LXXV.—*The Synthesis of* meso-*Alkyl and* meso-*Aryl Anthracene Derivatives. Part I.*

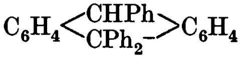
By Edward de Barry Barnett, James Wilfred Cook, and Ivor Gray Nixon.

The interest which attaches to the three-carbon transannular tautomerism exhibited by certain *meso*-alkyl anthracenes (Barnett, Cook, Matthews, *Ber.*, 1926, **59**, 1429, 2863) has rendered it desirable to review the methods available for the preparation of these compounds. Such methods fall roughly into two classes according as the *meso*-substituent is attached prior or subsequent to the closing of the central ring of the anthracene complex. The present communication deals with the former class of reaction.

(*A*). By treating methyl triphenylmethane-*o*-carboxylate with magnesium phenyl bromide, Haller and Guyot (*Bull. Soc. chim.*, 1904, **31**, 979) obtained a product which, when treated with hydrogen chloride in glacial acetic acid, passed into 9 : 9 : 10-triphenyl-9 : 10-dihydroanthracene (II).

(I.)

$C_6H_4{<}\begin{matrix}CHPh_2\\ CPh_2\cdot OMe\end{matrix}$


$C_6H_4{<}\begin{matrix}CHPh\\ CPh_2\end{matrix}{>}C_6H_4$
(II.)

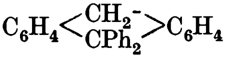
They described their product as a methyl ether (I), but offered no evidence of the presence of the methoxyl group other than ultimate analysis, which in this case is totally insufficient to differentiate between the free hydroxy-compound and its methyl ether (Found : C, 89·7; H, 6·2. $C_{32}H_{26}O$ requires C, 90·1; H, 6·1. $C_{33}H_{28}O$ requires C, 90·0; H, 6·4%), and it has now been found that the compound is, as would be expected, the free hydroxy-compound, since identical products are obtained from the methyl and the ethyl ester.

With diphenylmethane-*o*-carboxylic acid (*o*-benzylbenzoic acid), which is easily accessible, a synthesis similar to the above might be expected to take place. To a limited extent this is true, as the esters of this acid, on treatment with magnesium phenyl bromide, yield an oily product (undoubtedly III) which is easily and almost quantitatively dehydrated to 9 : 9-diphenyl-9 : 10-dihydroanthracene (IV). Attempts to extend this synthesis by replacing the magnesium phenyl bromide by magnesium ethyl, *iso*propyl or naphthyl bromide or by magnesium benzyl chloride were not successful, as no crystalline substance could be obtained from the viscid products of the reaction.

The hydroxy-compound (III) is not the sole product of the action of magnesium phenyl bromide on the esters of *o*-benzylbenzoic acid, a second product being formed at the same time to which formula (V) is given, this formula being based on analysis and molecular-weight determinations, the oxidation of the substance to *o*-dibenzoylbenzene, and on the fact that its formation is independent of the alcoholic radical (methyl, ethyl, or phenyl) in the ester.

(III.)

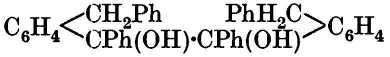
$C_6H_4{<}\genfrac{}{}{0pt}{}{CH_2Ph}{CPh_2\cdot OH}$



$C_6H_4{<}\genfrac{}{}{0pt}{}{CH_2\text{-}}{CPh_2}{>}C_6H_4$

(IV.)

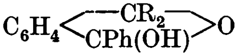
(V.)



$C_6H_4{<}\genfrac{}{}{0pt}{}{CH_2Ph \qquad PhH_2C}{CPh(OH)\cdot CPh(OH)}{>}C_6H_4$

This pinacol obviously originates by the reduction of the ketone (*o*-benzylbenzophenone) which must be the first product of the action of magnesium phenyl bromide on the esters of *o*-benzylbenzoic acid, and, although the reducing action of Grignard solutions is well known, this appears to be the first case recorded in which they have been found to cause pinacol condensation.

(*B*). By treating diphenylphthalide with magnesium phenyl bromide, Guyot and Catel (*Bull. Soc. chim.*, 1906, **35**, 551, 562) obtained a compound which they described as a hydroxyphthalan (VI, R = Ph), tetraphenylphthalan (VIII) being obtained by employing a large excess of the Grignard solution (Schlenk and Brauns, *Ber.*, 1915, **48**, 727).

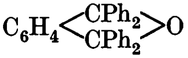


$C_6H_4{<}\genfrac{}{}{0pt}{}{CR_2}{CPh(OH)}{>}O$

(VI.)

$C_6H_4{<}\genfrac{}{}{0pt}{}{CR_2\cdot OH}{COPh}$

(VII.)



$C_6H_4{<}\genfrac{}{}{0pt}{}{CPh_2}{CPh_2}{>}O$

(VIII.)

Guyot and Catel's compound cannot be dehydrated to give diphenylanthrone by treatment either with hydrogen chloride in glacial acetic acid or with concentrated sulphuric acid, but it does give diphenylanthrone on heating to 300°.

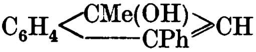
Similar compounds (R = Me or Et) are obtained by the action of magnesium phenyl bromide on dimethyl- and diethyl-phthalide; these, however, on heating do not pass into the corresponding dialkylanthrones, but lose water in a different direction to give unsaturated substances which are probably represented by formulæ (IX) and (X), although the possibility that they may be indene derivatives (*e.g.*, XI) is not excluded.

$C_6H_4{<}\genfrac{}{}{0pt}{}{CMe\colon CH_2}{COPh}$

(IX.)

$C_6H_4{<}\genfrac{}{}{0pt}{}{CEt\colon CHMe}{COPh}$

(X.)



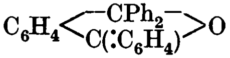
$C_6H_4{<}\genfrac{}{}{0pt}{}{CMe(OH)}{CPh}{\geqslant}CH$

(XI.)

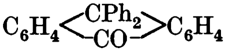
No proof of the hydroxyphthalan structure (VI) is at present available, and the hydroxy-ketonic structure (VII) is suggested by Beilstein (" Handbuch," 4th Ed., Vol. VIII, p. 223). It is possible that the two formulæ may represent phases of an isodynamic change and it is proposed to investigate this point at a later date and at the same time to examine the dehydration products more closely. In the meantime the hydroxyphthalan structure is retained in the following, although the dehydration which takes place on heating is better explained by formula (VII).

(*C*). Arylhydroxyphthalans (VI or VII) have been obtained from the esters of phthalic acid by Guyot and Catel (*loc. cit.*) and by Weiss and Heidrich (*Monatsh.*, 1924, **45**, 210). Shibata (J., 1909, **95**, 1449) treated diethyl phthalate with magnesium phenyl bromide and after purifying his product by distillation under reduced pressure (b. p. 280—295°/8 mm.) isolated a colourless, crystalline substance which he described as diphenylphenylenephthalan (XII), and he based certain conclusions concerning the structure of the benzene ring on its formation. The formula given by Shibata appeared in the highest degree improbable and repetition of his experiments has proved that this supposed phenylene compound is really diphenylanthrone (XIII), the formation of which is undoubtedly due to dehydration of the hydroxyphthalan (VI or VII) first formed.

(XII.)



$$C_6H_4{<}\genfrac{}{}{0pt}{}{-CPh_2-}{C(:C_6H_4)}{>}O$$



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CPh_2}{CO}{>}C_6H_4$$

(XIII.)

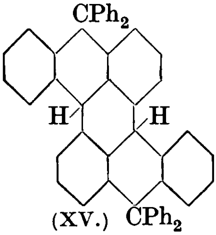
Shibata's conclusions as regards the structure of the benzene ring are therefore valueless.

The action of magnesium phenyl bromide on *o*-dibenzoylbenzene also leads to the hydroxyphthalan (VI or VII) and from this to diphenylanthrone.

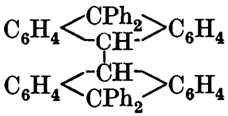
(*D*). Liebermann and Lindebaum (*Ber.*, 1905, **38**, 1804), by heating 9-bromo-10 : 10-diphenyl-9 : 10-dihydroanthracene (XIV) alone or with naphthalene, obtained a product which they described as tetraphenylheptacyclene and to which they gave formula (XV), without, however, bringing forward any experimental evidence in

$$C_6H_4{<}\genfrac{}{}{0pt}{}{CPh_2}{CHBr}{>}C_6H_4$$

(XIV.)



(XV.)



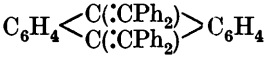
$$\begin{matrix} C_6H_4{<}\genfrac{}{}{0pt}{}{CPh_2}{CH}{>}C_6H_4 \\ | \\ C_6H_4{<}\genfrac{}{}{0pt}{}{CH}{CPh_2}{>}C_6H_4 \end{matrix}$$

(XVI.)

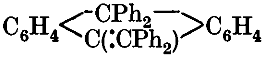
its favour. The formation of a compound of this structure by the above reaction is not very probable, and an exactly similar, insoluble and highly stable substance is formed when diphenylanthrone is submitted to the pinacol reduction with zinc and hydrochloric acid in acetic acid solution, and also when 9 : 9-diphenyl-9 : 10-dihydroanthracene is heated to 250° in oxygen or is heated with benzal chloride or benzophenone chloride. Owing to the extreme insolubility of these substances and to the fact that they do not melt, it is impossible to state with certainty that they are identical, but it seems extremely probable that they are identical with the so-called tetraphenylheptacyclene and have formula (XVI). The impossibility of purifying them by recrystallisation renders it difficult to be certain that the molecule does not contain two hydrogen atoms less than the number required by the formula given ($C_{52}H_{38}$ requires C, 94·3; H, 5·7. $C_{52}H_{36}$ requires C, 94·6; H, 5·45%).

(*E*). Padova (*Ann. Chim.*, 1910, **19**, 400) found that dihydroanthracene condensed with benzophenone chloride to give bisdiphenylmethylenedihydroanthracene (XVII), the compound obtained by Staudinger (*Ber.*, 1908, **41**, 1362) by the action of diphenylketen on anthraquinone. 9 : 9-Diphenyldihydroanthracene behaves in the same way with benzophenone chloride and gives 9 : 9-diphenyl-10 : 10-diphenylmethylene-9 : 10-dihydroanthracene (XVIII), in which it has not been found possible to reduce the double bond.

(XVII.)



$$C_6H_4{<}\genfrac{}{}{0pt}{}{C(:CPh_2)}{C(:CPh_2)}{>}C_6H_4$$



$$C_6H_4{<}\genfrac{}{}{0pt}{}{\text{-}CPh_2\text{—}}{C(:CPh_2)}{>}C_6H_4$$

(XVIII.)

Padova (*loc. cit.*) claimed to have reduced his compound by means of sodium and boiling benzyl alcohol, but we have not been able to repeat this.

EXPERIMENTAL.

*ωω-Diphenyl-*o*-tolyldiphenylcarbinol.*—The methyl and *ethyl* esters of triphenylmethane-*o*-carboxylic acid were prepared in the usual way by esterification with the alcohol and hydrochloric acid. The former (m. p. 98°) has been prepared by Haller and Guyot (*loc. cit.*), by a different method. The latter, after being twice recrystallised from alcohol, formed a colourless, crystalline powder, m. p. 69° (Found: C, 83·2; H, 6·6. $C_{22}H_{20}O_2$ requires C, 83·5; H, 6·3%).

In each case, an ethereal solution of the ester was added to an ethereal solution of magnesium phenyl bromide (2 mols.) with cooling in a freezing mixture, and the whole was boiled for 4 hours and then poured on to a mixture of ice and solid ammonium chloride. The solid which separated and that which was obtained by distilling off the ether from the ethereal solution were identical and in each case, after recrystallisation from toluene–light petroleum, melted at 218°, and a mixture of the specimens made from each ester showed no depression of melting point.

o-*Benzylbenzoic Acid.*—The statement by Ullmann (*Annalen*, 1896, **291**, 23) that *o*-benzoylbenzoic acid cannot be reduced beyond the phthalide stage by means of ammonia and zinc dust is incorrect, the following method having been found to be the most convenient one for the preparation of *o*-benzylbenzoic acid. Technical *o*-benzoylbenzoic acid (150 g.) was dissolved in 1 l. of concentrated ammonia (*d* 0·880) diluted with 300 c.c. of water, and a few c.c. of copper sulphate solution were added, followed by 300 g. of zinc dust in several portions with cooling. The whole was heated on the water-bath until a filtered sample, when acidified, gave a precipitate which was completely soluble in sodium carbonate (about 2 days). The filtrate and washings were then acidified with hydrochloric acid, and the precipitate was dissolved in sodium carbonate solution, reprecipitated with hydrochloric acid, and finally recrystallised from aqueous acetic acid. The yield was 117 g. of snow-white material, m. p. 118°.

Gresley (*Annalen*, 1886, **234**, 234) states that *o*-benzylbenzoic acid on treatment with sulphuric acid does not give anthrone but is oxidised to anthraquinone. This is erroneous, for when a solution of benzylbenzoic acid in concentrated sulphuric acid is kept for 2 hours at the ordinary temperature an almost quantitative yield of anthrone is obtained, and indeed this is a convenient method of preparing anthrone.

The *methyl* and *ethyl* esters were prepared in the usual way by means of the alcohol and hydrochloric acid and formed oils, b. p. 320° and 325°, respectively. The *phenyl* ester was obtained from the acid, phenol, and thionyl chloride in pyridine solution (Barnett and Nixon, *Chem. News*, 1924, **129**, 190) and was used in the crude state.

9 : 9-*Diphenyl*-9 : 10-*dihydroanthracene* (IV).—To an ethereal solution of magnesium phenyl bromide prepared from 8 g. of magnesium and 48 g. of bromobenzene and cooled in a freezing mixture, an ethereal solution of 32 g. of ethyl *o*-benzylbenzoate was added slowly. After boiling for an hour, or being kept at the ordinary temperature over-night, the whole was poured into ice and dilute hydrochloric acid, and the solid (15 g.; see below) collected. After washing and drying, the ether was removed from the ethereal solution. The viscid residue, which refused to crystallise, was heated for an hour on the water-bath with a glacial acetic acid solution of hydrogen chloride. The resulting diphenyldihydroanthracene (18 g.), m. p. 200°, was quantitatively oxidised to diphenylanthrone by chromic acid in glacial acetic acid.

Similar results were obtained when the methyl and the phenyl ester were used in place of the ethyl ester.

s-oo′-*Dibenzylbenzpinacol* (V).—The solid by-product insoluble in ether obtained as described above, after recrystallisation from benzene–light petroleum, chloroform–light petroleum, and methyl ethyl ketone, formed a colourless, crystalline powder, m. p. 175°. Its hot benzene solution showed a strong green fluorescence which vanished on cooling (Found: C, 87·8; H, 6·5; *M*, in ethylene dibromide, 540. $C_{40}H_{34}O_2$ requires C, 87·9; H, 6·2%; *M*, 546).

When 1 g. of the above pinacol in 20 c.c. of boiling glacial acetic acid was treated slowly with a concentrated aqueous solution of 3 g. of chromic acid, oxidation took place rapidly and, on cooling and dilution, a solid was obtained which, after recrystallisation, was identified as *o*-dibenzoylbenzene by direct comparison with an authentic sample.

Attempts to convert the pinacol into a dianthranyl derivative, an acetate, and a benzoate gave oily products only. The pinacol was not regenerated from these oils on boiling with alcoholic alkali, but they were converted into *o*-dibenzoylbenzene by oxidation with chromic acid. It is therefore likely that loss of water with formation of an α-pinacolin had taken place, but owing to the uninviting nature of the products the matter was not further investigated.

Dimethylphenylhydroxyphthalan (VI or VII; R = Me).—An ethereal solution of 8 g. of dimethylphthalide was added with water-cooling to an ethereal solution of magnesium phenyl bromide prepared from 2 g. of magnesium and 12 g. of bromobenzene. After boiling for 2 hours, the whole was poured on to ice and hydrochloric acid, and the ethereal layer was washed with sodium hydroxide solution and with water, dried over sodium sulphate, concentrated, and diluted with light petroleum. The m. p., 118°, of the resulting crystals (9·7 g.) was not altered by further recrystallisation from benzene–light petroleum (Found: C, 80·0; H, 6·8. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%).

o-iso*Propenylbenzophenone* (IX).—On distillation at atmospheric pressure, the above phthalan (10 g.) gave water and a product, b. p. 305°, which was dried in ethereal solution and distilled under reduced pressure; the yellow oil, b. p. 208—209°/45 mm., obtained became solid on cooling and after recrystallisation from aqueous alcohol formed colourless needles, m. p. 44° (Found: C, 86·2; H, 6·4. $C_{16}H_{14}O$ requires C, 86·5; H, 6·3%).

o-*iso*Propenylbenzophenone at once decolorised a solution of bromine in carbon tetrachloride. After 1 g. in 15 c.c. of glacial acetic acid had been boiled for an hour with addition of a concentrated aqueous solution of 5 g. of chromic acid, a solid was obtained, on cooling and dilution, which was reprecipitated from its solution in aqueous sodium carbonate and then identified as *o*-benzoylbenzoic acid by direct comparison with an authentic sample.

Diethylphenylhydroxyphthalan (VI or VII; R = Et) was prepared from diethylphthalide and magnesium phenyl bromide in exactly the same way as the corresponding dimethyl derivative described above and formed colourless, glistening crystals, m. p. 94—95° (Found: C, 80·2; H, 7·5. $C_{18}H_{20}O_2$ requires C, 80·5; H, 7·5%). On heating, it lost water and passed into an unsaturated oil which was not further examined.

Attempts to prepare the dibenzyl analogue from dibenzylphthalide were not successful, most of the dibenzylphthalide being recovered unchanged.

Action of Magnesium Phenyl Bromide on Ethyl Phthalate.—The experiment was carried out essentially as described by Shibata (*loc. cit.*), and the product identified as diphenylanthrone by direct comparison with an authentic sample.

Action of Magnesium Phenyl Bromide on o-*Dibenzoylbenzene.*—Finely powdered *o*-dibenzoylbenzene (14·5 g.) was added with cooling to an ethereal solution of magnesium phenyl bromide prepared from 1·25 g. of magnesium and 8 g. of bromobenzene. After boiling for 6 hours, the whole was poured into ice and dilute sulphuric acid, unchanged *o*-dibenzoylbenzene (2·5 g.) removed by filtration, and the ether distilled off. The residue, after purification by distillation in steam and drying in ethereal solution, was heated at 300° for ½ hour, and after recrystallisation was identified as diphenylanthrone by direct comparison with an authentic sample.

In both the above preparations of diphenylanthrone it is probable that triphenylhydroxyphthalan (VI or VII; R = Ph) intervenes, as it was found that this substance passed into diphenylanthrone when heated at 300° for ½ hour. Dehydration to diphenylanthrone, however, could not be effected either with concentrated sulphuric acid or with hydrogen chloride in acetic acid.

Tetraphenyltetrahydrodianthranyl (XVI).—(*a*) Diphenylanthrone (4·4 g.) and 2·5 g. of zinc dust were boiled with 50 c.c. of glacial acetic acid, and 5 c.c. of fuming hydrochloric acid were added slowly. After 5 hours, the solid was collected, extracted with hydrochloric acid and with boiling glacial acetic acid, and then recrystallised from a very large volume of boiling nitrobenzene, in which, however, it was almost insoluble. The resulting cream-coloured powder did not melt at 320° (Found: C, 93·9; H, 5·75. $C_{52}H_{38}$ requires C, 94·3; H, 5·7%).

(*b*) Diphenyldihydroanthracene was heated for 2 hours in a current of oxygen at 250°, and the product repeatedly extracted with boiling xylene to remove impurities. After being washed with ether and dried, it formed a colourless, crystalline powder which did not melt at 340° (Found: C, 94·3; H, 5·9%).

(*c*) An insoluble product similar to the above was obtained when diphenyldihydroanthracene was heated at 250° with benzal chloride.

9 : 9-*Diphenyl*-10 : 10-*diphenylmethylene*-9 : 10-*dihydroanthracene* (XVIII).—9 : 9-Diphenyl-9 : 10-dihydroanthracene (6·6 g.) and benzophenone chloride (5 g.) were heated for 2 hours at 250°, and coloured resinous by-products removed by washing with ether. The residual solid (7·8 g.) was dissolved in boiling xylene, and a small amount of an insoluble substance (probably tetraphenyltetrahydrodianthranyl) removed by filtration. On cooling, a colourless, crystalline powder separated which, after further recrystallisation, melted at 286° (Found: C, 94·0; H, 5·8. $C_{39}H_{28}$ requires C, 94·4; H, 5·6%).

The above compound was recovered unchanged after attempts to reduce it with zinc and hydrochloric acid in boiling glacial acetic acid, with sodium in boiling amyl and benzyl alcohols, and with hydriodic acid and red phosphorus at 180° for 7 hours.

10-*Chloro*-9 : 9 : 10-*triphenyl*-9 : 10-*dihydroanthracene*.—Five g. of triphenyldihydroanthranol (m. p. 204°, prepared from diphenylanthrone and magnesium phenyl bromide as described by Haller and Guyot, *Compt. rend.*, 1904, **139**, 9, but without the use of benzene as a solvent) were dissolved in 25 c.c. of benzene, and dry hydrogen chloride passed through the boiling solution for 20 minutes. On cooling and addition of ether, a solid was obtained which, after recrystallisation from benzene–ether, formed a colourless powder, m. p. 193—194°. It contained solvent of crystallisation which it lost at 120° (Found: Cl, 8·0. $C_{32}H_{23}Cl$ requires Cl, 8·0%). This chloro-compound, when boiled in benzene solution with copper powder in an atmosphere of carbon dioxide, gave a yellow solution which became more deeply coloured on heating. This solution probably contained a free radical, but further investigation has been postponed pending the publication of the work of another investigator.

9 : 9 : 10-*Triphenyl*-9 : 10-*dihydroanthracene* (II).—The preparation of this compound by the reduction of triphenyldihydroanthranol with zinc dust and acetic acid as described in the literature gave poor results, and it was found much better to reduce 15 g. of triphenyldihydroanthranol in 150 c.c. of boiling amyl alcohol by the addition of 7·5 g. of sodium. The solid which separated when the hot liquid was poured into water was washed with alcohol

and, after recrystallisation from benzene–alcohol (yield, 12 g.), melted at 230° (the m. p. given in the literature is 220°).

9 : 10-*Diphenyl*-9 : 10-*dihydroanthracene* was obtained most conveniently by reducing 1 g. of 9 : 10-diphenylanthracene in 25 c.c. of boiling amyl alcohol by the addition of 1 g. of sodium. The solution at first became yellow, but the yellow colour subsequently vanished with the fluorescence. The mixture was poured into water, the amyl alcohol removed with steam, and the product recrystallised from benzene–light petroleum.

Action of Aluminium Chloride on 9 : 9-*Diphenyl*-9 : 10-*dihydroanthracene.*—Diphenyldihydroanthracene (5 g.) and aluminium chloride (10 g.) were boiled for 6 hours with 50 c.c. of carbon disulphide. After decomposition with dilute hydrochloric acid, the carbon disulphide solution was washed with water, the solvent removed by distillation, and the product recrystallised from acetic acid and from alcohol. It then melted at 155—157°, alone or when mixed with an authentic sample of 9-phenylanthracene.

By the action of aluminium chloride on 9 : 10-diphenyl-9 : 10-dihydroanthracene, a product was obtained, m. p. 215—220°, which appeared to consist chiefly of 9 : 10-diphenylanthracene, since it did not depress the melting point of this substance; repeated recrystallisation, however, failed to raise the melting point.

The action of aluminium chloride on 9 : 9 : 10-triphenyl-9 : 10-dihydroanthracene in the cold led only to the recovery of the unchanged material, although the fluorescence of the solution and the low melting point of the crude recovered material indicated that re-establishment of the " bridge " had taken place to a slight extent. When the experiment was carried out in boiling carbon disulphide solution, only resinous products were obtained.

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