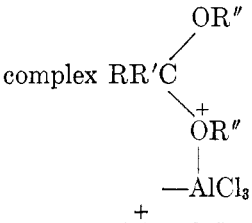
Communications TO THE EDITOR

Reduction of Acetals to Ethers by Means of Lithium Aluminum Hydride–Aluminum Chloride

Sir:

Acetals and ketals are not reduced by lithium aluminum hydride.[1] However, Doukas and Fontaine have described the reduction of a spirostanol (ketal) to a furostanol (ether) by means of ethereal lithium aluminum hydride containing hydrogen chloride or hydrogen bromide (but not other acids).[2] It appeared to us that the reagent in this reduction might be lithium aluminum hydride–aluminum chloride (or bromide).[3] Evidence for this view has now been obtained by the reduction of benzaldehyde diethyl acetal to benzyl ethyl ether (72% yield, b.p. 75–77°/23 mm., n_D^{20} 1.4889; lit.[4] b.p. 70–71.5°/12 mm., n_D^{20} 1.4954), of acetophenone diethyl ketal to α-phenethyl ethyl ether (59% yield, b.p. 88–90°/36 mm., n_D^{25} 1.4849; lit.[5] b.p. 89°/31 mm., n_D^{25} 1.4846), of butyraldehyde diethyl acetal to *n*-butyl ethyl ether (*ca.* 47% yield, b.p. 90–92°/745 mm., n_D^{25} 1.3790; lit.[6] b.p. 92.3°/760 mm., n_D^{25} 1.3798—part of this material was recovered as an azeotrope with ethanol) and of cyclohexanone diethyl ketal to cyclohexyl ethyl ether (61% yield, b.p. 147–149°/750 mm., n_D^{20} 1.4351; lit.[7] b.p. 148.5–149.5°/763 mm., n_D^{20} 1.43505) by means of the lithium aluminum hydride–aluminum chloride (1:4 ratio) reagent. The four ether products were identical in infrared spectra with authentic samples.

The reduction of acetals and ketals, RR′C(OR″)$_2$ to ethers RR′CHOR″ by means of $LiAlH_4$–$AlCl_3$ may involve chloroethers RR′ClOR″ as intermediates, in as much as such α-chloroethers are known to be reduced readily to ethers.[1] Alternatively, it may involve hydride displacement on the complex



, possibly *via* the resonating cation $RR'\overset{+}{C}—OR'' \longleftrightarrow RR'C=\overset{+}{O}R''$. An analogy is available in the reduction of α-aminoethers to amines by means of $LiAlH_4$ alone.[1] We are undertaking further work to elucidate the course of the acetal reduction and to extend its scope.

After this work was completed, a report appeared describing the hydrogenolysis of *p*-methoxybenzyl ethers, p-$CH_3OC_6H_4CH_2OR$ to the corresponding toluenes, p-$CH_3OC_6H_4CH_3$ by means of $LiAlH_4$–$AlCl_3$.[8] It might be noted that these ethers are vinylogs of acetals, and that their reduction by the mixed reagent is related to the reduction of *p*-aminobenzyl alcohols to *p*-aminotoluenes by $LiAlH_4$ alone in similar fashion as the reduction of acetals is related to that of α-aminoethers.

This work is a contribution from the Radiation Project of the University of Notre Dame, supported in part under Atomic Energy Commission contract AT(11-1)-38 and Navy equipment loan contract Nonr-06900.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, IND.

ERNEST L. ELIEL
MARK RERICK

Received April 24, 1958

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