Further evidence of low temperature activity was revealed by micro-scale dehydration of ethanol, in which an activated alumina at 340° gave about equal quantities of ethylene and ether, while our catalyst gave ethylene exclusively at 250°.

We have observed cracking with a magnesium exchanged acid mordenite, and isomerization of cyclohexene over acid mordenite and its aluminum exchanged derivative.

Further work is in progress on several of the more interesting aspects of this material.

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RECEIVED JUNE 28, 1961

LITHIUM N-DIHYDROPYRIDYLALUMINUM HYDRIDE—A SELECTIVE REDUCING AGENT FOR HIGHLY ELECTROPHILIC CARBONYL COMPOUNDS

Sir:

We have reported previously that pyridine is an excellent solvent for the reduction of ketones and the metalation of certain weakly acidic hydrocarbons by lithium aluminum hydride.[1] Carboxylic acids and esters also are cleanly reduced to alcohols in this medium. In contrast to the above results, which are obtained when lithium aluminum hydride is *added to* pyridine solutions of substrate, a highly selective reducing agent is formed when the hydride and pyridine are allowed to interact *before* addition of the substrate. This species,[2] lithium N-dihydropyridylaluminum hydride (I), acts as a weak hydride donor, reacting only with highly electrophilic carbonyl groups. Its rate of formation is quite rapid (but not as fast as the reduction of a ketone when one is present[1]), as indicated by the results of a series of benzophenone reductions carried out by aliquots taken periodically from a solution of lithium aluminum deuteride in pyridine and analyzing the resultant mixture of benzhydrol and benzhydrol-α-D by infrared spectroscopy.

TABLE I

REDUCTIONS OF BENZOPHENONE BY LiAlD₄ IN PYRIDINE

"Age" of solution	% C–H
6 min.	2
10	7
30	21
2 hr.	50
24	71
50	77

The postulate that hydride transfer from the dihydropyridine ring is the path involved in carbonyl reduction is strengthened by the above data, as well as by the novel behavior of the complex (see below). This latter factor rules out the possibility that the results shown in Table I are due merely to reversal of the nucleophilic addition of the hydride to the pyridine ring. Such isotope scrambling could account for the observed C–H/C–D ratios, but the selectivity of I, as compared with the powerful reducing action of lithium aluminum hydride, is not explainable in terms of such an hypothesis.

(1) P. T. Lansbury, *J. Am. Chem. Soc.*, **83**, 429 (1961).
(2) F. Bohlmann, *Chem. Ber.*, **85**, 390 (1952).

The tentative assignment of a 1,2-dihydropyridine structure to the complex is based on the previously observed orientation in closely-related nucleophilic additions of organometallics and metal hydrides to N-heteroaromatics.[2,3]
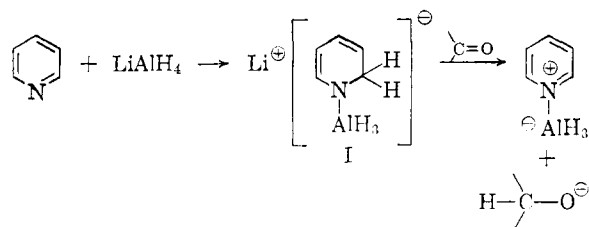
The specific reducing properties of I are illustrated by the facile reductions of benzophenone, 2,4'-dichlorobenzophenone and hexachloroacetone to the carbinols, whereas 1-naphthoic acid and methyl 1-naphthoate are recovered unchanged even after overnight exposure to excess complex. On the other hand, the reduction of such acids and esters in pyridine solution proceeds normally to alcohols when lithium aluminum hydride is added. This selective action of I may be used advantageously for reduction of ketone groups in certain polyfunctional compounds. Several examples, in which the simplicity of execution is illustrated, are recorded: To a 60-ml. serum bottle containing 50 ml. of anhydrous pyridine is added 0.50 g. of powdered lithium aluminum hydride. After the initial exothermic reaction, during which the solution acquires a dull orange coloration, the bottle is stoppered tightly and aged for at least one day, after which the lithium aluminum hydride is essentially consumed (see above). A ten milliliter aliquot (containing *ca*. 2.6 mmoles of I) of this solution[4] is withdrawn by a hypodermic syringe and transferred to 1–1.5 mmoles of substrate, dissolved in pyridine, the solution then being kept overnight before hydrolysis and work-up in the usual manner.[1] Under such conditions of prolonged contact with excess reducing agent, o-(α-naphthoyl)-benzoic acid gave 76% 3-α-naphthylphthalide, whereas the methyl ester gave a 78% yield of this lactone. In both cases, infrared examination of the crude products showed only lactone absorption (1745 cm.$^{-1}$) in the carbonyl region.[5] Furthermore, o-benzoylbenzoic acid and and its methyl ester were reduced to 3-phenylphthalide in 93% and 62% yields, respectively. As above, the crude reduction products consisted essentially only of the lactone (carbonyl absorption at 1740 cm.$^{-1}$).

If a ratio of lithium aluminum hydride to o-(α-naphthoyl)-benzoic acid comparable to that used in the above reductions involving I is employed, according to the earlier procedure,[1] the conversion to diol is complete within 15 minutes. This con-

(3) (a) K. Ziegler and R. Zeiser, *Ber.*, **63**, 1847 (1930); (b) E. A. Braude, J. Hannah and R. P. Linstead, *J. Chem. Soc.*, 3249 (1960), and references cited therein; (c) H. S. Mosher, "Heterocyclic Compounds," R. C. Elderfield, editor, John Wiley and Sons, Inc., New York, N. Y., 1950, Volume 1, Chap. 8.

(4) Solutions aged for up to ten days still retain their reducing powder.

(5) This method of reducing this ketoacid appears to be far superior to sodium borohydride in methanol, from which the starting material is recovered unchanged after five hours at room temperature.

trast in reactivity serves to emphasize the ability of the complex to reduce only the more electrophilic carbonyl groups in polyfunctional compounds, hence this reagent seems to have great potential in organic synthesis.

We are actively examining other selective reductions as well as the further characterization of lithium N-dihydropyridylaluminum hydride,[6] which may be isolated as a pale yellow crystalline solid from concentrated pyridine solutions.

Acknowledgment.—We gratefully acknowledge the generous support of this research by the National Science Foundation.

(6) It is especially desirable to ascertain whether I possesses a 1,2- or a 1,4-dihydropyridine moiety.

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EVIDENCE FOR GA(I) AS AN INTERMEDIATE IN THE REACTION OF GALLIUM METAL WITH AQUEOUS PERCHLORIC ACID

Sir:

Evidence recently has been obtained for the existence of Ga(I) in the gallium dihalides[1] and in certain addition compounds of the gallium dihalides,[2] as well as in the anodic oxidation of gallium in glacial acetic acid.[3] There appears to be no published evidence, however, for the existence of Ga(I) in aqueous solutions,[4] although reference has been made to the persistence of reducing properties following the dissolution of gallium metal in aqueous hydrochloric acid.[5]

We wish to report certain observations on the stoichiometry of the reaction of gallium metal with perchloric acid which provides strong evidence for the participation of Ga(I) as an intermediate species in the reaction. The pertinent experimental observations are that in the reaction of the metal with hot 11 M (72 wt. %) perchloric acid each mole of Ga(III) produced is accompanied by the formation of *one-half* mole of H_2 and *one-fourth* mole of Cl^- ion.[6] No other reduction products are formed in significant amount, in conflict with the implication by Foster that chlorine and other products are formed.[7] The results from a typical experiment are tabulated

Gallium metal used	3.10 mmoles (0.2164 g.)
Hydrogen gas produced	1.55 mmoles (34.8 ml. S.T.P.)
Chloride produced	0.78 mmole
Cl^-/Ga ratio	0.248
H_2/Ga ratio	0.50

The observed stoichiometry can be accounted for quantitatively by the mechanism

(1) R. K. McMullan and J. D. Corbett, *J. Am. Chem. Soc.*, **80**, 4761 (1958).

(2) S. M. Ali, F. M. Brewer, J. Chadwick and G. Garton, *J. Inorg. and Nuclear Chem.*, **9**, 124 (1959).

(3) A. W. Davidson and F. Jirik, *J. Am. Chem. Soc.*, **72**, 1700 (1950).

(4) The second edition of Latimer's "Oxidation Potentials," 1952, for example, discusses aqueous gallium chemistry in terms of the +2 and +3 oxidation states.

(5) L. A. Woodward and A. A. Nord, *J. Chem. Soc.*, 3721 (1956).

(6) The original observation concerning the Cl^-–Ga(III) proportion was made in the course of some work recently carried out in collaboration with L. I. Katzin at the Argonne National Laboratory.

(7) L. S. Foster, "Inorganic Syntheses," Vol. II, 1946, p. 26.

$$Ga(0) + H^+ = Ga(I) + \tfrac{1}{2}H_2(g) \quad (1)$$
$$4Ga(I) + 8H^+ + ClO_4^- = 4Ga^{3+} + Cl^- + 4H_2O \quad (2)$$
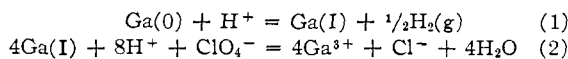
The proposed mechanism involves highly selective behavior of Ga(0) and Ga(I) with respect to oxidation; the metal reacting predominantly with H^+ rather than ClO_4^- or the intermediate chlorine compounds which must be involved in step two of the above mechanism, and the Ga(I) reacting predominantly with ClO_4^- rather than H^+ despite the fact that H^+ is certainly a sufficiently strong oxidizing agent to convert it to the tervalent state. On the basis of the present interpretation, gallium(I) joins the rather small group of ions which is capable of reducing perchlorate ion in aqueous solution.[8] The reluctance of Ga(I) to reduce H^+ provides an explanation for the slow rate of dissolution of the metal in the halogen acids as compared with $HClO_4$ and for the observed reducing properties of the solution after the metal is completely dissolved.

(8) W. R. King and C. S. Garner, *J. Phys. Chem.*, **58**, 29 (1954).

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CRYSTALLINE POLYMERS OF THE 2,3-EPOXYBUTANES—STRUCTURE AND MECHANISM ASPECTS

Sir:

It was suggested previously,[1,2] based on indirect evidence,[3] that the stereoregular polymerization of propylene oxide to high molecular weight isotactic polymer occurs by a front-side displacement at its asymmetric carbon atom. We recently polymerized the *trans*- and *cis*-2,3-epoxybutanes to high yields of different crystalline high polymers.[4] We now have evidence, based on polymerizing D(+)-2,3-epoxybutane to optically inactive crystalline polymer, which indicates that the stereoregular polymerization of *trans*-2,3-epoxybutane occurs by a rearward displacement on either of its equivalent asymmetric carbon atoms.

D(+)-2,3-epoxybutane, prepared by the procedure of Lucas and Garner,[5,6] ($[\alpha]^{25}D$ +58.8°, lit.[5] +59.0°) was polymerized (1.0 g.) with an *i*-Bu₃-Al–0.5 water catalyst[7] (0.4 millimole Al) in *n*-heptane (6.1 g.) for 2 hr. at −78°. This polymerization, which was almost instantaneous, gave a 97% conversion to highly crystalline, heptane-insoluble polymer [(ln η_{rel})/C 1.0 (0.1%, CHCl₃, 25°), m.p. 96°] which was essentially optically inactive

(1) M. Osgan and C. C. Price, *J. Polymer Sci.*, **34**, 153 (1959).

(2) E. J. Corey, *Tetrahedron Letters*, **2**, 1 (1959).

(3) C. C. Price and M. Osgan, *J. Am. Chem. Soc.*, **78**, 4787 (1956).

(4) E. J. Vandenberg, *J. Polymer Sci.*, **47**, 489 (1960).

(5) H. J. Lucas and H. K. Garner, *J. Am. Chem. Soc.*, **70**, 992 (1948).

(6) The starting D(−)-2,3-butanediol was kindly supplied (98% purity based on rotation) by Dr. R. W. Jackson and Dr. R. F. Anderson, U. S. D. A., Northern Utilization Research and Development Division, Peoria, Illinois. The final D(+)-2,3-epoxybutane was, by gas chromatography, 96.7% *trans*-2,3-epoxybutane, 0.5% *cis*-2,3-epoxybutane and 3.2% diethyl ether (ether added to remove water by azeotropic distillation).

(7) E. J. Vandenberg, *J. Polymer Sci.*, **47**, 486 (1960).