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

DEPARTMENT OF CHEMISTRY
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The Preparation of Grignard Reagents from Magnesium Amalgams

BY EUGENE G. ROCHOW

Magnesium amalgams have been used for the preparation of magnesium alkyls and aryls,[1] and for the coupling of ketones with chloro-esters and chloro-ethers.[2,3,4] 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, $MgHg_2$ and MgHg. Below 168° the equilibrium condition at the low magnesium end is a mixture of $MgHg_2$ 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 $MgHg_2$. Since $MgHg_2$ 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 $MgHg_2$ 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.[5] 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After refluxing the amalgam with the solution of methyl bromide for several hours, samples of the ether layer were withdrawn for determination of total CH_3MgX by evolution of methane with water. The increase of CH_3MgX 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 $MgHg_2$ 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_2Mg compound under such conditions.[1]

The odor of mercury dimethyl was detected in some of the experiments. Metallic mercury does not react with RMgX to form R_2Hg,[6] 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 $MgHg_2$ does not participate in the Grignard reaction as readily as magnesium, and that mercury therefore has an inhibiting effect on the reaction.

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

(2) Sommelet, *Ann. chim. phys.*, (8) **9**, 484 (1906). Superficial amalgamation by addition of a trace of $HgCl_2$ 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.

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

RESEARCH LABORATORY
GENERAL ELECTRIC COMPANY
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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.

The preparation of a number of analogous addition compounds was attempted with several amines and hydroxy compounds. Usually a solid formed on mixing equimolecular amounts of the materials at room temperature, but sometimes chilling was required. Recrystallization was effected by cooling a solution of the addition compound in ether or petroleum ether.

A typical example of the preparation of these compounds is as follows. A solution of 10 g. of dicyclohexylamine in 10 ml. of petroleum ether was mixed with 5 g. of cyclohexanol in 10 ml. of petroleum ether. The clear solution was strongly chilled to deposit crystals which were filtered out, washed with petroleum ether and dried in air; m. p. 47–48°. *Anal.* Calcd. for $(C_6H_{11})_2NH \cdot C_6H_{11}OH$: N, 4.99. Found: N, 4.87.

The table gives data on a number of these materials. Several recrystallized products melted below room temperature, but the existence of a compound is shown by the analysis of the melt.

The only known reference[1] on this subject is an article by Fougue, who described the formation of a hydrate (m. p. 23°) and an alcoholate (m. p. 28°) of dicyclohexylamine, but who did not discover the apparent generality of this behavior. It is, furthermore, quite surprising that these materials were not found earlier in view of the large amount of work done on reactions of cyclohexanol with ammonia and of cyclohexanone and hydrogen with ammonia, where conditions for isolation of an addition compound must have been at least as favorable as in this case.

(1) Fougue, *Compt. rend.*, **166**, 394 (1918).

TABLE I

AMINE–ALCOHOL ADDITION COMPOUNDS

Amine	Alcohol	M. p., °C.	Nitrogen, % Calcd.	Found
Dicyclohexyl-	Cyclohexanol	47–48	4.99	4.87
Dicyclohexyl-	2-Me-cyclohexanol	59–60	4.74	4.65
Dicyclohexyl-	1,2-Cyclohexanediol	64–66	4.72	4.72
Dicyclohexyl-	1,3-Cyclohexanediol	64–66	4.72	4.72
Dicyclohexyl-	1,4-Cyclohexanediol	90–91	4.72	4.59
Dicyclohexyl-	*o*-Cyclohexylcyclohexanol	43–45	3.86	3.61
Dicyclohexyl-	*p-t*-Butylcyclohexanol	75–76	4.15	4.12
Dicyclohexyl-	*β*-Phenethyl alcohol	Below	4.62	4.27
Dicyclohexyl-	1,3-Butanediol	room	5.16	5.10
Dicyclohexyl-	Benzyl alcohol	temp.	4.84	4.72
Dibenzyl-	Cyclohexanol	Below	4.72	4.63
Piperidine	1,3-Cyclohexanediol	room	6.96	6.78
Cyclohexyl-	Cyclohexanol	temp.	7.04	6.84

RESEARCH LABORATORIES
THE GOODYEAR TIRE & RUBBER COMPANY
AKRON, OHIO

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COMMUNICATIONS TO THE EDITOR

STEROLS. LXXXI. CONVERSION OF SARSASAPOGENIN TO PREGNANEDIOL-3(α),20(α)

Sir:

In studying the reaction of sarsasapogenin with acetic anhydride at 200° we have obtained a product in good yield (after alkaline hydrolysis) of the composition $C_{27}H_{44}O_3$, m. p. 171–173°, which we are tentatively designating as pseudosarsasapogenin. *Anal.* Calcd. for $C_{27}H_{44}O_3$: C, 77.8; H, 10.6. Found: C, 77.8; H, 10.6. Pseudosarsasapogenin upon mild oxidation with chromic anhydride in acetic acid gives a good yield of an unsaturated diketone, m. p. 201–203°. *Anal.* Calcd. for $C_{21}H_{30}O_2$: C, 80.2; H, 9.6. Found: C, 80.1; H, 9.6. This diketone upon reduction with sodium and ethanol gave a product, m. p. 236–239°, which gave no depression with an authentic sample of pregnanediol-3(α),20(α), m. p. 237–239°. *Anal.* Calcd. for $C_{21}H_{36}O_2$: C, 78.8; H, 11.3. Found: C, 78.7; H, 11.3. Acetylation of this reduction product with hot acetic anhydride gave an acetate of m. p. 177–179° which gave no depression with an authentic sample of the diacetate of pregnanediol-3(α),20(α) m. p. 177–179°. *Anal.* Calcd. for $C_{25}H_{40}O_4$: C, 74.2; H, 10.0. Found: C, 74.2; H, 10.0.

The ready availability of sarsasapogenin makes it now one of the most suitable sources of hormones such as progesterone, testosterone and desoxycorticosterone. The details of the work concerning the preparation and reactions of pseudosarsasapogenin, and its conversion to the above hormones will be published in a forthcoming issue of THIS JOURNAL.