

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]
**THE CONSTITUTION AND THE DISSOCIATION OF THE
GRIGNARD REAGENT¹**

BY HENRY GILMAN AND ROBERT E. FOTHERGILL

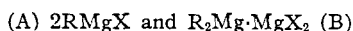
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Introduction

It is possible to write a large number of formulas for the Grignard reagent prepared in ether. The so-called central element to which might be attached the largest number of other elements and groups can be magnesium (variously coordinated) or oxygen or a halogen. Or we might have combinations of two or more of such central atoms, and structures involving residual valences of carbon and even of hydrogen. Then there are electronic interpretations of the structure, which because of the polar characteristics of organomagnesium halides may have formal, classical bonds replaced by electrostatic forces after some representations of the structure of compounds like magnesium chloride.

If we omit the diethyl ether, which is not a *necessary*² part of the molecule, it is possible to simplify matters considerably by restricting discussion arbitrarily to two formulas to which most attention has been directed recently.³ These formulas are



One of several ways of deciding between these two formulas is to determine whether MgX_2 is an integral part of the Grignard reagent. Some light can be thrown on this by use of the very interesting recent studies of Gomberg and Bachmann⁴ on the following equilibrium



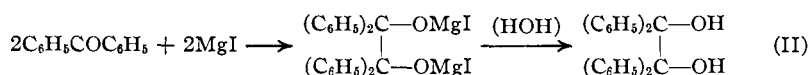
The magnesian halide formed in accordance with Reaction I can be characterized in a number of ways, particularly by its reaction with benzophenone to give benzopinacol

¹ An account of this work was read at the Spring Meeting of the American Chemical Society held at Columbus, Ohio, in April, 1929.

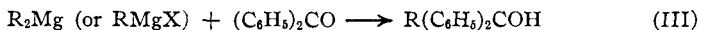
² It is possible to prepare $RMgX$ compounds with no ether, and it is possible to remove all ether from $RMgX$ compounds. These so-called "individual organomagnesium halides" show the general reactions of the corresponding compounds containing ether.

³ It is out of the question, because of space limitations, to give a complete (even though uncritical) consideration of the large amount of work on the constitution of organomagnesium halides. Some leading references are Grignard, *Compt. rend.*, **130**, 1322 (1900); **185**, 507 (1927); *Bull. soc. chim.*, **41**, 759 (1927); Jolibois, *Compt. rend.*, **155**, 353 (1912); Meisenheimer and co-workers, *Ber.*, **54**, 1655 (1921); **61**, 708, 720 (1928); Ivanoff, *Compt. rend.*, **185**, 505 (1927); Terentieff, *Z. anorg. Chem.*, **156**, 73 (1926); Kierzek, *Bull. soc. chim.*, **41**, 1299 (1927); Schlenk and Schlenk, *Ber.*, **62**, 921 (1929). A list of general references may be found in Footnote 3 on p. 748 of an article by Gilman, Fothergill and Parker, *Rec. trav. chim.*, **48**, 748 (1929).

⁴ Gomberg and Bachmann, *THIS JOURNAL*, **49**, 236, 2584 (1927).



If the Grignard reagent has Formula B and if, also, the MgX_2 part of the molecule has an attachment to the rest of the molecule of a kind that will permit its reaction with magnesium to give magnesiumous halide (Reaction I), then on the addition to the Grignard reagent of one equivalent of magnesium and two equivalents of benzophenone, benzopinacol should result in equivalent quantities, together with a tertiary alcohol formed as follows



The results reported at this time of several experiments made with typical organomagnesium halides show that the Grignard reagents are better represented by the RMgX formula. We do not mean by this that no benzopinacol was formed. Actually some benzopinacol was obtained in many of the reactions. This, of course, might have been predicted because the reaction between an RX compound and magnesium is not simple⁵ and invariably leads to the formation of small (and in some cases large) quantities of MgX_2 .⁶ Obviously the presence of such MgX_2 compounds, formed incidentally to side reactions, would make it possible for benzopinacol to be formed in accordance with Reactions I and II. The quantity of benzopinacol formed in this way is apparently proportional to the quantity of MgX_2 formed. This was strikingly illustrated in two experiments carried out with *n*-butylmagnesium iodide. In one case the butyl iodide was added rapidly to the magnesium in ether, and in the other experiment it was added slowly. In the former case the yield of Grignard reagent is lower⁶ because of the larger formation of magnesium iodide, and in agreement with this a greater quantity of benzopinacol was obtained in the experiment carried out with a more rapid addition of the butyl iodide.

Furthermore, no benzopinacol was obtained in the reactions involving organomagnesium chlorides.⁷ This is in strict agreement with the experiments of Gomberg and Bachmann,⁴ in which it was shown that magnesium chloride, very probably because of its sparing solubility, does not react with magnesium after Reaction I to give magnesiumous chloride ($-\text{MgCl}$).

⁵ Gilman and Fothergill, *THIS JOURNAL*, **50**, 3334 (1928). This paper discusses some side reactions in the preparation of alkylmagnesium halides. Related work is by Gilman and Kirby, *ibid.*, **51**, 1571 (1929).

⁶ Very recent work on the yields of some Grignard reagents, with leading references to earlier work, is to be found in papers by Gilman, Zoellner and Dickey, *ibid.*, **51**, 1576, 1583 (1929).

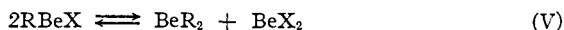
⁷ With the exception of the special cases of *tert*-butylmagnesium and triphenylmethylmagnesium chlorides; see the latter part of the Introduction and also the Experimental Part.

From such evidence it appears that there is little or no $R_2Mg \cdot MgX_2$ in the Grignard reagent. This found some support in a reaction carried out between magnesium diethyl, magnesium iodide, magnesium and benzophenone in which no benzopinacol was obtained. One interpretation of this reaction is that the magnesium diethyl and magnesium iodide reacted as follows

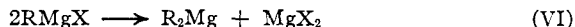


In other words, an R_2Mg compound cannot exist apparently to any appreciable extent in the presence of an MgX_2 compound, and it must have such an existence if Formula B ($R_2Mg \cdot MgX_2$) is correct.

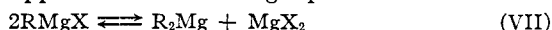
However, all of the preceding discussion gives but a partial picture of things. In the first place, Gilman and Schulze⁸ have presented convincing evidence for the following equilibrium with the related organoberyllium compounds



Also, they called attention at that time to the probability of the same equilibrium with Grignard reagents, basing such a conclusion on the effect of heat on some Grignard reagents incidental to the preparation of ether-free crystalline organomagnesium halides.⁹ Those experiments showed that Grignard reagents were converted to R_2Mg compounds on the application of heat.



The experiment with magnesium diethyl (previously referred to) shows that Reaction VI can also go from right to left. Since then we¹⁰ have actually succeeded in distilling from the Grignard reagent (by a modification of the technique used by Gilman and Schulze⁸ in the organoberyllium studies) the R_2Mg compound. In addition, the Experimental Part of this report contains an account of a second experiment with magnesium diethyl which may lend support to the following equilibrium



All available evidence certainly confirms an equilibrium of this type with the $RMgX$ form as the *chief* component of most Grignard reagents.

But this is not all. Some Grignard reagents undergo dissociation in the following manner



This is strikingly illustrated in the reaction between triphenylmethylmagnesium chloride, $(C_6H_5)_3CMgCl$, *free of metallic magnesium*, and benzophenone. In strict accordance with Reaction VIII the magnesiumous

⁸ Gilman and Schulze, *THIS JOURNAL*, **49**, 2904 (1927); *J. Chem. Soc.*, 2663 (1927).

⁹ Doctoral thesis of L. C. Heckert, Iowa State College, 1927.

¹⁰ Gilman and Brown, *Rec. trav. chim.*, **48**, (1929). In confirmation of the reaction between magnesium diethyl and magnesium iodide to give ethylmagnesium iodide, Mr. Brown has shown that magnesium diphenyl with magnesium iodide gives phenylmagnesium iodide.

chloride¹¹ reduces benzophenone to benzopinacol, and the free radical or its equivalent (the peroxide) is formed. The dissociation postulated in Reaction VIII finds support in related unpublished studies. First, it is possible to prepare triphenylmethylmagnesium iodide from triphenylmethyl and magnesium iodide ($-\text{MgI}$).¹² This is, incidentally, a new method of theoretical interest for the preparation of Grignard reagents and lends support to earlier¹³ experimental studies on the intermediate formation of free radicals in the preparation of Grignard reagents. Second, the molecular weight determinations of triphenylmethylmagnesium chloride and its reactions with hydrogen, oxygen and nitrous oxide lend further support to Reaction VIII.¹⁴

There is then a large amount of convincing evidence for both the equilibrium¹⁵ represented by Reaction VII and the dissociation pictured by Reaction VIII. It remains to be determined to what extent the equilibrium and to what degree the dissociation takes place with a variety of Grignard reagents. From a purely theoretical basis it would be a relatively easy matter to assume that the equilibrium and the dissociation are properties of *all* Grignard reagents to *some* extent. Whatever results may come from future experiments, it is possible from the results of the present studies to have, as a working basis in the interpretation of some Grignard reactions, the postulate that Grignard reagents in solution may be a mixture of RMgX , R_2Mg , MgX_2 , $\text{R}-$ and $-\text{MgX}$ in a series of equilibria.

¹¹ This does not appear to be in harmony with the statement that magnesium chloride does not react with magnesium to give magnesium chloride, an experiment verified by us. It may be argued that if Reaction VIII is correct, then a Grignard reagent like triphenylmethylmagnesium chloride should go irreversibly to form triphenylmethyl, magnesium and magnesium chloride, inasmuch as the magnesium chloride should (in accordance with Reaction I) proceed irreversibly to give the sparingly soluble magnesium chloride. But because such a reaction (leading to the formation of triphenylmethyl, magnesium chloride and magnesium) appears not to take place, one may conclude that the respective equilibria and rates of reaction are such as to make Reaction VIII a correct expression of the state of things under our experimental conditions. In this connection attention should also be directed to Menshutkin's studies [*Z. anorg. Chem.*, **49**, 34, 207 (1906)] on the tendency of magnesium halide etherates to form metastable supersaturated solutions.

¹² Studies by J. H. McGlumphy.

¹³ Gilman and Fothergill, *THIS JOURNAL*, **50**, 3334 (1928); Gilman and Kirby, *ibid.*, **51**, 1571 (1929). See, also, an earlier theoretical consideration by Gomberg and Bachmann, *ibid.*, **49**, 236 (1927), and Pickens, *Science*, **62**, 226 (1925).

¹⁴ Studies by J. A. Leermakers, a preliminary account of which was presented at the Iowa Academy of Science Meeting held at Fairfield, Iowa, in April 1929. See, also, Gilman and Pickens, *Science*, **62**, 226 (1925), and Gilman and Heck, *Ber.*, **62**, 1379 (1929).

¹⁵ See, also, Grignard, *Compt. rend.*, **185**, 507 (1927); *Bull. soc. chim.*, **41**, 759 (1927), and the elegant studies that have just been published by Schlenk and Schlenk, *Ber.*, **62**, 920 (1929).

Experimental Part

The primary objective of the several experiments was to isolate the benzopinacol¹⁶ from other reaction products. After preparing the Grignard reagent in the customary manner, another equivalent of magnesium turnings and 50 to 100 cc. of dry benzene were added. We used magnesium turnings because preliminary experiments showed that the yield of benzopinacol prepared from such turnings and iodine and benzophenone was equal to the yield of benzopinacol obtained when magnesium powder was used. Gomberg and Bachmann⁴ have shown that the rate of reaction is more rapid with magnesium powder.

The calculated quantity of a benzene solution of benzophenone was added with stirring to the cooled solution of Grignard reagent and the heat of reaction was generally great enough to cause the ether-benzene solution to reflux. External heat was not applied in any of the experiments. After adding the benzophenone, the reaction mixtures were stirred or shaken vigorously for varying lengths of time. In long runs when the flask was not tightly stoppered an inert atmosphere was used.

At the conclusion of an experiment, any precipitate that formed was allowed to settle, the clear supernatant solution was decanted and to this solution was added an ether-benzene washing of the precipitate. The solution and the precipitate were hydrolyzed separately, first with water and then with dilute hydrochloric acid.¹⁷

The acid layers were extracted once or twice with an ether-benzene mixture, and the combined extract and ether-benzene layers were dried with anhydrous sodium sulfate, after which the solvents were removed by distillation from a water-bath followed by a current of dry air. The residues from the solution and from the precipitate were then extracted with 100 to 200 cc. of petroleum ether (40-60°), and after this treatment benzopinacol remained.¹⁸ If the precipitate of the reaction mixture were

¹⁶ Others have obtained benzopinacol from the reaction between benzophenone and the Grignard reagent. Actually it was the formation of benzopinacol from a reaction between benzophenone, magnesium and an aryl halide that led Gomberg and Bachmann⁴ to a study of magnesium halides. Prior to that time, Schmidlin, *Ber.*, 39, 4198 (1906), obtained benzopinacol from benzophenone, triphenylmethylmagnesium chloride and an excess of magnesium. Subsequently Lagrave, *Ann. chim.*, [10] 8, 363 (1927), isolated small quantities of benzopinacol from benzophenone and various Grignard reagents. He very correctly attributed the formation of the small quantities of benzopinacol to a secondary reaction between some magnesium iodide and a slight excess of magnesium.

¹⁷ Any unused magnesium in the precipitate was removed prior to the acid hydrolysis.

¹⁸ Benzopinacol is partly soluble in petroleum ether. This was shown in a thirteen-hour extraction of 10 g. of benzopinacol in a Soxhlet extractor by 150 cc. of petroleum ether. Two and four-tenths grams of benzopinacol was dissolved in this way. Accordingly, our yields of benzopinacol are, in some cases, slightly less than those actually

not washed well with the ether-benzene mixture, some of the halogen-magnesium pinacolate (dissolved in the ether-benzene mixture) would remain with the precipitate (the halogen-magnesium tertiary alcoholate) and a mixture of pinacol and tertiary alcohol, $R(C_6H_5)_2COH$, would result on hydrolysis. This small quantity of pinacol can be separated largely from the tertiary alcohol by dissolving the mixture in hot glacial acetic acid; then, on cooling, the pinacol crystallizes first.

In those experiments concerned with the dissociation of the Grignard reagent, the reagent was prepared in the usual manner and then filtered through cotton or glass wool packed in a tube.¹⁹ The benzophenone was then added to the filtered solution of the Grignard reagent and the reaction carried out and worked up as previously described.

A general account of the results of the several experiments is given in Table I and particular details and comments are included in the footnotes accompanying it.

Magnesium Diethyl, Magnesium Iodide and Magnesium.—The magnesium diethyl was prepared by heating 38.9 g. (0.15 mole) of mercury diethyl with 7.3 g. (0.3 atom) of magnesium turnings in a sealed tube at 100–120° for thirty-six hours. The magnesium iodide solution was prepared⁴ from 14.6 g. of magnesium and 38.1 g. of iodine. All transfers and operations were carried out in a special apparatus and in a stream of dry and pure hydrogen. There was little evidence of reaction when the ether solution of magnesium diethyl was added to the magnesium iodide and magnesium. After adding 109.2 g. (0.6 mole) of benzophenone in 100 cc. of benzene, stirring was continued for five hours and then the mixture was allowed to settle overnight. The pink supernatant solution yielded 1.3 g. or 1.18% of benzopinacol.

Inasmuch as a deep pink color formed near the particles of magnesium, more solvent was then added and the precipitate was stirred intermittently, for an additional twenty-five hours, during a total time of one hundred hours. The red solution was then decanted and worked up separately from the precipitate. This solution yielded 7.8 g. or 7.1% of benzopinacol. Crystallization of the products obtained from the precipitate gave 5.0 g. of benzopinacol and 20.1 g. of ethyldiphenylcarbinol. The total yield of benzopinacol, based on benzophenone, was 14.1 g. or 12.83%.²⁰

In a second experiment an atmosphere of nitrogen was used and the reaction mixture was stirred for only one-half hour subsequent to addition of benzophenone, and then hydrolyzed. No benzopinacol was obtained from the yellow solution of the reaction mixture and the yield of ethyldiphenylcarbinol was 22.9 g. or 18.0%.

present. Also, it must be remembered that we are dealing here with mixed solvents, because the benzopinacol is being extracted not only by petroleum ether but also by any benzophenone and tertiary alcohol dissolved by the petroleum ether. The Soxhlet extractor was used only in the benzylmagnesium chloride experiment.

¹⁹ Another way of filtering solutions from magnesium is to use a mat of sintered glass fused into a glass tube. Such a filter has been used by Gilman and Brown in their studies on magnesium dialkyls and diaryls (see ref. 10 of this paper).

²⁰ There are several possible explanations for the formation of benzopinacol in this long-time run. One of them involves the following reaction: $2(C_6H_5)_2(C_2H_5)COMgI \longrightarrow ((C_6H_5)_2(C_2H_5)C-O)_2Mg + MgI_2$. The magnesium iodide thus formed would react with the magnesium present to give magnesiumous iodide, which in turn would reduce the benzophenone to benzopinacol.

TABLE I
 REACTANTS AND PRODUCTS

Expt.	Reactants				Products				
	RMgX	Mole	Mg, g. atom	Benzophenone, mole	Benzopinacol G.	%	Tertiary alcohol G.	%	
1	CH ₃ MgI ^a	0.2	0.2	0.4	0.04	0.057	(C ₆ H ₅) ₂ (CH ₃)COH	22.1	27.9
2	CH ₃ MgI ^b	.3	.3	.3	2.0	3.6	(C ₆ H ₅) ₂ (CH ₃)COH	48.3	81.3
3	C ₂ H ₅ MgCl ^c	.3	.3	.3	0.0	0.0	(C ₆ H ₅) ₂ (C ₂ H ₅)COH	2.85	4.5
4	<i>n</i> -C ₄ H ₉ MgI ^d	.3	.3	.3	5.5	10.0	(C ₆ H ₅) ₂ (C ₄ H ₉)COH	21.0	36.3
5	<i>n</i> -C ₄ H ₉ MgI ^e	.3	.3	.3	9.5	17.3	(C ₆ H ₅) ₂ (C ₄ H ₉)COH	15.1	26.1
6	<i>n</i> -C ₄ H ₉ MgI ^f	.2	.0	.2	0.0	0.0
7	<i>tert.</i> -C ₄ H ₉ MgCl ^g	.3	.0	.3	0.0	0.0
8	C ₆ H ₅ MgBr ^h	.2	.2	.4	0.0	0.0	(C ₆ H ₅) ₃ COH	38.5	36.9
9	C ₆ H ₅ MgBr ⁱ	.3	.3	.3	Trace	Trace	(C ₆ H ₅) ₃ COH	61.9	79.3
10	C ₆ H ₅ CH ₂ MgCl ^j	.3	.3	.3	0.0	0.0	(C ₆ H ₅) ₂ (C ₆ H ₅ CH ₂)COH	70.0	85.2
11	C ₆ H ₅ CH ₂ MgBr ^k	.2	.2	.4	0.55	0.75	(C ₆ H ₅) ₂ (C ₆ H ₅ CH ₂)COH	10.4	9.5
12	C ₆ H ₅ CH ₂ MgBr ^l	.25	.0	.25	0.0	0.0	(C ₆ H ₅) ₂ (C ₆ H ₅ CH ₂)COH	35.0	51.0
13	(C ₆ H ₅) ₃ CMgCl ^m	.03	.0	.043	1.73	22.0	(C ₆ H ₅) ₂ ((C ₆ H ₅) ₃ C)COH	1.0	7.8
14	(C ₆ H ₅) ₃ CMgBr ⁿ	.03	.0	.043	2.49	31.6	(C ₆ H ₅) ₂ ((C ₆ H ₅) ₃ C)COH	0.55	4.3

^a All of the yields given in Table I are based on the quantity of benzophenone taken for each experiment. Unless otherwise stated iodine was not used as a catalyst in the preparation of the several Grignard reagents. The diphenylmethylcarbinol, (C₆H₅)₂(CH₃)COH, and unused benzophenone formed an oil that did not separate well by fractional crystallization from petroleum ether. It was partly for this reason that the excess of benzophenone was not used in many of the other experiments. Where such an excess was not used, the results, of course, are not of the same accuracy as in the other experiments where an excess was used. However, the differences at best are very slight in those experiments carried out with a selected Grignard reagent and with and without an excess of benzophenone (*cf.* Expts. 1 and 2, 8 and 9). Actually, from these comparative experiments (1 and 2, 8 and 9) more benzopinacol was isolated when the excess of benzophenone was not used. In this experiment the mixture was stirred for one hour prior to hydrolysis. There was no red color in the solution at the end of addition of ketone and the whitish precipitate was tinged slightly with a greenish yellow color. When about one-half of the ketone had been added there was a faint red color.

^b In this run with methylmagnesium iodide, the solution took on a reddish color and the red precipitate which formed did not diminish appreciably after shaking for twenty minutes. As with all other solid products isolated in this study, the identity of the benzopinacol was confirmed by a mixed melting-point determination with an authentic specimen.

^c The addition of benzophenone in 50 cc. of benzene to the ethylmagnesium chloride and magnesium caused the formation of a white precipitate. An orange color formed momentarily at the spot of addition of benzophenone but when all of the ketone had been added no color was left in the solution. The mixture was stirred for one hour prior to hydrolysis.

^d A white precipitate formed and the solution was of a purple color. Stirring was continued for three hours after the addition of ketone and at the end of the three-hour period the solution had become a pink color. From the precipitate of the reaction mixture there were obtained 15.1 g. or 27.4% of crude benzohydrol, $(C_6H_5)_2CHOH$, melting at 64–65°, and 9.3 g. or 17.8% of dibenzohydril ether, $((C_6H_5)_2CH)_2O$. In all of the experiments with *n*-butylmagnesium iodide, a vacuum distillation was carried out with the oil that did not crystallize from petroleum ether. The dibenzohydril ether may owe its formation to the effect of heat on benzohydrol and benzopinacol.

^e This experiment was like Expt. No. 4, excepting that *n*-butylmagnesium iodide was prepared by the *rapid* addition of butyl iodide to magnesium in ether, thus favoring the greater formation of magnesium iodide as a side-product.

Part of the benzopinacol (5.0 g. or 9.1%) came from the solution, and the remainder was obtained from the precipitate as 19.9 g. of a solid which melted between 66 and 160° and which proved to be a mixture of benzopinacol and benzohydrol. An attempt was made to separate this mixture by converting the benzopinacol in it to benzopinacolone by the method of Gomberg and Bachmann,⁴ which involves boiling the pinacol in glacial acetic acid for a few minutes with a trace of iodine. On cooling the acetic acid solution, there separated pure benzopinacol instead of the expected benzopinacolone. In this manner the mixture gave 4.5 g. of benzopinacol and 15.4 g. of benzohydrol.

^f In this third run with *n*-butylmagnesium iodide the object was to determine whether there was any dissociation of the Grignard reagent. Accordingly, the ketone was added to a filtered solution of *n*-butylmagnesium iodide free of magnesium. A white precipitate formed and the solution turned brown with a trace of pink, which may have been indicative of some reduction of the benzophenone. The mixture was stirred for three hours and among the reaction products was 9.9 g. or 26.9% of benzohydrol which melted at 67–68° and which was obtained from the precipitate portion of the reaction mixture. The tertiary alcohol from this experiment was not worked up.

^g In a first experiment with *tert*-butylmagnesium chloride, the Grignard reagent was prepared by the use of a bare trace of iodine as a catalyst. Because this experiment was carried out to determine whether any dissociation occurred, the Grignard solution was filtered through a funnel packed with glass wool. The solution took on a red color and the precipitate which formed did not dissolve after shaking for a few minutes. The quantity of benzopinacol formed was 0.45 g. or 0.98%. By a vacuum distillation of the residues left after evaporation of the petroleum ether solutions of both parts of the reaction mixture, there was obtained 30.6 g. or 63.7% of an oil distilling at 147–165° (4 mm.). This was probably *tert*-butyldiphenylcarbinol or dehydration products. In the experiment listed as No. 7 in Table I, no iodine was used as a catalyst and the Grignard solution was filtered through a plug of cotton instead of glass wool. A white precipitate formed and with it a reddish colored solution which gradually changed to greenish yellow. No benzopinacol was isolated. Some benzophenone (2.4 g.) was recovered. Nothing was done with the tertiary alcohol fraction in this experiment.

^h In this experiment with phenylmagnesium bromide, stirring was continued for two hours after addition of the ketone. The solution containing a white precipitate was of a yellow color prior to hydrolysis. In this experiment, as in the others in which an excess of benzophenone was used, there was a residue composed of a mixture of tertiary alcohol and benzophenone which did not lend itself to ready separation by means of

fractional crystallization from petroleum ether: The quantity of benzophenone recovered was 25.4 g. or 34.8%.

[†] Stirring was continued for three hours in this run and the trace of benzopinacol isolated is very probably due to the trace of iodine used in the preparation of the phenylmagnesium bromide. The trace of benzopinacol was obtained from 1.7 g. of a solid (melting at 145–150°) which was separated from the solution part of the reaction mixture. It was obtained in a pure condition by recrystallization from a mixture of alcohol and chloroform, followed by two crystallizations from glacial acetic acid.

[‡] On the first addition of benzophenone to the benzylmagnesium chloride prepared with a trace of iodine, a small quantity of white precipitate formed; this dissolved completely by the time all of the ketone had been added. The faint lavender colored solution was stirred for one hour and then worked up in the usual manner. The benzyldiphenylcarbinol was not very soluble in petroleum ether, so that any small quantity of benzopinacol could not be isolated by extraction with 300 cc. of petroleum ether. A 3.5-hour extraction with 250 cc. of petroleum ether in a Soxhlet extractor failed to separate any benzopinacol (see ref. 18). A recrystallization of a portion of the tertiary alcohol from glacial acetic acid gave no trace of benzopinacol.

^{*} The mixture was stirred for four hours and the yellowish solution present prior to hydrolysis contained a white precipitate. The quantity of benzophenone recovered was 38.5 g. or 52.9%.

[‡] In this experiment the object was to determine whether benzylmagnesium bromide dissociated. On adding the benzophenone to the filtered Grignard solution, a momentary purple color formed at the spot of addition and when all of the ketone had been added the solution was of a yellow-brown color. No precipitate formed. A recrystallization of a part of the benzyldiphenylcarbinol from glacial acetic acid gave no benzopinacol.

^m The triphenylmethylmagnesium chloride and bromide, respectively, used in Expts. 13 and 14 were prepared in accordance with the directions of Gilman and Zoellner, *THIS JOURNAL*, **51**, Nov. (1929). When benzophenone in benzene was added to the filtered benzene solution of Grignard reagent an intense red color formed. The solution was shaken for a few minutes and then hydrolyzed. In addition to the products listed in Table I, there was obtained 4.3 g. or 55.3% of triphenylmethyl peroxide. There was an excess of benzophenone because a small quantity of it was recovered directly from the petroleum ether extract of the crude pinacol. This experiment was carried out in a nitrogen atmosphere.

ⁿ This experiment was like that with the triphenylmethylmagnesium chloride. The yield of triphenylmethyl peroxide was 4.5 g. or 57.9%. Evidently there was an excess of benzophenone because a portion of the petroleum ether extract of the crude pinacol gave some benzophenone-oxime when treated in the customary manner with hydroxylamine. This experiment was carried out in a nitrogen atmosphere.

Summary

Evidence is presented for the following equilibrium, $2RMgX \rightleftharpoons R_2Mg + MgX_2$, and the following dissociation, $RMgX \longrightarrow R^- + ^-MgX$, of Grignard reagents.

AMES, IOWA