrow 4HAlCl_2 + AlCl_3 + LiCl} \qquad (14)$$

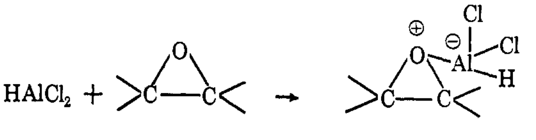
$$\mathrm{LiAlH_4 + 4AlCl_3} \begin{cases} \nearrow \mathrm{3HAlCl_2 + LiAlCl_3H + AlCl_3} & (15) \\ \searrow \mathrm{4HAlCl_2 + LiAlCl_4} & (16) \end{cases}$$

When lithium aluminum hydride and aluminum chloride were allowed to react in diethyl ether in 1:4 ratio at 0°, a clear solution was produced. On warming to room temperature a small amount (less than 2% of the total product) of a black solid precipitated which was mostly lithium chloride containing some Al–H compound. Removal of the diethyl ether solvent under vacuum followed by benzene extraction of the product resulted in nearly quantitative separation of the $HAlCl_2$ and $AlCl_3$ from LiCl. Thus it appears that the only difference between the "mixed hydride" reagents ($LiAlH_4/AlCl_3$, 1:3 and 1:4 or higher ratios) lies in the amount of excess of aluminum chloride mixed with the hydridoaluminum halide.

We have attempted to establish the existence of $LiAlCl_3H$ in solution by both nmr and infrared analysis. Scanning at 10-kc range we could not observe the Al–H proton resonance in $HAlCl_2 \cdot Et_2O$ or $HAlCl_2 \cdot Et_2O + LiCl$. One would expect the proton signal to be a very much broadened sextet due to the large quadrupole moment of the aluminum atom (spin $^5/_2$). Apparently the signal is so broad as not to be observable.

Infrared analysis was not conclusive in establishing proof for the existence of $LiAlCl_3H$. A weak band at 5.60 μ was observed for the $HAlCl_2$–LiCl solution in addition to the strong band at 5.27 μ whereas only the strong band at 5.27 μ and a much weaker band at 5.60 μ was observed for pure $HAlCl_2$. Unfortunately AlH_3 also absorbs strongly at 5.60 μ and therefore this band could be attributed to a small impurity of AlH_3 resulting from disproportionation of $HAlCl_2$. Thus it appears that although solubility considerations necessitate the formation of $LiAlCl_3H$, we were not able to prove the existence of this complex in solution.

The fact that Eliel has found "mixed hydride" reduction ($LiAlH_4/AlCl_3$, 1:4) of triphenylethylene oxide produces 2,2,2-triphenylethanol indicates that $[AlCl_3H]^-$ is not involved since attack by this species should result in the formation of 1,1,2-triphenylethanol. Therefore it seems probable that reduction involves attack by $HAlCl_2$, in the case of epoxides, at the epoxide oxygen atom. The resulting adduct consists of an



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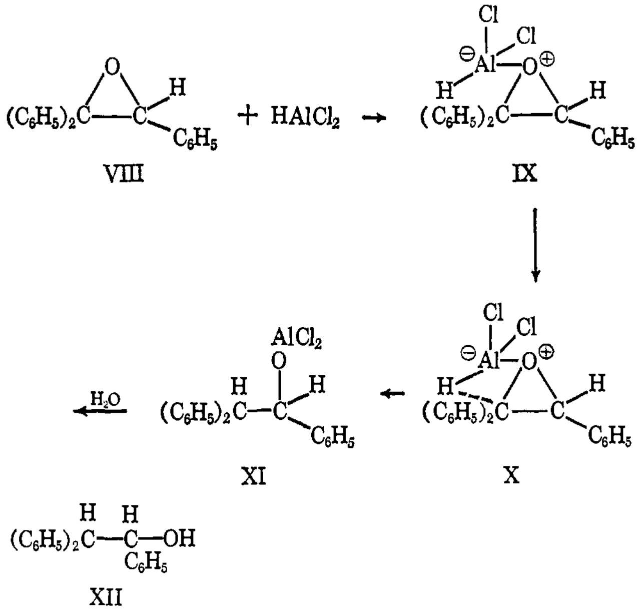
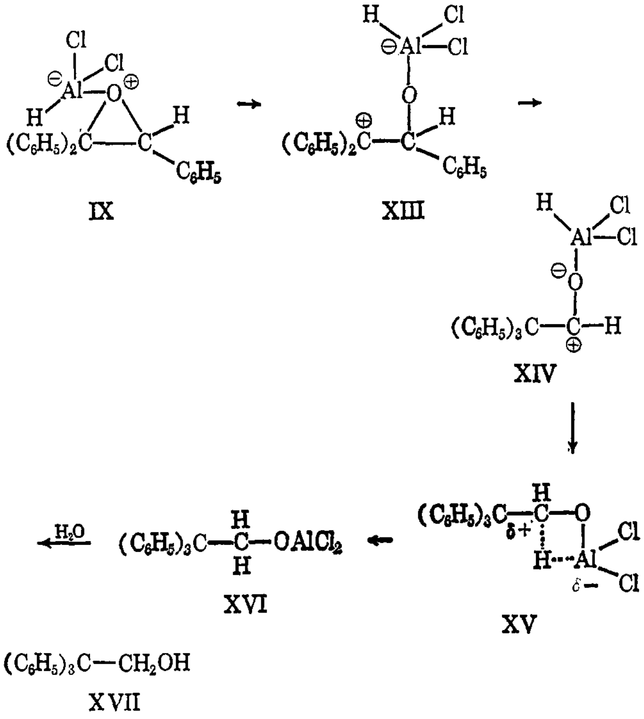
Al–H bond in close proximity to attack the ring carbon atom, in a four-center transition state. However, if the

Scheme I. Complex Formation Followed by Reduction

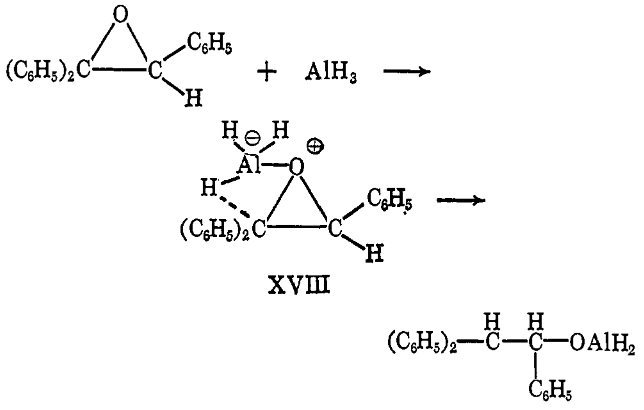


Scheme II. Complex Formation Followed by Migration



attacking Lewis acid is a strong acid such as $AlCl_3$ or $HAlCl_2$, the epoxide ring opening to form a carbonium ion should be fast and thus reduction and migration are competing reactions (Scheme I and II). Eliel has shown that the product formed through migration of the phenyl group (2,2,2-triphenylethanol) is the major one indicating that carbonium ion formation and subsequent phenyl migration is faster than reduction.

On the other hand if the attacking species is a much weaker Lewis acid than $HAlCl_2$, such as AlH_3, complexation at the epoxide oxygen atom is expected; however, ring opening should not be nearly so rapid.[15] In this case reduction could be the major reaction *via* a four-center transition state. This proposal is consistent with a report by Eliel that triphenylethylene oxide is reduced by $3LiAlD_4 + AlCl_3$, which produces AlD_3 *in situ*, to XX.



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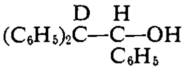
XIX



$$(C_6H_5)_2\overset{D}{C}-\underset{C_6H_5}{\overset{H}{C}}-OH$$

XX

Thus it appears that the reaction of $LiAlH_4$ and $AlCl_3$ in 3:1, 1:1, 1:3, and 1:4 ratio produces AlH_3, H_2AlCl, $HAlCl_2$, and $HAlCl_2 + AlCl_3$, respectively, and that the first step in the reduction of an organic functional group such as an epoxide involves complexation of the aluminum species at the oxygen atom. If the aluminum species is a strong Lewis acid such as $HAlCl_2$ or $AlCl_3$, then ring opening to form a carbonium ion is very rapid followed by migration and then reduction. However, if the complexing Lewis acid is weak such as AlH_3, then the resulting complex is relatively stable and thus reduction proceeds by a four-center transition state to produce the expected alcohol. Whether or not AlH_3, reduces epoxides through a four-center transition state or a carbonium ion could be easily tested by reduction of optically active 1-phenyl-1-ethyl ethylene oxide. Reduction *via* a four-center transition state should result in the formation of optically active 2-phenyl-1-butanol whereas reduction *via* a carbonium ion should result in the formation of racemic 2-phenyl-1-butanol.

Since we have prepared the hydridoaluminum halides in pure form as the diethyl etherates and triethyl aminates, we are now studying the effect of both the halogen and solvating species of $H_nAlX_{3-n}\cdot$solvent on the product distribution by reaction with styrene oxide and triphenylethylene oxide. By reducing these compounds with different combinations of $HAlCl_2$, LiCl, and $AlCl_3$ and comparing the product ratio to what is observed by the "mixed hydride" reagent, we hope to determine the nature of the attacking species.

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[15] Strong Lewis acids such as $AlCl_3$ and BCl_3 are known to cleave ethers such as diethyl ether and tetrahydrofuran much more rapidly than AlH_3 and B_2H_6.

A Polarographic and Spectroscopic Study of Dibenzothiophene and Some of Its Isologs

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Abstract: The polarographic reduction potentials and ultraviolet absorption spectra of dibenzofuran, dibenzothiophene, dibenzoselenophene, and various derivatives of these compounds have been measured. The effects of methyl substituents on the reduction potentials of dibenzofuran and biphenyl have been shown to be in accord with the predictions of LCAO–MO theory. For dibenzothiophene agreement *is not* obtained if the 3d orbitals of the sulfur are included in the conjugated system in the way originally suggested by Longuet-Higgins, and this is in accord with a previous interpretation of the esr spectra of the radical anion of this compound. The shifts in the positions of the ultraviolet spectral bands, produced by methyl substitution, are discussed.

In an earlier paper[1] we reported the electron spin resonance spectra of the radical anions of dibenzofuran, dibenzothiophene, and certain of their methyl derivatives and obtained good agreement between their ring proton hyperfine splitting and the predictions of LCAO–MO theory. Two models were used to describe the sulfur atom in dibenzothiophene, one in which only its occupied $3p_z$ orbital entered into con-

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[1] R. Gerdil and E. A. C. Lucken, *J. Am. Chem. Soc.*, 87, 213 (1965).