[Contribution from the Chemistry Laboratory of the University of Michigan]

THE REACTION BETWEEN TRIPHENYLMETHYL, MAGNESIUM AND A SMALL AMOUNT OF MAGNESIUM HALIDE. THE COMPOSITION OF THE GRIGNARD REAGENT

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In studying the action of a mixture of magnesium and magnesium halide on ketones, 1,2-diketones and on aromatic acids,[1] it was observed that a molecule of magnesium halide was split off from the halogen-magnesium compounds initially formed in the reaction. In virtue of this regeneration of magnesium halide, a small amount of halide in the mixture could suffice for complete reaction of a large amount of the ketones or acids, provided the mixture was heated.

It has now been found that a Grignard reagent may be made to undergo a similar loss of magnesium halide

$$2(C_6H_5)_3CMgX \rightleftarrows (C_6H_5)_3CMgC(C_6H_5)_3 + MgX_2 \qquad (1)$$

Recently[2] it was shown that triphenylmethylmagnesium bromide, and the iodide, can be prepared in excellent yields from triphenylmethyl and a mixture of magnesium and magnesium halide, according to the following formulation

$$2(C_6H_5)_3C + Mg + MgX_2 \longrightarrow 2(C_6H_5)_3CMgX \qquad (2)$$

It is now found that a small amount of magnesium halide suffices for complete conversion of triphenylmethyl to its magnesium derivatives. To be sure, the reaction is slower than is the case when a large amount of halide is present, but nevertheless it is complete. Either magnesium halide, as such, or a small amount of triphenylbromomethane may be added to the triphenylmethyl and magnesium; in the latter case, the carbinol bromide is first of all changed to the radical and magnesium bromide.[2] Since the radical does not react with metallic magnesium without halide present, the magnesium halide must be continuously reproduced according to Equation 1, being made available for further reaction. At the end of the reaction there exists an equilibrium mixture of triphenylmethylmagnesium halide, magnesium triphenylmethyl and magnesium halide.

It is considered that a similar equilibrium mixture may exist in the case of this and all other Grignard reagents even when the amount of metal halide is equivalent to a full mole, as is the case with such reagents prepared from the alkyl halides. Schlenk and Schlenk, Jr.,[3] employing a different method, came to a similar conclusion. Gilman and co-workers[4] consider

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[1] Gomberg and Bachmann, This Journal, **49**, 247, 2584 (1927); **50**, 2762 (1928).

[2] Gomberg and Bachmann, *ibid.*, **52**, 2455 (1930).

[3] Schlenk and Schlenk, Jr., *Ber.*, **62**, 920 (1929).

[4] Gilman and Fothergill, This Journal, 51, 3149 (1929); Gilman and Brown, *Rec. trav. chim.*, **48**, 1133 (1929).

that there is little or no $R_2Mg{\cdot}MgI_2$ in the Grignard reagent under ordinary conditions in ether solution but that the amount varies markedly with the nature of the solvent, reactant and temperature.

Experimental

Triphenylmethyl + Mg.—A mixture of 9.8 g. of triphenylmethyl and 0.52 g. of magnesium ribbon in 120 cc. of ether–benzene (1:2) was heated for forty-eight hours in an atmosphere of nitrogen. At the end of this time no weighable amount of magnesium had reacted. In another experiment no magnesium was dissolved after one hundred hours, and the triphenylmethyl used was recovered unchanged.

Triphenylmethyl + Mg + MgI_2 (42%).—Twelve grams of triphenylmethyl, 3 g. of magnesium iodide and 0.77 g. of magnesium ribbon were heated in an atmosphere of nitrogen in a mixture of 40 cc. of ether and 70 cc. of benzene. After twenty hours, the clear solution was filtered from excess of magnesium and hydrolyzed. The magnesium loss was 0.59 g.; this represents 97% of the calculated value. The magnesium hydroxide produced on hydrolysis required 46.05 cc. of *N* acid for neutralization; theoretical value on basis of triphenylmethyl, 50.0 cc. From the ether–benzene solution there was obtained 11 g. (92%) of triphenylmethane.

Similar results were obtained when magnesium bromide was used in place of the iodide, even when the amount of halide corresponded to only 0.05 mole for a mole of triphenylmethyl.

Triphenylmethyl (0.9 mole) + Triphenylbromomethane (0.1 mole) + Mg.—A mixture of 13.4 g. of triphenylmethyl and 1.98 g. of triphenylbromomethane was heated with 1.19 g. of magnesium ribbon in 200 cc. of ether–benzene (2:3). The reaction started immediately. After three days the solution was filtered; loss in magnesium, 0.83 g.; theoretical value, 0.82. Dry carbon dioxide was passed into the solution for six hours. Hydrolysis yielded 8.5 g. of triphenylacetic acid or 50% of the calculated amount. From this single experiment, it would appear that the reaction between magnesium triphenylmethyl and carbon dioxide is considerably slower than carbonation of triphenylmethylmagnesium bromide. Gilman and Brown[5] report that phenylmagnesium bromide reacts with *n*-valeronitrile more readily than does an equivalent solution of magnesium diphenyl.

In another experiment in which 13.4 g. of triphenylmethyl and 1.80 g. of triphenylbromomethane were allowed to react with magnesium, 0.80 g. of metal was dissolved; calculated, 0.80. Hydrolysis gave 11.3 g. of triphenylmethane; calculated, 14.8.

Summary

A small amount of magnesium iodide (or bromide) can suffice to convert triphenylmethyl and magnesium to the magnesium derivatives of triphenylmethyl. The reaction takes place in two steps: (a) $2(C_6H_5)_3C + Mg + MgX_2 = 2(C_6H_5)_3CMgX$; (b) $2(C_6H_5)_3CMgX \leftrightarrows MgX_2 + (C_6H_5)_3CMgC(C_6H_5)_3$. The latter step makes the MgX_2 available for continuous reaction.

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[5] Gilman and Brown, THIS JOURNAL, **52**, 1183 (1930).