CCXII.—*The Production of Pinacols in the Reaction between a Carboxylic Ester and a Grignard Reagent.*

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THE reaction between a carboxylic ester and a Grignard reagent yields a pinacol if metallic magnesium is present (Boyd and Hatt, J., 1927, 898), and its production is explained by supposing that the corresponding ketone is formed at an intermediate stage of the reaction.

Gomberg and Bachmann (*J. Amer. Chem. Soc.*, 1927, **49**, 236) have shown that in the reduction of a ketone by magnesium and magnesium iodide the halogenomagnesium pinacolate (I) or the corresponding metal ketyl is first formed.

$$(1)\ 2\text{CORR}' \xrightarrow[\text{MgI}_2]{\text{Mg}+} 2\text{CRR}'\cdot\text{OMgI} \rightleftharpoons \underset{\text{(I.)}}{[\text{OMgI}\cdot\text{CRR}'\cdot]_2}$$

When less magnesium iodide than that required by equation (1) is used, reduction is not so rapid: the halogenomagnesium pinacolate (I) first formed dissociates into the magnesium pinacolate, $\begin{array}{l}\text{CRR}'\cdot\text{O}\\ |\\ \text{CRR}'\cdot\text{O}\end{array}\!\!>\!\text{Mg}$ (II) and magnesium iodide, and the latter then takes part in the reduction of a further quantity of the ketone, the final product consisting chiefly of (II).

In attempts, therefore, to improve the small yields of benzpinacol previously obtained (*loc. cit.*, p. 907), the reaction between magnesium phenyl bromide and methyl benzoate was brought about in presence of magnesium and larger quantities of magnesium iodide. The results were unexpected. When the reaction was carried out at 30—60° in the presence of sufficient magnesium and magnesium iodide to give a theoretical yield of (I), no benzpinacol could be isolated. When the Grignard reagent was added rapidly to the ester, the strong purple colour of the metal ketyl appeared for a while, but vanished so soon as the addition was complete.

Such observations suggested that (I) is first formed but afterwards destroyed. A possible explanation is the subsequent formation (equation 2) of a compound analogous to Schlenk's disodiobenzophenone (*Ber.*, 1914, **47**, 486) which by reason of its close resemblance to the magnesium alkyl halides might be expected to possess considerable reactivity (Gilliland and Blanchard, *J. Amer. Chem. Soc.*, 1926, **48**, 411). However, no evidence of its formation was obtained when benzophenone was shaken for long periods with excess of

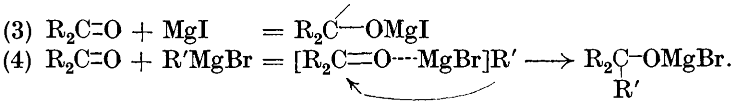
$$(2)\ 2\text{Ph}_2\underset{|}{\text{C}}\cdot\text{OMgI} + \text{Mg} + \text{MgI}_2 = 2\text{Ph}_2\underset{\text{MgI}}{\underset{|}{\text{C}}}\cdot\text{OMgI}$$

magnesium and magnesium iodide in ether–benzene : an ethereal solution of the iodomagnesium benzpinacolate in presence of magnesium and magnesium iodide showed no special reactivity towards either methyl benzoate, magnesium phenyl bromide or bromobenzene.

The harmful effect of excess of magnesium iodide is apparent in other cases. Ethyl *o*-chlorobenzoate and magnesium phenyl bromide in presence of magnesium and a little magnesium iodide gave 27% of the corresponding pinacol, but when sufficient magnesium and magnesium iodide to produce the theoretical quantity of the pinacol were used the yield fell to 5%. From ethyl *o*-toluate and magnesium phenyl bromide the maximum yield of pinacol (45%) was obtained when 10% of the theoretical quantity of magnesium iodide was present.

In a study of the effect of substituents in the benzene nuclei of the ester and of the Grignard reagent on the yield of pinacol, the standard procedure adopted was approximately that indicated in Expt. 4 (J., 1927, 906). The table summarises the results. Cases (1) and (8) are complicated by the fact that separation of triarylmethoxymagnesium bromide commenced during the early stages of the reaction and prevented good contact between the metal and the liquid.

The experiments indicate that substitution of ethyl benzoate in the ortho-position generally favours the production of pinacols; the effect, however, depends much on the nature of the substituent. This result would be expected if the two reactions which are in competition were represented by equations (3) and (4).



$$(3)\quad R_2C{=}O + MgI = R_2\overset{\diagup}{C}{-}OMgI$$

$$(4)\quad R_2C{=}O + R'MgBr = [R_2C{=}O\cdots MgBr]R' \longrightarrow R_2\underset{R'}{C}{-}OMgBr.$$

The great effect of the methyl group in the ortho-position and its slight effect in other positions are clearly indicated by cases (2) and (5).

In the table, *a* = % yield of pinacol calculated from 0·1 mol. of ester; *b* = % yield of carbinol calculated from 0·1 mol. of ester.

No.	Ester (0·1 mol.).	Grignard reagent (0·2 mol.).	*a*.	*b*.
1	$C_6H_5{\cdot}CO_2Me$	$C_6H_5{\cdot}MgBr$	2	44
2	$o\text{-}C_6H_4Me{\cdot}CO_2Et$	$C_6H_5{\cdot}MgBr$	40	23
3	$o\text{-}C_6H_4Me{\cdot}CO_2Et$	$p\text{-}C_6H_4Me{\cdot}MgBr$	52	6
4	$o\text{-}C_6H_4Me{\cdot}CO_2Et$	$o\text{-}C_6H_4Me{\cdot}MgBr$	0	—
5	$p\text{-}C_6H_4Me{\cdot}CO_2Et$	$C_6H_5{\cdot}MgBr$	3	37
6	$o\text{-}C_6H_4Cl{\cdot}CO_2Et$	$C_6H_5{\cdot}MgBr$	27	31
7	$o\text{-}C_6H_4Br{\cdot}CO_2Et$	$C_6H_5{\cdot}MgBr$	9	5
8	$o\text{-}OMe{\cdot}C_6H_4{\cdot}CO_2Me$	$C_6H_5{\cdot}MgBr$	0	52
9	$o\text{-}C_6H_4Cl{\cdot}CO_2Et$	$o\text{-}C_6H_4Me{\cdot}MgBr$	0	—
10	$\alpha\text{-}C_{10}H_7{\cdot}CO_2Et$	$C_6H_5{\cdot}MgBr$	4	22

No pinacol is formed in cases (4) and (9) where an ortho-substituent is present both in the ester and in the Grignard reagent. The result is surprising, since, in absence of magnesium, ethyl *o*-toluate and magnesium *o*-tolyl bromide gave a 66% yield of the ketone. Di-*o*-tolyl ketone reacted in ether–benzene solution with the amounts of magnesium and magnesium iodide required for the formation of the iodomagnesium pinacolate, giving a deep purple solution the hydrolysis of which yielded di-*o*-tolylcarbinol (25%) and a little ketone. The purple colour of the solution was discharged by oxygen or iodine, but very little iodine reacted even after prolonged treatment, and the quantity of ketone regenerated was small.

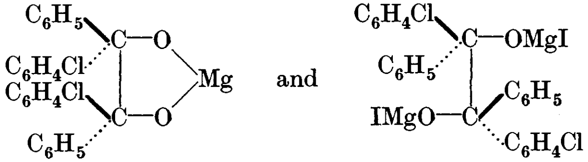
$$2(C_7H_7)_2\underset{\diagdown}{C}{-}OMgI + I_2 = 2(C_7H_7)_2C{=}O + 2MgI_2.$$

The results indicate that the iodomagnesium pinacolate is formed but is extremely unstable. Probably it undergoes intermolecular oxidation and reduction analogous to the reactions so well known in the triarylmethyls and diarylnitrogens.

Cohen and Montagne (*Rec. trav. chim.*, 1919, **38**, 120) obtained a diphenyldi-α-naphthylpinacol of m. p. 158°. The substance now obtained melts at 199° and is possibly the second form, m. p. 220°, of this pinacol, recently described by Bachmann and Shankland (*J. Amer. Chem. Soc.*, 1929, **51**, 306). s-2 : 2′-*Dichlorobenzpinacol* has been obtained of m. p. 164°, differing from the pinacol of m. p. 178° described by Koopal (*Rec. trav. chim.*, 1915, **34**, 115) : the two pinacols can be readily distinguished by their crystalline form. The product of the reaction between ethyl *o*-chlorobenzoate and magnesium phenyl bromide contained both pinacols, that of m. p. 181° being present only in small quantity. Both pinacols were also produced when *o*-chlorobenzophenone was reduced with magnesium and magnesium iodide, but in this case the pinacol of m. p. 181° was present in the larger quantity. Magnesium phenyl bromide transforms the pinacol of m. p. 181° into a bromomagnesium pinacolate which, on hydrolysis, yields chiefly the pinacol of m. p. 164°; the conversion, however, is not complete. The properties of the two pinacols indicate that they are the *meso*- and racemic forms. The transformation of one form into the other is then readily explained if it is assumed that, in the free radicals into which the halogenomagnesium pinacolates dissociate, the groups attached to the unsaturated carbon atom either readily change positions or occupy identical positions (compare Jones and Mason, *J. Amer. Chem. Soc.*, 1927, **49**, 2528; Schlenk and Bergmann, *Annalen*, 1928, **463**, 109). In solution the free radical would then be in equilibrium with both configurations of the halogenomagnesium pinacolate and hydrolysis would lead to the two forms of the pinacol. This explanation was also advanced by Bachmann and Shankland. The position of equilibrium would be expected to depend greatly on the nature of the halogenomagnesium pinacolates. In the present case the substitution of bromine for iodine appears to effect a considerable displacement of this position.

The isolation of two forms of pinacol in some cases may be due to another cause. In the reaction between ethyl *o*-chlorobenzoate and magnesium phenyl bromide the yield of pinacol was 27%, but the amount of magnesium halide present was insufficient to maintain this pinacol as the halogenomagnesium pinacolate, and both (I) and (II) must have been present. (The quantity of magnesium halide present can be calculated approximately from the amount of iodine used to start the Grignard reaction and from the yield of diphenyl.) If like groups, and especially the *o*-chlorophenyl groups, are assumed to repel one another (Böeseken, *Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 371), the stable configurations in each case would be:

(III.)



(IV.)

Because of the presence of free radicals the pinacolates will be able to assume these configurations, hydrolysis of which would yield the racemic pinacol from (III) and the *meso*-pinacol from (IV). It was this hypothesis which led to attempts to isolate *two* forms of the pinacol from the products of the reaction between an ester and a Grignard reagent. The complications encountered have prevented a complete test in this case. Experiments in this direction are being continued.

Diphenyldi-*o*-tolylpinacol has been rearranged to the corresponding pinacolin and the phenyl group has been found to migrate in preference to the *o*-tolyl group. This is in agreement with the behaviour of *o*-halogen-substituted benzpinacols (Koopal, *loc. cit.*). The experiments of Elbs (*J. pr. Chem.*, 1887, **35**, 477) seem to indicate that 2 : 5-dimethylphenyl migrates in preference to the phenyl group.

EXPERIMENTAL.

The yields of pinacol recorded in the table were obtained under the following standard conditions: 0·2 g.-mol. of the Grignard reagent was added during 1¾—2 hours to a well-stirred solution of 0·1 g.-mol. of the ester in ether at 50° in the presence of 0·1 g.-atom of magnesium, in an atmosphere of nitrogen; after being heated for a further hour, the mixture was decomposed with ice and dilute acid.

The experiment with ethyl α-naphthoate and magnesium phenyl bromide described below is typical of the series.

Action of Magnesium Phenyl Bromide on Ethyl α-Naphthoate (10).—The Grignard reagent was prepared from 0·2 g.-mol. of bromobenzene, 0·22 g.-atom of magnesium, 0·1 g. of iodine, and 100 c.c. of ether in accordance with the optimum conditions recommended by Gilman and McCracken (*Rec. trav. chim.*, 1927, **46**, 463). It was added under the conditions described above to 0·1 g.-mol. of ethyl α-naphthoate and 0·1 g.-atom of magnesium in 50 c.c. of ether. The mixture was decomposed with ice and after a while dilute sulphuric acid was slowly run in until the magnesium hydroxide just dissolved, the mixture being shaken vigorously. The filtered ethereal solution was washed with dilute sulphurous acid and water and dried, and the ether removed; fractional crystallisation of the residue from light petroleum produced only diphenyl-α-naphthylcarbinol. From the residual oil, 0·8 g. of diphenyl was isolated by steam distillation. The final residue on fractional crystallisation from light petroleum–ether yielded two fractions (0·88 g.), m. p. 185—190°; subsequent fractions consisted of diphenyl-α-naphthylcarbinol (total yield, 7 g.), which was identified by conversion into 9-phenylnaphthaphenofluorene, m. p. 193—194° (Kovache, *Ann. Chim.*, 1918, **10**, 184).

The two fractions, crystallised once from acetone and light petroleum (b. p. 60—80°) and once from chloroform and alcohol, formed prisms, m. p. 199°. The melt did not crystallise on cooling. The substance was identified as diphenyldi-α-naphthylpinacol by analysis (Found: C, 86·3; H, 5·8. Calc. for $C_{34}H_{26}O_2$: C, 87·5; H, 5·6%), by the dirty purple colour developed with cold concentrated sulphuric acid, and by the green colour produced at first in hot alcoholic potash. Bachmann and Shankland (*loc. cit.*) give m. p. 220°.

Action of Magnesium Phenyl Bromide on Methyl o-*Anisate* (8).—The addition of the Grignard reagent produced at once a white precipitate which gradually formed a hard white mass; no colour developed. 15 G. of diphenyl-*o*-anisylcarbinol, m. p. 128—129°, were obtained. Practically the only by-products were those formed in the preparation of the Grignard reagent.

Action of Magnesium Phenyl Bromide on Ethyl o-*Bromobenzoate* (7).—Addition of the Grignard reagent produced a red-brown colour. The products of decomposition, by treatment with alcohol and then with light petroleum, gave 2·4 g. of a substance, m. p. 140—150°. This, crystallised several times from chloroform and acetone, formed colourless rhombs, m. p. 166°, of *s*-2 : 2′-dibromobenzpinacol (Found: Br, 30·65. Calc. for $C_{26}H_{20}O_2Br_2$: Br, 30·6%). Koopal (*loc. cit.*) gives m. p. 168°.

From the mother-liquors remaining after the isolation of the pinacol, by treatment with dry hydrogen chloride in benzene solution, 1·9 g. of *o*-bromotriphenylchloromethane, m. p. 116—118°, were isolated.

In a second experiment the Grignard reagent was added during 7·5 hours. Only 0·34 g. of the pinacol (1·3%) could be isolated. In addition 2 g. of *o*-bromotriphenylcarbinol, m. p. 101—103·5°, were obtained. Distillation of the residual oils under reduced pressure yielded *o*-bromotriphenylmethane (7·7 g.), m. p. 84—85°, and other products which were not identified.

Action of Magnesium Phenyl Bromide on Ethyl o-*Chlorobenzoate* (6).—A red-brown solution remained after the addition of the Grignard reagent. When the products of decomposition, washed and freed from ether, were poured into alcohol, s-2 : *2′-dichlorobenzpinacol* crystallised at once. Further separations were obtained by evaporation and by the addition of light petroleum (yield, 6·9 g.). An oil (A) remained. The pinacol, recrystallised several times from chloroform and alcohol, gave rhombic crystals, m. p. 164° (decomp.) (Found : Cl, 16·3; M, cryoscopic in benzene, 415, 420. $C_{26}H_{20}O_2Cl_2$ requires Cl, 16·3%; M, 435). It was identified by rearrangement to the pinacolin, m. p. 139·5—140·5°, and by the fleeting blue coloration produced with alcoholic potash.

Reduction of the products of the reaction with alcoholic potash with zinc dust and alcoholic potash yielded *o*-chlorodiphenylcarbinol, m. p. 63°.

Later fractions from the crystallisation of the pinacol, when recrystallised many times, gave a mixture, m. p. 163—169°, in which, under the microscope, rhombic crystals of the pinacol of m. p. 164° and small elongated rectangular plates of the pinacol of m. p. 181° were easily distinguished.

The oil (A), when freed from alcohol and treated with light petroleum, gave 3·3 g. of *o*-chlorotriphenylcarbinol, m. p. 93° after crystallising from acetic acid. The residues, treated with hydrogen chloride in light petroleum–benzene, gave 6·2 g. of *o*-chlorotriphenylchloromethane.

In a second experiment, 0·1 g.-atom of magnesium and 0·1 g.-atom of iodine were warmed in 33 c.c. of ether and 17 c.c. of benzene until the liquid became colourless. The mixture was stirred well and 0·1 g.-mol. of ethyl *o*-chlorobenzoate was added rapidly, followed by the Grignard reagent as in the first experiment. The subsequent procedure was as in that experiment. From the reaction products 1·05 g. of pinacol (4·8%) and 10 g. of the carbinol were isolated. Crystallised twice from chloroform and alcohol, the pinacol melted at 163—164° and consisted only of the low-melting form.

Reduction of o-Chlorobenzophenone.—(1) *With zinc dust and acetic acid.* *o*-Chlorobenzophenone, prepared after the method of Koopal (*loc. cit.*) and crystallised from light petroleum containing a little chloroform, melted at 45·5°.

7·5 G. of zinc dust were added gradually with frequent shaking to a solution of 5 g. of the ketone in 50 c.c. of glacial acetic acid. The mixture was heated for 2 hours at 50°, kept over-night, and then poured into water. The insoluble material was dried, and extracted with chloroform. The extract was concentrated somewhat and alcohol added, 3·7 g. of pinacol, seen under the microscope to consist of long rectangular plates and a much smaller quantity of rhombic crystals, being obtained. The two constituents were isolated in a pure condition by fractional crystallisation from chloroform and alcohol. The pinacol crystallising in rectangular plates is the *s*-2 : 2′-dichlorobenzpinacol of Koopal and when pure melts at 181° (decomp.) (Found : Cl, 16·6; *M*, cryoscopic in benzene, 415, 417. Calc. for $C_{26}H_{20}O_2Cl_2$: Cl, 16·3%; *M*, 435). Koopal gives m. p. 178°, and Cohen, 174—175° (*Rec. trav. chim.*, 1919, **38**, 120). They isolated only the one form. The pinacol crystallising in rhombs melts at 164° and is identical with the low-melting form already described.

In a second experiment the reduction of the ketone with zinc dust and acetic acid was allowed to proceed at room temperatures for 5 days (compare Montagne, *Rec. trav. chim.*, 1907, **26**, 253). The yield of pinacol was slightly improved (4·1 g.) and both forms were present in approximately the same proportion as in the first experiment.

(2) *With magnesium and magnesium iodide.* A mixture of 0·02 g.-atom of magnesium, 0·02 g.-atom of iodine, 13·5 c.c. of ether, and 6·5 c.c. of benzene was refluxed until it became colourless. It was then cooled, the air replaced by nitrogen, 0·02 g.-mol. of *o*-chlorobenzophenone dissolved in 8 c.c. of benzene added, and the whole shaken. After 4 hours, when all the magnesium had dissolved, the resulting red solution was decomposed with ice and acidified with dilute sulphuric acid. The ethereal solution was separated, washed with dilute sulphurous acid and water, and dried. Evaporation of the ethereal solution left an oil from which, by solution in chloroform and addition of alcohol, 2·9 g. of crystalline material were obtained. A small amount of oil remained. From the crystalline material, by fractional crystallisation from chloroform and alcohol, *s*-2 : 2′-dichlorobenzpinacol of m. p. 181° and a new substance (A), m. p. 180—183°, were obtained. They could be readily distinguished, for the substance (A) formed stout prisms with pyramid-like ends, was much more soluble in chloroform, and was not decomposed at its

melting point but resolidified on cooling. In addition a small amount of the pinacol of m. p. 164° was present. The yield of the substance (A) was increased by raising the temperature at which the reduction of the ketone was carried out, much smaller amounts of the pinacols then being obtained.

Action of Magnesium Phenyl Bromide on s-2 : 2′-*Dichlorobenzpinacol* (m. p. 181°).—To 1·6 g. of the pure pinacol and 8 c.c. of dry benzene, in an atmosphere of nitrogen, was added an ethereal solution of magnesium phenyl bromide in excess of that required for the formation of the bromomagnesium pinacolate. The clear purple-red solution obtained was decomposed with ice after 3 days. 0·95 G. of crystalline material was isolated from the reaction products. By fractional crystallisation this was found to consist chiefly of the low-melting form, which was isolated in a state of purity (m. p. 163°). A much smaller amount of the pinacol of high melting point was present, which was not obtained quite free from its isomeride. An experiment in which the solution of the bromomagnesium pinacolate was refluxed for 2 hours and then decomposed yielded the two forms of pinacol in essentially the same proportion and also a small amount of the substance (A).

Action of Magnesium Phenyl Bromide on Ethyl p-*Toluate* (5).—The experimental conditions were those described for case (10). After decomposition with ice the products of the reaction were purified by steam distillation and the residue was fractionally crystallised from light petroleum, 0·65 g. of diphenyldi-*p*-tolylpinacol being obtained, m. p. 162—163° after crystallising twice from chloroform and alcohol. Other products consisted of 8·3 g. of diphenyl-*p*-tolylcarbinol, m. p. 75—77°, and 2 g. of the corresponding chloromethane, m. p. 97—98°.

Preparation of Di-p-*tolyl*-o-*tolylchloromethane*.—A filtered solution of the Grignard reagent prepared from 0·4 g.-mol. of *p*-bromotoluene, 0·5 g.-atom of magnesium, and 200 c.c. of ether was cooled to 0°, and 0·09 g.-mol. of ethyl *o*-toluate added gradually. After a while the mixture was refluxed for 6 hours, cooled, and decomposed in the usual way. The ethereal layer was separated and freed from ether and the residue was steam-distilled to remove di-*p*-tolyl. The oil remaining was dissolved in light petroleum and dried. Passage of dry hydrogen chloride through the solution in presence of a little fused calcium chloride caused the separation of *di*-p-*tolyl*-o-*tolylchloromethane* (13·4 g.) (Found : Cl, 11·5. $C_{22}H_{21}Cl$ requires Cl, 11·0%), which crystallised from light petroleum (b. p. 40—60°) in colourless needles, m. p. 106°.

Action of Magnesium p-*Tolyl Bromide on Ethyl* o-*Toluate* (3).—0·001 G.-mol. of magnesium iodide was added to the ethereal solution containing the ester and magnesium metal. The addition of the

Grignard reagent produced a bright red solution, which was filtered from the excess of magnesium metal and decomposed with ice and dilute sulphuric acid. A white crystalline mass remained, m. p. 162° after being washed with ether. The ethereal solution of the reaction products was evaporated and the residual oil poured into alcohol. Further crops of the same substance were obtained (yield, 11 g.). From the residue 0·8 g. of di-*p*-tolyl and 2 g. of di-*p*-tolyl-*o*-tolylchloromethane were obtained as described above. The product of m. p. 162° was identified as *di*-p-*tolyldi*-o-*tolylpinacol*. Crystallised several times from chloroform and ether, it melted at 174° (decomp.) (Found: C, 85·3; H, 7·3. $C_{30}H_{30}O_2$ requires C, 85·3; H, 7·2%). Hot alcoholic potash decomposed the pinacol, giving the characteristic blue coloration. Heated in air at 145°, the pinacol gave a clear melt in 25 minutes, undergoing no loss in weight. The melt did not crystallise on cooling, but when reduced with zinc dust and alcoholic potash yielded p-*tolyl*-o-*tolylcarbinol*, which crystallised from light petroleum (b. p. 40—60°) in colourless prisms, m. p. 61—61·5° (Found: C, 84·7; H, 7·5; *M*, by Rast's method, 224. $C_{15}H_{16}O$ requires C, 84·9; H, 7·6%; *M*, 212).

Preparation of Di-o-*tolyl Ketone.*—7·6 G. of ethyl *o*-toluate in 10 c.c. of ether were added to a filtered solution of the Grignard reagent from 20 g. of *o*-bromotoluene, 2·4 g. of magnesium, and 60 c.c. of ether. The mixture was refluxed for 2 hours and then decomposed in the usual manner. From the ethereal layer, by steam distillation, after removal of the more volatile products, an oil was obtained which solidified (6·5 g.). After crystallising several times from light petroleum, it melted at 70·5° (yield, 66%). It was identified as di-*o*-tolyl ketone by analysis and by conversion into the oxime, m. p. 103—104·5° (Grignard, Bellet, and Courtot, *Ann. Chim.*, 1919, **12**, 381). 0·47 G. of the ketone, reduced with zinc dust and alcoholic potash for 5 days at 25°, gave 0·36 g. of di-*o*-tolylcarbinol (m. p. 119·5°) identical with that previously described (J., 1927, 908).

Action of Magnesium and Magnesium Iodide on Di-o-*tolyl Ketone.*—The conditions were as described under (2) on p. 1629 (0·038 g.-atom each of magnesium and iodine, 27 c.c. of ether, 13 c.c. of benzene). Soon after the addition of di-*o*-tolyl ketone (4 g., *i.e.*, 0·019 g.-mol., in 8 c.c. of benzene) the liquid became deep purple. After 2 days' shaking, the liquid was filtered and decomposed, the ethereal solution dried, and the solvents removed in a vacuum. From the residue, by treatment with light petroleum and finally by steam distillation, 0·95 g. of di-*o*-tolylcarbinol was obtained, m. p. 118—119·5° after crystallising from alcohol; it was identified by means of a mixed melting point.

A second experiment, in which 0·019 g.-mol. of the ketone was treated with 0·019 g.-atom each of magnesium and of iodine until all the magnesium had dissolved (5 hours), yielded 1·0 g. of the carbinol and, by steam distillation, 0·1 g. of di-*o*-tolyl ketone (m. p. 66—68°). A residual brown oil was not identified.

*Rearrangement of Diphenyldi-*o*-tolylpinacol.*—A mixture of 1·33 g. of the pinacol, 6·5 g. of glacial acetic acid, and 0·01 g. of iodine was refluxed for 6 hours (compare Gomberg and Bachmann, *loc. cit.*); it was then poured into water and the acetic acid was neutralised. The product, extracted, washed, and dried in ether, crystallised from alcohol, containing a little ether, in colourless prisms (1 g.), m. p. after recrystallisation 93·5—94·5°, containing alcohol of crystallisation, which was expelled at 80° (Found : $C_2H_5{\cdot}OH$, 11·2. $C_{28}H_{24}O,C_2H_5{\cdot}OH$ requires $C_2H_5{\cdot}OH$, 10·9%). The removal of the alcohol did not alter the melting point (Found : C, 89·05; H, 6·8. $C_{28}H_{24}O$ requires C, 89·3; H, 6·4%). The *substance* appears to be a diphenyldi-*o*-tolylpinacolin.

In a second experiment, 4 g. of the pinacol, 20 c.c. of glacial acetic acid, and 0·04 g. of iodine were refluxed for 12 hours. The crystalline material obtained when the product was poured into water (yield, 3·6 g.) melted at 129° after recrystallisation from alcohol and ether (Found : C, 89·15; H, 6·6; *M*, by Rast's method, 356. $C_{28}H_{24}O$ requires C, 89·3; H, 6·4%; *M*, 376). It was proved to be o-*toluoyldiphenyl-*o*-tolylmethane* by refluxing it with 10% alcoholic potash for 60 hours, whereby it was completely converted into *o*-toluic acid (m. p. 103°) and diphenyl-*o*-tolylmethane (m. p. 82—83°). After the pinacolin of m. p. 93·5—94·5° had been kept in a tube for a month it melted at 131°. A mixed melting-point determination established its identity with the pinacolin of m. p. 129°.

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