CXXX.—*The Mechanism of the Reaction between a Carboxylic Ester and a Grignard Reagent.*

By DAVID RUNCIMAN BOYD and HAROLD HERBERT HATT.

FEW synthetic processes of organic chemistry have been more extensively used than that which leads to the formation of tertiary alcohols by the action of magnesium alkyl, or aryl, halides upon ethereal salts. The mechanism of the process, however, is still in some respects obscure. In his original papers dealing with this subject (*Compt. rend.*, 1901, **132**, 336; *Ann. Chim.*, 1901, **24**, 433), Grignard states that the reaction probably takes place in three stages :

(i) $\text{R·CO·OEt} \xrightarrow{\text{R}'\text{·MgBr}} \text{R·CR}'(\text{OMgBr})\text{·OEt}$.

(ii) $\text{R·CR}'(\text{OMgBr})\text{·OEt} \xrightarrow{\text{R}'\text{·MgBr}} \text{R·CR}'_2\text{·OMgBr} + \text{EtO·MgBr}$.

(iii) $\text{R·CR}'_2\text{·OMgBr} \xrightarrow{\text{H}_2\text{O}} \text{R·CR}'_2\text{·OH} + \text{HO·MgBr}$.

This scheme is reproduced in several well-known text-books.

An alternative view assumes that a ketone is formed as an intermediate product:

$$\text{R·CO·OEt} + \text{R}'\text{·MgBr} = \text{R·CO·R}' + \text{EtO·MgBr};$$

and that the tertiary alcohol results from the action of the Grignard reagent upon the ketone. This mechanism was suggested by Reformatsky for the analogous case of an organo-zinc iodide reacting with an ethereal salt (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 881); it has been advocated by several writers, notably by Stadnikov (*Ber.*, 1914, **47**, 2133). Gomberg (*J. Amer. Chem. Soc.*, 1917, **39**, 2011) refers to Stadnikov's work as providing some evidence in support of the ketone hypothesis; but a consideration of Stadnikov's papers has led us to the conclusion that the evidence offered there is illusory.

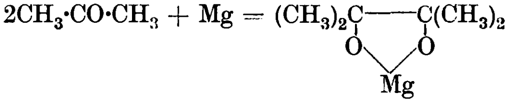
Ketones have, it is true, been obtained by Blaise and Courtot (*Compt. rend.*, 1905, **140**, 370) by the action of water on the addition compounds which are formed on treating the esters of certain unsaturated acids with magnesium methyl iodide at 0°, *e.g.*,

$$\text{CH}_2\text{:C(CH}_3\text{)·CO·OEt} \longrightarrow \text{CH}_3\text{·CH}_2\text{·CH(CH}_3\text{)·CO·CH}_3.$$

These results, however, are not out of harmony with Grignard's views. The appearance of a ketone amongst the products of the reaction may be attributed to the stability, under the conditions of the experiment, of the magnesium addition compound arising in stage (i) of the Grignard scheme. The experiments of Blaise and Courtot provide no evidence in support of the hypothesis that the formation of a ketone is a necessary step in the production of a tertiary alcohol. In order to establish the correctness of this view, it is necessary to show that the free ketone is present in the reaction mixture during the experiment. Such evidence we are now able to bring forward.

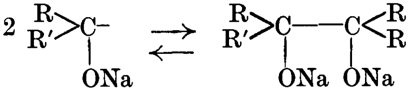
In connexion with investigations on derivatives of the triaryl carbinols, which have been in progress for some time, we have had frequent occasion to employ the Grignard reaction for the preparation of tertiary alcohols from ethereal salts, and in the course of this work we have found that if metallic magnesium is added to the reaction mixture the presence of a ketone is readily detected. When magnesium phenyl bromide, for example, was allowed to react with ethyl *o*-toluate in the presence of metallic magnesium, the products of the reaction included diphenyldi-*o*-tolylpinacol (38%) in addition to diphenyl-*o*-tolylcarbinol (23%). The addition of the Grignard reagent to the ester and magnesium was invariably followed by the development of a deep red colour, which persisted, provided air was excluded, until the reaction mixture was treated with water.

The formation of pinacols under the conditions described is easily understood in the light of the observations of Couturier and Meunier, who found (*Bull. Soc. chim.*, 1905, **33**, 454) that magnesium amalgam reacts smoothly with acetone, giving an addition compound from which the corresponding pinacol is obtained on treatment with water:



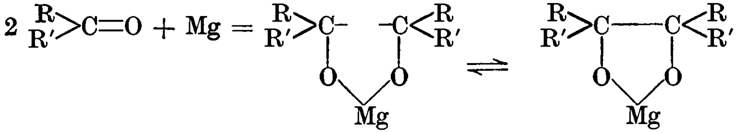
$$2\mathrm{CH_3{\cdot}CO{\cdot}CH_3} + \mathrm{Mg} = \underset{\mathrm{Mg}}{\underbrace{\mathrm{(CH_3)_2}\underset{\mathrm{O}}{\mathrm{C}}\text{——}\underset{\mathrm{O}}{\mathrm{C}}\mathrm{(CH_3)_2}}}$$

The more recent investigations of Schlenk (*Ber.*, 1911, **44**, 1182; 1913, **46**, 2840) have shown, further, that ketones combine with metallic sodium (or magnesium activated by iodine) to give intensely coloured metal ketyls, containing tervalent carbon, and that metallic pinacolates result from the union of two of these unsaturated molecules:



$$2\,\genfrac{}{}{0pt}{}{\mathrm{R}}{\mathrm{R'}}{>}\underset{\mathrm{ONa}}{\mathrm{C}}{-}\ \rightleftarrows\ \genfrac{}{}{0pt}{}{\mathrm{R}}{\mathrm{R'}}{>}\underset{\mathrm{ONa}}{\mathrm{C}}\text{——}\underset{\mathrm{ONa}}{\mathrm{C}}{<}\genfrac{}{}{0pt}{}{\mathrm{R}}{\mathrm{R'}}$$

The phenomena observed in our experiments (production of pinacols and development of colour) are thus very simply explained if it is assumed that the ester reacts with the Grignard reagent to form a ketone and that some of the ketone escapes transformation to a tertiary alcohol by combining with metallic magnesium (activated by contact with the Grignard reagent): *



$$2\,\genfrac{}{}{0pt}{}{\mathrm{R}}{\mathrm{R'}}{>}\mathrm{C{=}O} + \mathrm{Mg} = \underset{\mathrm{Mg}}{\underbrace{\genfrac{}{}{0pt}{}{\mathrm{R}}{\mathrm{R'}}{>}\underset{\mathrm{O}}{\mathrm{C}}{-}\quad{-}\underset{\mathrm{O}}{\mathrm{C}}{<}\genfrac{}{}{0pt}{}{\mathrm{R}}{\mathrm{R'}}}}\ \rightleftharpoons\ \underset{\mathrm{Mg}}{\underbrace{\genfrac{}{}{0pt}{}{\mathrm{R}}{\mathrm{R'}}{>}\underset{\mathrm{O}}{\mathrm{C}}\text{——}\underset{\mathrm{O}}{\mathrm{C}}{<}\genfrac{}{}{0pt}{}{\mathrm{R}}{\mathrm{R'}}}}$$

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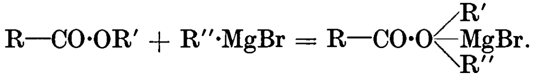
* Since this work was completed a paper has been published by Gomberg and Bachmann (*J. Amer. Chem. Soc.*, 1927, **49**, 236) in which it is shown that ketones are converted into pinacols by magnesium in the presence of a Grignard reagent or, more effectively, by treating the ketone with a mixture of magnesium and magnesium iodide. The activation of the magnesium in

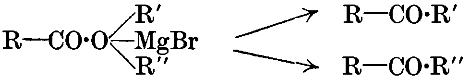
Grignard's scheme, on the other hand, cannot be reconciled with the observed phenomena and must therefore be rejected in favour of the ketone hypothesis.

There remains the question, By what mechanism is the ketone produced from the ester? On theoretical grounds, it appears probable that the Grignard reagent and the ethereal salt react in the first place to give an additive compound, and that the ketone results from the decomposition of this primary complex. Some experimental evidence in support of this view is on record. Stadnikov (*loc. cit.*) found that benzhydryl acetate reacts, in the cold, with magnesium ethyl iodide to give an addition compound, from which the original ester can be recovered on treatment with water. Addition compounds of a somewhat similar character have been obtained from certain ketones (compare Klages, *Ber.*, 1902, **35**, 2633). Stadnikov explains his observations by postulating the formation of an oxonium compound:



$$R{-}CO{\cdot}OR' + R''{\cdot}MgBr = R{-}CO{\cdot}O\left\langle\begin{matrix}R'\\MgBr\\R''\end{matrix}\right.$$

The groups R′ and R″ in this complex are assumed by Stadnikov to be similarly situated, and the conclusion is drawn that two different ketones may result from its decomposition:



$$R{-}CO{\cdot}O\left\langle\begin{matrix}R'\\MgBr\\R''\end{matrix}\right. \quad \begin{matrix}\nearrow R{-}CO{\cdot}R'\\ \searrow R{-}CO{\cdot}R''\end{matrix}$$

Stadnikov claims to have obtained experimental proof of the correctness of this hypothesis from the results of a study of the action of magnesium phenyl bromide upon (*a*) benzyl benzoate and (*b*) benzhydryl acetate.

The principal product of reaction (*a*) is triphenylcarbinol; but, in addition to this, Stadnikov isolated a small quantity of a substance, m. p. 72—73°, which he assumed to be triphenylethylene.

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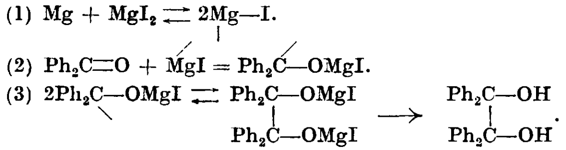
both cases is attributed by Gomberg and Bachmann to the formation of a magnesous iodide:



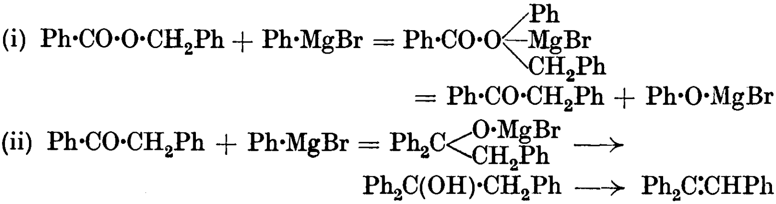
$$(1)\ Mg + MgI_2 \rightleftharpoons 2\overset{}{\underset{|}{Mg}}{-}I.$$

$$(2)\ Ph_2C{=}O + \overset{/}{Mg}I = Ph_2\overset{/}{C}{-}OMgI.$$

$$(3)\ 2Ph_2\underset{\diagdown}{C}{-}OMgI \rightleftharpoons \begin{matrix}Ph_2C{-}OMgI\\|\\Ph_2C{-}OMgI\end{matrix} \longrightarrow \begin{matrix}Ph_2C{-}OH\\|\\Ph_2C{-}OH\end{matrix}.$$

Very large yields of pinacols (92—99·6%) were obtained from eight ketones by Gomberg and Bachmann; and these authors have proved that the *simultaneous* action of both magnesium and magnesium iodide is demanded in the reduction of ketones.

On this assumption, he argues that phenyl benzyl ketone must have been formed as an intermediate product :



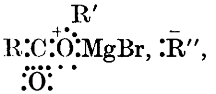
$$\text{(i)}\ \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}CH_2Ph + Ph{\cdot}MgBr = Ph{\cdot}CO{\cdot}O}\!<\!\begin{matrix}\mathrm{Ph}\\ \mathrm{MgBr}\\ \mathrm{CH_2Ph}\end{matrix} = \mathrm{Ph{\cdot}CO{\cdot}CH_2Ph + Ph{\cdot}O{\cdot}MgBr}$$

$$\text{(ii)}\ \mathrm{Ph{\cdot}CO{\cdot}CH_2Ph + Ph{\cdot}MgBr = Ph_2C}\!<\!\begin{matrix}\mathrm{O{\cdot}MgBr}\\ \mathrm{CH_2Ph}\end{matrix} \longrightarrow \mathrm{Ph_2C(OH){\cdot}CH_2Ph} \longrightarrow \mathrm{Ph_2C{:}CHPh}$$

No evidence is given in support of the formula $\mathrm{Ph_2C{:}CHPh}$ except the analytical data : C, 93·34; H, 6·64%. These figures, however, are in excellent agreement with the composition of diphenyl (C, 93·46; H, 6·54%). The melting point given for the supposed triphenylethylene is the same as that of diphenyl, and the description of the crystalline form and solubility agrees with the assumption that the compound was diphenyl. On repeating Stadnikov's experiment we obtained the substance he describes, and identified it as diphenyl by the melting point of a mixture with an authentic specimen and by conversion into the dibromide.

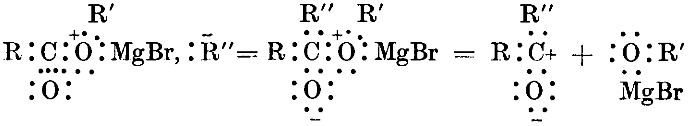
Amongst the products of reaction (*b*), Stadnikov obtained a hydrocarbon, m. p. 121—122°, which he assumed to be methyltriphenylethylene. The formation of the compound is explained as due to a series of changes similar to those given for case (*a*), and involving the production of benzhydryl methyl ketone as an intermediate step. Again, no evidence is brought forward in proof of the formula $\mathrm{CPh(CH_3){:}CPh_2}$, except the analytical data. The figures given agree equally well with the compositions of several other substances,. Methyltriphenylethylene has recently been prepared by methods which leave no doubt as to its constitution (Levy, *Bull. Soc. chim.*, 1921, **29**, 890); it melts at 89—90°.

There is thus no experimental foundation for the view that an ester, R·CO·OR′, can react with a Grignard reagent, R″·MgBr, to give a ketone with the formula R·CO·R′. Hence Stadnikov's oxonium formula, in its original form, must be rejected, since it suggests possibilities of reaction which are not realised in practice. If, however, the Stadnikov formula is written in electronic fashion,



$$\mathrm{R{:}\underset{:\ddot{O}:}{\overset{R'}{\ddot{C}}}{:}\overset{+}{\ddot{O}}{:}MgBr,\ {:}\overset{-}{R}''},$$

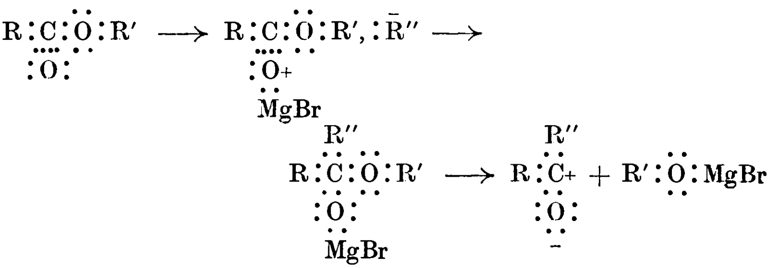
it becomes apparent that the groups R′ and R″ are not similarly situated. R″ is negatively charged and retained in the molecule by the electrostatic attraction of the positive oxonium oxygen atom; R′, on the other hand, is attached by a co-valency to the oxygen. The rearrangement of the oxonium compound will naturally take place by a movement of the radical R″, the radical R′ retaining its original position. Hence only one ketone will be formed.



$$\mathrm{R}:\underset{:\mathrm{O}:}{\mathrm{C}}:\overset{\mathrm{R}'}{\overset{+}{\mathrm{O}}}:\mathrm{MgBr},\ :\overset{-}{\mathrm{R}}'' = \mathrm{R}:\underset{\underset{-}{:\mathrm{O}:}}{\overset{\mathrm{R}''}{\mathrm{C}}}:\overset{\mathrm{R}'}{\overset{+}{\mathrm{O}}}:\mathrm{MgBr} = \mathrm{R}:\underset{\underset{-}{:\mathrm{O}:}}{\overset{\mathrm{R}''}{\mathrm{C}}}{}^{+} + :\underset{\mathrm{MgBr}}{\mathrm{O}}:\mathrm{R}'$$

(I.) (II.)

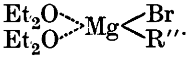
The magnesium complex (II) may be expected to break down with extreme ease, giving free ketone and the aryloxy-magnesium halide. The ketone thus liberated will be in a highly reactive form, and rapid combination with a Grignard reagent, or with activated magnesium, may be anticipated. This hypothesis appears to us to be the most satisfactory way of interpreting the phenomena. It is possible, however, that the formation of the primary addition compound may be due to the residual affinity of the carbonyl oxygen (compare v. Braun and Kirschbaum, *Ber.*, 1919, **52**, 1725, for the analogous case of a ketone addition compound), and not to that of the ethereal oxygen :



$$\mathrm{R}:\underset{:\mathrm{O}:}{\mathrm{C}}:\mathrm{O}:\mathrm{R}' \longrightarrow \mathrm{R}:\underset{\underset{\mathrm{MgBr}}{:\mathrm{O}^{+}}}{\mathrm{C}}:\mathrm{O}:\mathrm{R}',\ :\overset{-}{\mathrm{R}}'' \longrightarrow$$

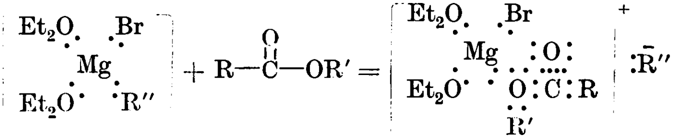
$$\mathrm{R}:\underset{\underset{\mathrm{MgBr}}{:\mathrm{O}:}}{\overset{\mathrm{R}''}{\mathrm{C}}}:\mathrm{O}:\mathrm{R}' \longrightarrow \mathrm{R}:\underset{\underset{-}{:\mathrm{O}:}}{\overset{\mathrm{R}''}{\mathrm{C}}}{}^{+} + \mathrm{R}':\mathrm{O}:\mathrm{MgBr}$$

Either view can be combined with the interesting suggestions of Meisenheimer and Casper (*Ber.*, 1921, **54**, 1655), who regard the Grignard reagent as a magnesium complex compound containing two molecules of ether,



$$\begin{matrix}\mathrm{Et_2O}\\ \mathrm{Et_2O}\end{matrix}>\mathrm{Mg}<\begin{matrix}\mathrm{Br}\\ \mathrm{R}''\end{matrix}.$$

The primary reaction between this compound and an ethereal salt may be represented as follows :



$$\left[\begin{matrix}\mathrm{Et_2O}\cdot & \cdot\mathrm{Br}\\ & \mathrm{Mg} \\ \mathrm{Et_2O}\cdot & \cdot\mathrm{R}''\end{matrix}\right] + \mathrm{R}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{OR}' = \left[\begin{matrix}\mathrm{Et_2O}\cdot & \cdot\mathrm{Br} & \\ & \mathrm{Mg} & :\mathrm{O}: \\ \mathrm{Et_2O}\cdot & \underset{\mathrm{R}'}{\mathrm{O}}: & \mathrm{C}:\mathrm{R}\end{matrix}\right]^{+} :\overset{-}{\mathrm{R}}''$$

Considered as a practical method for the preparation of pinacols, the new process presents advantages in certain cases, since it starts from the ester, which is usually more accessible than the ketone. Indirectly it provides a method for the synthesis of ketones and secondary alcohols, pinacols being readily decomposed into these products. The yield of pinacol, however, varies greatly in different cases. It appears to be dependent upon the constitutions of both the ester and the Grignard reagent: the study of the reaction from this point of view is being continued.

One other point of some practical importance may be noticed. In the preparation of triphenylcarbinol from magnesium phenyl bromide the crude carbinol is always associated with other compounds which lower its melting point and render its isolation in good yield less easy than might be expected. One of these compounds, diphenyl (invariably formed during the preparation of the Grignard reagent), is well known and easily removed. But the literature contains references to other by-products whose constitutions have not been elucidated. Schroeter, in an experiment on the preparation of triphenylcarbinol from carbon dioxide and magnesium phenyl bromide (*Ber.*, 1903, **36**, 3005), obtained a substance (A), m. p. 165°, which he suggests may be a molecular compound of triphenylcarbinol with benzophenone; and also a small quantity of a substance (B), m. p. 81°. From the description given of the properties of (A) there can be little doubt that it was an impure specimen of benzpinacol. As to the constitution of (B), Schroeter offers no opinion. A compound melting at about the same temperature (83—84°) was recently obtained by Stadnikov (*Ber.*, 1924, **57**, 1)] from methyl benzoate by prolonged boiling with a Grignard reagent prepared from bromobenzene. This compound was regarded by Stadnikov as the methyl ether of triphenylcarbinol, and an elaborate series of equations is given to account for its formation. We have repeated Stadnikov's experiment several times and have also tried various modifications of the conditions, but on no occasion have we detected the presence of the methyl ether of triphenylcarbinol amongst the products of the reaction between methyl benzoate and magnesium phenyl bromide.

We have, however, observed the occurrence of a small quantity of the *ethyl* ether of triphenylcarbinol as a by-product in the preparation of the carbinol from methyl benzoate and magnesium phenyl bromide in certain cases when ethyl alcohol was used as the crystallisation medium.

The methyl and ethyl ethers of triphenylcarbinol may easily be confused; their melting points do not differ by more than a degree (m. p. of methyl ether, 82°; m. p. of ethyl ether, 83°. Richter's

Lexikon), and their percentage compositions are almost identical. They can readily be distinguished by a mixed melting point determination, but Stadnikov makes no mention of such an observation. In the circumstances, we are of opinion that the compound, m. p. 83—84°, obtained by him from methyl benzoate was the ethyl ether of triphenylcarbinol and not, as he supposed, the methyl compound. Schroeter's substance, m. p. 81°, was, doubtless, also the ethyl ether of the carbinol.

EXPERIMENTAL.

In the preparation of the Grignard reagents, iodine was employed in small quantity to activate the magnesium.

The Action of Magnesium Phenyl Bromide on Ethyl o-*Toluate.*—Bistrzycki and Gyr (*Ber.*, 1904, **37**, 1248) obtained a 40% yield of diphenyl-*o*-tolylcarbinol from methyl *o*-toluate and magnesium phenyl bromide; they do not record the formation of any by-products. In our experiments, the ethyl ester was used.

Expt. 1. The product obtained on decomposing the magnesium complex with ice and dilute sulphuric acid was steam-distilled, and the residue crystallised from light petroleum and alcohol. The yield of carbinol, m. p. 98—98·5°, was 28·5%.

Expt. 2. 41 G. of the ester, dissolved in 60 c.c. of ether, were added to a Grignard reagent prepared from 13·5 g. of magnesium, 98 g. of bromobenzene and 200 c.c. of ether. In the hope of improving the yield, the procedure was modified as follows. After decomposition of the magnesium compound, the ethereal layer was removed, and the ether distilled off. On pouring the residual oil into alcohol, fine, white needles (A), m. p. 155°, immediately separated. Further small quantities of (A) were deposited from the solution on keeping, the total yield being 6·7 g. The residue left on evaporation of the alcoholic solution was steam-distilled, and the non-volatile portion crystallised from alcohol. In this way, 20·3 g. of diphenyl-*o*-tolylcarbinol were obtained. From the oil remaining after this crystallisation, 7·35 g. of diphenyl-*o*-tolylchloromethane were precipitated on passing hydrogen chloride gas through an ethereal solution containing fused calcium chloride.

The product (A), after several crystallisations from aqueous alcohol, melted at 160°. It crystallised well from benzene (needles, rapidly efflorescing in the air), or glacial acetic acid. It was identified as *diphenyldi-*o*-tolylpinacol* by analysis (C, 85·1; H, 6·9. $C_{28}H_{26}O_2$ requires C, 85·2; H, 6·65%) and by conversion into a mixture of phenyl-*o*-tolylcarbinol and phenyl *o*-tolyl ketone. Transformation into the secondary alcohol and ketone was brought about either by heating for some hours at 120—125° or by treatment with hot alcoholic potash. On treatment with this reagent, it dissolved, imparting a characteristic, fleeting, deep-blue colour to the solution (compare Schlenk and Thal, *Ber.*, 1913, **46**, 2840). The oily product of the reaction, on being rubbed with light petroleum, gave crystals of phenyl-*o*-tolylcarbinol, identified by melting point (91·5°, after three crystallisations from ether–light petroleum) and by analysis (C, 84·9; H, 7·3. Calc. for $C_{14}H_{14}O$: C, 84·8; H, 7·1%). The oil left after separation of the phenyl-*o*-tolylcarbinol boiled at 286—288°, and on treatment with alkaline-alcoholic hydroxylamine gave an oxime, m. p. 101·5—103·5° after crystallisation from aqueous alcohol. Smith (*Ber.*, 1891, **24**, 4046) gives 105° as the melting point of *anti*-phenyl-*o*-tolylketoxime.

The yields of pinacol and carbinol in this experiment were, respectively, 13·6% and 39·7%. Cohen, who prepared diphenyldi-*o*-tolylpinacol by reduction of phenyl *o*-tolyl ketone (*Rec. trav. chim.*, 1919, **38**, 113), gives 163° as the melting point.

Expt. 3. The formation of pinacol in the preceding experiment was attributed to the presence in the reaction mixture of some metallic magnesium left over in the preparation of the Grignard reagent. This view was confirmed by removing any undissolved metal as completely as possible before allowing the reagent to mix with the ester. For this purpose, the Grignard reagent was filtered through an asbestos pad before entering the solution of ester (7·5 g.) in dry ether. The reaction product, after treatment in the usual way, was poured into alcohol, kept for 9 days, and inoculated with diphenyldi-*o*-tolylpinacol; 0·02 g. of product, m. p. 154°, was then obtained (equivalent to a yield of 0·26% of pinacol). On addition of light petroleum to the oily liquid, from which the pinacol had separated, diphenyl-*o*-tolylcarbinol (1·29 g.) crystallised; and the mother-liquor from this crystallisation, on long standing, deposited 0·77 g. of the *ethyl ether* of diphenyl-*o*-tolylcarbinol (large, colourless prisms, m. p. 96°), identified by the melting point of a mixture with a specimen prepared from diphenyl-*o*-tolylcarbinyl chloride (Found: OEt, 11·56. $C_{20}H_{17}OEt$ requires OEt, 14·9%).

Expt. 4. In order to obtain a maximum yield of pinacol, the reaction was carried out in the presence of a considerable excess of magnesium. The Grignard reagent, prepared from 16·2 g. of bromobenzene, 5 g. of magnesium, and 50 c.c. of dry ether, was filtered from the excess of magnesium, and the excess of metal was introduced into a solution of 7·5 g. of ethyl *o*-toluate in 30 c.c. of dry ether. The Grignard reagent was then added gradually (3 hours) to the ester solution, which was stirred and refluxed gently. Heating was continued for an hour after all the reagent had been added. All these operations were carried out in an atmosphere of dry nitrogen. The reaction mixture remained throughout a deep red-orange colour. The product, treated in the usual way, gave 3·62 g. of pinacol (38%) and 2·92 g. of carbinol (23·3%).

The Action of Magnesium Phenyl Bromide on Methyl Benzoate.—In the following experiments, no attempt was made to exclude dry atmospheric oxygen.

Expt. 1. A Grignard reagent (prepared from 24·4 g. of bromobenzene, 7·5 g. of magnesium, and 70 c.c. of ether) was mixed with an ethereal solution of 20·9 g. of methyl benzoate, to which had been added the magnesium remaining over in the preparation of the magnesium phenyl bromide. The product was decomposed with ice and dilute sulphuric acid and extracted with ether. The semi-crystalline mass left on evaporation of the ether gave, on fractional crystallisation from ethyl alcohol, 8·7 g. (43·5%) of triphenylcarbinol (m. p. 160—161°) and 0·6 g. (2·2%) of benzpinacol, melting at 166—167° (m. p. after two crystallisations from aqueous alcohol, 185—186°). The benzpinacol was identified by conversion into benzhydrol (m. p. 67°) and benzophenoneoxime (m. p. 142—143°). The oil which did not crystallise in this treatment was steam-distilled. The steam distillate on fractional distillation yielded 10·08 g. of methyl benzoate, 0·3 g. of diphenyl, and 1·12 g. of residue. From the 1·12 g. of residue there resulted, on treatment with alkaline-alcoholic hydroxylamine, 0·46 g. of benzophenoneoxime, m. p. 142—143° after two crystallisations from aqueous alcohol (mixed m. p. 142—143°). The oil remaining after the steam distillation amounted to 2·55 g., and this when fractionally crystallised yielded, besides triphenylcarbinol, some colourless crystals melting between 70° and 78°. These, on recrystallisation from methyl alcohol, melted at 81—82°; they were identified as the ethyl ether of triphenylcarbinol. Mixed with a specimen of this ether (m. p. 80—82°), the crystals melted at 81·5°. A mixture of the substance with the methyl ether of triphenylcarbinol (m. p. 83—84°) melted at 60—63°, softening at 58°. A mixture of the methyl and ethyl ethers of triphenylcarbinol melted at 66—70°, softening at 53°.

Expt. 2. The Grignard reagent (prepared from 24·1 g. of bromobenzene, 4·5 g. of magnesium, and 70 c.c. of ether) was filtered and added slowly to an ethereal solution of 20·9 g. of methyl benzoate, containing 2·5 g. of magnesium turnings and a little metallic mercury. The reaction product, worked up in the usual way, yielded 2·15 g. (7·8%) of benzpinacol and 8·3 g. (41·5%) of triphenylcarbinol.

Expt. 3. Methyl benzoate (14 g.) was added fairly rapidly to a

Grignard reagent prepared from 34 g. of bromobenzene, 4·8 g. of magnesium, and 100 c.c. of ether. After the first reaction had ceased, the mixture was refluxed in a water-bath for 15 hours. The product was worked up as in Expt. 1, but the ethereal solution before evaporation was shaken with dilute aqueous sodium hydroxide in order to remove any free sulphuric acid. The following yields were obtained: triphenylcarbinol, 13·3 g. (49·7%); benzpinacol, 0·11 g.; and the ethyl ether of triphenylcarbinol, 1·62 g. (5·7%). The last compound was identified by a mixed melting point (83°), and conversion into the carbinol (mixed m. p. 160—161°) by treatment with concentrated sulphuric acid and glacial acetic acid.

The Action of Magnesium o-*Tolyl Bromide on Ethyl* o-*Toluate*.—The reaction was carried out exactly as described under Expt. 4 for the preparation of diphenyldi-*o*-tolylpinacol. The Grignard reagent was prepared from 16·5 g. of *o*-bromotoluene, 4·6 g. of magnesium, and 50 c.c. of ether; the undissolved magnesium being transferred to the solution of ethyl *o*-toluate (6·7 g.) in 30 c.c. of ether.

Immediately the Grignard reagent entered the ester solution, a deep reddish-violet colour was observed, which persisted until treatment of the reaction products with ice and dilute sulphuric acid. The ethereal layer on evaporation left an oil. From this residual oil, after rubbing with alcohol, a crystalline powder separated, m. p. 158° (yield 0·46 g.); and, on keeping, a further 0·02 g. of crystals (m. p. 148—153°) was obtained. This substance was very soluble in hot benzene, moderately easily soluble in alcohol, and insoluble in light petroleum. It was analysed after recrystallisation from benzene (Found: C, 85·2; H, 7·25. Calc. for $C_{30}H_{30}O_2$: C, 85·3; H, 7·2%). From its analysis, its decomposition on melting, and the evanescent deep green colour which it gives on dissolving in hot alcoholic sodium ethoxide, the substance is evidently *tetra*-o-*tolylpinacol*. The yield of pinacol was 5·2%.

The oil left after crystallisation of the pinacol was steam-distilled. From the distillate, 0·2 g. of a crystalline substance was obtained, melting, after crystallisation from aqueous alcohol, at 118—122°. The residue from the steam distillation was extracted with ether, and the ethereal solution was dried and evaporated. An oil was thus obtained which, on being rubbed with light petroleum containing a little ether, gave 0·51 g. of the same crystalline substance. After crystallisation from aqueous alcohol, it melted at 119—119·5°. A mixed melting-point determination showed that it was not di-*p*-tolyl. Analysis after recrystallisation pointed to *di*-o-*tolylcarbinol* (Found: C, 84·7; H, 7·7. $C_{15}H_{16}O$ requires C, 84·9;

H, 7·6%). The substance dissolved in concentrated sulphuric acid, giving a strong red colour. The di-*o*-tolylcarbinol may arise from hydrolysis of the pinacol by magnesium hydroxide during the decomposition of the reaction products with ice. Tri-*o*-tolylcarbinol has not, so far, been isolated, and the study of this reaction is being continued.

The Action of Magnesium Phenyl Bromide on Benzyl Benzoate (Stadnikov, *Ber.*, 1914, **47**, 2140).—Benzyl benzoate was prepared from benzoyl chloride and benzyl alcohol by a Schotten–Baumann reaction. It was purified by fractionating it twice under reduced pressure. The ester was brought into reaction with magnesium phenyl bromide, the same amounts of reagents and the same procedure being used as directed by Stadnikov (*loc. cit.*). In the main, the products of the reaction were those recorded by Stadnikov; thus we obtained 0·25 g. of benzoic acid and 29·1 g. of triphenylcarbinol. The steam distillate was separated into two fractions, as he directs, and from the first there were obtained 5·9 g. of bromobenzene (b. p. 146—147°), 6·8 g. of benzyl alcohol (b. p. 201—205°), and a small amount of a crystalline residue. From the second fraction, 6 g. of benzyl alcohol (b. p. 204—210°) were obtained, together with 0·89 g. of the crystalline material supposed to be triphenylethylene. This substance melted at 62—67°, and, after two crystallisations from aqueous ethyl alcohol, formed colourless plates, m. p. 70—71°. The yield of pure product was 0·57 g. (Stadnikov obtained 0·55 g.). Mixed with diphenyl (m. p. 69—69·5°), the substance melted at 69·5—70·5°.

It was brominated by dissolving 0·5 g. in 3 g. of carbon disulphide and adding 3 g. of bromine. After refluxing for 6 hours, the carbon disulphide was evaporated under reduced pressure, and the crystalline product washed with caustic soda solution, water, and alcohol (yield, 0·72 g.). After two crystallisations from benzene, it formed small, colourless needles, m. p. 164·5°.

4 : 4′-Dibromodiphenyl, prepared in precisely the same manner from 0·5 g. of diphenyl and crystallised twice from benzene, melted at 163—164°. For the mixed melting point, the value 163·5—164·5° was obtained.

Postscript.—Barnett, Cook, and Nixon (this vol., p. 504) have recorded the formation of *s*-*oo*′-dibenzylbenzpinacol as one of the products of the action of magnesium phenyl bromide on ethyl *o*-benzylbenzoate. The announcement of our results led these authors to repeat this experiment, and in a private communication they inform us that, in agreement with our observations, they obtained no pinacol when a filtered solution of magnesium phenyl bromide was employed.

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