LIX.—*The Action of Aldehydes on the Grignard Reagent. Part II.*

By JOSEPH MARSHALL.

WHEN an aldehyde (1 mol.) is added to a cold, ethereal solution of magnesium in an alkyl or aryl haloid, it is noticed that the precipitate which is formed on the addition of each drop of aldehyde is redissolved until about one-third of the whole has been added, after which the precipitate remains undissolved, and finally the ether is filled with a greyish, crystalline mass, which may be heated on the water-bath during several hours without undergoing any visible change. If, however, a further quantity of an aldehyde is added to the mixture, although only very little heat is developed, a considerable alteration in the character of the pre-

precipitate is observed, a heavy, brownish, viscous mass taking the place of the original crystalline precipitate. If, after some hours, the ether is poured away from the lower layer and is mixed with dilute acid, it is found that only a trace of the aldehyde is present, so that evidently combination has taken place between the aldehyde and the original product of the reaction. The products of the hydrolysis of the viscous mass by dilute acid are very different from that obtained by the decomposition of the original crystalline material.

It was shown in a previous paper (T., 1914, **105**, 527) that the products obtained by the action of benzaldehyde (2 mol.) on magnesium phenyl bromide (1 mol.) are benzophenone and benzyl alcohol. The reaction may be expressed by the equations:

diphenylcarbinol being oxidised to benzophenone and benzaldehyde being reduced to benzyl alcohol.

It is of interest to note that Sabatier and Murat (*Compt. rend.*, 1913, **157**, 1496) state that the chief product of the reaction between benzaldehyde and magnesium phenyl bromide is tetraphenylethane, whilst diphenylcarbinol is produced only to the extent of 3 per cent., and is accompanied by diphenylmethane and benzophenone. These results are explained by assuming that a part of the diphenylcarbinol is reduced to tetraphenylethane and diphenylmethane at the expense of the remainder of the carbinol, which is converted into benzophenone.

In the light of the experiments recorded in the present paper, another explanation of the results of Sabatier and Murat is suggested. It is well known that a certain amount of diphenyl is produced in the reaction between magnesium and bromobenzene, and accordingly a small quantity of magnesium remains undissolved. If to the solution containing an excess of magnesium a quantity of benzaldehyde equivalent to the bromobenzene is added, it is evident that there is, in reality, an excess of the aldehyde, which will react with the magnesium diphenylcarbinyl bromide, and on hydrolysis a certain amount of benzophenone will be produced. During the hydrolysis, also, hydrogen is liberated, owing to the solution of the excess of magnesium, and it is probable that the reduction of diphenylcarbinol (or, more probably, magnesium diphenylcarbinyl bromide) to tetraphenylethane or diphenylmethane is effected by the hydrogen thus formed. In the experiments made by the author, any excess of metal was removed before the aldehyde was added, and in every such case the yield of

diphenylcarbinol (or benzophenone) was more than 50 per cent. of the total possible amount. In order to test the explanation of the results of Sabatier and Murat, suggested above, an experiment was made in which a large excess of magnesium was left in contact with the reaction mixture. The yield of tetraphenylethane in this experiment was 45 per cent., whilst the fraction containing diphenylcarbinol and benzophenone diminished to less than 10 per cent.

If a similar reaction occurs when a magnesium alkyl haloid is allowed to react with an excess of benzaldehyde, the products of the reaction should be a phenyl alkyl ketone and benzyl alcohol, and this has been found to be the case, for example, in the reaction between magnesium methyl iodide and an excess of benzaldehyde, benzyl alcohol and acetophenone have been isolated. Since acetophenone condenses with benzaldehyde, a further excess of benzaldehyde may lead to the formation of phenyl styryl ketone; this substance has also been isolated in the reaction. In the earlier paper (*loc. cit.*) it was stated that the crystalline compound obtained in this reaction was methyldeoxybenzoin, but there is no doubt that it is phenyl styryl ketone contaminated with a small quantity of dibenzoylmethane, from which it is only separated with difficulty. It may be pointed out that the relation between dibenzoylmethane and the hydrate of phenyl styryl ketone is the same as that between acetophenone and phenylmethylcarbinol.

A similar result was obtained when an excess of benzaldehyde was allowed to react with magnesium dimethylcarbonyl iodide, the chief product of the reaction being styryl methyl ketone.

The results obtained by the action of an excess of an aliphatic aldehyde on magnesium carbonyl haloids were similar to those already described in the case of benzaldehyde. Thus, when an excess of acetaldehyde was allowed to react with magnesium phenyl bromide, the substances isolated were acetophenone and benzoylacetone, formed according to the scheme:

The whole of these results may be explained by the assumption that the excess of the aldehyde present in each experiment is capable of reacting as an oxidising agent, being itself reduced to a primary alcohol. Although aldehydes are usually regarded as reducing agents, the formation of benzoic acid from benzaldehyde in the presence of sodium hydroxide is a well-known example in which one molecule of the aldehyde behaves as an oxidising agent towards a second molecule. If the equation for this reaction is compared with an equation representing the oxidation of phenyl-

methylcarbinol to acetophenone by means of benzaldehyde, it will at once be noticed that the two are very similar:

If the hydrate of benzaldehyde is written in each equation, the similarity between them is still more evident:

The assumption may therefore be made that any mechanism which explains the formation of benzoic acid from benzaldehyde will also account for the production of acetophenone from phenylmethylcarbinol.

It has been shown by Claisen (*Ber.*, 1887, **20**, 646) that when sodium methoxide is brought into contact with benzaldehyde, the first product of the reaction which can be isolated is the ortho-compound $\text{C}_6\text{H}_5\cdot\text{C}(\text{ONa})(\text{O}\cdot\text{CH}_3)\cdot\text{OCH}_2\cdot\text{C}_6\text{H}_5$, which, by suitable means, may be converted into benzyl benzoate. Also, Kohn [Keane] and Trantom (T., 1899, **75**, 1155) have brought forward evidence which indicates the intermediate production of a similar compound when sodium hydroxide reacts with benzaldehyde. The suggestion is therefore made that in the reaction between benzaldehyde and magnesium phenylmethylcarbinyl bromide a similar ortho-derivative of acetophenone is produced, the two reactions being contrasted in (5) and (6):

This substance may then condense with an excess of benzaldehyde, after which further oxidation may take place:

Finally, just as the benzoic acid derivative yields on hydrolysis benzyl alcohol and sodium benzoate, the derivative of acetophenone

is decomposed by the addition of water into benzyl alcohol and acetophenone:

The fact that benzyl alcohol is not produced until the hydrolysis of the reaction product is effected is strong evidence in favour of the foregoing explanation of the reaction, for if benzyl alcohol were formed by the direct action of the aldehyde on the carbinyl haloid, it should be found dissolved in the ether, whereas experiment has shown that this is not the case. Again, if the alcohol were present as the compound $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{O}\cdot\text{MgBr}$, acetophenone should be present in the ethereal layer, which again is contrary to the experimental results; neither of the equations (10) or (11), therefore, can represent the facts of the case:

The mechanism of the formation of the ortho-compounds is the only point which still requires elucidation. Although no direct experimental evidence in support of the present suggestion can be brought forward, there is, at any rate, some indirect evidence in its favour.

It is suggested that the first stage in the oxidation of benzaldehyde is the elimination of a molecule of water from two molecules of the hydrate of benzaldehyde. This may be effected by two different methods, either as in (12) or (13):

It is improbable that (12) represents the reaction, since benzoin would be almost certainly isolated, whilst Keane and Trantom have shown that no trace of this substance can be found. The loss of a second molecule of water is supposed to be the second step in the reaction, whereby hydroxydiphenylethylene oxide is produced:

It may be noted that this substance is isomeric with two molecules of benzaldehyde, whilst it differs from the hypothetical

intermediate product suggested by Keane and Trantom, namely, $C_6H_5 \cdot C(OH) : C(OH) \cdot C_6H_5$.

Derivatives of ethylene oxide are known to undergo change with extreme ease (Tiffeneau, *Ann. Chim. Phys.*, 1907, [viii], **10**, 176, etc.), and the addition of a molecule of sodium hydroxide to this compound will result in the formation of the ortho-compound suggested by Keane and Trantom:

A similar series of reactions will account for the formation of the ortho-derivative of acetophenone:

If a magnesium tertiary carbinyl haloid were employed in the place of a secondary compound, it is evident that no oxidation by an excess of the aldehyde would take place, since the formation of an intermediate ethylene oxide derivative would be impossible. This was put to the test by allowing benzaldehyde to react with magnesium diphenylmethylcarbinyl bromide, when no trace of an oxidation product could be found.

If the above explanation of the course of the reaction is correct, it is possible that a reaction may take place between a magnesium secondary carbinyl haloid and a ketone, for the formation of an ethylene oxide derivative from these substances is possible, according to the equation

If a compound of this constitution is formed, it will be impossible to foretell what will be the products of its hydrolysis, for the original substances may be reproduced, or benzophenone and phenylmethylcarbinol may be formed. Experiment showed that

combination of magnesium diphenylcarbinyl bromide with acetophenone actually occurred, whilst the products obtained from the reaction were diphenylcarbinyl ether and acetophenone.

Finally, experiments have been made to determine the nature of the action of ethyl acetate on magnesium carbinyl haloids, and it has been found that good yields of the acetates of the carbinols are produced. The reaction may be regarded as a case of double decomposition, and may be formulated :

It was shown in the earlier paper that formic ester reacts in such a manner with a magnesium carbinyl bromide as to yield, on hydrolysis, the bromide of the carbinol. This reaction may now be explained by assuming that the carbinyl formate is first formed as in (20), and is converted into the bromide by the action of magnesium ethoxybromide.

Further experiments in connexion with this subject are in progress, but it was thought desirable at this stage to correct the observations recorded in the former paper.

EXPERIMENTAL.

Action of Benzaldehyde on Magnesium Phenylbromide.

Several experiments were carried out in order to determine the conditions necessary for the production of tetraphenylethane. The yield of diphenylcarbinol produced by the reaction of equimolecular proportions of these substances was about 55 per cent. of the theoretical, and this was not affected by heating the Grignard product during several hours, or by alteration of the temperature at which the substances were allowed to react. In one experiment, however, 24 grams of magnesium (2 mols.) were allowed to react with an ethereal solution of 75 grams (1 mol.) of bromobenzene, and to the solution (still containing a large quantity of undissolved magnesium) was added a solution of 50 grams of benzaldehyde. The mixture was then poured into a mixture of ice and dilute hydrochloric acid. The chief product of this reaction was tetraphenylethane, of which 30 grams were obtained; the fraction containing benzhydrol could not be obtained in a crystalline condition.

Action of Benzophenone on Magnesium Phenyl Bromide.

This experiment was made in order to determine whether an excess of magnesium would lead to the formation of hexaphenylethane in a manner analogous to the formation of tetraphenyl-

ethane in the previous experiment. The only product of the reaction, however, was triphenylcarbinol, of which a 60 per cent. yield was obtained.

Action of Benzaldehyde on Magnesium p-Tolyl Iodide.

Two experiments were made, in one of which, (a), the amount of benzaldehyde was less than one molecular proportion, whilst in the second, (b), two molecular proportions of the aldehyde were added to the Grignard reagent. The chief product in (a) was phenyl-*p*-tolylcarbinol (m. p. 58°), whilst in (b) benzyl alcohol and phenyl-*p*-tolyl ketone were isolated. The latter substance solidified only when it was brought into contact with a specimen of the ketone obtained by Gattermann's method. It was recrystallised from alcohol, and melted at 60°. The oxime was prepared and analysed.

In these experiments, di-*p*-tolyl was formed in considerable quantity, and was best removed by pouring away the ethereal layer from the Grignard product before the decomposition of the latter with dilute acid.

Action of Benzaldehyde on Magnesium Methyl Iodide.

This reaction was carried out in the manner described in the former paper, but the products of the reaction were examined in more detail.

The fraction of the product boiling below 150°/15 mm. was kept over solid calcium chloride for some time to remove benzyl alcohol, and the remaining liquid was found to be pure acetophenone. This was obtained easily in a crystalline condition, and the oxime and the phenylhydrazone were prepared as confirmation of the nature of the substance.*

The fraction of the product boiling at 200—225°/15 mm. was recrystallised from alcohol, and the substance thus obtained melted at 53°. In order to separate from it a small quantity of impurity, it was dissolved in ether, and the solution was saturated with hydrogen chloride. The crystals which separated were recrystallised from alcohol (m. p. 112°), and were then allowed to remain in contact with a solution of sodium ethoxide.

The precipitated sodium chloride was removed, a little water was added to the clear filtrate, and, on keeping, crystals similar to the original substance were obtained, which, however, melted at 58°. These were compared with a specimen of phenyl styryl

* It has been found that in order to obtain phenylmethylcarbinol free from acetophenone, considerably less than the calculated quantity of benzaldehyde must be added to the solution of magnesium methyl iodide.

ketone prepared by condensing benzaldehyde with acetophenone in the presence of a solution of sodium hydroxide, and the two substances were found to be identical. Analyses of the hydrochloride and the dibromide (m. p. 169°) were published in the earlier paper. As a confirmatory test, the specimens were heated separately with phenylhydrazine, after which sufficient alcohol was added to each to produce a clear solution. The solutions, which were strongly fluorescent, deposited crystals melting at 135° , and a mixture of the two specimens had the same melting point. Each specimen gave the dark greenish-blue coloration when treated with nitrous acid which is characteristic of 1:3:5-triphenylpyrazoline, and the identity of the substance was established by an analysis.

The ethereal solution from which phenyl styryl ketone hydrochloride separated was distilled in a vacuum, and a fraction boiling at 220° was collected. This solidified on cooling, and it was partly soluble in dilute sodium hydroxide solution. The filtered alkaline solution was acidified, and the precipitate thus obtained was recrystallised from alcohol, when it melted at $80-81^{\circ}$. An alcoholic solution of the substance gave a reddish-violet coloration when a drop of a solution of ferric chloride was added to it. (Found: C=80.1; H=5.5. $C_{15}H_{12}O_2$ requires C=80.3; H=5.3 per cent.)

One gram of the substance was dissolved in a small quantity of alcohol, a small excess of an aqueous solution of hydroxylamine was added, and the mixture was boiled under a reflux condenser until no further precipitate was formed. The substance was separated and recrystallised from alcohol, from which solvent it was deposited in shining plates, melting at 141° . (Found; N=5.99. $C_{15}H_{11}ON$ requires N=6.3 per cent.)

The properties of the latter two substances and their analyses agree with those of dibenzoylmethane and 1:3-diphenylisooxazole respectively, and further confirmation of the identity of dibenzoylmethane was obtained by the preparation from it of monobromodibenzoylmethane (m. p. 92°) and of 1:3:5-triphenylpyrazole (m. p. 139°).

Action of Benzaldehyde on Magnesium Ethyl Iodide.

An ethereal solution of 79 grams ($1\frac{1}{2}$ mol.) of benzaldehyde was added to the well-cooled Grignard reagent obtained by the solution of 12 grams of magnesium in 78 grams of ethyl iodide, during which process the greyish, crystalline precipitate of magnesium phenylethylcarbonyl iodide, which first separated, was converted into a heavy, brown, viscous mass. The mixture was gently heated during twenty-four hours, the two layers were then poured

separately into cold dilute acid, and, after washing with dilute sodium carbonate solution, the two ethereal solutions were distilled. From the upper, ethereal layer, the only substance which could be separated was a small amount of benzaldehyde; this part of the reaction product did not contain benzyl alcohol. From the lower, viscous layer, two fractions were separated, namely, a colourless liquid, b. p. $90-155^{\circ}/15$ mm., weighing 86 grams (*A*), and a yellowish liquid, b. p. $160-240^{\circ}$, weighing 16 grams (*B*). From the distillate (*A*), 20 grams of benzaldehyde were separated in the form of the sodium hydrogen sulphite compound, whilst the residue distilled at $200-215^{\circ}$ under the atmospheric pressure. This was oxidised by means of a dilute solution of potassium dichromate and sulphuric acid, when a further quantity of benzaldehyde (15 grams) was obtained, as well as 20 grams of pure phenyl ethyl ketone. There must have been present, therefore, in this fraction about 16 grams of benzyl alcohol and a mixture of phenylethylcarbinol and propiophenone.

Fraction (*B*), on keeping, became filled with a mass of crystals which, after being collected, washed with light petroleum, and recrystallised from hot alcohol, were obtained in colourless needles, melting at $84-85^{\circ}$ (compare Abell, T., 1901, **79**, 929).

Dibenzoylthane is readily soluble in cold benzene, and is dissolved readily by boiling alcohol or light petroleum. It is not soluble in dilute sodium hydroxide solution, nor does an alcoholic solution of the substance produce any coloration when treated with ferric chloride. (Found: C = 81.10; H = 5.94. $C_{16}H_{14}O_2$ requires C = 80.7; H = 5.9 per cent.)

To a solution of 1.2 grams in alcohol, 0.8 gram of very finely powdered hydrazine sulphate was added, and, finally, 1 gram of sodium hydrogen carbonate. After the mixture had been kept overnight, water was added, and the precipitate was recrystallised from alcohol, in which it is not readily soluble. The compound melted at 223° , and agreed in its properties with 3:5-diphenyl-4-methylpyrazole (Abell, *loc. cit.*).

The combination of dibenzoylthane with phenylhydrazine is easily effected by warming equimolecular proportions of the two substances on the water-bath. The product separates from alcohol in colourless, silky needles, which melt at 125° :

0.1550 gave 15.5 c.c. N_2 at 16° and 742 mm. N = 9.26.

$C_{22}H_{18}N_2$ requires N = 9.03 per cent.

1:3:5-Triphenyl-4-methylpyrazole is readily soluble in carbon tetrachloride, and this solution does not react with a solution of bromine in the same solvent. The substance is soluble in concen-

trated mineral acids, but no action is observed when nitrous acid is added to the acid solutions of the compound.

3: 5-Diphenyl-4-methylisooxazole is slowly precipitated when a solution of the diketone in dilute alcohol is boiled with a small excess of hydroxylamine hydrochloride. It forms shining plates, which melt at 127° :

0.235 gave 15.5 c.c. N_2 at 16° and 750 mm. $N=6.17$.

$C_{16}H_{13}ON$ requires $N=6.0$ per cent.

Bromodibenzoylthane is produced by allowing a solution of the ketone in carbon tetrachloride to react with a solution of the calculated quantity of bromine. The substance may be recrystallised from dilute alcohol, from which it separates in colourless prisms, melting at 65° :

0.1585 gave 0.0963 AgBr. $Br=25.70$.

$C_{16}H_{13}O_2Br$ requires $Br=25.23$ per cent.

Action of Benzaldehyde on Magnesium Propyl Iodide.

This reaction was carried out in the same manner as in the preceding experiment. Sixty-eight grams of propyl iodide were used, and the yellow fraction, which contained ethyldibenzoylmethane, weighed 23 grams. This fraction solidified on cooling, and, after purification by draining and recrystallisation from alcohol, dibenzoylpropane was obtained in long, colourless needles.

It melts at 87° (compare Auger, *Ann. Chim. Phys.*, 1891, [vi], 22, 351), and is readily soluble in the common organic solvents. It is insoluble in water and in dilute alkali solutions, and its alcoholic solution is not coloured on the addition of a drop of a solution of ferric chloride. It is decomposed by sodium ethoxide in alcoholic solution into sodium benzoate and phenyl propyl ketone (semicarbazone, m. p. 187°). (Found: $C=81.16$; $H=6.47$. $C_{17}H_{16}O_2$ requires $C=81.0$; $H=6.3$ per cent.)

Bromodibenzoylpropane, $C_6H_5 \cdot CO \cdot CBr(C_2H_5) \cdot CO \cdot C_6H_5$, may be prepared in the usual manner. It separates from alcohol in hexagonal prisms, which melt at 52° .

Dibenzoylpropane reacts with hydroxylamine hydrochloride when the solutions are boiled for some hours. On adding a little water, 1: 3-diphenyl-2-ethylisooxazole separates in long, colourless, silky needles, which melt at 93° . (Found: $N=5.3$. Calc.: $N=5.6$ per cent.) It is not altered by heating to the boiling point or by the action of phosphorus pentachloride.

Equivalent quantities of dibenzoylpropane and phenylhydrazine were heated on the water-bath during four hours, after which the

reaction mixture was distilled in a vacuum, when almost the whole of the substance passed over at $265^{\circ}/15$ mm. The distillate solidified on cooling, and was recrystallised from light petroleum.

1:3:5-*Triphenyl-4-ethylpyrazole* forms colourless needles, which melt at $84-85^{\circ}$:

0.1620 gave 15.4 c.c. N_2 at 17° and 750 mm. $N=8.85$.

$C_{23}H_{20}N_2$ requires $N=8.6$ per cent.

Action of Benzaldehyde on Magnesium isoPropyl Iodide.

This experiment was carried out in the usual manner, and a much greater proportion of unused benzaldehyde was recovered than in the preceding experiments. The chief product was a mixture of phenylisopropylcarbinol and phenyl isopropyl ketone, only a very small amount of a substance with a higher boiling point than that of this mixture being obtained. From the fraction of higher boiling point was isolated less than 0.5 gram of a substance which crystallised from alcohol or light petroleum in bright yellow needles, melting at 110° . The quantity available was too small to admit of examination.

Action of Benzaldehyde on Magnesium Benzyl Bromide.

When magnesium is allowed to react with the calculated quantity of benzyl bromide dissolved in anhydrous ether, the proportion of magnesium which remains undissolved is much greater than in the experiments previously described. In some cases, the formation of 10 per cent. of dibenzyl was observed. Hence, in order to obtain pure phenylbenzylcarbinol by this method, it is necessary either to take considerably more benzyl bromide than is theoretically needed, or to diminish the amount of benzaldehyde to considerably less than one molecular proportion. Unless this precaution is adopted, the amount of phenyl benzyl ketone produced is so great as to render it almost impossible to obtain the carbinol in a pure condition. In the present experiment, the separation of these substances has not been attempted, since phenyldibenzoylmethane has a much higher boiling point than either deoxybenzoin or phenylbenzylcarbinol.

Dibenzoylphenylmethane is not readily soluble in hot alcohol, and is almost insoluble in the cold solvent. It separates from the solution in colourless needles, which melt at 149° :

0.1570 gave 0.4845 CO_2 and 0.0784 H_2O . $C=84.17$; $H=5.56$.

$C_{21}H_{16}O_2$ requires $C=84.00$; $H=5.33$ per cent.

The only reference to dibenzoylphenylmethane in the literature is in a paper by Japp and Lauder (T., 1896, **69**, 742), where a

substance, which melts at 119° , is described as having the composition required by this compound, although it does not react with phenylhydrazine.

The substance obtained in the present experiment reacts with phenylhydrazine when the two compounds are heated together on the water-bath during four hours. The product crystallises from alcohol, in which it is much more readily soluble than the original ketone, in needles, melting at 167° . An analysis showed that the substance was 1 : 3 : 4 : 5-tetraphenylpyrazole.

Bromodibenzoylphenylmethane is produced by mixing equivalent amounts of the ketone and bromine dissolved in carbon tetrachloride, and crystallises from alcohol in colourless prisms, melting at 147° .

Dibenzoylphenylmethaneoxime is obtained by boiling an alcoholic solution of the ketone with a small excess of free hydroxylamine during four hours. It crystallises from alcohol in fine needles, which melt at 153° :

0.2635 gave 13 c.c. N_2 at 15° and 750 mm. $N=4.61$.

$C_{21}H_{17}O_2N$ requires $N=4.44$ per cent.

The substance is soluble in dilute sodium hydroxide solution, and is reprecipitated on the addition of dilute acid. When heated above its melting point, or when an ethereal solution is mixed with phosphorus pentachloride, it loses a molecule of water, and is converted into 3 : 4 : 5-triphenylisooxazole, which is almost insoluble in alcohol and ether, and crystallises in needles, melting at 212° :

0.2359 gave 12 c.c. N_2 at 15° and 750 mm. $N=4.80$.

$C_{21}H_{15}ON$ requires $N=4.72$ per cent.

Action of Benzaldehyde on Magnesium Dimethylcarbinyl Iodide.

In the earlier paper, a substance, boiling at $165^{\circ}/15$ mm., of unknown constitution, was mentioned as constituting the chief product of this reaction. This substance has now been obtained in a crystalline condition, and proved to be styryl methyl ketone by analysis and by the preparation of the oxime (m. p. 116°) and of the phenylhydrazone (m. p. 156°). The latter substance may be easily converted into 1 : 5-diphenyl-3-methylpyrazoline by heating carefully to its boiling point. If the product is distilled in a vacuum, the distillate (boiling at about 250°) solidifies on cooling, and, after three recrystallisations from light petroleum, is obtained in colourless needles, which melt at 114° . Solutions of the pure substance in light petroleum or alcohol are not fluorescent. If a trace of sodium nitrite is added to the solution of the pyrazoline

derivative in hydrochloric acid, a vivid magenta coloration is produced. These two observations are contrary to those recorded in the literature, but have previously been made by Knorr (*Ber.*, 1893, **26**, 114).

Action of Acetaldehyde on Magnesium Phenylmethylcarbinyl Bromide.

A solution of magnesium phenyl bromide and acetaldehyde (4 mol.) was heated during twenty hours. After decomposing the reaction mixture with dilute acid, the ethereal extract was washed with a dilute solution of sodium hydroxide, and then distilled in a vacuum. The chief product was acetophenone, but a small quantity of a substance of higher boiling point was obtained, which was probably impure phenyl propenyl ketone. It reacted with phenylhydrazine to form a substance which was strongly fluorescent in solution, and of which an acid solution was coloured deep blue on the addition of nitrous acid; these properties are characteristic of 1:3-diphenyl-5-methylpyrazoline.

The solution of sodium hydroxide which had been employed to wash the ethereal extract of the reaction product was acidified with dilute acetic acid. A precipitate was obtained which, after filtration, was redissolved in alkali, and again precipitated with acid. The substance was then recrystallised from dilute alcohol, when it formed needles, melting at 59—60°. An alcoholic solution of the substance was coloured deep red by the addition of ferric chloride. An analysis showed that the substance was benzoyl acetone, and it was further characterised by the preparation from it of phenylmethylisooxazole, which forms shining plates, melting at 68—69°.

Action of Acetaldehyde on Magnesium isoPropyl Iodide.

This experiment was carried out in the usual manner, and the products which were isolated and identified were acetone and isopropyl alcohol. A small quantity of a yellow liquid, which boiled at 120—140°, was also obtained. This was soluble in water, and reacted violently with phenylhydrazine to form 1-phenyl-3:5-dimethylpyrazoline (Knorr, *Ber.*, 1887, **20**, 1105). The original liquid must therefore have been ethylideneacetone, but the quantity obtained was too minute to admit of complete purification and analysis.

Action of Benzaldehyde on Magnesium Diphenylmethylcarbinyl Bromide.

In an experiment in which benzaldehyde was allowed to react with the Grignard product obtained by the mixture of acetophenone with magnesium phenyl bromide, the only products which were isolated were diphenylmethylcarbinol and dibenzoylmethane. The latter substance was evidently produced by the action of the aldehyde on a small excess of acetophenone.

Action of Acetophenone on Magnesium Diphenylcarbinyl Bromide.

The grey, crystalline mass produced by the action of benzaldehyde on magnesium phenyl bromide was heated with one molecular proportion of acetophenone during twenty hours. There was no visible change in the character of the mass, but it was found that the acetophenone had combined in some manner with the magnesium compound, for only a trace of it was present in the upper layer at the end of the reaction. From the lower layer was obtained, on hydrolysis, a product containing nearly the whole of the acetophenone, and a substance which was found to be benzhydryl ether, m. p. 110° . (Found: C=89.35; H=6.41. $C_{26}H_{22}O$ requires C=89.14; H=6.28 per cent.)

Action of Ethyl Acetate on Magnesium Phenylmethylcarbinyl Iodide.

The Grignard product obtained by the addition of benzaldehyde to magnesium methyl iodide was mixed with one molecular proportion of pure ethyl acetate. The crystalline deposit immediately dissolved, a small quantity of heat being developed. After washing the ethereal solution with dilute acid, it was distilled under diminished pressure, and almost the whole of the product was a liquid boiling at $105\text{--}108^{\circ}/15$ mm. This liquid was found to be phenylmethylcarbinyl acetate, for it was hydrolysed by an alcoholic solution of potassium hydroxide, yielding acetic acid and phenylmethylcarbinol.

A similar result was obtained by the action of ethyl acetate on magnesium diphenylcarbinyl bromide, a good yield of the carbinyl acetate being produced.

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