

3. Ether extraction indicated the presence of 55.86% of lipid iodine.
4. No thyroxine could be detected in the extract of shrimp waste when tested by the Kendall method.

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THE REDUCING ACTION AND CONSTITUTION OF THE GRIGNARD REAGENT

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A. Reducing Action

The occurrence in the literature of over fifty references to the reduction of various compounds, chiefly aldehydes, ketones and esters, brought about by Grignard reagents indicates the frequency with which this side reaction is encountered. During the past year alone, from papers and a note have appeared dealing primarily with this subject.¹

An examination of the various experiments leads one to the conclusion that the reduction may be due to a number of causes. It may be brought about by the action of unused magnesium and the magnesium halide which is always present,² by the action of magnesium alcoholate on an excess of the aldehyde or ketone,³ or by the action of the Grignard reagent itself. It would seem that, strictly speaking, only the last type of reduction should be considered as the reducing action of the Grignard reagent, but even in this case reduction may be brought about in at least two ways. Where dissociation of the Grignard reagent into the free hydrocarbon radical and magnesium halide may take place, the latter may cause reduction.⁴

In other cases reduction takes place at the expense of the hydrocarbon radical with the formation of unsaturated hydrocarbon.⁵ It should be

¹ (a) Hatt, *J. Chem. Soc.*, 1623 (1929); (b) Conant and Blatt, *THIS JOURNAL*, 51, 1227 (1929); (c) Blicke and Powers, *ibid.*, 51, 3378 (1929); (d) Grignard and Delarue, *Bull. soc. chim.*, [4] 47, 237 (1930); (e) Davies, Dixon and Jones, *J. Chem. Soc.*, 1916 (1930).

² Boyd and Hatt, *ibid.*, 131, 898 (1927) and Ref. 1a; Lagrave, *Ann. chim.*, [10] 8, 369 (1927). See also Gomberg and Bachmann, *THIS JOURNAL*, 49, 236 (1927).

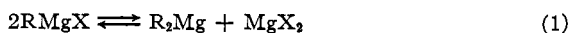
³ Marshall, *J. Chem. Soc.*, 105, 527 (1914); 107, 509 (1915); 127, 2184 (1925); Meisenheimer, *Ann.*, 446, 76 (1926).

⁴ Gilman and Fothergill, *THIS JOURNAL*, 51, 3149 (1929).

⁵ Of the several theories that have been proposed for this last type of reduction, the assumptions (1) that after a primary addition of RMgX to the aldehyde or ketone, unsaturated hydrocarbon is lost and the remaining HMgX adds to the carbonyl group [Hess and Rheinboldt, *Ber.*, 54, 2043 (1921); Hess and Wustrow, *Ann.*, 437, 256 (1924); Rheinboldt and Roleff, *Ber.*, 57, 1921 (1924); Meisenheimer, *Ann.*, 442, 180 (1925); Rheinboldt and Roleff, *J. prakt. Chem.*, 109, 175 (1925)] and (2) that the free radicals $\text{RR}'\text{C}(\text{OMgX})$ — and R'' — are intermediate products in the reaction of a ketone RCOR'

noted that the products of these various types of reduction are not the same. Magnesium halide or magnesium and magnesium halide seem to lead to the formation of pinacols, whereas magnesium alcoholate and undissociated Grignard reagent yield alcohols.^{5,6}

With the appearance of the excellent work of Schlenk and Schlenk⁷ on the composition of the Grignard reagent in which direct evidence was advanced for the equilibrium



it seemed desirable to determine whether solutions of R_2Mg alone would cause reduction. In choosing a reaction for study it was thought advisable to use one that normally caused a very large amount of reduction. The reaction of isobutylmagnesium iodide and benzophenone reported by Blicke^{1c} to give a 74% yield of benzhydrol satisfied this condition, and the ease with which the reduction product was isolated seemed to be an added advantage. Isobutyl bromide was used in place of isobutyl iodide because it is more readily prepared and probably rearranges to the tertiary halide less readily.

Schlenk's method⁷ was used for preparing solutions of di-isobutyl magnesium. It was found that the equilibrium (1) is shifted so far to the right in the Grignard reagent prepared from isobutyl bromide that approximately 75% of the active Grignard reagent is present in the form of di-isobutyl magnesium. Precipitation of the halogen-containing compounds with 1,4-dioxane therefore gave a ready means of obtaining fairly concentrated solutions of di-isobutyl magnesium (0.1–0.14 equivalent or 0.05–0.07 mole per 100 cc. of solution). These solutions could be prepared containing less than 0.1 equivalent per cent. of the active Grignard reagent combined with halogen, as determined by analysis for halogen.⁸ In all of with R^mMgX (Blicke, Ref. 1c) seem to be the most satisfactory. The latter theory, however, leads one to predict the formation of pinacols in the absence of excess of magnesium. Until recently, the only case where this occurred was with triphenylmethylmagnesium chloride.⁴ Recently, Davies, Dixon and Jones¹⁸ report the isolation of benzpinacol from the reaction of amylmagnesium halides with benzophenone. Unfortunately, they siphoned or decanted their solutions from the excess magnesium. That this may not be sufficient is shown by the experiments of Gilman and Fothergill (Ref. 4, note g) with *tert.*-butylmagnesium chloride. Since the appearance of the work of Davies, Dixon and Jones, we have re-examined 60 g. of the combined solid fractions obtained in the reaction of isobutylmagnesium bromide and benzophenone and have been unable to find any indication of the presence of benzpinacol.

⁶ An entirely different type of reduction seems to take place in the action of Grignard reagents on azobenzene [Rheinboldt and Kirbig, *J. prakt. Chem.*, [2] 118, 1 (1928)] and in the reaction of certain bromides with magnesium [Krestinsky, *Ber.*, 55, 2770 (1922)].

⁷ Schlenk and Schlenk, *ibid.*, 62, 920 (1929); see also Gilman and Fothergill, Ref. 4.

⁸ One of the referees has pointed out that a small amount of MgX_2 because of the equilibria involved might suffice to convert a large amount of R_2Mg to $RMgX$. We do

the work reported in this paper, perfectly clear filtered solutions of the Grignard reagent were used and always in 10% excess.

We have found that solutions of di-isobutyl magnesium reduce benzophenone to benzhydrol to the extent of at least 64% of the theoretical amount. The high percentage of di-isobutyl magnesium present in the original Grignard solution (approximately the same as the amount of reduction reported by Blicke) seemed to indicate that it was the sole reducing agent. However, when benzophenone in benzene solution is added to the original Grignard reagent, a copious precipitate is soon formed from which the reduction product is isolated; when added to a solution of di-isobutyl magnesium, no precipitate is formed and the reduction product is obtained on decomposing the solution and crystallizing the benzhydrol from the other reaction products. On comparing the relative amounts of benzhydrol isolated in each case, it would appear that more reduction takes place when the original Grignard reagent is used (83.5%) than when a solution of di-isobutyl magnesium is used (64.2%). Because of the greater difficulty in isolating the benzhydrol in the second case, however, the amount formed is undoubtedly larger than was actually isolated. Whether or not the amount of reduction was identical, it was certainly greater than 64% in both cases.

Blicke assumed the precipitate from which the benzhydrol was isolated in the first case to have the formula $(C_6H_5)_2CHOMgBr$, having shown that a similar precipitate is formed on adding a solution of benzhydrol to the Grignard reagent prepared from ethyl bromide. No analyses were given. We have determined the ratio of the benzhydrol to the basic hydroxyl groups and to the halogen after the precipitate is decomposed with water, and find that it agrees with this formula. It would appear therefore that solutions containing only di-isobutyl magnesium can cause reduction of benzophenone to the extent of at least 64%, the reduction product probably existing in the form $(C_6H_5)_2CHOMgOCH(C_6H_5)_2$, which is soluble in ether. When, on the other hand, the original Grignard reagent is used, only isobutylmagnesium bromide causes reduction, the reduction product precipitating entirely in the form $(C_6H_5)_2CHOMgBr$, and this in spite of the fact that 75% of the active Grignard reagent is in the form of di-isobutyl magnesium.

B. Constitution of the Grignard Reagent

In order that reduction may be brought about entirely by means of isobutylmagnesium bromide, the equilibrium (1) must shift very rapidly, not feel that this is likely, however, because Gomberg and Bachmann (Ref. 2) and more recently Bachmann [THIS JOURNAL, 52, 4412 (1930)] find that in reactions depending on similar equilibria the rate is slower when only a small amount of MgX_2 is present than when an equivalent quantity of MgX_2 is present, whereas in our experiments reaction always takes place very rapidly. The suggestion is, nevertheless, one to be kept in mind since the rates of attaining equilibrium may be vastly different in different reactions.

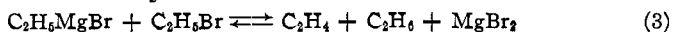
because so far as one can tell by the evolution of heat and immediate precipitation of the reduction product (after precipitation once starts), the reduction is practically instantaneous. This would not be a serious drawback, however, because Schlenk⁷ has shown that although the equilibrium in the case of ethylmagnesium iodide is only slowly attained, the equilibrium in the case of phenylmagnesium bromide must be reached quite rapidly. The reduction of benzophenone by di-isobutyl magnesium, however, must also, as evidenced by the evolution of heat, be practically instantaneous. It is difficult to see, therefore, why the original Grignard reagent which is in the form of di-isobutyl magnesium to the extent of 75% should shift entirely to the form isobutylmagnesium bromide during the reduction when either compound may cause reduction.

At this point it occurred to us to determine what would happen if a solution of anhydrous magnesium bromide in absolute ether were added to the solution containing the reduction product formed by the action of di-isobutyl magnesium. It was found that a compound is rapidly precipitated (again after precipitation once starts) which so far as can be determined from analysis, appearance and behavior is identical with that formed when benzophenone is added to the original Grignard reagent. This would mean, assuming Blicke's formula to be correct, that the reaction

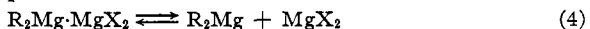


is likewise a very rapid one.

Considerable work has been done in attempts to decide between the formulas RMgX and $\text{R}_2\text{Mg}\cdot\text{MgX}_2$ for the Grignard reagent.⁹ The majority of this work seems to favor the RMgX formula, but with the possible exception of the results of Job and Dubien¹⁰ on the order of the reaction



of which no experimental details are given, the writer does not believe that any of the work gives conclusive evidence for either formula. Until such evidence is presented, it would appear that the reactions discussed in this paper are best explained by assuming that no isobutylmagnesium bromide exists in the original Grignard solution, that the equilibrium existing in this solution is best represented as



and that the insoluble compound has the composition $[(\text{C}_6\text{H}_5)_2\text{CH—O}]_2\cdot\text{Mg}\cdot\text{MgBr}_2$, where the dots simply represent some form of molecular complex. Such reactions involving the formation of simple addition products would be expected to take place more rapidly than metathetical

⁹ For references to this work see Note 3 in the paper by Gilman and Fothergill (Ref. 4).

¹⁰ Job and Dubien. *Bull. soc. chim.*, [4] 39, 583 (1926); *Compt. rend.*, 184, 155 (1927).

reactions in a slightly ionizing solvent such as anhydrous ether, and a single compound, the dialkyl magnesium, would be responsible for reduction.

Experimental

Isobutyl Bromide.—Isobutyl alcohol, b. p. 106–107.5°, was mixed with a 50% excess of constant-boiling hydrobromic acid and the mixture slowly distilled through a 1-m. column until the temperature reached 120°. The distillate was saturated with salt, the bromide layer separated, returned to the flask containing the residue of hydrobromic acid and distilled again. This operation was repeated until the bromide layer had a specific gravity of approximately 1.2. It was then washed twice with concd. sulfuric acid, once with 5% sodium carbonate solution, then with water and dried over calcium chloride. This product was carefully fractionated three times through a 1-m. column, the main portion boiling at 91–93°. Analysis according to the method of Michael¹¹ showed 5.1% of tertiary butyl bromide. After vigorously stirring this product for thirty minutes at 25° with fifty times its weight of water, drying over anhydrous potassium carbonate, and distilling, analysis showed 0.96% tertiary butyl bromide.

Grignard Reagent.—The entire preparation and filtering operations were carried out in an atmosphere of hydrogen. About 10 cc. of a mixture of 137 g. (1 mole) of isobutyl bromide and 150 cc. of absolute ether was added to 24.5 g. of fine, bright magnesium turnings in a one-liter three-necked flask fitted with condenser, stirrer and dropping funnel. The reaction started almost immediately without the addition of iodine and 100 cc. of absolute ether was rapidly added. The balance of the bromide-ether mixture was then added slowly from the separatory funnel with stirring over a period of three hours. During this time the solution was under hydrogen at a pressure only slightly greater than atmospheric. Another 100 cc. of ether was added and the solution filtered under hydrogen pressure into a graduated cylinder and diluted to a total volume of 590 cc. The apparatus was so arranged that the solution could be transferred from the three-necked flask to a Büchner funnel with slight hydrogen pressure, filtered under a pressure of 10 pounds into the graduated cylinder, diluted to the desired volume and transferred from the graduated cylinder to a measuring buret entirely in the absence of air. The Büchner funnel had a Jena glass filter disk of porosity 3 and a 3-mm. layer of tightly packed ignited kieselguhr was used as a filtering medium.

The filtered solution was perfectly clear but still had the pale brownish-gray color characteristic of Grignard reagents. Analysis of 5-cc. portions by titration¹² with standard 0.2 *N* acid showed 0.001325 mole per cubic centimeter of solution. This corresponds to a total yield of Grignard reagent of 78.2%. (The actual yield of Grignard reagent, as determined in other runs in which the filtration was omitted and hence losses avoided, was approximately 86%.)

Analysis of the Grignard Solution for Di-isobutyl Magnesium.—A 3G3 Jena-Büchner funnel with sintered glass filter disk was fitted through a cork with a 50-cc. glass-stoppered separatory funnel and a stopcock for applying hydrogen pressure. The apparatus was swept out with hydrogen, 5 cc. of absolute ether run into the funnel to moisten the glass filtering disk (no other filtering medium was used) and 5 cc. of the Grignard reagent run into the separatory funnel from a buret. To this was quickly added 1.5 cc. of a solution of pure 1,4-dioxane in absolute ether (1 g. per 2 cc. of solution). The separatory funnel was closed with a well-greased stopper and shaken. The mixture was then run into the Büchner funnel and filtered with hydrogen pressure. The sepa-

¹¹ Michael, *Ann.*, 379, 287 (1911).

¹² Gilman and co-workers, *THIS JOURNAL*, 45, 150 (1923); 51, 1576 (1929).

ratory funnel and precipitate were washed three times with 5-cc. portions of ether, filtering each time with pressure. The filtrate was decomposed with 50 cc. of water, the ether removed by heating on a hot-plate, and the magnesium hydroxide titrated with standard acid.¹³ The average amount of acid, calculated as 1 *N*, was 4.967 cc., indicating that approximately 75% of the active Grignard solution was in the form of di-isobutyl magnesium.

Preparation of Di-isobutyl Magnesium Solution.—Three hundred cubic centimeters of the Grignard reagent from isobutyl bromide was placed in a 500-cc. glass-stoppered flask previously swept out with hydrogen, and cooled in an ice-salt bath to 0°. To this was added with shaking 66 cc. of a solution of dioxane in ether (50 g. per 100 cc.). The temperature did not rise above 20°. After thorough shaking the mixture was poured into four 100-cc. centrifuge tubes and tightly stoppered. After centrifuging for fifteen minutes at about 2000 r. p. m., a clear upper layer had formed. This still gave a slight precipitate with dioxane solution and a total of 7 cc. more was added to each tube, when practically no more precipitate formed. The tubes were again centrifuged and then decanted into a hydrogen filled bottle. This solution is perfectly clear and water white, being entirely free from the grayish color of the original Grignard solution. The concentration of active Grignard reagent as determined by titration with standard acid was 0.00101 equivalent per cubic centimeter. The solution gave a weak test for halogen. To 10 cc. of the solution was added 100 cc. of water and then 10 cc. of 6 *N* nitric acid. This solution was titrated with an approximately 0.1 *N* standard silver nitrate solution. An amount equivalent to 0.0079 cc. of *N* silver nitrate was required, indicating 0.078% of the Grignard reagent combined with halogen.

Reducing Action of the Original Grignard Solution.—In an Erlenmeyer flask fitted with a thermometer and a 50-cc. dropping funnel was placed 41.5 cc. (0.055 equiv.) of the Grignard solution and this diluted with 13.5 cc. of absolute ether to make the equivalent concentration of active Grignard reagent the same as that of the di-isobutyl magnesium solution prepared above. The flask was placed in an ice-salt mixture and when the temperature had dropped to 0°, a solution of 9.1 g. (0.05 mole) of benzophenone dissolved in 10 cc. of dry benzene was slowly added, shaking after each addition. The rate of addition was such that the temperature was kept between 0 and 5°. With the addition of each drop of benzophenone solution, a deep wine red color was imparted to the solution, which soon disappeared. After a short time a white precipitate began to form which settled out very readily. The formation of a red color each time the solution of benzophenone was added took place at the end of the reaction just as at the beginning. The mixture was allowed to warm up to room temperature and then filtered on a Büchner funnel with suction, washing the precipitate three times with 10-cc. portions of dry benzene. The filtrate and precipitate were decomposed separately with a saturated solution of ammonium chloride and extracted three times with 50-cc. portions of ether. The ether solutions were evaporated in a tared beaker placed on a watch glass, at first over a warm hot-plate and finally in a vacuum desiccator over phosphorus pentoxide.¹⁴ There was obtained from the precipitate 7.7 g. of benzhydryl melting at 65–67° or 83.5% of the calculated amount. The filtrate yielded 1.3 g. of an oil from which nothing could be crystallized. Assuming this to be diphenyl isobutyl carbinol, it would correspond to 10.8%, making the total recovery 94.3%.

Reducing Action of Di-isobutyl Magnesium Solutions.—The procedure followed

¹³ Whenever an appreciable amount of ether is present it is necessary to remove it in order to get a satisfactory end-point with phenolphthalein. This is in agreement with the work of Hall [*Ind. Eng. Chem., Anal. Ed.*, 2, 244 (1930)] on the analysis of ether.

¹⁴ Excessive heating must be avoided to prevent the formation of dibenzhydryl ether which seems to take place at times even at temperatures near 100°.

was the same as in the previous experiment, using 110 cc. (0.11 equiv.) of di-isobutyl magnesium solution and 18.2 g. (0.10 mole) of benzophenone in 20 cc. of dry benzene. As in the preceding experiment, a deep red color developed after each addition of benzophenone, which soon disappeared on shaking. This reaction differed from the preceding one, however, in that no precipitate formed. After all of the benzophenone had been added, the solution was allowed to warm up to room temperature and a clear pale yellow solution resulted. The entire solution was decomposed with a saturated ammonium chloride solution, extracted three times with 50-cc. portions of ether, and the ether and benzene removed as before. There was obtained 18.5 g. of an oil which partially solidified on standing. Filtration was rather difficult so the whole was dissolved in 10 cc. of 95% alcohol, cooled until crystallization was complete, and filtered with suction. The filtrate was cooled again in an ice-salt mixture and filtered. A total of 10.4 g., m. p. 59–64°, was obtained. The combined alcoholic solution, including alcoholic washings of funnel, beakers and filter papers, was evaporated at 25 mm. and finally heated at 100° for ten minutes at this pressure. After standing for several days crystals appeared and on stirring a paste of crystals resulted. On filtering, oily crystals were obtained which weighed 1.4 g. and after clay plating melted at 59–65°, making the total recovery of benzhydrol 11.8 g. or 64.2% of the calculated amount. The total amount of oil remaining was 3.8 g., so that a loss of 2.9 g. occurred. The difference between the original weight and the weight of benzhydrol is 6.7 g. Assuming this to be diphenyl isobutyl carbinol it amounts to 27.9% of the calculated amount, making the total yield of products 92.1%. The actual amount of benzhydrol formed must be considerably greater than was actually isolated.

Analysis of Precipitate Formed on Adding Benzophenone to the Original Grignard Reagent.—A Grignard solution was prepared as previously described except that one-third quantities were used and the final solution was less dilute. Analysis by titration with standard acid showed it to contain 0.001927 equivalent of active Grignard reagent per cubic centimeter. Two 20-cc. (0.0385 equiv.) portions of this solution were treated with solutions of 6.3 g. (0.0347 mole) of benzophenone in 10 cc. of dry benzene. The precipitates were centrifuged, the clear liquid decanted and the precipitate washed four times with 30-cc. portions of dry benzene, stirring the precipitate and centrifuging each time. After the last centrifuging the tube was swirled so as to remove an upper gelatinous layer with the benzene when the latter was decanted. No attempt was made to obtain all of the precipitate, the sole object being to get a pure product. Ether was added to the precipitate to facilitate removal and the whole transferred to an Erlenmeyer flask, where it was decomposed with 100 cc. of distilled water. The solutions were extracted four times with 50-cc. portions of alcohol-free ether and the ether evaporated from the solution in a tared beaker, at first over a warm hot-plate and finally in a vacuum desiccator over phosphorus pentoxide.

The aqueous layers were boiled to remove ether and after cooling titrated with approximately 0.5 *N* standard nitric acid. These same solutions were then diluted to 500-cc. and 50-cc. portions acidified with nitric acid and titrated with approximately 0.1 *N* standard silver nitrate solution. The results are given in Table I.

TABLE I

ANALYSIS OF PRECIPITATE FROM ORIGINAL GRIGNARD REAGENT AND BENZOPHENONE

| Sample | G. | Benzhydrol equiv. | M. p., °C. | <i>N</i> HNO ₃ , cc. | Equiv. of basic OH | <i>N</i> AgNO ₃ , cc. | Equiv. of halogen |
|--------|------|-------------------|------------|---------------------------------|--------------------|----------------------------------|-------------------|
| 1 | 4.28 | 0.0233 | 66–67.5 | 23.02 | 0.0230 | 23.20 | 0.0232 |
| 2 | 4.17 | .0227 | 67.5–68 | 22.80 | .0228 | 22.81 | .0228 |

These results show that on decomposing the precipitate with water

there is obtained one equivalent of benzhydrol for one equivalent each of basic hydroxyl and halogen.

Analysis of the Precipitates Formed on Adding a Solution of Anhydrous Magnesium Bromide to a Solution of the Reaction Product of Benzophenone and Di-isobutyl Magnesium.—Anhydrous magnesium bromide was prepared according to the method of Lerch.¹⁵ On allowing the powdered fused salt to stand for several hours under absolute ether with occasional shaking, a lower yellow layer formed which according to Menschutkin¹⁶ contains around 40% of magnesium bromide at room temperature. By dissolving 35 cc. of this lower layer in a mixture of 45 cc. of dry benzene and 30 cc. of absolute ether, a solution was obtained which could be diluted with a considerable quantity of ether without causing the separation of two layers, and a clear solution resulted when small amounts were mixed with a large volume of ether. Analysis for halogen showed it to contain 0.00089 mole of magnesium bromide per cubic centimeter.

When this solution was added to a solution of the product of the reaction of benzophenone and di-isobutyl magnesium prepared as above, an immediate precipitate was formed. On carrying out a fractional precipitation and analyzing the precipitates, it was found that the first precipitate after decomposition with water gave practically no benzhydrol or basic hydroxyl but a large amount of halogen. The second precipitate gave a considerable quantity of benzhydrol (0.0082 equiv.) and a practically equal amount of basic hydroxyl (0.0098 equiv.) but a somewhat higher amount of halogen (0.0147 equiv.). This indicated that an excess of dioxane had been present in the di-isobutyl magnesium solution.

A solution of di-isobutyl magnesium was then prepared using a smaller excess of dioxane. To 100 cc. of the Grignard solution containing 0.001927 equivalent of active Grignard reagent per cubic centimeter was added 20 g. of dioxane dissolved in 20 cc. of ether. After centrifuging, the clear solution still gave a slight precipitate when more dioxane was added. Analysis for active Grignard reagent showed 0.00141 equivalent per cubic centimeter and for halogen 0.0000198 equivalent per cubic centimeter or 1.4 equivalent per cent.

To 65 cc. (0.092 equiv.) of this solution was added 15 g. (0.082 mole) of benzophenone dissolved in 25 cc. of dry benzene under the conditions previously given. A clear pale yellow solution resulted. This solution should require 51.5 cc. of the solution of anhydrous magnesium bromide prepared above to give an amount equivalent to the active Grignard reagent present in the di-isobutyl magnesium solution. On adding a small amount of the magnesium bromide solution, no precipitate formed, indicating that no excess dioxane was present. On adding 30 cc. of the anhydrous magnesium bromide solution, a heavy precipitate formed. The total mixture was divided into two parts and centrifuged. The clear liquids were decanted and combined and a second 10 cc. of magnesium bromide solution was added. The precipitate was centrifuged and another 10-cc. portion of magnesium bromide solution added. Only a small precipitate formed

¹⁵ Lerch, *J. prakt. Chem.*, [2] **28**, 338 (1883).

¹⁶ Menschutkin, *Z. anorg. Chem.*, **49**, 207 (1906).

this time and it was entirely different in appearance from the previous precipitates in that it was yellow and gelatinous rather than white and crystalline. A final addition of magnesium bromide solution gave no further precipitate. The various precipitates were each washed four times with 20-cc. portions of a mixture of 150 cc. of dry benzene and 100 cc. of dry ether. All washings were discarded and any gelatinous layer on top of the crystalline precipitates was removed and discarded. The precipitates were then analyzed as before. The results are given in Table II.

TABLE II

ANALYSIS OF PRECIPITATES FROM MAGNESIUM BROMIDE AND THE REACTION PRODUCT OF BENZOPHENONE AND DI-ISOBUTYL MAGNESIUM

| Precipitate | Benzhydrol | | M. p. | N HNO ₃ , cc. | Equiv. of basic OH | N AgNO ₃ , cc. | Equiv. of halogen |
|-------------|------------|--------|---------|-----------------------------|-----------------------|------------------------------|----------------------|
| | G. | equiv. | | | | | |
| 1—Part A | Lost | | | 15.62 | 0.0156 | 15.85 | 0.0158 |
| 1—Part B | 3.47 | 0.0189 | 65–66.5 | 18.56 | .0186 | 18.69 | .0187 |
| 2 | 2.62 | .0142 | 62–66.5 | 14.04 | .0140 | 14.13 | .0141 |
| 3 | 0.01 | .00005 | | 1.469 | .0015 | 3.20 | .0032 |

The main portion of the precipitate, therefore, gives analytical results identical with the precipitate formed from the original Grignard reagent and benzophenone.

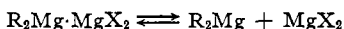
Summary

1. Solutions of di-isobutyl magnesium which are practically halogen free have been shown to reduce benzophenone to benzhydrol, as well as the original Grignard reagent containing halogen.

2. The Grignard reagent prepared from isobutyl bromide at a concentration of about 1.3 molar exists to the extent of 75% in the form of di-isobutyl magnesium.

3. When the original Grignard reagent is used to reduce benzophenone, the reduction product precipitates as a white crystalline compound which yields, on decomposition with water, one mole of benzhydrol, one equivalent of basic hydroxyl, and one equivalent of halogen. When a solution of di-isobutyl magnesium is used, the reduction product remains in solution presumably in the form $[(C_6H_5)_2CHO]_2Mg$, but which can be precipitated by the addition of a solution of anhydrous magnesium bromide to give a compound identical by analysis with that obtained from the original Grignard solution.

4. It is believed that the constitution of the Grignard reagent represented by the equilibrium



best fits these facts and that the ether-insoluble benzhydryl magnesium salt has the composition $[(C_6H_5)_2CHO]_2Mg \cdot MgBr_2$.