and the nature of the overall electrode process is seen to be the same. Differences in behavior are essentially due to differences in the solvation of the "ions" and in the nature of the double layer in AHF compared with water.

Registry No. In, 7440-74-6; Tl, 7440-28-0; Sn, 7440-31-5; Pb, 7439-92-1; Cd, 7440-43-9; As, 7440-38-2; Sb, 7440-36-0; Bi, 7440-69-9; Hg, 7439-97-6; Hg_2Cl_2, 10112-91-1; Hg_2Br_2, 15385-58-7; Hg_2I_2, 15385-57-6.

References and Notes

(1) To whom correspondence should be addressed.

(2) H. H. Hyman and J. J. Katz, "Non Aqueous Solvent Systems", T. C. Waddington, Ed., Academic Press, London, 1965, pp 47–81.

(3) H. H. Hyman, L. A. Quarterman, M. Kilpatrick, and J. J. Katz, *J. Phys. Chem.*, **65**, 123 (1961).

(4) R. J. Gillespie and K. C. Moss, *J. Chem. Soc. A*, 1170 (1966).

(5) L. B. Asprey, M. J. Reisfield, and N. A. Matwiyoff, *J. Mol. Spectrosc.*, **34**, 361 (1970).

(6) R. J. Gillespie and D. A. Humphreys, *J. Chem. Soc. A*, 2311 (1970).

(7) P. A. W. Dean, R. J. Gillespie, R. Hulme, and D. A. Humphreys, *J. Chem. Soc. A*, 341 (1971).

(8) G. D. Koerber and T. DeVries, *J. Am. Chem. Soc.*, **74**, 5008 (1952).

(9) A. F. Clifford, W. D. Pardieck, and M. A. Wadley, *J. Phys. Chem.*, **70**, 3241 (1966).

(10) For a review of these early reports, see ref 11.

(11) A. M. Bond, T. A. O'Donnell, and A. B. Waugh, *J. Electroanal. Chem.*, **39**, 137 (1972).

(12) I. D. MacLeod, A. M. Bond, and T. A. O'Donnell, *J. Electroanal. Chem.*, **45**, 89 (1973).

(13) A. M. Bond, I. Irvine, and T. A. O'Donnell, *Inorg. Chem.*, **14**, 2408 (1975).

(14) A. M. Bond and J. R. Thackeray, *Chem. Instrum.*, **4**, 299 (1972).

(15) J. Shamir and A. Netzer, *J. Sci. Instrum.*, **1**, 770 (1968).

(16) D. DeFord and D. N. Hume, *J. Am. Chem. Soc.*, **73**, 5321 (1951).

(17) G. T. Hefter, personal communication, University of Melbourne, 1973.

(18) J. Heyrovsky and J. Kuta, "Principles of Polarography", Academic Press, London, 1966, p 214.

(19) R. D. W. Kemmitt and D. W. A. Sharp, *Adv. Fluorine Chem.*, **4**, 209 (1965).

(20) A. M. Bond and G. T. Hefter, *J. Electroanal. Chem.*, **42**, 1 (1973).

(21) T. Biegler, *J. Electroanal. Chem.*, **6**, 373 (1963).

(22) M. F. A. Dove and A. F. Clifford, "Chemistry in Non Aqueous Ionizing Solvents", Vol. III, C. C. Addison, Ed., Oxford-Pergamon, New York, N.Y., 1967, p 258.

(23) C. G. Barraclough, R. W. Cockman, and T. A. O'Donnell, *Inorg. Chem.*, **16**, 673 (1977).

(24) I. D. MacLeod, Ph.D. Thesis, University of Melbourne, 1973.

(25) R. J. Gillespie, *Acc. Chem. Res.*, **1**, 202 (1968).

(26) J. P. Brenet and K. Traore in "Transfer Coefficients in Electrochemical Kinetics", Academic Press, London, 1971, p 89.

(27) T. Biegler, *J. Electroanal. Chem.*, **6**, 365 (1963).

(28) T. Biegler, *J. Electroanal. Chem.*, **6**, 357 (1963).

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Reaction of Lithium Aluminum Hydride with Copper(I) and Mercury(II) Salts. Nature of the Reactive Species in the Conjugate Reducing Agent $LiAlH_4$–CuI

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The reaction of lithium aluminum hydride in tetrahydrofuran solution with solid copper(I) iodide in 1:1, 1:2, 1:3, and 1:4 mole ratios has been studied over the temperature range 0 to −78 °C using a combination of low-temperature infrared techniques and intermediate isolation. Copper(I) tetrahydridoaluminate ($CuAlH_4$) and copper(I) hexahydridoaluminate (Cu_3AlH_6) appear to be the major hydride species present at low temperature (−78 °C) while copper, hydrogen, and iodoalane (H_2AlI) are the major products at higher temperatures. Lithium aluminum hydride and mercury(II) chloride or iodide produce AlH_3, H_2AlX, $HAlX_2$, and AlX_3 (X = Cl, I) in addition to mercury and hydrogen depending on the initial reactant mole ratio: $LiAlH_4 + (n/2)HgX_2 \rightarrow LiX + (n/2)Hg + (n/2)H_2 + H_{4-n}AlX_{n-1}$, where n = 1–4. A mixture of diphenylaluminum hydride and triphenylaluminum is produced when lithium aluminum hydride and phenylmercuric chloride are allowed to react in 1:1 mole ratio in benzene.

Introduction

A reagent prepared by mixing solid copper(I) iodide and a tetrahydrofuran solution of lithium aluminum hydride in a 4:1 mole ratio at 0 °C effects conjugate reduction of α,β-unsaturated ketones in 100% yield and with 100% regioselectivity.[2] Similar reagents prepared by mixing a variety of other transition metal salts including titanium(III) chloride, iron(III) chloride, copper(I) chloride, mercury(II) iodide, and mercury(II) chloride with lithium aluminum hydride were less effective than CuI but still showed considerable promise as reagents for conjugate reduction of enones. This study was undertaken to characterize the reaction of selected transition metal halides (primarily CuI but also including HgX_2 and RHgX) with lithium aluminum hydride and hopefully determine the species responsible for conjugate reduction.[2]

A survey of the reactions of several transition metal halides and lithium aluminum hydride is given by Wiberg.[3] Of particular importance to this study are previous studies of the reaction of CuI[4,5] and HgI_2[6] with lithium aluminum hydride. The reaction of CuI and lithium aluminum hydride in a 4:1 mole ratio has been studied in the mixed solvents pyridine and ether at room temperature.[4,5] Copper(I) hydride containing 4–20% pyridine and 10–20% copper(I) iodide was prepared by allowing the reaction to proceed for 8 h followed by filtration to remove the insoluble aluminum iodide and addition of ether in order to precipitate the CuH (eq 1). Attempts

$$4CuI + LiAlH_4 \xrightarrow[2.\ ether]{1.\ py} LiI + AlI_3 + 4CuH \tag{1}$$

have also been made to prepare mercury(II) hydride by the reaction of mercury(II) iodide with lithium aluminum hydride in 1:2 molar ratio in diethyl ether at a variety of temperatures.[6] These workers reported mercury, hydrogen, lithium iodide, and aluminum hydride as the ultimate products of the reaction (eq 2) at temperatures above −125 °C.

$$HgI_2 + 2LiAlH_4 \rightarrow Hg + H_2 + 2LiI + 2AlH_3 \tag{2}$$

Experimental Section

Techniques and Reagents. Unless stated otherwise in a specific experiment, the normal techniques for handling air- and moisture-sensitive compounds were used.[7]

Fisher purified copper(I) iodide was repurified by dissolving in aqueous saturated KI, treating with decolorizing charcoal, and filtering. After precipitation with deoxygenated water, the CuI was collected by filtration. Dry CuI as a light yellow powder was obtained by repeated washing with absolute ethyl alcohol and anhydrous ether followed by vacuum-drying for 12 h.[5] A standard solution of lithium aluminum hydride was prepared by mixing an excess of Ventron $LiAlH_4$ powder and dry tetrahydrofuran and heating at reflux temperature for 4 h, followed by filtration. The solution was standardized for aluminum by EDTA titration. Mercury(II) iodide

Table I. Analysis of the Reaction of CuI and $LiAlH_4$ in 4:1 and 2:1 Mole Ratios at 0 °C in THF[a]

			Amt, mmol					
			Reactants		Products			
Expt	Reacn time, min	CuI:$LiAlH_4$	CuI	$LiAlH_4$	H_2	I^{-1} (H_2O sol)	I^{-1} (OH^- sol)	Observn
1	5	4	1.90	0.47	0.084	0.80 (43%)	1.0 (52%)	Red-brown product
2	30	4	2.70	0.68	0.096	1.35 (50%)	1.2 (45%)	Red-brown product
3	30[b]	2	2.02	1.01	1.06	1.80 (90%)	(0%)	Black product

[a] Measurement of the amount of hydrogen produced and the extent of halide-hydride exchange in CuI-$LiAlH_4$ mixtures. [b] A large amount of gas was produced and the product turned black within 30 s.

and chloride were dried by heating at 90–100 °C under vacuum for 4 h. Standard tetrahydrofuran solutions of these salts were prepared in the drybox. The reagents AlI_3,[8] $I_2AlH{\cdot}2THF$,[9] and $IAlH_2{\cdot}2THF$[9] were prepared using literature methods. All solvents were freshly distilled from an appropriate metal hydride under nitrogen prior to use. Phenylmercuric chloride from Alfa Inorganics was used without further purification.

Analyses. Samples were hydrolyzed with either water or water and nitric acid. The quantity of iodide as LiI or X_nAlI_{3-n} was determined after water hydrolysis using the Volhard procedure. Extraction of the residue remaining after water hydrolysis with hot, 10% aqueous NaOH followed by acidification with H_2SO_4 and a second Volhard titration gave an estimate of the quantity of CuI in the sample. Hydrolysis with water and nitric acid followed by heating with a gas burner converted all I^- in the sample to I_2. Heating was continued until all of the I_2 had been removed. Copper in this sample was determined by electrodeposition and the aluminum which remained was determined by EDTA titration. Lithium was determined by flame photometry after hydrolysis of the sample with H_2O–HNO_3. Hydride in samples was determined by hydrolysis of the sample and measuring the amount of evolved hydrogen using a standard vacuum line equipped with a gas buret, Toepler pump, and separation traps. Hydrogen was also liberated from some samples by pyrolysis. In the case of pyrolysis the moles of hydrogen gas produced were adjusted in accordance with the general property that pyrolysis produces $^1/_2$ mol of H_2/mol of M–H.

Reaction of CuI with $LiAlH_4$ in THF at 0 °C. Copper(I) iodide was transferred in the drybox into a glass ampule containing a small Teflon-coated stirring bar. The ampule consisted of an O-ring joint for connection to the vacuum line and a small glass bulb of approximately 25-mL volume. A side arm fitted with a 1-mm ground glass stopcock (Dow Corning silicone stopcock grease) was located near the top of the glass bulb. The tube immediately above the stopcock had been expanded considerably giving a volume of approximately 1 mL. Both the O-ring joint and side arm were capped with serum stoppers to preserve the inert atmosphere. Two milliliters of THF was syringed into the tube and the tube was attached to the vacuum system and evacuated while cooling with liquid nitrogen. The THF–CuI slurry was then warmed to 0 °C and stirred magnetically for a minimum of 10 min. A THF solution of $LiAlH_4$ was then syringed into the 1-mL bulb and added dropwise using the 1-mm stopcock. The reaction was quenched by cooling with liquid nitrogen after a specific reaction time and the quantity of hydrogen gas present was measured. The ampule was removed and the frozen sample hydrolyzed with water. Iodide in this water sample was determined after filtration. The residue was extracted with hot, aqueous 10% NaOH and the iodide in this sample was determined. The results of three experiments with varying CuI and $LiAlH_4$ reactant ratios and reaction times are given in Table I.

Reaction of CuI and $LiAlH_4$ in THF at −40 °C. Analysis of the Solution Content with Respect to Time. Copper(I) iodide (0.011 mol), $LiAlH_4$ (0.011 mol), and 50 mL of THF at −40 °C were stirred magnetically. The reaction was interrupted after 0.25, 1, 2, 4, 6, and 8 h by centrifuging and withdrawing aliquots of the clear solution. These aliquots were analyzed for Cu^+, I^-, Al^{3+}, and Li^+. The content of the solution in mole percent of each element relative to the total amount of each element present initially with respect to time was determined. These data are plotted in Figure 1.

Reaction of CuI and $LiAlH_4$ in THF at −78 °C. To a −78 °C slurry of 2.667 g of CuI (0.0140 mol) and 20 mL of THF in a 100-mL flask was added 9.61 mL of a 1.46 M solution of $LiAlH_4$ in THF. The resultant mixture turned red-brown finally producing a definite red-brown precipitate after about 2 h. After 5 h the mixture was centrifuged using a centrifuge cup which had been precooled to −78 °C. The liquid was removed and the solid washed with two separate 20-mL portions of precooled THF. After removal of the last washing, 20 mL of THF was added to form a slurry. Two 1-mL aliquots of this slurry were withdrawn using a precooled syringe. The H^-:Al^{3+}:Cu^+:Li^+:I^- ratio was found to be 4.0:1.0:1.0:0.58:0.51. *None of the I^- was present as unreacted CuI.* The slurry was found to be stable at −78 °C.

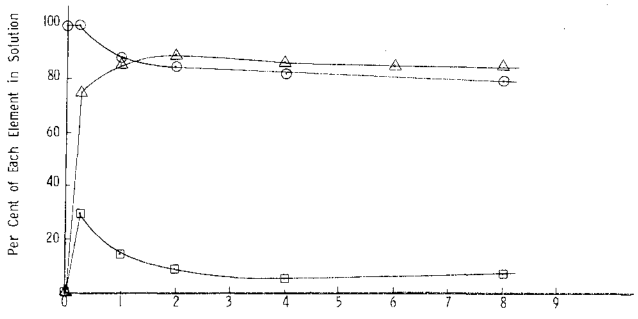

Figure 1. Plot of percent Al^{3+} (○), Cu^+ (□), and I (△) in THF solution vs. reaction coordinate for reaction of CuI and $LiAlH_4$ in 1:1 mole ratio at −40 °C.

Reaction of CuI and $LiAlH_4$ in THF at −78 °C Followed by Repeated Washings at −40 °C. To a −78 °C slurry of 6.99 g of CuI (0.0368 mol) and 125 mL of THF was added 25.2 mL of 1.46 M $LiAlH_4$ (0.37 mol) in a Schlenk tube. Rapid magnetic stirring of the reaction mixture gave a voluminous red-brown precipitate after 30 min. After being stirred at −78 °C for 4 h, the reaction mixture was allowed to warm to −40 °C. No gas evolution was noted at −40 °C and the precipitate remained red-brown. Analysis of an aliquot of the clear liquid revealed that more than 50% of the aluminum was in solution. The mixture was centrifuged and the liquid removed. The resulting solid was washed with seven 20-mL portions of THF precooled to −40 °C. No Al^{3+} or I^- was found in the last washing. THF (25 mL) was added to the resulting red-brown solid forming a slurry. Aliquots (2.0 mL) of this slurry were removed for analysis. The H^-:Al^{3+}:Cu^+:Li^+:I^- ratio was found to be 5.7:1.0:3.0:0.03:0.03. The slurry was stable at −78 °C.

Low-Temperature Infrared Studies of the Reactions of CuI and $LiAlH_4$ or AlH_3. An Air Products low-temperature Cryo-Tip, Model Ac-1-110, Vacuum shroud, Model WM X-1, and optical sample holder fitted with NaCl salt plates and indium gaskets were used for low-temperature infrared studies of THF solutions of selected metal hydrides and reaction mixtures. The cell path length was approximately 3 mm depending on the thickness of the indium gaskets. Spectra in the region 2000–1500 cm^{-1} were obtained against THF compensation using a variable-path-length compensating cell and PE Model 621 infrared spectrometer. Solutions of metal hydrides normally stable under ambient conditions were syringed into the sample holder and cooled to the desired temperature. Relatively less stable hydrides were generated in a 100-mL flask precooled to the desired temperature. Portions of this reaction mixture were forced into the precooled sample holder under nitrogen pressure by means of an inert tube connection.

Infrared spectra of 0.01 M $LiAlH_4$ and 0.01 M AlH_3 in THF were obtained in the range ambient to −120 °C. Single bands centered at 1695 and 1735 ± 5 cm^{-1}, respectively, were observed at all temperatures.

Infrared Analysis of the Reaction of CuI and $LiAlH_4$ in a 1:1 Mole Ratio at −40 °C. To a slurry of 0.2569g of CuI (0.001 35 mol) and

100 mL of THF at −40 °C was added 0.93 mL of 1.45 M $LiAlH_4$ solution in THF (0.001 35 mol). A portion of the resulting mixture was immediately forced into the low-temperature infrared cell which had been precooled to −40 °C. The initial, intense band centered at 1700 cm^{-1} was observed to shift to 1735 cm^{-1} in about 1 min. The band at 1735 cm^{-1} remained at that position for the entire time (90 min) that the reaction mixture was monitored.

Infrared Analysis of the Reaction of CuI and $LiAlH_4$ in a 4:1 Mole Ratio at −40 °C. To a slurry of 0.7443 g of CuI (3.92 mmol) and 100 mL THF at −40 °C was added 0.70 mL of 1.45 M $LiAlH_4$ in THF (1.0 mmol). A portion of the resulting mixture was immediately forced into the −40 °C infrared cell. An intense band at 1735 cm^{-1} was observed when the first scan had been recorded (reaction time of approximately 30 s). After 2 min, a new low-intensity band at approximately 1780 cm^{-1} was observed and the band at 1735 cm^{-1} was absent. The band at 1780 cm^{-1} was observed to decrease in intensity as the reaction proceeded. After 30 min, the observed spectrum nearly matched the baseline spectrum of neat THF at −40 °C vs. THF compensation.

Infrared Analysis of the Reaction of CuI and AlH_3 in a 1:1 Mole Ratio at −40 °C. To a slurry of 0.26 g of CuI (1.4 mmol) in 100 mL of THF at −40 °C was added 1.4 mL of a 1.0 M solution of AlH_3 in THF. A portion of the resulting mixture was immediately forced into the −40 °C infrared cell. An intense band at 1735 cm^{-1} was observed at approximately 30-s reaction time. After 5 min, this band was no longer present and a new low-intensity band appeared at 1780 cm^{-1}. The intensity of this band was found to decrease with time.

Reaction of $nHgI_2$ and $LiAlH_4$, Where n = 0.5, 1.0, 1.5, or 2.0. A THF solution of mercury(II) iodide was added to a THF solution of $LiAlH_4$ in four different 100-mL reaction flasks to give HgI_2:$LiAlH_4$ mole ratios of 0.5, 1.0, 1.5, and 2.0. The volume of THF present in each flask was adjusted to give a concentration of 0.200 M for aluminum assuming complete solubility of the aluminum species. Addition of HgI_2 to $LiAlH_4$ at room temperature was accompanied by immediate gas evolution and formation of a black-gray color. After a reaction time of 12 h, clear solutions and drops of mercury metal were observed in the cases where n = 0.5 and 2.0. A substantial amount of white precipitate was also present in the cases where n = 1.0 and 1.5. Infrared spectra of all solutions were recorded at room temperature. In the case of n = 0.5 an intense absorption was observed at 1737 cm^{-1}. The H^-:Al^{3+} ratio of the solution was found to be 2.7:1.0 and 96% of the aluminum was in solution. In the cases where n = 1.0, 1.5, and 2.0 very weak and broad absorptions were observed at approximately 1800 cm^{-1}. Analysis of the solution for I^- and Al^{3+}, where n = 2, revealed that 95% of the aluminum was in solution, the I^-:Al^{3+} ratio was 3.53 and a small amount of HgI_2 was present. The products of the reactions where n = 1.0 and 1.5 were filtered in the drybox, washed with THF, and hydrolyzed with dilute H_2SO_4. In the case where n = 1.0 the I^-:Al^{3+} ratio was found to be 0.80 and 60% of the aluminum was present. In the case where n = 1.5, the I^-:Al^{3+} ratio was found to be 1.90 and 60% of the aluminum was present.

Reaction of $nHgCl_2$ and $LiAlH_4$, Where n = 1.0 or 1.5. A THF solution of mercury(II) chloride was added to a THF solution of $LiAlH_4$ in two different 100-mL flasks to give $HgCl_2$:$LiAlH_4$ reactant mole ratios of 1.0 and 1.5. The volume of THF present in each flask was adjusted to give a concentration of 0.50 M based on soluble aluminum species. The reagents were mixed at 0 °C, allowed to warm to room temperature, and stirred for 12 h. The infrared spectrum of the solution where n = 1.0 revealed a band at 1790 cm^{-1}. Analysis of this solution revealed a H^-:Al^{3+}:Cl^- ratio of 1.69:1.00:2.08 with 98% of the aluminum in solution. When n = 1.5, an intense band at 1850 cm^{-1} was observed. The H^-:Al^{3+}:Cl^- ratio was found to be 0.90:1.0:2.90 with 100% of the aluminum in solution.

Reaction of C_6H_5HgCl and $LiAlH_4$ in a 1:1 Mole Ratio in Benzene. Solid phenylmercuric chloride (25 g, 0.080 mol) and excess solid $LiAlH_4$ (6.1 g, 0.16 mol) were mixed magnetically in a 250-mL flask containing 80 mL of benzene at room temperature. Gas evolution and formation of elemental mercury and a fine, white precipitate was noted during the first 1 min of reaction. The reaction appeared to be over in 30 min, although it was allowed to proceed at room temperature for 12 h. The reaction mixture was filtered yielding a clear filtrate which appeared to be saturated with product(s) giving a granular precipitate upon standing. This precipitate redissolved when the solution was heated at the reflux temperature. Removal of benzene under vacuum at room temperature gave a white solid which was analyzed for Al^{3+}, H^-, and Cl^-. No Cl^- was present and the percent by weight of Al^{3+} and H^- was consistent with a mixture of 75% $(C_6H_5)_2AlH$ and 25% $(C_6H_5)_3Al$. The conversion of C_6H_5 groups to these two products based on the amount of phenylmercuric chloride used as limiting reagent was 60%.

Results and Discussion

The results summarized in Table I indicate that only 50% of the CuI actually reacts at 0 °C when $LiAlH_4$ is allowed to react with CuI in THF in a 1:4 ratio over a 5–30-min period. There is relatively little thermal decomposition of the hydridic intermediates when the reaction time is as long as 30 min (experiments 1 and 2, Table I) and the reaction product remains red-brown during the reaction. In contrast, nearly all of the CuI reacted when the CuI:$LiAlH_4$ reactant mole ratio was 2:1 and the reaction time was 30 min. Moreover, 1.06 mmol of H_2 was produced from 2.02 mmol of CuI suggesting complete pyrolysis of the CuH product. Although the reaction was allowed to proceed for 30 min in order to measure the H_2 evolved quantitatively, the majority of the H_2 evolved was produced in the first 30 s.

These data can be explained by eq 3 and 4. Formation of

$$4CuI + LiAlH_4 \rightarrow LiI + IAlH_2 + 2Cu_2HI \qquad (3)$$

$$2CuI + LiAlH_4 \rightarrow LiI + IAlH_2 + Cu + H_2 \qquad (4)$$

a mixed hydrido–iodo complex of copper(I) is suggested in eq 3 because of the unusual thermal stability of this "CuH" exchange product as compared with its instability when "excess" CuI is not present (eq 4). Moreover, pure copper(I) hydride reportedly decomposes to hydrogen and copper metal rapidly above −20 °C.[10] This product apparently decomposes slowly at 0 °C producing H_2 and copper metal.

The reaction of CuI and $LiAlH_4$ was monitored using infrared spectroscopy over the range 2000–1500 cm^{-1} at −40 °C in an effort to determine the fate of soluble hydridoaluminum species. The reaction temperature was lowered to −40 °C due to thermal instability of the hydride products observed at 0 °C, particularly in cases where the CuI:$LiAlH_4$ mole ratio is 2:1 or less (eq 4). The observed spectral changes in the reactions of CuI and $LiAlH_4$ in 1:1 and 4:1 mole ratios and in the reaction of CuI and AlH_3 in a 1:1 mole ratio are consistent with the reaction scheme

$$LiAlH_4 \xrightarrow{CuI} AlH_3 \xrightarrow{CuI} IAlH_2 \xrightarrow{CuI} \text{no reaction} \qquad (5)$$

Aluminum–hydride stretching frequencies centered at 1700, 1735, and 1780 cm^{-1} were observed at various stages during the reaction (see Experimental Section). These bands are assigned to Al–H stretching in $LiAlH_4$, AlH_3, and H_2AlI, respectively. The Al–H stretching frequencies of $LiAlH_4$ and AlH_3 in THF at ambient temperature have previously been reported at 1690 and 1730 cm^{-1}, respectively.[11] The Al–H stretching frequency for $H_2AlI{\cdot}2THF$ in the solid state has been reported near 1780 cm^{-1}.[9] The position of these bands was found to be independent of temperature in this study. We observed a band centered at 1780 cm^{-1} which decreased in intensity with respect to time when H_2AlI was generated by the reaction of H_3Al with either I_2 or AlI_3 according to eq 6 and 7, respectively. Decreasing intensity of the 1780-cm^{-1} band

$$H_3Al + {}^1/_2I_2 \rightarrow H_2AlI + {}^1/_2H_2 \qquad (6)$$

$$2H_3Al + AlI_3 \rightarrow 3H_2AlI \qquad (7)$$

is likely due to precipitation of the relatively insoluble[9] THF complex ($H_2AlI{\cdot}2THF$) with time.

These studies reveal that iodoalane is the principal hydride product present in THF at 0 °C when the initial reactant mole ratio of CuI:$LiAlH_4$ is 2 or larger. Independently synthesized iodoalane (eq 6) gave nearly 100% 1,4 reduction of model enones. Iodoalane is therefore likely to be the active reagent responsible for giving conjugate reduction in situ reactions of

CuI and $LiAlH_4$ with enones.[2]

Several attempts were made to prepare and isolate copper(I) hydride and/or derivatives of CuH by the reaction of CuI and $LiAlH_4$ in 1:1 mole ratio at several temperatures in THF. Figure 1 is a plot of the percent of Al^{3+}, Cu^+, and I^- in solution against reaction coordinate when the reaction temperature is −40 °C. Rapid increase in the I^- concentration is consistent with rapid metathesis producing LiI. Increase in the Cu^+ concentration followed by a sharp decrease accompanied by a decrease in the Al^{3+} solubility is consistent with formation of an insoluble complex metal hydride of these metals.

Attempts were made to isolate complex metal hydrides of copper(I) and aluminum at −78 and −40 °C. Reaction of CuI and $LiAlH_4$ in a 1:1 mole ratio at −78 °C followed by washing of the insoluble red-brown precipitate with THF at −78 °C gave a slurry that exhibited a $H^-:Al^{3+}:Cu^+:Li^+:I^-$ ratio of 4.0:1.0:1.0:0.58:0.51. Double titration for I^- revealed that none of the I^- was present as unreacted CuI suggesting that LiI which is only sparingly soluble in THF at −78 °C is still present. The observed ratio for $H^-:Al^{3+}:Cu^+$ is consistent with $CuAlH_4$ or an equimolar mixture of CuH and AlH_3. Unfortunately, it is not possible to definitely distinguish between these two possibilities due to the fact that AlH_3 is essentially insoluble in THF at −78 °C. It is worthy of note that $CuAlH_4$ has been suggested previously as a possible complex metal hydride of copper(I).[12,13]

Nearly all of the LiI and a considerable amount of AlH_3 can be dissolved by repeated washing of this solid with THF at −40 °C. The $H^-:Al^{3+}:Cu^+$ ratio of the resulting red-brown slurry was found to be 6:1:3. This product is likely copper(I) hexahydridoaluminate (Cu_3AlH_6) in view of the fact that the last THF washings contained little or no aluminum hydride. Preferential stability of copper(I) hexahydridoaluminate relative to copper(I) tetrahydridoaluminate or a physical mixture of copper(I) hydride and aluminum hydride parallels the thermodynamic stability found for alkali metal hexahydridoaluminates relative to alkali metal tetrahydridoaluminates.[14,15] The fact that Cu_3AlH_6 is formed indicates that $CuAlH_4$ and not a mixture of CuH and AlH_3 are products of the reaction of $LiAlH_4$ and CuI in a 1:1 ratio. It is reasonable to assume that AlH_3 can be extracted from $CuAlH_4$ producing a molar excess of CuH which then reacts with $CuAlH_4$ to produce Cu_3AlH_6 (see eq 8 and 9).

$$CuAlH_4 \xrightarrow{THF} CuH + AlH_3 \qquad (8)$$

$$2CuH + CuAlH_4 \rightarrow Cu_3AlH_6 \qquad (9)$$

This suggestion is not unreasonable on the basis that more stable complex metal hydrides, such as $LiAlH_4$, release AlH_3 when extracted with $N(CH_3)_3$ resulting in the formation of Li_3AlH_6.[16]

The reaction of CuI and $LiAlH_4$ in THF at 0 °C was shown to produce iodoalane which has important applications in organic synthesis.[2] Attempts to generate iodoalane by reaction at room temperature lead to decomposition of this reagent[2] due presumably to the autocatalytic action of copper metal which is produced as a by-product. Several attempts were made to prepare haloalanes in THF by the reaction of mercury(II) halides and $LiAlH_4$. Mercury(II) halides were chosen because metallic mercury, the expected decomposition product of HgH_2, does not catalyze decomposition of aluminum hydrides.

Reactions of HgX_2 and $LiAlH_4$ where the initial mole ratio of HgX_2:$LiAlH_4$ is 0.5, 1.0, 1.5, and 2.0 and X is chlorine or iodine were evaluated. A combination of chemical and infrared analyses reveals that AlH_3, H_2AlX, $HAlX_2$, and AlX_3, respectively, are the principal aluminum products. These reactions are consistent with eq 10–13 and the more general eq 14. When X = I and n = 2 or 3, the aluminum products are not soluble in THF[9] while THF-soluble products are produced in all other cases.

$${}^1/_2HgX_2 + LiAlH_4 \rightarrow H_3Al + {}^1/_2Hg + {}^1/_2H_2 + LiX \qquad (10)$$

$$HgX_2 + LiAlH_4 \rightarrow H_2AlX + Hg + H_2 + LiX \qquad (11)$$

$$^3/_2HgX_2 + LiAlH_4 \rightarrow HAlX_2 + {}^3/_2Hg + {}^3/_2H_2 + LiX \qquad (12)$$

$$2HgX_2 + LiAlH_4 \rightarrow AlX_3 + 2Hg + 2H_2 + LiX \qquad (13)$$

$$(n/2)HgX_2 + LiAlH_4 \rightarrow H_{4-n}AlX_{n-1} + (n/2)Hg + (n/2)H_2 + LiX \qquad (14)$$

$$n = 1\text{–}4;\ X = Cl, I$$

Successful preparation of haloalanes by the reaction of mercury(II) halides and $LiAlH_4$ suggested that it might be possible to prepare alkyl- or arylaluminum hydrides by the reaction of alkyl- or arylmercury(II) halides and $LiAlH_4$. Reaction of phenylmercuric chloride and excess $LiAlH_4$ in benzene gave a mixture containing 75% $(C_6H_5)_2AlH$ and 25% $(C_6H_5)_3Al$ with 60% of the phenyl moiety converted to these products. These results suggest initial metathesis producing phenylaluminum hydride (eq 15) followed by phenylmercury–aluminum hydride exchange (eq 16 and 17).

$$LiAlH_4(s) + C_6H_5HgCl(s) \rightarrow LiCl(s) + Hg(l) + H_2(g) + C_6H_5AlH_2 \qquad (15)$$

$$C_6H_5AlH_2 + C_6H_5HgCl(s) \rightarrow {}^1/_2Hg(l) + {}^1/_2H(g) + {}^1/_2HgCl_2(s) + (C_6H_5)_2AlH \qquad (16)$$

$$(C_6H_5)_2AlH + C_6H_5HgCl(s) \rightarrow {}^1/_2Hg(l) + {}^1/_2H_2(g) + {}^1/_2HgCl_2(s) + (C_6H_5)_3Al \qquad (17)$$

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Registry No. CuI, 7681-65-4; $LiAlH_4$, 16853-85-3; AlH_3, 7784-21-6; HgI_2, 7774-29-0; $HgCl_2$, 7487-94-7; C_6H_5HgCl, 100-56-1; $(C_6H_5)_2AlH$, 880-08-0; $(C_6H_5)_3Al$, 841-76-9; H_2AlI, 58602-50-9; Cu_3AlH_6, 62126-19-6; $CuAlH_4$, 62126-20-9.

References and Notes

(1) On leave from the University of Northern Colorado, Greeley, Col. 80639.

(2) E. C. Ashby and J. J. Lin, *Tetrahedron Lett.*, 4453 (1975); E. C. Ashby, J. J. Lin, and R. A. Kovar, *J. Org. Chem.*, **41**, 1939 (1976).

(3) E. Wiberg and E. Amberger, "Hydrides of the Elements of Main Groups I-IV", Elsevier, Amsterdam, 1971, pp 460–462, and references therein.

(4) E. Wiberg and W. Henle, *Z. Naturforsch., B*, 7, 250 (1952).

(5) J. A. Dilts and D. F. Shriver, *J. Am. Chem. Soc.*, **90**, 5769 (1968).

(6) E. Wiberg and W. Henle, *Z. Naturforsch., B*, **6**, 461 (1951).

(7) D. F. Shriver, "The Manipulation of Air Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.

(8) G. W. Watt and J. L. Hall, *Inorg. Synth.*, **4**, 117 (1953).

(9) D. L. Schmidt and E. E. Flagg, *Inorg. Chem.*, **6**, 1262 (1967).

(10) G. M. Whitesides, J. San Filippo, Jr., E. R. Sterdronsky, and C. P. Casey, *J. Am. Chem. Soc.*, **91**, 6542 (1969).

(11) E. C. Ashby, J. J. Watkins, and H. S. Prasad, *Inorg. Chem.*, **14**, 583 (1975).

(12) G. Monnier, *Ann. Chim. (Paris)*, **2**, 14 (1957).

(13) E. C. Ashby and H. S. Prasad, *Inorg. Chem.*, **14**, 1608 (1975).

(14) E. C. Ashby and P. Kobetz, *Inorg. Chem.*, **5**, 1615 (1966).

(15) V. I. Mikheeva and S. M. Arkhipov, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **12**, 1066 (1967).