[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

The Preparation of Dialkylmagnesium Compounds from Grignard Reagents

BY ARTHUR C. COPE

Schlenk's dioxane precipitation method[1] for the removal of the RMgX and MgX_2 components of the Grignard reagent $2RMgX \rightleftharpoons R_2Mg + MgX_2$ is now in common use for the preparation of ether solutions of dialkylmagnesium compounds. There is need for proof that the system is in mobile equilibrium, however, and for evidence concerning the accuracy of the dioxane method of analysis, since the equilibrium may shift during precipitation. Research in this Laboratory on these problems has revealed several factors which affect the yield of R_2Mg obtainable from Grignard reagents. They are reported in this communication.

The amount of R_2Mg obtained from all of the Grignard reagents investigated increased with increasing temperature. Thus the data summarized in Table I show that the amount of diphenylmagnesium present in solutions of phenylmagnesium bromide increased by about 10% for a 50° temperature rise. The point of equilibrium was also determined in *n*-butyl ether, in order to determine the effect of still higher temperatures. Both phenylmagnesium bromide and methylmagnesium iodide proved to be much less disproportionated in butyl ether than in ethyl ether at the same temperature. The data are recorded in Table II. Preliminary experiments at low temperatures showed a continued decrease in the amount of R_2Mg present and an apparently rapid rate of equilibration, for in solutions of ethylmagnesium iodide, ethylmagnesium bromide and phenylmagnesium bromide the amount of R_2Mg present decreased by approximately 30, 20 and 10%, respectively, on cooling from room temperature to −20 to −30° in forty to fifty seconds.

TABLE I

EFFECT OF TEMPERATURE ON THE DISPROPORTIONATION OF C_6H_5MgBr

Concn. of C_6H_5MgBr[a] Basic Mg, N	Br^-, N	Basic Mg present as $(C_6H_5)_2Mg$, % at T, °C. −15	0	20	35
0.1325	0.1381	59.5	62	67	69
.2178	.2257	62	64	68	70
.2772	.2897	61.5	65	69	70

[a] The slight apparent increase in $(C_6H_5)_2Mg$ with increasing concentration may be due to a rise in temperature during precipitation, which in the case of the most dilute of the above solutions amounted to 5°.

TABLE II

DISPROPORTIONATION OF C_6H_5MgBr AND CH_3MgI IN BUTYL ETHER

RMgX	Concentration Basic Mg, N	X^-, N	Basic Mg present as R_2Mg, % at T, °C. 20	60	100	140
C_6H_5MgBr	0.1108	0.1752	24	39	56	65
CH_3MgI	.2803	.2739	0.2			20

Another factor influencing the yield of R_2Mg obtainable from phenylmagnesium bromide is the reversibility of the precipitation; the yields of diphenylmagnesium increased if the precipitate with dioxane was allowed to stand in contact with the solution. Thus a 0.1818 *N* solution of phenylmagnesium bromide was found to contain 67% of diphenylmagnesium by the usual method of analysis. On allowing the precipitated samples to stand for one, two, three, twenty-four and seventy-two hours before separation of the precipitate by centrifuging, however, the amounts of diphenylmagnesium increased to 72, 73, 74, 75 and 75%, respectively. This reversibility of the precipitation is not general, for the yields of dimethylmagnesium from methylmagnesium iodide and methylmagnesium chloride did not increase on allowing the precipitated solutions to stand.

From these results, in the preparation of dialkylmagnesium compounds from Grignard reagents for synthetic purposes, the precipitation should be made by the addition of dioxane to refluxing solutions of the alkylmagnesium halides in order to obtain maximum yields. Due to the high disproportionation of the common Grignard reagents[1b,2,3] (especially the chlorides), all of the ordinary dialkylmagnesium compounds with the exception of dimethylmagnesium are thus available for practical synthetic use. Methylmagnesium iodide and methylmagnesium bromide are not highly disproportionated, however, so that Bartlett[4] was able to obtain dimethylmagnesium from methylmagnesium bromide in only 4% yield. Investigation of the disproportionation of methylmagnesium iodide at higher tempera-

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(1) (a) Schlenk and Schlenk, *Ber.*, **62**, 920 (1929); (b) Schlenk, *ibid.*, **64**, 735 (1931).

(2) Johnson and Adkins, THIS JOURNAL, **54**, 1943 (1932).

(3) Cope, *ibid.*, **56**, 1580 (1934).

(4) Bartlett and Berry, *ibid.*, **56**, 2683 (1934).

tures and of methylmagnesium chloride showed that dimethylmagnesium can also be prepared in the fair yield of 50% from the chloride (Table III).

TABLE III

EFFECT OF TEMPERATURE ON THE DISPROPORTIONATION OF CH_3MgX

CH_3MgX	Concentration Basic Mg, N	Concentration X^-, N	Basic Mg present as $(CH_3)_2Mg$, % at T, °C. 20	35	80 (in benzene)[a]	100[b]
CH_3MgI	0.2232	0.2331	2	10	17.5	44
CH_3MgCl	.2418	.1894	47	50		54

[a] The benzene solution was obtained by dissolving the liquid residue of methylmagnesium iodide etherate remaining after distilling off the ether in benzene. Note that the disproportionation is higher in benzene at 80° than in ether at 35°. The use of benzene as a solvent at 80° was recently assumed to decrease the disproportionation of cyclohexylmagnesium bromide by Miller and G. B. Bachman [*ibid.*, **57**, 767 (1935)]. Further work on the effect of solvents on the equilibrium was discontinued following the notice by these authors that they intended to study the problem.

[b] The samples at 100° were obtained by distilling off the ether and heating the residue at 100°. The methylmagnesium iodide etherate was a liquid, the chloride a white crystalline solid and mechanical difficulties probably account for the relatively low yield in the latter case.

All of the solutions of methylmagnesium chloride prepared contained more basic magnesium than chloride ion. Consequently the precipitate always formed in the preparation of this reagent is magnesium chloride etherate, not only from the Wurtz reaction, but also from the Grignard equilibrium. Thus, in the solution of methylmagnesium chloride described in Table III, 21.5% of the total basic magnesium was present as dimethylmagnesium regardless of any disproportionation of the methylmagnesium chloride remaining in solution. This amount was fairly constant for several preparations which had the following concentrations: (a) basic Mg, 0.2481 N, Cl^-, 0.1963 N (therefore 21% $(CH_3)_2Mg$; (b) basic Mg, 0.5404 N, Cl^-, 0.4168 N (therefore 23% $(CH_3)_2Mg$). A similar precipitation of magnesium chloride etherate was observed by Schlenk[1a] from benzylmagnesium chloride but precipitation was slow in that case, beginning only after several days, while with methylmagnesium chloride, concentrations similar to the above are observed immediately after preparation of the reagent.

Experimental Part

The Grignard reagents used in this investigation were prepared and stored under nitrogen. They were filtered through a plug of asbestos inserted in a stopcock sealed to the side of the flask in which they were prepared. If they were allowed to stand for a short time before filtering (or twelve hours in the case of methylmagnesium chloride), most of the filtration amounted to a decantation and could be made quite rapidly. The analyses for percentage R_2Mg were made as previously described.[3] The amount of dioxane used in each case to precipitate the halides was four moles to each mole of halide ion in the sample, made up to 10 cc. with the ether used in preparing the Grignard reagent. This amount was an excess, and apparently the excess employed does not affect the results given by the method. In all cases, the dioxane solution was at the same temperature as the solution being precipitated. In making the rapid cooling measurements, the samples were immersed in a carbon dioxide–ether mixture. In the other cases, since the equilibria appear to be established rapidly, the solutions were held at the recorded temperature for only fifteen minutes. The removal of halide ion from the solutions was practically complete in all cases, no more than 0.4% of the original quantity remaining in any case. For the measurements in which the ether was removed, the centrifuge tubes were fitted with a small dry exit tube and heated to the indicated temperature (80 or 100°) while the ether distilled off. In the measurements in benzene 20 cc. of dry benzene was then added and the tubes stoppered, while in the 100° determinations the tubes were stoppered and the residues heated at that temperature for fifteen minutes. The precipitation was made by adding 2 cc. of pure dioxane in each of these cases. In the samples precipitated in the absence of a solvent, dry ether was added to the tubes as soon as the rather vigorous reaction with dioxane was over and the rest of the determination made as before. Since heat is evolved during the precipitations, no attempt was made to control the temperature with an accuracy greater than 1°. The order of accuracy of the measurements is indicated by the average deviation of the duplicate analyses which were made in each case, which was 0.5% for basic magnesium; 0.2% for halide ion; 1% for per cent. R_2Mg.

Summary

The extent of the disproportionation $2RMgX \rightleftharpoons R_2Mg + MgX_2$ depends upon the solvent

employed and increases with increasing temperature, as determined by the dioxane precipitation method.

The precipitate formed during the preparation of the Grignard reagent from methyl chloride contains magnesium chloride etherate from the disproportionation of methylmagnesium chloride, so that the reagent contains 20% of dimethylmagnesium in addition to that formed by the disproportionation of the methylmagnesium chloride remaining in solution.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Photobromination of Tetrachloroethylene and of Chloroform with Special Reference to the Effects of Oxygen

BY JOHN WILLARD AND FARRINGTON DANIELS

Oxygen, present as an incidental impurity, is known to have a marked effect on the rate of certain chemical reactions,[1] and very likely it is a factor in others where its influence has not yet been suspected. The matter is of interest both from a theoretical and from a practical standpoint.

The photobromination of cinnamic acid has been under investigation in this Laboratory for several years[2] and it seemed desirable to investigate also the photobromination of the very simple molecules, tetrachloroethylene for addition, and chloroform for substitution. These two substances are valuable for investigational purposes not only on account of their simple structure but also on account of the fact that they have high vapor pressures and can be studied in the gas phase as well as in the liquid phase.

All of the photochemical work described here was carried out with a large quartz monochromator and capillary lamps of high intensity,[3] and a large area thermopile.[4]

Photobromination of Tetrachloroethylene

Experimental Procedure

Tetrachloroethylene.—Chlorine was passed into Eastmen tetrachloroethylene and exposed to light.[5] After washing several times with sodium hydroxide and with water the liquid was dried with calcium chloride and twice distilled through a Widmer column in an all-glass still, the middle fraction being retained. It was further purified by freezing in an all-glass reservoir equipped with a dozen taps which could be opened with magnetically operated hammers.

Bromine.—Merck reagent quality bromine was distilled from potassium bromide onto phosphorus pentoxide which had been resublimed in a stream of oxygen. It was then fractionally distilled four times and fractionally crystallized three times, all steps in the purification process being carried out in an all-glass system. After degassing in the manner to be described shortly, it was distilled into a dozen small bulbs.

Oxygen.—Commercial tank oxygen was liquefied in a liquid air trap and the middle-boiling fraction was used to fill a series of bulbs of 1 cc. or less in volume. The pressure of oxygen was determined with a glass manometer.

Degassing Liquids.—Dissolved oxygen was removed from the reservoirs of liquid tetrachloroethylene and bromine by a repeated cycle of freezing with liquid air, evacuation with a mercury vapor pump, melting and brief boiling. When gas from the frozen liquid was no longer able to support a discharge from a Tesla coil, the material was deemed to be sufficiently free from oxygen. It was usually necessary to go through a series of six or seven freezings and evacuations before the oxygen and other permanent gases were sufficiently removed to meet this criterion.

Apparatus.—The experiments were carried out in a fused quartz cell 1 × 2 cm. in cross section and 8 cm. deep. The cell was equipped with a head as illustrated in Fig. 1. Side arm A contains bulbs of reactants which may be shaken into depression C to be broken by the glass-enclosed hammer B. D-E-G is a sealed-in, magnetically-operated stirrer designed to give efficient stirring in the illuminated portion of the cell, without interrupting the beam of light. It consists of the quartz-enclosed iron core D, the quartz landing button E and the quartz rod which terminates in the stirring button G. When an experiment is in progress the circuit through the solenoid M is opened and closed about twice a second by means of a contact operated by a metronome or by a cam on a pulley wheel. This jerks the stirrer up several centimeters and then allows it to fall under its own weight to the point where E is stopped by the quartz platform, F. In falling rapidly the button G sets into motion a body of liquid which travels on into the illuminated region of the cell. The button G has to be 5 mm. or less in diameter, in order to pass through the neck

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[1] See, among others, Deanesly, THIS JOURNAL, **56**, 2501 (1934); Bauer and Daniels, *ibid.*, **56**, 2014 (1934); Dunnicliff and Joshi, *J. Ind. Chem. Soc.*, **6**, 121 (1929); Kistiakowsky, "Photochemical Processes," Chemical Catalog Company, New York City, 1929, pp. 118, 119, 166, 183.

[2] Bauer and Daniels, THIS JOURNAL, **54**, 2564 (1932).

[3] Heidt and Daniels, *ibid.*, **54**, 2381, 2384 (1932).

[4] Damon, Ph.D. Thesis, University of Wisconsin, 1932.

[5] Dickinson and Leermakers, THIS JOURNAL, **54**, 3853 (1932).