Lithium *n*-Butyl and Polyhalogen Compounds.—When lithium *n*-butyl solutions were allowed to react with trimethylene bromide and carbon tetrachloride, complex liquid hydrocarbon mixtures were obtained. With *o*-dichlorobenzene heavy, tarry products slightly fluorescent in solution were produced. Hexabromobenzene gave a dark insoluble powder. A similar powder was obtained when lithium phenyl was used instead of lithium *n*-butyl. When tetrachloro-ethylene was used a violent explosion occurred.

Summary

1. The reaction between lithium *n*-butyl and various halogen compounds has been studied.

2. In general the simple reaction of replacement of halogen by the *n*-butyl group does not occur.

3. The products which were formed suggest that the first step in the reaction of lithium *n*-butyl and a halogen compound is the formation of free radicals. These then undergo further reactions which differ widely for different groups.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

MAGNESIUM DIETHYL AND ITS REACTION WITH ACETYL CHLORIDE

BY HENRY GILMAN AND F. SCHULZE

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Introduction

Magnesium diethyl was apparently first prepared by Hallwachs and Schafarik[1] by heating magnesium with ethyl iodide. They described it as a solid, although the reactions of the liquid or oily fraction indicate that some magnesium diethyl was contained in the excess ethyl iodide. Later, Cahours[2] carried out the preparation from the same materials but he described his product as a liquid. Löhr[3] then prepared magnesium diethyl by heating magnesium with ethyl iodide and also by heating magnesium with mercury diethyl. His product was a solid. Fleck[4] extended Löhr's work on magnesium dialkyls, and, among other reactions, made a careful study of the reaction between magnesium diethyl and acetyl chloride.

We have prepared magnesium diethyl by the preferred method of Löhr[3] and Fleck,[4] namely, by heating magnesium with mercury diethyl

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[1] Hallwachs and Schafarik, *Ann.*, **109**, 206 (1859).

[2] Cahours, *Ann.*, **114**, 227 (1860).

[3] Löhr, *Ann.*, **261**, 48 (1891).

[4] Fleck, *Ann.*, **276**, 129 (1893).

in a sealed tube. However, we had no success in a few experiments even when Löhr's directions were carefully followed until a very small amount of mercuric chloride was used as a catalyst.[5] The magnesium diethyl so obtained was a solid and not a liquid.

Fleck[4] obtained trimethylcarbinol from the reaction between magnesium *dimethyl* and acetyl chloride. This is exactly as one would expect. However, he got the same carbinol from magnesium *diethyl* and acetyl chloride. This is certainly what one would not expect. Fleck did not expect to get this compound; instead he looked for dimethylethylcarbinol. He was quite aware of the apparently abnormal course of his reaction between magnesium diethyl and acetyl chloride; but there was no doubt in his mind because the product from magnesium diethyl was identical with that from magnesium dimethyl. He repeated the reaction between magnesium diethyl and acetyl chloride several times, and finally "left this quite striking observation unexplained."

In our work with beryllium alkyls, acetyl chloride was used as one of the reagents and it gave the normal or expected products. The same is true with magnesium diethyl, for it has been shown that dimethylethylcarbinol and not trimethylcarbinol is obtained from magnesium diethyl and acetyl chloride.

Experimental Part

It was not found possible to prepare magnesium diethyl by heating magnesium powder with mercury diethyl in an evacuated sealed tube at 130°, even when the heating was continued for 3 days. At a somewhat higher temperature, about 150°, the tube exploded after a short period of heating. However, when fresh mercury diethyl and a small amount of mercuric chloride were heated with magnesium powder at 130° a reaction set in at once. The reaction product was a light gray or brown powder, spontaneously inflammable in the air. On opening the reaction tube there was considerable pressure.

The material was removed from the tubes by dissolving it in 50 cc. of ether. The ether solutions gave a strong positive color test[6] for reactive organometallic compounds, a test not shown by mercury diethyl. A violent reaction took place when an ether solution of acetyl chloride was added to the magnesium diethyl in ether.[7] When a negative color test[6]

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[5] The same catalyst has given decidedly successful results in the preparation of organoberyllium compounds. Also, it has been used to bring about reaction between magnesium and some RX compounds that react very slowly with magnesium in ether. Mention of this catalyst, as well as many others, was made in a preliminary paper presented by Gilman, Schulze and Peterson at the Philadelphia, 1926, meeting of the American Chemical Society. The paper has been submitted for publication.

[6] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

[7] There is no apparent heat of reaction or heat of solution when anhydrous ether is added to magnesium diethyl.

was given (showing that an excess of acetyl chloride was present) the mixture was hydrolyzed by pouring it onto cracked ice containing a small amount of hydrochloric acid. On working up the extract in the customary manner by removing the ether, there remained a liquid with a pronounced camphor-like odor. This distilled between 120 and 125°, with the last portion coming over at about 130°. In order to further characterize this water-insoluble carbinol, it was converted to the corresponding chloride by passing in hydrogen chloride until no more of this gas was absorbed. The methyldiethylchloromethane when distilled in a microdistillation flask boiled at 115–118°. Its refractive index was 1.4037.

An authentic specimen of methyldiethylcarbinol was prepared from methyl ethyl ketone and ethylmagnesium bromide. It boiled at 120–122°. Treatment with hydrogen chloride gave the methyldiethylchloromethane boiling at 115–118°, and having a refractive index of 1.4034 as determined under the same conditions used for the unknown chloride.

The similarity of the carbinols and the chlorides obtained from them leaves no doubt as to the formation of methyldiethylcarbinol from magnesium diethyl and acetyl chloride.

Summary

Magnesium diethyl prepared by heating magnesium powder with mercury diethyl in the presence of mercuric chloride as a catalyst is a solid and not a liquid. When treated with acetyl chloride it gives methyldiethylcarbinol and not trimethylcarbinol as previously reported.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY]

A NEW PROCEDURE FOR THE QUANTITATIVE ESTIMATION OF SELENIUM IN ORGANIC COMPOUNDS

BY EDWIN H. SHAW, JR., AND E. EMMET REID

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Introduction

During the recent investigation of some organic selenium compounds the authors[1] felt the need of a simple and direct method of estimating selenium. Most of the methods described in the literature depend on a Carius tube combustion which is slow and tedious. As combustion with sodium peroxide in the Parr bomb has been so successful with sulfur,[2] and has supplanted the Carius method with halogens,[3] it seemed advisable to adapt this method to the determination of selenium. The only novelty is in the use of the fusion method. Two commonly used methods have

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[1] Shaw and Reid, THIS JOURNAL, **48**, 520 (1926).

[2] Parr, *ibid.*, **30**, 768 (1908).

[3] Lemp and Broderson, *ibid.*, **39**, 2069 (1917).