Notes

Contribution from the Ethyl Corporation,
Baton Rouge, Louisiana

Preparation of Sodium Hydride Complexes of Diethylzinc and Zinc Chloride[1]

By Paul Kobetz and Warren E. Becker

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The literature contains only two references to a complex between an alkali metal hydride and a zinc compound. Wittig and Hornberger[2] reported that a complex $Zn(C_6H_5)_2 \cdot LiH$ could be isolated as an etherate from the reaction between diphenylzinc and lithium hydride. Frey and co-workers[3] mentioned a complex between sodium hydride and diethylzinc; however, no attempts to characterize the complex were made.

Preparation of Sodium Hydride Complexes of Diethylzinc and Zinc Chloride.—We have found that sodium hydride will form an adduct with both diethylzinc and zinc chloride in glycol ethers. With monoglyme or diglyme as solvent, one mole of sodium hydride dissolved rapidly per two moles of diethylzinc to give a soluble product, but no additional sodium hydride would dissolve. Attempts to isolate the compound resulted in decomposition. The reaction would not take place in aliphatic or aromatic hydrocarbons, nor in diethyl ether or tetrahydrofuran.

Anal. Gas composition on hydrolysis of $NaH \cdot 2Zn(C_2H_5)_2$: H_2, 20; C_2H_6, 80. Found: H_2, 19.7; C_2H_6, 79.3.

The corresponding adduct of sodium hydride and zinc chloride was prepared in solution by stirring 20 g. (0.15 mole) of zinc chloride and 4.0 g. (0.17 mole) of sodium hydride in glycol ethers. The solid reactants dissolved very slowly, requiring 2–24 hr. While the reaction was proceeding, in the presence of solid sodium hydride, two competing reactions apparently occurred, for precipitation of zinc metal and sodium chloride and some gas evolution were observed. These side reactions were more rapid in reactions run at elevated temperatures. The product solution after filtration contained active hydrogen as well as sodium, zinc, and chlorine, and apparently was stable at room temperature. After several weeks of storage, hydrolysis gave rapid gas evolution, indicating retention of hydride content. Attempts to isolate the solute by removing solvent under vacuum resulted in decomposition.

Anal. Calcd. ratios for $NaH \cdot 2ZnCl_2$ in solution: Na/Zn/Cl/H = 1/2/4/1. Found: Na/Zn/Cl/H = 1.0/2.0/5.6/0.8.

Ethylation of the Sodium Hydride Complexes.—A solution of $NaH \cdot 2Zn(C_2H_5)_2$ in diglyme readily added ethylene under 450 p.s.i.g. at 100°. Reaction was complete within 2 hr. Analysis of the gases obtained from hydrolysis of the product showed only ethane and no hydrogen.

Attempts to add ethylene to $NaH \cdot 2ZnCl_2$ at 100° and at 25° under 550–850 p.s.i.g. of ethylene were unsuccessful. The mixture decomposed, leaving a residue containing zinc metal.

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[1] Presented in part before the Inorganic Division, 142nd National ACS Meeting, Atlantic City, N. J., September, 1962.

[2] G. Wittig and P. Hornberger, *Ann.*, **577**, 11 (1952).

[3] F. W. Frey, P. Kobetz, G. C. Robinson, and T. O. Sistrunk, *J. Org. Chem.*, **26**, 2950 (1961).

Contribution from the Ethyl Corporation
Baton Rouge, Louisiana

Some New Reactions of Complex Metal Hydrides of Aluminum[1]

By Paul Kobetz, Warren E. Becker,
Richard C. Pinkerton, and Julian B. Honeycutt, Jr.

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The literature contains only a few references to the reaction of a complex metal hydride with an acetylene. The reaction of $LiAlH_4$ with acetylene was studied by Ziegler.[2] He reported an addition reaction to give $LiAl(CH{=}CH_2)_3H$. Bailey and Pfeifer[3] observed hydrogen evolution in the reaction of $LiAlH_4$ with 1-hexyne. This might suggest ultimate formation of $LiAl(C{\equiv}CC_4H_9)_4$; however, no such product was isolated. Smith and co-workers[4] also inferred the preparation of $LiAl(C{\equiv}CC_4H_9)_4$ from the amount of hydrogen evolved in the reaction of $LiAlH_4$ with 1-hexyne in ether.

We have now studied the related reaction between acetylene and $NaAlR_3H$ where R is ethyl or isobutyl. In this reaction hydrogen evolution is vigorous. We have isolated the solid product; elemental analysis shows it to have the empirical formula $Na(R_3AlC{\equiv}CAlR_3)Na$.

Redistribution Reactions between $NaAlH_4$ and $NaAlR_4$.—Ziegler[5–7] has reported the preparation of sodium alkylaluminum hydride compounds from the reaction of sodium hydride with trialkylaluminum compounds and with alkylaluminum hydrides. We have prepared these identical compounds by the redistribution reactions between $NaAlH_4$ and $NaAlR_4$.

A phase diagram for the system $NaAlH_4$–NaAl-

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[1] Presented in part before the Inorganic Division, 142nd National ACS Meeting, Atlantic City, N. J., September, 1962.

[2] K. Ziegler, *European Scientific Notes*, **6**, No. 13, 178 (1952).

[3] W. J. Bailey and C. R. Pfeifer, *J. Org. Chem.*, **20**, 1337 (1955).

[4] G. B. Smith, D. H. McDaniel, E. Biehl, and C. A. Hollingsworth, *J. Am. Chem. Soc.*, **82**, 3560 (1960).

[5] K. Ziegler and H. Gellert, U. S. Patent 2,826,598, March 11, 1958.

[6] K. Ziegler, E. Holzkamp, R. Köster, and H. Lehmkuhl, *Angew. Chem.*, **67**, 213 (1955).

[7] K. Ziegler, H. Lehmkuhl, and E. Linder, *Chem. Ber.*, **92**, 2320 (1959).

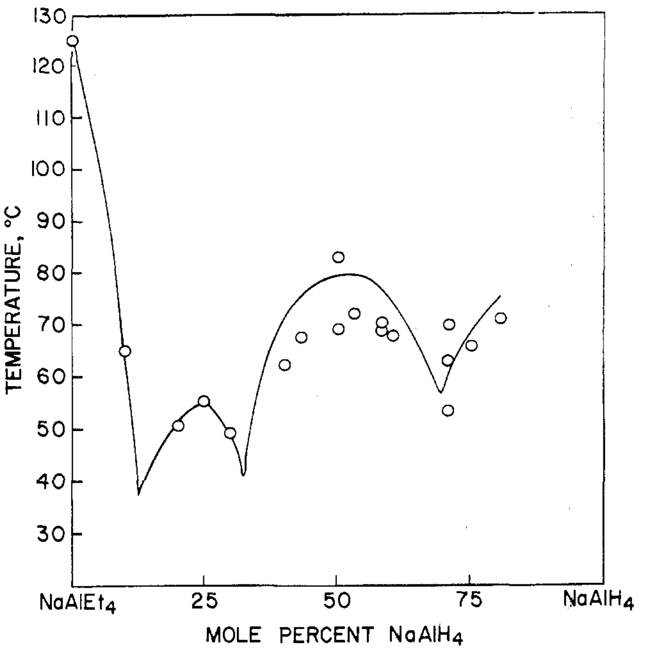

Fig. 1.—The NaAl $(C_2H_5)_4$–$NaAlH_4$ system.

$(C_2H_5)_4$ (Fig. 1) shows maxima corresponding to the compositions $NaAl(C_2H_5)_3H$ and $NaAl(C_2H_5)_2H_2$, but there is no evidence for $NaAl(C_2H_5)H_3$. An attempt to prepare this compound by the redistribution of $NaAlH_4$ and $NaAl(C_2H_5)_4$ in 3 : 1 mole ratio gave a material insoluble in toluene and another material which was soluble. Elemental analysis of the latter material showed that it had a composition corresponding to the formula $3NaAl(C_2H_5)_4 \cdot 2NaAlH_4$; however, no conclusions concerning the nature of this material can be drawn.

We do not know the exact mechanism of exchange involved in the redistribution reactions. Either a dissociation mechanism involving NaH or NaC_2H_5 or a complex intermediate involving single- or double-bridged bonds would explain the results.

Triethylaluminum Adducts of $LiAlH_4$.—We have found that triethylaluminum can be added to $LiAlH_4$ according to the equation

$$LiAlH_4 + nAl(C_2H_5)_3 \longrightarrow LiAlH_4 \cdot nAl(C_2H_5)_3$$

where n has values of from 1 to 4. If more than 4 moles are added, the additional $Al(C_2H_5)_3$ forms a separate phase. Solid products were isolated from these reactions, but it is probable that several species are present. For example, the adduct $LiAlH_4 \cdot 2Al(C_2H_5)_3$ may be in equilibrium with $LiAl(C_2H_5)_2H_2 \cdot 2(C_2H_5)_2AlH$. The fact that a residue enriched in alkyl groups can be obtained by the addition of petroleum ether to any of the adducts is evidence for redistribution of the groups. An observed increase in specific conductivity with increasing $Al(C_2H_5)_3$ content of the $LiAlH_4$–$Al(C_2H_5)_3$ system also suggests a redistribution reaction. Triethylaluminum itself is a non-conductor.

The mechanism of redistribution of the adducts is still unclear. Infrared data indicate the existence of hydrogen-bridged aluminum atoms (5.7 μ) and the absence of a mixed alkyl–hydrogen bridge (7.5 μ) such as has been found in dilute solutions of $(C_2H_5)_2AlH$ in $Al(C_2H_5)_3$.[8]

Ziegler has described[7] a similar system in which exchange also occurs. He was able to distil $Al(C_2H_5)_3$ away from a mixture of $(C_2H_5)_2AlH$ and $NaAl(C_2H_5)_4$, leaving a residue of $NaAl(C_2H_5)_2H_2$.

Experimental[9]

Equipment.—Most reactions were carried out in a three-necked round-bottomed flask fitted with a stirrer, condenser, heating mantle, and a nitrogen purge when necessary.

Analyses.—The bimetallic alkyl or alkyl hydride compounds were prepared for analysis by slow hydrolysis of a weighed sample. The aluminum was determined by titration with the sodium salt of ethylenediaminetetraacetic acid, and the sodium and lithium by flame photometry.

Active aliphatic and hydride groups were determined by hydrolysis using water (or dilute acid, if necessary), followed by mass spectrometric analysis of the gases evolved.

Infrared spectra were obtained using a Model 21 Perkin-Elmer infrared spectrophotometer.

Conductivity Measurements.—The cell used for conductivity measurements consisted of a pair of platinum bands mounted on a glass spindle dipping into a small well. The electrodes were platinized and the cell constant was determined before each series of runs. The specific resistance of the system was found using a Wheatstone bridge operated at about 1 kc. In order to balance the capacity of the cell, a large capacitor was introduced into the comparator arm of the bridge. An oscilloscope was used to indicate the null point.

Freezing Point Determinations.—Freezing point determinations were made in a 25 by 150 mm. glass tube containing a mechanically driven glass stirrer. The molten organometallic compound was allowed to cool slowly and the cooling curve was recorded on a recording potentiometer. An iron–constantan thermocouple was used in the measurements. An inert nitrogen atmosphere was maintained over the compound at all times.

Reagents.—Commercial triethylaluminum and triisobutylaluminum were used without further purification. Sodium aluminum hydride (95% purity) was obtained from the Ethyl Corporation.

Lithium aluminum hydride and sodium hydride, obtained from Metal Hydrides, Inc., were used without additional purification. The lithium aluminum hydride was used as received. The sodium hydride was obtained as a suspension in oil. After the oil was removed by filtration, the product was washed with toluene and hexane and dried under vacuum. Acetylene, purified grade, was obtained from the Matheson Company. It was further purified by passing it through concentrated sulfuric acid and activated alumina.

Sodium triethylaluminum hydride was prepared by a modification of Ziegler's method.[5,6] Sodium hydride (9 g., 0.38 mole) was slowly added to 40 g. (0.35 mole) of triethylaluminum in 150 ml. of toluene. The reaction was rapid. The slurry was filtered to remove excess sodium hydride. After most of the toluene was removed by vacuum distillation, 150 ml. of dry hexane was added to precipitate the product. The white crystalline solid had a melting point of 57–59° (uncorrected) and specific conductivity, K_{100}, of 0.0281 ohm^{-1} cm.$^{-1}$.

Anal. Calcd. for $NaAl(C_2H_5)_3H$: Al, 19.53. Found: Al, 19.63.

Sodium diethylaluminum hydride was prepared by slowly adding 5.5 g. of sodium hydride to 20 g. of a diethylaluminum hydride–triethylaluminum mixture (78% $(C_2H_5)_2AlH$ and 22% $Al(C_2H_5)_3$) in 100 ml. of toluene. The reaction was very fast.

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[8] R. L Hudson, private communication.

[9] Reaction products were worked up in a dry nitrogen box with a circulating purification system containing a heated tube packed with copper to remove oxygen and a Dry Ice trap to remove water. The oxygen content was less than 0.1%.