

his values by the density of ammonia, an odd coincidence.

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### The Preparation of Grignard Reagents from Magnesium Amalgams

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Magnesium amalgams have been used for the preparation of magnesium alkyls and aryls,<sup>1</sup> and for the coupling of ketones with chloro-esters and chloro-ethers.<sup>2,3,4</sup> In view of the high reactivity of dilute amalgams of magnesium toward oxygen and water, it seemed interesting to investigate the formation of methylmagnesium halides from such amalgams, and then to follow with experiments on other less reactive halides.

The phase diagram for the system Mg-Hg shows two compounds, MgHg<sub>2</sub> and MgHg. Below 168° the equilibrium condition at the low magnesium end is a mixture of MgHg<sub>2</sub> crystals and liquid, and hence the reported solubility of magnesium in mercury (3% at 250°, 1% at 100° and probably 0.1% at room temp.) must refer to the solubility of MgHg<sub>2</sub>. Since MgHg<sub>2</sub> contains 5.71% magnesium by weight, amalgams of this or greater concentration of magnesium will be solids, and amalgams in the range 5 to 0.1% magnesium will normally be mixtures of MgHg<sub>2</sub> with increasing proportions of liquid.

Amalgams containing from 0.1 to 1.0% of magnesium were prepared in an all-glass apparatus under an atmosphere of purified nitrogen.<sup>5</sup> The dissolution of magnesium in mercury is strongly exothermic, so no external heating was required. After cooling in the stream of nitrogen, 50 cc. of a 0.1 N solution of methylmagnesium chloride was added through the condenser and methyl bromide was admitted. The purpose of the methylmagnesium chloride was to eliminate difficulties in starting, which would have confused the results obtained.

After refluxing the amalgam with the solution of methyl bromide for several hours, samples of

(1) Fleck, *Ann.*, **276**, 129 (1893).

(2) Sommelet, *Ann. chim. phys.*, (8) **9**, 484 (1906). Superficial amalgamation by addition of a trace of HgCl<sub>2</sub> was used here to start the reaction.

(3) Darzens, *Compt. rend.*, **151**, 883 (1910).

(4) Grignard, *Bull. soc. chim.*, **128**, 1285 (1926).

(5) The dilute amalgams are very sensitive to traces of oxygen and moisture, and it was found that the ordinary purification methods had to be supplemented by passing the gas through a 1% Mg amalgam before use.

the ether layer were withdrawn for determination of total CH<sub>3</sub>MgX by evolution of methane with water. The increase of CH<sub>3</sub>MgX over that added at the start was calculated as % yield based on the magnesium. Typical results were:

% Mg in amalgam	Yield of RMgX, %
0.1	0
0.5	4.1
1.0	25.3

Unreacted magnesium was evident in the mercury layer in each case as soon as the amalgam was exposed to the air. Attempts were made to displace a possible equilibrium between MgHg<sub>2</sub> and RMgX, but the results indicated that there was no such equilibrium. Dilute magnesium amalgams did not seem to react at all with methyl chloride, and the iodide is reported to form the R<sub>2</sub>Mg compound under such conditions.<sup>1</sup>

The odor of mercury dimethyl was detected in some of the experiments. Metallic mercury does not react with RMgX to form R<sub>2</sub>Hg,<sup>6</sup> but mercury halides would do so readily, and such halides might have been formed in small quantity.

The experiments indicate that the yield of RMgX from magnesium amalgams increases with the concentration of magnesium in the amalgam, and with the increasing possibility of free magnesium in the amalgam mixture. It may be concluded that MgHg<sub>2</sub> does not participate in the Grignard reaction as readily as magnesium, and that mercury therefore has an inhibiting effect on the reaction.

(6) Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., Chapter 4.

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### Addition of Compounds of Dicyclohexylamine

BY CHARLES F. WINANS

In the hydrogenation of cyclohexanone in the presence of ammonia to form cyclohexylamine, a crystalline compound, m. p. 46°, formed in the cooled residue after distilling cyclohexylamine. This solid was found only when there was an insufficient amount of ammonia for complete reaction of the carbonyl group. Distillation of this product separated it into equivalent amounts of cyclohexanol and dicyclohexylamine, which recombined with evolution of heat to give the original crystalline material.