at 230 mμ (ε 71400), 272 mμ (ε 6500), 283 mμ (ε 7480), 292 mμ (ε 5000), 329 mμ (shoulder, ε 2800), 341 mμ (ε 4000).

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THE WORCESTER FOUNDATION FOR
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Attempted Oxygenolysis of Some Halide-$LiAlH_4$ and Nitrile-$LiAlH_4$ Reaction Products

LOUIS M. SOFFER

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The literature contains several instances of the reaction of oxygen with hydride reduction complexes to yield hydroxylic products. Thus Hochstein and Brown[1] obtained 1-phenyl-1,3-propanediol (25%) from the reduction of cinnamyl alcohol, Soffer and Katz[2] isolated α-phenyl-β-aminoethanol (7%) from the reduction of phenylacetonitrile, and Cotman[3] reduced polyvinyl chloride to a polyethylene containing approximately one hydroxyl per 25 carbon atoms. In the first two instances these products were taken as evidence for a carbon-metal bond, probably carbon-aluminum. In the last, several alternate explanations were made, of which one assumed the presence of a carbon-lithium bond, and another, the oxidation of aluminohydride ion to an oxyaluminohydride ion which displaced chloride, thus leading to a product which on hydrolysis would yield a secondary hydroxyl group.

In addition, Badger and coworkers obtained the cyclic ether of 4,5-bishydroxymethylphenanthrene from the reduction of 4,5-bisbromomethylphenanthrene.[4] Although an ordinary basic hydrolysis of dibromide to diol cannot be definitely excluded, it seemed possible that the incorporation of oxygen might occur by the reaction of a carbon-metal species with atmospheric oxygen.

$$R\text{—}Br \xrightarrow{LiAlH_4} R\text{—}Al\langle \xrightarrow{O_2} R\text{—}OAl\langle \xrightarrow{HOH} ROH$$

The purpose of this study was to attempt the oxygenolysis of simple halides and nitriles under varying conditions and thus obtain additional information on the role of carbon-metal species in hydride reductions.

Assuming that a reaction of oxygen with a carbon-metal bond occurs, it could conceivably be influenced by many factors in the overall process, such as the nature of the substrate, the molar ratio of hydride and substrate, the manner in which the hydride reaction was performed (with reference to solvent, temperature, and whether by direct or reverse addition[2]), the manner in which oxygen was supplied (concurrent with the hydride-substrate reaction, or following it), as well as by the temperature and time of contact with oxygen. A number of experiments using some of the many possible reaction conditions are summarized in Table I. It can be seen that in no case, except the previously reported run 11, were hydroxylic materials isolated. The products obtained were normal for reductions without attempted oxygenolysis, but yields were considerably lower. The low recoveries were undoubtedly due to the difficulties experienced in extraction of the large quantities of gelatinous, post-hydrolysis reaction mixture.[5] The low yields of expected products can be explained likewise, and by the consumption of hydride by oxygen. Although it is regarded as unlikely that significant amounts of hydroxylic materials could have been present in the reaction mixture, the low recoveries preclude the definite conclusion that no hydroxylic products were formed.

Run 5 was made as a test of Cotman's hypothesis[3] that oxyaluminohydride ions are responsible for the displacement of halide with hydroxyl. Oxygen was passed into the hydride suspension solution at 65° for 4.5 hr., after which benzyl bromide was added and the mixture stirred at 65° for 17 hr. The isolation of toluene and benzyl bromide indicated that the reaction of hydride with oxygen had been incomplete and that little or no reaction occurred between benzyl bromide and the oxidized hydride. The failure to obtain any product other than a 10% yield of phenylacetaldehyde in run 9 can be attributed to the factors of low temperature and concurrent admission of oxygen.

Thus, under the conditions of our experiments, the attempted oxygenolysis of halide-hydride and aliphatic nitrile-hydride reduction complexes were unsuccessful, affording no evidence for a carbon-metal bond in such species. A single test of Cotman's "oxyaluminohydride hypothesis" for the production of hydroxyl during halide-hydride reductions failed to support the hypothesis.

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(1) F. A. Hochstein and W. G. Brown, *J. Am. Chem. Soc.*, **70**, 3484 (1948).

(2) L. M. Soffer and M. Katz, *J. Am. Chem. Soc.*, **78**, 1705 (1956).

(3) J. D. Cotman, Jr., *J. Am. Chem. Soc.*, **77**, 2790 (1955).

(4) G. M. Badger, J. E. Campbell, J. W. Cook, R. A. Raphael, and A. I. Scott, *J. Chem. Soc.*, 2326 (1950). The ether was obtained by sublimation of the actual reduction product which was undoubtedly 4,5-bishydroxymethylphenanthrene. The dehydration of the latter material to the ether was demonstrated by these workers to occur very readily.

(5) Extraction was particularly difficult in the runs where oxygen input was concurrent with the substrate-hydride reaction.