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.

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

Contribution from the Ethyl Corporation
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Some New Reactions of Complex Metal Hydrides of Aluminum[1]

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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).

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[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).