[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE REDUCTION OF BENZOPHENONE TO BENZOPINACOL BY MEANS OF MAGNESIUM AMALGAM AND SOME OBSERVATIONS CONCERNING MAGNESIOUS CHLORIDE

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Introduction

In a recent paper by Gilman and Fothergill[1] it was shown that triphenylmethylmagnesium chloride probably dissociates in the following manner

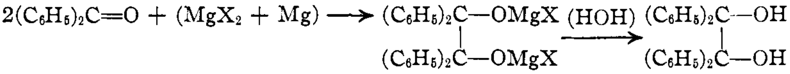
$$(C_6H_5)_3CMgCl \rightleftharpoons (C_6H_5)_3C— + —MgCl \qquad (I)$$

Evidence for such dissociation was the molecular weight determination, reduction of benzophenone to benzopinacol, catalytic reduction and the reaction with nitrous oxide.[2]

Attention was directed at that time to a serious objection that might be raised against a dissociation leading to the formation of the hypothetical magnesious chloride (—MgCl). If Reaction I were correct, then it is possible that the reaction might proceed irreversibly to give triphenylmethyl (or hexaphenylethane) and magnesium and magnesium chloride ($MgCl_2$). Such a possibility is reasonable on the basis of the following equilibrium.

$$2MgCl \rightleftharpoons Mg + MgCl_2 \qquad (II)$$

Gomberg and co-workers,[3] in some excellent studies, have shown that Reaction II, with magnesium iodide and magnesium bromide, is very largely displaced toward the right so that the quantity of magnesious halide (—MgX) present in solution is extremely small. They also established the fact that the binary system ($MgCl_2$ + Mg) quite unlike the binary systems ($MgBr_2$ + Mg) and (MgI_2 + Mg) does not reduce benzophenone, in the following manner, to benzopinacol.



$$2(C_6H_5)_2C{=}O + (MgX_2 + Mg) \longrightarrow \begin{array}{l}(C_6H_5)_2C—OMgX\\ \quad\; |\\ (C_6H_5)_2C—OMgX\end{array} \xrightarrow{(HOH)} \begin{array}{l}(C_6H_5)_2C—OH\\ \quad\; |\\ (C_6H_5)_2C—OH\end{array} \qquad (III)$$

But, because Gilman and Fothergill[1] actually obtained benzopinacol from benzophenone and triphenylmethylmagnesium chloride (apparently free of any magnesium), it seemed altogether reasonable that magnesious chloride, formed in accordance with Reaction I, reduced benzophenone to benzopinacol (Reaction III) like magnesious bromide or ($MgBr_2$ + Mg) and magnesious iodide or (MgI_2 + Mg).

The reduction (Reaction III) goes rapidly with (MgI_2 + Mg), less quickly with ($MgBr_2$ + Mg) and not at all with ($MgCl_2$ + Mg). Gom-

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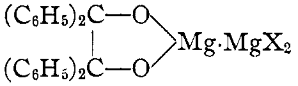
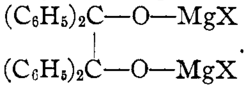
[1] Gilman and Fothergill, THIS JOURNAL, **51**, 3149 (1929).

[2] Gilman and Leermakers, *ibid.*, **52**, (1930).

[3] (a) Gomberg and Bachmann, *ibid.*, **49**, 236 (1927); (b) Gomberg and Bachmann, *ibid.*, **49**, 2666 (1927); (c) Gomberg and Bachmann, *ibid.*, **49**, 2584 (1927); (d) Gomberg and Bailar, Jr., *ibid.*, **51**, 2229 (1929); Gomberg and Van Natta, *ibid.*, **51**, 2238 (1929).

berg and Bachmann[3a] attributed the absence of reduction with ($MgCl_2$ + Mg) to the sparing solubility of magnesium chloride in the ether–benzene mixture used as a medium. However, because magnesium chloride is soluble, even though to an extremely slight extent, in an ether–benzene mixture, it occurred to us that the system ($MgCl_2$ + Mg) should reduce benzophenone if the reaction were heated for an extended time. Previously, Gilman and Fothergill[1] confirmed the results of Gomberg and Bachmann[3a] on the absence of reduction by ($MgCl_2$ + Mg). The results of the present study complete such verification because benzophenone when heated in a sealed tube for 35 *days* at 130° with ($MgCl_2$ + Mg) gave neither the characteristic color indicative of reduction[3] nor any benzopinacol.

Other experiments were carried out to see if evidence might not be secured for the —MgCl postulated in Reaction I. It was found that benzophenone is reduced to benzopinacol by magnesium and mercuric chloride. We are of the opinion that such reduction is due to magnesium amalgam and not to the system ($MgCl_2$ + Mg), because as just stated ($MgCl_2$ + Mg) without mercury did not effect reduction, and also because magnesium and mercury (very probably as magnesium amalgam) did reduce benzophenone to the pinacol.[4] In their first study Gomberg and Bachmann[3a] reported that magnesium amalgam did not reduce the ketone, but later[3c] they reported that such reduction did occur but in an erratic fashion. We also tried magnesium cleaned with iodine and with a Grignard reagent (methylmagnesium iodide), but observed no reduction.

The results, on the whole, are not too easy of correct interpretation. It is clear that although magnesium alone will not effect reduction, magnesium in an activated form (as the amalgam by mercury or by mercuric halide) will reduce the carbonyl group. Quite naturally this raises a question whether reduction by the system (MgI_2 + Mg) or ($MgBr_2$ + Mg) might not be due to an activation of the metal by the magnesium halide, somewhat after the manner of its activation by the mercuric halide. If this were the case, an answer must be found to the need of an equivalent quantity of magnesium halide (or halogen). Possibly as in some other catalytic reactions (like some Friedel–Crafts reactions) the catalyst is required at moderate temperatures in equivalent molecular quantities because it is "accidentally removed" or tied up by the formation of complexes with intermediate compounds, the formation of which it accelerates. In such an event the formula of the intermediate halogen magnesium pinacolate might be  $\left.\begin{array}{l}(C_6H_5)_2C{-}O\\ \qquad\quad|\\ (C_6H_5)_2C{-}O\end{array}\right\rangle Mg\cdot MgX_2$ and not  $\begin{array}{l}(C_6H_5)_2C{-}O{-}MgX\\ \qquad\quad|\\ (C_6H_5)_2C{-}O{-}MgX\end{array}$. Gomberg and co-workers[3] have already considered

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[4] See also Schlenk and Thal, *Ber.*, **46**, 2847 (1913).

the former compound as derivable from the latter by the application of heat.

It may not be an easy matter to answer the question whether the reduction is due to magnesious halide (—MgX) from the system (MgX_2 + Mg), or to the catalyzing or activating effect of the magnesium halide (MgX_2) on the magnesium. Possibly they are one and the same thing, or both processes are involved in concurrent reactions.[5]

TABLE I

RESULTS OF EXPERIMENTS

Run	Mg		$(C_6H_5)_2CO$		$HgCl_2$,	Pinacol		Time of heating,	Temp.,
no.	G.	Atom	G.	Moles	G.	G.	%	Days	°C.
1	2.4	0.1	18.2	0.1	0.5	1.2	6.7	8	130
2[a]	1.2	.05	9.1	.05	None	None		35	130
3	1.2	.05	9.1	.05	None	None		8	130
4	1.2	.05	9.1	.05	0.5	None		8	130
5	0.0	.0	9.1	.05	None	None		8	130
6[b]	1.2	.05	9.1	.05	0.5	0.7	7.7	6	25
7[c]	1.2	.05	9.1	.05	None	0.3	3.3	35	130
8[d]	1.2	.05	9.1	.05	None	None		12	130
9[e]	1.2	.05	9.1	.05	None	None		1	25

[a] In this experiment 4.8 g. (0.05 mole) of magnesium chloride was used. Another experiment like this was run for eight days at 130° and no benzopinacol was obtained.

[b] In this experiment the reaction tube was shaken mechanically at room temperature.

[c] Ten g. of mercury was used in this experiment. No color appeared in the reaction mixture until it had been heated for fourteen days. When this run was worked up a yellow oil was isolated. It would not crystallize at low temperatures nor could it be made to yield a crystalline product from alcohol, ether, benzene, acetic acid, ligroin or methyl alcohol.

[d] The magnesium was first cleaned in this experiment by treating it with iodine. Of course, the iodine and magnesium iodide were then completely removed by an ether–benzene mixture washing in an inert atmosphere.

The magnesium which was cleaned by permitting it to react with methyl iodide in ether gave no color and no benzopinacol when heated with benzophenone for twenty-four hours at 130° in an ether–benzene mixture.

[e] In this experiment, 3.1 g. (0.05 mole) of magnesium fluoride was used. Our interest here was with other studies concerned with the preparation of phenylmagnesium fluoride from magnesium diphenyl. The reaction tube in this experiment was shaken mechanically at room temperature.

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[5] If a definite answer can be given, we feel quite certain that it will come from Gomberg and co-workers. This field is properly reserved to its discoverers who have done much with it and in a short time. Our interests lie only with such applications of their developments as concern the Grignard reagents. We (H. G.) are at present sympathetically inclined to the attractive magnesious halide conception [see Gilman and Fothergill, THIS JOURNAL, **50**, 3334 (1928); and Gilman and Kirby, *ibid.*, **51**, 1571 (1929)], but some of our students feel that a sufficiently strong case has not been made against that interpretation which involves an activated or catalyzed magnesium.

Experimental Part

All of the experiments were carried out in sealed tubes and with purified materials. Operations such as filtration were effected in an inert atmosphere.

Two and four-tenths g. (0.1 atom) of 30–80 mesh magnesium, 18.2 g. (0.1 mole) of benzophenone, 90 cc. of an ether–benzene mixture (in the ratio of 1:2), and the mercuric chloride or magnesium chloride, if used, were placed in a previously constricted, nitrogen filled Carius tube. The tube was evacuated, until the solvents boiled vigorously, and sealed off. It was then placed on a steam-plate, the temperature of which was 130°. At the end of the heating period, the tube was opened under a stream of nitrogen, the contents filtered through a nitrogen filled Erlenmeyer flask into the bottom of which was sealed a sintered glass filter, and the filtrate was allowed to run into a flask provided with a nitrogen atmosphere.

After adding dilute hydrochloric acid, the ether–benzene layer was separated, washed with water, dried over sodium sulfate and the solvents removed by distillation. One hundred cc. of dry petroleum ether (40–60°) was added and the insoluble pinacol was filtered, digested with 20 cc. of petroleum ether, filtered, dried and weighed.

Because benzopinacol decomposes near its melting point, parallel comparative melting points were always made with pure benzopinacol. The melting points varied from 183 to 189° depending on the rate of heating of the melting-point bath. Mixed melting-point determinations were always made with pure benzopinacol.

The separation of benzopinacol from benzophenone by means of 40–60° petroleum ether is very satisfactory when all of the benzene is removed from the mixture of pinacol and ketone. This was accomplished by blowing dry air over the warm mixture after the major portion of the solvents had been removed by distillation.

The results of a miscellany of experiments are given in Table I and the footnotes which accompany it.

Summary

In connection with the possible existence of magnesious chloride, a study has been made of some factors affecting the reduction of benzophenone to benzopinacol.

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