3. A tentative molecular structure for the trimeric form has been suggested.
4. Dihydroxy-acetone is oxidized by saturated aqueous solutions of copper sulfate at 80° to hydroxypyruvic acid.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE COUPLING ACTION OF THE GRIGNARD REAGENT. II METHYLMAGNESIUM IODIDE AND THE BENZYL HALIDES

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Introduction

It was pointed out in the first paper of this series[2] that the Grignard reagent reacts with a number of alkyl halides as a coupling agent removing the halogen atoms and uniting the resulting residues. The reaction is analogous to the Wurtz reaction, the Grignard reagent here playing the role of the metal in the Wurtz synthesis. No agreement, however, has been reached as to what becomes of the Grignard reagent itself in the reaction. Various equations have been written for the reaction; one of these (1) supposes the generation of a hydrocarbon by a coupling together of the radicals attached to magnesium, and another (2) assumes the formation of an alkyl halide. Späth[3] has shown that where R′ is an alkyl group other than methyl, the reaction probably takes place according to Equation 3, the two radicals reacting to form equal quantities of a saturated and an ethylenic hydrocarbon.

$$2RX + 2R'MgX = R-R + R'-R' + 2MgX_2 \qquad (1)$$
$$2RX + R'MgX = R-R + R'X + MgX_2 \qquad (2)$$
$$2RX + 2R'MgX = R-R + R'_{-H} + R'_{+H} + 2MgX_2 \qquad (3)$$

Equation 1 was proposed by Schmidlin.[4] By treating triphenylmethyl chloride with phenylmagnesium iodide he obtained a 27% yield of triphenylmethyl along with some tetraphenylmethane and a small amount of diphenyl. He formulated his results by the following equation: $2(C_6H_5)_3CCl + 2C_6H_5MgI = 2(C_6H_5)_3C + C_6H_5—C_6H_5 + 2MgICl$.

By treating iodoform and carbon tetrachloride with phenylmagnesium bromide, Binaghi and Oddo[5] and Binaghi[6] obtained *sym.*-tetraphenylethane and hexaphenylethane, respectively. They assume the intermediate formation of diphenylchloromethane in the one case and of triphenyl-

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[1] National Research Fellow in Chemistry.

[2] Fuson, THIS JOURNAL, **48**, 830 (1926).

[3] Späth, *Monatsh.*, **34**, 1965 (1913).

[4] Schmidlin, *Ber.*, **43**, 1141 (1910).

[5] Binaghi and Oddo, *Gazz. chim. ital.*, [II] **51**, 330 (1921).

[6] Binaghi, *ibid.*, **53**, 879 (1923).

chloromethane in the other. These compounds then undergo coupling with the production of *bromobenzene.* The authors, accordingly, formulate their results according to Equation 2 as follows: $2C_6H_5MgBr + I_2CHI = 2MgBrI + (C_6H_5)_2CHI$; $2(C_6H_5)_2CHI + C_6H_5MgBr = (C_6H_5)_2CHCH(C_6H_5)_2 + C_6H_5Br + MgI_2$; $CCl_4 + 3C_6H_5MgBr = 3MgBrCl + (C_6H_5)_3CCl$; $2(C_6H_5)_3CCl + C_6H_5MgBr = (C_6H_5)_3CC(C_6H_5)_3 + C_6H_5Br + MgCl_2$.

The purpose of the present investigation was to study quantitatively the coupling reaction between alkyl halides and the Grignard reagent to see whether Equation 1 or 2 or some other equation correctly represents the stoichiometric relationships obtaining between the reacting substances and the products of the reaction.

It was desirable that the coupling reaction to be studied be as nearly quantitative as possible. A preliminary study of the coupling tendencies of a variety of alkyl halides showed that the reaction of the benzyl halides with methylmagnesium iodide fulfilled the requirements. The yields of the coupling products are 65 to 80% and the one side reaction, alkylation, does not constitute a serious difficulty.

The reaction was first studied by Houben,[7] who treated benzyl chloride with methylmagnesium iodide, obtaining a 25% yield of *ethylbenzene* and some *dibenzyl,* the latter being attributed to a reaction between benzyl chloride and magnesium. Späth[8] treated benzyl chloride with methylmagnesium iodide, obtaining a 37% yield of ethylbenzene and a large amount of dibenzyl. He reported also the formation of *1,2,3-triphenylpropane.* Studies now in progress, however, seem to indicate that this product may be due to a side reaction. In the present investigation it has been shown that *ethane* also is produced. Under the conditions obtaining in this work, dibenzyl, ethylbenzene and ethane were found to be the sole products.

Method

The dibenzyl and ethylbenzene are easily separated by fractional distillation and by this method the yields of these compounds were determined. Accurate measurement of the evolved gas, however, was found to be very difficult. An attempt was first made to carry out the reaction in *iso*-amyl ether and to use an apparatus similar to that of Zerewitinoff[9] but it was found that in this ether the reaction does not take place. The apparatus described below was, therefore, devised for use with ethyl ether solutions.[10] As will be seen, it gives an accurate measure of the gas.

[7] Houben, *Ber.*, **36**, 3083 (1903).

[8] Ref. 3, p. 1991.

[9] Zerewitinoff, *Ber.*, **40**, 2023 (1907); **41**, 2233 (1908). See also Hibbert and Sudborough, *J. Chem. Soc.*, **85**, 933 (1904).

[10] A method of this type was used by (a) Grignard [*Ann. chim.*, [7] **24**, 433 (1901)], who obtained pure methane and ethane from reactions carried out in ethyl ether. He freed the gases from ether vapor by passing them through concentrated sulfuric acid.

Apparatus.—The apparatus is shown in Fig. 1. The reaction vessel was a three-necked, 100cc. flask A equipped with a dropping funnel, mechanical stirrer (with a mercury seal) and a condensing coil B immersed in an ice-bath. The connections at a, b and c were made with rubber stoppers which were covered with shellac to insure gas-tightness. The apparatus was, moreover, carefully tested for leaks. The reaction vessel was immersed in a bath C when it was desired to regulate the temperature.

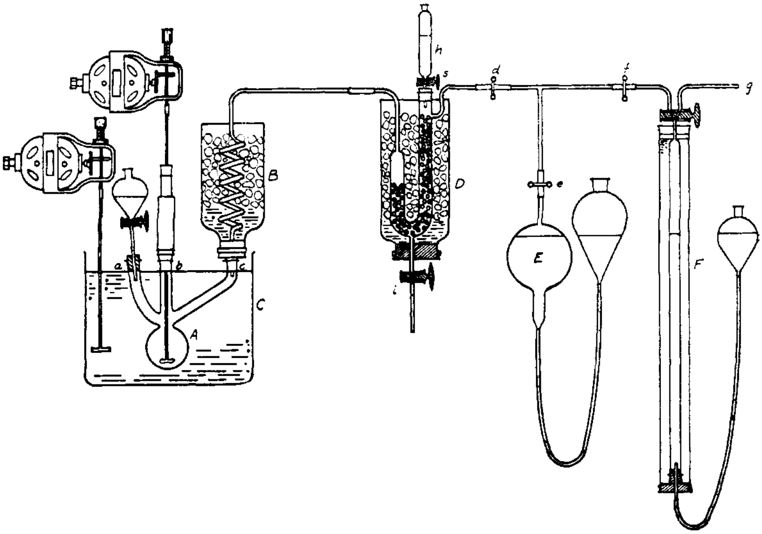

Fig. 1.

The condensing coil was connected by means of capillary tubing to a tower D built in the form of a U and filled with glass pearls partially covered with concd. sulfuric acid. It was equipped with a dropping funnel h and an outlet i so arranged that the sulfuric acid could be removed when desired. The tower was surrounded by an ice-bath in order to keep the acid cold and to maintain the enclosed gas at constant temperature. By means of this arrangement the gas was bubbled through fresh, cold sulfuric acid—a procedure which, according to Gilman and others,[10e] completely removes ether vapor. As will appear later, analysis of the gases obtained with this apparatus shows them, in fact, to be free from ether.

The tower was connected in turn to a T-joint leading on the one hand to

(b) Tschugaeff [*Ber.*, **35**, 3912 (1902)] also made quantitative measurements of gases evolved from ethyl ether solutions. More recently, (c) Moureu and Mignonac [*Compt. rend.*, **158**, 1624 (1914)] and (d) Ciusa [*Gazz. chim. ital.*, [II] **50**, 53 (1920)] have used a similar method. These authors used water to remove the ether vapor from the gas. Finally, the very precise and convenient method of (e) Gilman and others [THIS JOURNAL, **45**, 150 (1923)] for the quantitative estimation of Grignard reagents involves ethyl ether as solvent and concd. sulfuric acid for the removal of the ether vapor.

a 300cc. glass bulb E used as a gas trap, and on the other hand to a 50cc. gas buret F surrounded by a water jacket. The pinchcocks d, e and f enabled the connections between D, E and F to be changed as desired. The gas trap and the buret were filled with mercury and were equipped with leveling bulbs in the usual way.

Test of the Accuracy of the Method of Measurement of the Gas.—To determine the accuracy of the method, three tests were run with methylmagnesium iodide and pure benzoic acid. A weighed amount of the acid was introduced into the dropping funnel and enough absolute ether added to effect solution. This solution was dropped slowly into the reaction flask containing an excess of the Grignard reagent kept at 0°. The yields of methane obtained in the three runs were 99.0, 100.5 and 99.8%. These runs, however, were of short duration and were carried out at low temperature and in these respects are not comparable with the experiments with the alkyl halides, which lasted from two to four hours and which involved temperatures as high as 50°. A blank run was made, therefore, in which the Grignard solution alone was maintained at 40–60° for an hour. When the bath C was replaced and the system brought back to the starting temperature, it was found that the change in volume was negligible. It was concluded from this that the higher temperatures and the longer period of reaction do not materially affect the gas volume and that the results of the runs described here with benzoic acid are comparable with those obtained with the benzyl halides. From this fact and the data given above it appears that the error of the method is of the order of 1%.

The Reagent.—The methylmagnesium iodide solution was prepared by adding methyl iodide to an excess of magnesium in absolute ether. Mechanical agitation was used and after the addition of the halide was complete, the solution was refluxed for two or three hours to make sure that no methyl iodide remained unchanged. The starting materials were used in proportions calculated to give a solution containing 1.67 moles per liter of reagent. Analysis of some preparations showed the amount of active methylmagnesium iodide to be only about 80% of that calculated; the concentration of the solution in active reagent was, therefore, assumed to be 1.34 moles per liter in all cases even where no analyses were made. The amounts of reagent recorded in Table I were based on this value, being calculated by reference to the volume of stock solution taken. Since the reagent was always used in considerable excess, the accuracy of this figure was not of great importance.

To prepare this stock solution for use it was first concentrated by distilling the greater portion of the ether. A measured volume of the stock solution was siphoned into the reaction flask A which was then placed on a steam-bath, connected to a condenser and heated to drive off the ether. The volume of ether removed in this way was always 58% of the volume of stock solution taken. This concentrated solution was used in all of the runs; its concentration was approximately 3.2 moles per liter.

Procedure.—A measured amount of the ether solution of the Grignard reagent was introduced into the reaction flask A which was then connected to the rest of the apparatus by inserting the stoppers at a, b and c and painting the joints with shellac. The bath C was then put in place. The apparatus was closed everywhere except at s and allowed to stand for 15–20 minutes or until thermal equilibrium had been established between A and C. To facilitate this, both A and C were continually agitated. Finally this equilibrium was tested by closing stopcocks and noting the change in level of the mercury in the buret during a period of five minutes. If this change was found to be negligible, which was ordinarily the case, the temperatures of C and F were noted and the buret reading was taken. At this point also the apparatus was tested for gas-tightness.

A weighed amount of the alkyl halide was then introduced. This was done in two ways. The first method consisted in introducing the alkyl halide into a small, thin-walled bulb which was then sealed off and placed in the reaction flask A along with the solution of the reagent. By this method it was only necessary to break the bulb with the stirrer in order to bring about the reaction. Usually, however, the ensuing reaction was too rapid to be controlled and hence this method had to be used with great caution. By bringing the tip of the stirrer down against the bulb the latter could usually be broken without causing any considerable agitation of the liquid, and the alkyl halide being relatively heavy would settle to the bottom of the flask and thus would become mixed with the reagent only slowly. In this way the gas was evolved at a convenient rate. This method, although rather uncertain, was especially useful in the case of the benzyl halides since they are strongly lachrymatory and yet may be handled in this way without inconvenience.

The second method was simply to introduce the alkyl halide in weighed amount into the dropping funnel and allow it to flow into the reaction flask at the desired rate, washing down the last trace of the halide with a few cubic centimeters of absolute ether. The addition was carried out by maintaining the apparatus at slightly reduced pressure by suitable adjustment of the mercury leveling bulb.

Bath C was used only at the beginning and at the end of each run and was removed during the time that the reaction was actually taking place. When the reaction ceased, the bath was replaced and carefully brought back to the starting temperature. When it was found that the mercury level remained practically constant over a period of two or three minutes the pressure inside the apparatus was adjusted to atmospheric pressure and pinchcock d closed. Gas was then driven from the trap E into the buret until the latter was nearly full. The volume was read off and this portion of the gas was expelled through tube g. By repetition of this process the total volume of gas was measured.

The contents of the reaction flask were then poured onto ice and the basic magnesium salt was brought into solution by the addition of hydrochloric acid. The ether layer was separated and the residual aqueous layer washed with ether. The ether washing was united with the main ethereal solution and this was washed, first with dil. aqueous sodium thiosulfate to remove free iodine and finally with water. The solution was dried over calcium chloride and distilled at atmospheric pressure from a 50cc. distilling flask equipped with a short, sealed-in fractionating column. The ethylbenzene came over at 135–160° and the dibenzyl at 270–290°. Redistillation showed the substances to be nearly pure.

Identification of the Products

Dibenzyl.—The solid product was redistilled and crystallized from 95% alcohol. It melted at 50–51°. It was shown to be dibenzyl by the method of mixed melting points.

Ethylbenzene.—The liquid, upon redistillation, boiled at 135–136°. The boiling point given in the literature for ethylbenzene is 135.5–136°. The method of preparation in conjunction with the boiling point establishes the compound as ethylbenzene inasmuch as toluene and other compounds that might conceivably be formed in this reaction have boiling points remote from that observed.

Ethane.—The gaseous product was identified as ethane by analysis. A Hempel explosion pipet was used, the gas volumes being read over water. In four analyses the contractions (in volumes) were 2.55, 2.55, 2.58 and 2.56; the absorptions (in volumes) for the same runs were 1.95, 1.97, 1.94 and 1.95. For ethane, the calculated contraction and absorption are 2.50 and 2.00, respectively.

Determination of the Amount of Grignard Reagent used up in the Reaction.—This was accomplished by using a known amount of active reagent and by determining the excess that remained after the reaction was complete. One hundred cc. of methylmagnesium iodide solution (shown to contain 1.34 moles of active methylmagnesium iodide per liter) was treated with 17.99 g. (0.099 mole) of benzyl bromide. When the reaction was over, a solution of 5 cc. of ethyl alcohol in absolute ether was run in and the evolved methane collected. The yield was 888.5 cc. at 20° (760 mm.), or 0.037 mole. Since the number of moles of methylmagnesium iodide at the beginning was 0.134 the amount used up in the reaction is seen to be 0.097 mole. The benzyl chloride and methylmagnesium iodide reacted, therefore, in the ratio 0.099:0.097, that is, in equimolecular proportions.

Determination of Methyl Iodide

In order to determine any methyl iodide resulting from the coupling reaction the following procedure was used. In the first place, blank tests were run on the methylmagnesium iodide solutions used. A measured portion of the solution was introduced into a small flask and connected through a condenser to a receiver containing a solution of alcoholic silver nitrate. The flask was heated on the steam-bath until distillation ceased, the distillate being collected in the silver nitrate solution contained in the receiver. The silver iodide formed in the receiver was filtered off on a Gooch funnel, dried and weighed. These tests showed the methylmagnesium iodide solutions to contain only traces of methyl iodide.

To see if any methyl iodide had been produced in the coupling reaction, the reaction vessel A was removed and its volatile contents were distilled into alcoholic silver nitrate solution as in the tests described above for the blank runs. There was always a small amount of silver iodide, but this was usually about equal to that obtained from the tests on the reagent solution itself. Hence, while it is not possible to say whether any methyl iodide actually results from the coupling reaction it is certain that, if so, the amount so formed is negligibly small.

The Reaction of Methylmagnesium Iodide on Methyl Iodide

It is possible to formulate the coupling reaction of Type 1 as a coupling of Type 2 followed by alkylation, as shown by the following equations: $2C_6H_5CH_2X + CH_3MgI = C_6H_5CH_2CH_2C_6H_5 + CH_3I + MgIX$; $CH_3I + CH_3MgI = CH_3CH_3 + MgI_2$. If this mechanism is correct, we should expect that if methyl iodide were treated with methyl magnesium iodide *under the conditions that obtain in the coupling reaction*, ethane would be formed quantitatively. The following experiment was carried out to test this idea.

Forty cc. of methylmagnesium iodide solution containing 0.125 mole of reagent was placed in the reaction flask A and brought to a temperature of 22.8° by use of bath C. The apparatus was then closed and C replaced by a small bath in which the lower half of A was immersed. This bath was kept at a temperature of 40–50°. Ten g. of methyl iodide was then dropped in during the course of two hours, the reaction mass being stirred continuously. At the end of this time bath C was replaced, the flask cooled to the initial temperature and the evolved gas measured in the usual way. The yield of gas corrected to 20° and 760 mm. was 36.5 cc. or 21% of the amount of gas theoretically possible from the following reaction: $CH_3MgI + CH_3I = CH_3CH_3 + MgI_2$.

From this result it seems certain that methyl iodide cannot be an intermediate in the formation of ethane in the coupling reaction.

Results

The results obtained with benzyl chloride, benzyl bromide and benzyl iodide are shown in Table I. The table gives in moles the amounts of reagent and benzyl halide used and the amount in moles of each of the products—ethylbenzene, ethane and dibenzyl. Each column gives the results of a single run. The last three figures in each column represent the number of moles of each of the three products obtained for one mole of alkyl halide used. All of the runs were made under conditions standardized as accurately as possible and it is believed that the results are comparable. The three halides do not differ much among themselves and will, accordingly, be discussed together. The results lead to the following interpretation.

1. *Approximately 25% of the benzyl halide is methylated.* This reaction is $CH_3MgI + C_6H_5CH_2X = C_6H_5CH_2CH_3 + MgIX$. Since the separation of the ethylbenzene from dibenzyl by distillation involved considerable loss, it is certain that the actual yield was higher than those found—probably nearer 30 than 25%.

2. *Ethane and dibenzyl occur in equimolecular amounts.* This is true within a few per cent., and the difference is easily explained. The last two lines in the table show that the yield of ethane is in all cases approximately 5–10% in excess of that of dibenzyl, which is just what we should expect when we consider that the ethane is determined quantitatively, whereas the yield of dibenzyl is low because of unavoidable mechanical losses.

3. *Within the probable limits of experimental error the benzyl halide is accounted for as ethylbenzene or as dibenzyl.* The data show that about 65% of the benzyl halide is transformed into dibenzyl. This, added to the 25% changed to ethylbenzene, accounts for approximately 90% of the benzyl halide. The remaining 10% corresponds to the probable error due to mechanical losses.

4. *The benzyl halide and methylmagnesium iodide react in equimolecular proportions.* The evidence for this has been presented above.

TABLE I

THE ACTION OF METHYLMAGNESIUM IODIDE ON THE BENZYL HALIDES

	$C_6H_5CH_2Cl$			$C_6H_5CH_2Br$			$C_6H_5CH_2I$
Amt., moles:							
CH_3MgI	0.240	0.220	0.210	0.200	0.167	0.167	0.100
$C_6H_5CH_2X$	.132	.132	.100	.100	.108	.097	.070
$C_6H_5CH_2CH_3$	.035	.030	.025	.022	.025	.019	.007
$(C_6H_5CH_2)_2$	.041	.044	.033	.034	.036	.036	.026
CH_3CH_3	.044	.046	....	.038	.039	.037	.028
Yield (in moles per mole of $C_6H_5CH_2X$):							
$C_6H_5CH_2CH_3$	0.27	0.23	0.25	0.22	0.23	0.20	0.10
$(C_6H_5CH_2)_2$	.31	.33	.33	.34	.34	.37	.38
CH_3CH_3	.33	.35	....	.38	.36	.38	.40

From the above we can write the equation for the coupling reaction, which is the following: $2CH_3MgI + 2C_6H_5CH_2X = CH_3CH_3 + C_6H_5CH_2CH_2C_6H_5 + 2MgIX$. Considering, moreover, that no methyl iodide is produced we may now conclude that the coupling reaction in these cases proceeds exclusively according to the general equation (1): $2RX + 2R'MgX = R—R + R'—R' + 2MgX_2$.

Summary

When the benzyl halides react with methylmagnesium iodide in excess, the products are ethylbenzene, ethane and dibenzyl. 1,2,3-Triphenylpropane is not produced under these conditions.

Approximately 25% of the benzyl halide is methylated according to the equation: $C_6H_5CH_2X + CH_3MgI = C_6H_5CH_2CH_3 + MgIX$.

The remainder of the benzyl halide undergoes the coupling reaction forming ethane and dibenzyl according to the following equation: $2C_6H_5CH_2X + 2CH_3MgI = CH_3CH_3 + C_6H_5CH_2CH_2C_6H_5 + 2MgIX$.

An apparatus is described for measuring the gas evolved by reactions carried out in ethyl ether.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE VALENCE OF NITROGEN IN QUATERNARY AMMONIUM COMPOUNDS

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In quaternary ammonium salts nitrogen has usually been considered as having a valence of five but it has also been recognized that the fifth valence is of a type different from the other four. The older ideas concerning the stereochemistry of quinquivalent nitrogen as advanced by Van't Hoff,[2] Willgerodt[3] and Bischoff[4] predicted many isomers that have never been obtained experimentally. Werner[5] first advances the idea that in ammonium compounds the fifth group is not held directly by the nitrogen atom but rather by the entire ammonium group. He thought that the fourth valence might be different from the first three, but pointed out that if the four are identical, the stereochemistry of nitrogen in the ammonium ion would be the same as that of carbon. This idea is borne out by all the evidence available. Mills and Warren[6] have recently demonstrated that the pyramidal formula of Bischoff is impossible and that the tetrahedral structure of the ammonium ion is probably correct.

Lewis[7] states that in ammonium compounds nitrogen shares four pairs of electrons with other atoms, that is has a valence of four, and that the ammonium ion holds the fifth group by a polar or electrostatic bond. While he believes that phosphorus may share ten electrons, that is, have a true valence of five, as in phosphorus pentachloride, he does not think the shell of the nitrogen atom can ever accommodate more than eight electrons.

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[1] This communication is an abstract of a thesis submitted by F. D. Hager in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Van't Hoff, "Ansichten über die organischen Chemie," Vieweg u. Sohn, Braunschweig, **1878**, vol. 1, p. 80.

[3] Willgerodt, *J. prakt. Chem.*, [2] **41**, 291 (1890).

[4] Bischoff, *Ber.*, **23**, 1967 (1890).

[5] Werner, "Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie," Vieweg u. Sohn, Braunschweig, **1905**, p. 96; "Lehrbuch der Stereochemie," Fischer, Jena, **1904**, p. 311.

[6] Mills and Warren, *J. Chem. Soc.*, **127**, 2507 (1925).

[7] Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, **1923**, p. 111.