## CCXXIV.—*The Synthesis of* meso-*Alkyl and* meso-*Aryl Anthracene Derivatives.   Part II.*

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THE action of Grignard solutions upon anthraquinone, 2-methyl-anthraquinone, and alizarin dimethyl ether has been studied by Haller and Guyot (*Bull. Soc. chim.*, 1904, **31**, 797), Guyot and Staehling (*ibid.*, 1905, **33**, 1104), Haller and Comptesse (*Compt. rend.*, 1910, **150**, 1290), Guyot and Vallette (*Ann. Chim.*, 1911, **23**, 363), Padova (*ibid.*, 1910, **19**, 353), Kovaché (*ibid.*, 1918, **10**, 226), Sirker (*J.*, 1915, **107**, 1242), Clarke and Carleton (*Ber.*, 1908, **41**, 935; *J. Amer. Chem. Soc.*, 1911, **33**, 1966), and Ingold and Marshall (*J.*, 1926, 3080) and has been found to lead to the alkyl- or aryl-hydroxyanthrone (I) or the dialkyl- or diaryl-dihydroanthraquinol (II), the last class of compound being by far the most readily accessible.

<p style="text-align:center">(I.)   R·C·OH / CO   (II.)   R·C·OH / R·C·OH   C:X / C:X   (III.)</p>
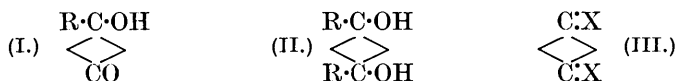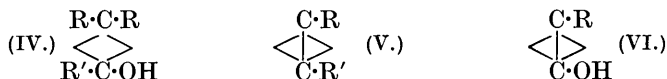
These last are stable towards alkaline reducing agents, although very easily reduced to the anthracene derivatives in acid solution, but when R is an alkyl group there is usually a marked tendency for loss of water to take place with the production of an alkylideneanthracene (III) or a polymerisation product of this. The yields of diol (II) recorded in different experiments are very varied. For example, by the action of magnesium phenyl bromide on anthraquinone, Haller and Guyot obtained only a 10% yield of the diol, Ingold and Marshall a 34% yield, and Kovaché an 80% yield. It has now been found that one of the chief reasons for the poor yields frequently obtained lies in the reducing action of the Grignard solution, which leads to the partial reduction of the anthraquinone to an anthraquinol :

<p style="text-align:center">CO / CO   + 2ArMgBr =   C·OMgBr / C·OMgBr   + Ar·Ar</p>
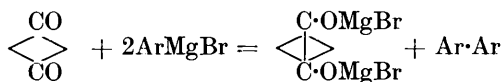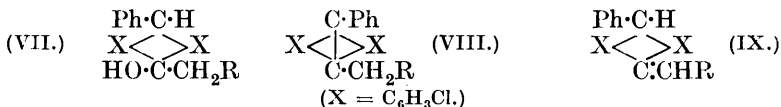
a reaction which is somewhat analogous to a pinacol condensation, but which takes place in the complete absence of metallic magnesium (compare Boyd and Hatt, this vol., p. 898). Occasionally the reduction proceeds further and a considerable quantity of the diarylanthracene may be formed.

The action of Grignard solutions on anthrones has been studied by Haller and Guyot (*Bull. Soc. chim.*, 1904, **31**, 797), Guyot and Staehling (*ibid.*, 1905, **33**, 1104, 1144), Jüngermann (*Ber.*, 1905, **38**, 2868), Krollpfeiffer and Branscheid (*ibid.*, 1923, **56**, 1617), Sieglitz and Marx (*ibid.*, 1923, **56**, 1619), Kehrmann, Monnier, and Ramm (*ibid.*, 1923, **56**, 169), Barnett and Matthews (*ibid.*, 1926, **59**, 1429), and Barnett, Cook, and Matthews (*ibid.*, 1926, **59**, 2863) and has been found to lead to a dihydroanthranol (IV), from which (when R = H) loss of water takes place extremely easily (for example, by treatment with an acid) with the formation of an alkyl- or aryl-anthracene (V).

$$\text{(IV.)} \quad \begin{matrix} R \cdot C \cdot R \\ \diamondsuit \\ R' \cdot C \cdot OH \end{matrix} \qquad \begin{matrix} C \cdot R \\ \diamondsuit \\ C \cdot R' \end{matrix} \text{ (V.)} \qquad \begin{matrix} C \cdot R \\ \diamondsuit \\ C \cdot OH \end{matrix} \text{ (VI.)}$$
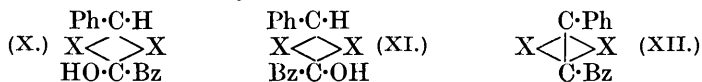
When neither R group represents a hydrogen atom the yields of the dihydroanthranol are excellent, although in this case the subsequent loss of water is impossible, but when one of these groups is a hydrogen atom the Grignard solution brings about considerable conversion of the anthrone into the enolic anthranol (VI) and poorer yields of the dihydroanthranol are obtained. The reaction is also complicated in some cases by reduction taking place which is probably due, at least in part, to loss of an alcohol from the dihydroanthranol first formed (compare Branscheid, *Dissert.*, Marburg, 1923). The method is, nevertheless, an extremely valuable one for the synthesis of both *meso*-alkyl- and *meso*-aryl-anthracenes, although of less general application than might be expected.

The action of magnesium alkyl halides on 1 : 5-dichloro-9-phenyl-anthrone gave oily products (probably VII) from which in some cases yellow and fluorescent (VIII) and/or colourless and non-fluorescent (IX) isomeric substances were obtained.

$$\text{(VII.)} \quad \begin{matrix} Ph \cdot C \cdot H \\ X \diamondsuit X \\ HO \cdot C \cdot CH_2R \end{matrix} \qquad \begin{matrix} C \cdot Ph \\ X \diamondsuit X \\ C \cdot CH_2R \end{matrix} \text{ (VIII.)} \qquad \begin{matrix} Ph \cdot C \cdot H \\ X \diamondsuit X \\ C{:}CHR \end{matrix} \text{ (IX.)}$$
$$(X = C_6H_3Cl.)$$

The action of magnesium benzyl chloride on 1 : 5-dichloro-9-phenylanthrone yielded a dihydroanthranol to which the *trans*-configuration is assigned (X), since it could not be converted into phenylbenzyldichloroanthracene (XII), all attempts at dehydration

leading either to the isolation of the unchanged material or to the production of indefinite substances from which no pure product could be isolated. A less amount of the *cis*-dihydroanthranol (XI) must have been formed simultaneously, as the liquors from the *trans*-isomeride gave, on evaporation, an oil from which phenyl-benzyldichloroanthracene (XII) was easily obtained as a yellow, fluorescent substance by treatment with acids :

$$\text{(X.)} \quad \begin{matrix} \text{Ph·C·H} \\ \text{X}{<}{>}\text{X} \\ \text{HO·C·Bz} \end{matrix} \qquad \begin{matrix} \text{Ph·C·H} \\ \text{X}{<}{>}\text{X} \\ \text{Bz·C·OH} \end{matrix} \text{ (XI.)} \qquad \begin{matrix} \text{C·Ph} \\ \text{X}{<}|{>}\text{X} \\ \text{C·Bz} \end{matrix} \text{ (XII.)}$$

The fact that phenyldichloroanthrone can yield alkylidene compounds whereas phenylanthrone yields only the anthracene derivatives is in harmony with previous observations on the stabilising influence of α-chlorine atoms on the derivatives of 9 : 10-dihydroanthracene, and the inter-conversion of the alkylidene compounds (IX) and the anthracene derivatives (VIII) would supply definite proof of the theory of transannular tautomerism (Barnett, Cook, and Matthews, *loc. cit.*). To this end a detailed examination of the products described in the present communication is now in progress.

Ingold and Marshall (*loc. cit.*) have shown that the 9 : 10-diaryl-anthracenes undergo a reversible deepening in colour when heated with an inert solvent of high boiling point and have attributed this to dissociation of the " bridge " bond leaving the *meso*-carbon atoms in the tervalent state. Liebermann, Glawe, and Lindenbaum (*Ber.*, 1904, **37**, 3337) and Schlenk (*Annalen*, 1912, **394**, 191) have previously brought forward evidence of the existence of anthracene derivatives in which one of the *meso*-carbon atoms is tervalent, although the latter observer was unable to detect dissociation of 9 : 10-diphenylanthracene. The present authors have confirmed qualitatively Ingold and Marshall's statements as regards the reversible deepening in colour of the diarylanthracenes in mesitylene solution, and have found that not only the diarylanthracenes mentioned in the sequel, but also the 9-phenyl-10-alkylanthracenes exhibit the same phenomenon. A similar remark applies to 9-phenylanthracene, although in this case the effect is so slight as to be barely perceptible. The colourless products to which the alkylidene formula (IX) has been attributed in the foregoing do not become coloured when their solutions in mesitylene are boiled, and this is regarded as additional evidence in favour of the structure assigned to them.

Ingold and Marshall assume, by analogy with the hexa-aryl-ethanes, that the formation of disodio- and dipotassio-compounds of the diarylanthracenes indicates the existence of a dissociable " bridge " bond. This argument is inadmissible, as anthracene

itself gives similar compounds (Schlenk, Appenrodt, Michael, and Thal, *Ber.*, 1914, **47**, 473) and, indeed, the formation of these compounds is merely a further example of the resemblance of the " bridge " to an ethylenic bond.

In any case, the dissociation of the diaryl- and arylalkyl-anthracenes is just as much in harmony with the orthoquinonoid formula as with the " bridge " formula and there appears to be no method of differentiating between these two structures. Arguments based on physical properties such as refractivity (compare Auwers, *Ber.*, 1920, **53**, 941) are fictitious, since the " bridge," if it does exist, does not behave like an ordinary single bond, although represented as such. In all its chemical properties it exactly resembles an ethylenic bond and in calculating a physical constant it should be treated as a double bond. If this is done, the " bridge " and the orthoquinonoid structures represent each a system containing seven double bonds and are therefore indistinguishable. The chief advantages of the " bridge " formula are that it represents reactions of transannular addition and loss somewhat more clearly than the orthoquinonoid formula does, and it does not predict the existence of two α- or two β-monosubstitution products which would be expected from the orthoquinoid structure in the absence of a conception of dynamic equilibrium. For these reasons, it is used in this communication and is regarded as the best symbolical representation of the anthracene molecule whether the " bridge " bond has any real existence or not.

EXPERIMENTAL.

9 : 10-*Diphenyl*-9 : 10-*dihydroanthraquinol* was prepared from anthraquinone and magnesium phenyl bromide in 50% yield without using the special precautions recommended by Kovaché. The pure product melted at 260—263° (Haller and Guyot give 247° and Ingold and Marshall 252—254°). To prove the formation of anthraquinol, the crude Grignard product was poured on ice and ammonium chloride, the ether removed by distillation in steam, and the resulting solid extracted with boiling dilute sodium hydroxide solution, all these operations being performed in an inert atmosphere. When air was blown through the deep red alkaline extract, anthraquinone was deposited, and after recrystallisation it was identified by the method of mixed melting points.

In another experiment in which the crude diol was recrystallised from xylene, 9 : 10-diphenylanthracene was isolated from the liquors and identified by direct comparison with an authentic sample.

9 : 10-Di-*p*-anisyl-9 : 10-dihydroanthraquinol * was prepared by

* This compound was previously prepared by Haller and Comptesse (*loc. cit.*), who also reduced it to dianisylanthracene.

Ingold and Marshall's method (*loc. cit.*) from anthraquinone and magnesium *p*-anisyl bromide.* The inherent improbability of their statement that octahydrodiphenylanthracene is obtained when this diol is heated with hydriodic acid and phosphorus at 150° led us to repeat the experiment and we have identified their product as 9 : 10-dihydroanthracene by direct comparison with an authentic sample. A previous example of facile loss of a *meso-* group on heating with hydriodic acid has been given by one of us (J., 1926, 1684).

1-*Chloro-*9 :10-*diphenylanthracene.*—By boiling 1-chloroanthraquinone for 4 hours with 4 mols. of an ethereal solution of magnesium phenyl bromide a crude product was obtained from which 1-chloro-9 : 10-diphenylanthracene was isolated by recrystallisation first from toluene and then from acetic acid. It then formed a yellow, crystalline powder, m. p. 185° (Found : Cl, 9·7. $C_{26}H_{17}Cl$ requires Cl, 9·7%). In addition to the above, the crude product also contained 1-chloroanthraquinone (due to atmospheric oxidation of the anthraquinol) and as it gave an indigo-blue colour with concentrated sulphuric acid the diol also was doubtless present. For the preparation of 1-chloro-9 : 10-diphenylanthracene, it was found best to remove the anthraquinone by extraction with alkaline hydrosulphite solution and then to reduce by boiling with zinc dust and acetic acid.

2-Chloro-9 : 10-diphenylanthracene was obtained as a yellow, crystalline powder, m. p. 194°, by reduction of the crude diol obtained from 2-chloroanthraquinone and magnesium phenyl bromide (Found : Cl, 9·7. Calc. : Cl, 9·7%). Subsequent to our preparation of this compound, it was described by Ingold and Marshall (*loc. cit.*).

1 : 5 - *Dichloro* - 9 : 10 - *diphenyl* - 9 : 10 - *dihydroanthraquinol.* — A vigorous reaction took place when 12 g. of 1 : 5-dichloroanthraquinone were added to a cold ethereal solution of magnesium phenyl bromide (4 mols.). After boiling for 6 hours, the whole was poured on ice and solid ammonium chloride, and volatile substances were removed by distillation with steam. The crude product contained much dichloroanthraquinone (due to atmospheric oxidation of the anthraquinol) and this was removed by repeated extraction with large volumes of boiling alkaline hydrosulphite solution. The residue, recrystallised from nitrobenzene and from xylene, formed a colourless, crystalline powder which melted to a red liquid at

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* 49 G. of pure *p*-bromoanisole were obtained when a solution of 52 g. of *p*-bromophenol in 200 c.c. of 10% potassium hydroxide solution was heated on the water-bath until neutral (about 2 hours) with 70 g. of methyl *p*-toluene-sulphonate, the whole being shaken from time to time. After addition of a large excess of alkali and heating for an hour to destroy the excess of the ester, the bromoanisole was removed by distillation with steam, dried in ethereal solution with calcium chloride, and distilled.

320° and gave an indigo-blue solution in concentrated sulphuric acid. The yield was 5 g. and numerous attempts under various conditions failed to improve it (Found : C, 71·9; H, 4·45. $C_{26}H_{18}O_2Cl_2$ requires C, 72·0; H, 4·2%). Unlike all other dihydroanthraquinols which have been studied up to the present, the above diol is extremely stable to reduction, and prolonged boiling with zinc dust and acetic acid, with or without the addition of hydrochloric acid, failed to convert it into diphenyldichloroanthracene.

1 : 5 : 9 : 10 - *Tetrachloro* - 9 : 10 - *diphenyl* - 9 : 10 - *dihydroanthracene* was obtained when dry hydrogen chloride was passed through a solution of the above diol in boiling tetralin, and also when 1 : 5-dichloro-9 : 10-diphenylanthracene was treated with a solution of chlorine in carbon tetrachloride. It formed colourless crystals which melted to a red liquid at 250° and liberated iodine from potassium iodide in acetic acid solution (Found : Cl, 30·3. $C_{26}H_{16}Cl_4$ requires Cl, 30·2%).

9-*Benzylanthracene*.—By the action of a well-cooled solution of magnesium benzyl chloride (3 mols.) on anthrone (1 mol.) there was obtained a colourless, crystalline compound, m. p. 50°. This dihydroanthranol (IV. R = H; R′ = C_7H_7) is less stable than its isomeride (Cook, J., 1926, 2160) and passes into 9-benzylanthracene on keeping over-night in a vacuum desiccator.

Neither *o*-tolyl- nor *p*-anisyl-anthracene could be obtained from anthrone by the action of magnesium tolyl or anisyl bromide, most of the anthrone being recovered unchanged.

Action of Grignard Solutions on 9-*Phenylanthrone*.—In all cases, 9 g. of finely powdered 9-phenylanthrone were added to an ethereal solution of the Grignard reagent (3 mols.), the whole being cooled in a freezing mixture. After remaining over-night at the ordinary temperature, the mixture was poured on ice and solid ammonium chloride, the ethereal layer washed, and the ether removed by distillation. The residual crude dihydroanthranol passed very easily into the alkylanthracene by heating with acetic acid alone or with the addition of acetic anhydride or a few drops of hydrochloric or dilute sulphuric acid. In order to establish the reaction, the dihydroanthranol was purified and analysed in three cases. Attempts to effect dehydration in such a way that an alkylidene derivative was formed were not successful. When the reaction was carried out with magnesium *iso*butyl bromide, only 9-phenylanthracene was obtained, a result which may be due to the reducing properties of the Grignard solution but is more probably to be attributed to loss of butyl alcohol from the crude dihydroanthranol. The same result was obtained when the Grignard solution was carefully freed from metallic magnesium.

9-Phenyl-10-α-naphthyldihydroanthranol was found to be more stable than the other dihydroanthranols, but it was converted into 9-phenyl-10-α-naphthylanthracene by boiling for 3 hours with acetic anhydride.

Phenyl-n-butylanthracene, phenylbenzylanthracene, and phenyl-α-naphthylanthracene are yellow in colour, but all the other hydrocarbons are colourless. They are all strongly fluorescent. The dihydroanthranols are all colourless and non-fluorescent.

The following table gives the m. p. and analytical figures for carbon and hydrogen, the calculated values being in brackets. The solvent from which final crystallisation was effected is given after the m. p.

Group.	Phenylalkyl (or aryl)-dihydroanthranol.	Phenylalkyl (or aryl)-anthracene.
Et	—	M. p. 110° (alcohol). 93·4, 6·5 ($C_{22}H_{18}$: 93·6, 6·4%).
Pr^a	M. p. 148—150° (much lower in a preheated bath) (benzene–light petroleum). 87·6, 7·2 ($C_{23}H_{22}O$: 87·9, 7·0%).	M. p. 115—116° (alcohol). 93·1, 6·7 ($C_{23}H_{20}$: 93·2, 6·75%).
Pr$^\beta$	—	M. p. 166—167° (methyl ethyl ketone–alcohol). 93·2, 6·9 ($C_{23}H_{20}$: 93·25, 6·75%).
Bu^a	—	M. p. 156° (ethyl acetate). 92·6, 7·1 ($C_{24}H_{22}$: 92·9, 7·1%).
isoAmyl	—	M. p. 203—204° (benzene–alcohol). 92·3, 7·45 ($C_{25}H_{24}$: 92·6, 7·4%).
Bz	M. p. 177° (benzene). 89·3, 6·2 ($C_{27}H_{22}O$: 89·5, 6·1%).	M. p. 155° (acetic acid). 94·0, 6·0 ($C_{27}H_{20}$: 94·2, 5·8%).
α-$C_{10}H_7$	M. p. 260—262° (toluene). 90·2, 5·65 ($C_{30}H_{22}O$: 90·4, 5·5%).	M. p. 244—245°* (benzene–alcohol). 94·5, 5·4 (Calc. : 94·7, 5·3%).

* Previously made by a different method by Guyot and Staehling (*Bull. Soc. chim.*, 1905, **33**, 1120), who gave the m. p. as 229°.

Action of Grignard Solutions on 1 : 5-*Dichloro*-9-*phenylanthrone.*—In all cases the reaction was carried out by adding finely powdered 1 : 5-dichloro-9-phenylanthrone (m. p. 254° and not 245° as erroneously given previously; Barnett and Matthews, *Ber.*, 1926, **59**, 670) to an ethereal solution of 3—4 mols. of the Grignard reagent, the whole being cooled in a freezing mixture. After remaining over-night at the ordinary temperature, the mixture was poured on ice and solid ammonium chloride. The washed and filtered ethereal solution was then evaporated to dryness. Under these conditions viscous oils which could not be made to crystallise were obtained with all the magnesium alkyl halides, and these were

therefore dissolved in acetic acid and heated on the water-bath with the addition of a little sulphuric or hydrochloric acid.

1 : 5-*Dichloro-9-phenyl*-10-*methylene*-9 : 10-*dihydroanthracene* (IX; R = H), after recrystallisation from ethyl acetate, formed a snow-white, crystalline powder which showed no fluorescence; m. p. 150° (Found : C, 74·6; H, 4·5; Cl, 20·8. $C_{21}H_{14}Cl_2$ requires C, 74·8; H, 4·2; Cl, 21·1%).

1 : 5-*Dichloro-9-phenyl*-10-*ethylidene*-9 : 10-*dihydroanthracene* (IX; R = Me). The crude dihydroanthranol, when boiled with acetic acid and a mineral acid, gave chiefly a red, resinous product, but by dissolving this in ethyl acetate, adding alcohol, and then allowing the solution to evaporate slowly at the ordinary temperature, a colourless product (about 0·5 g. from 7 g. of phenyldichloroanthrone) was obtained which, after recrystallisation from alcohol and then from ethyl acetate, melted at 159° (Found : C, 75·3; H, 4·9. $C_{22}H_{16}Cl_2$ requires C, 75·2; H, 4·6%).

n-*Propyl derivatives*. By treating the red resin obtained by heating the crude dihydroanthranol with acetic and hydrochloric acids as described above, a small amount of a colourless, non-fluorescent product was isolated which, after recrystallisation from methyl alcohol, melted at 135°. This was undoubtedly 1 : 5-*dichloro-9-phenyl*-10-*propylidene*-9 : 10-*dihydroanthracene* (IX; R = Et) (Found : C, 75·3; H, 5·1. $C_{23}H_{18}Cl_2$ requires C, 75·6; H, 4·9%).

In another experiment, in which the crude dihydroanthranol was treated with acetic and sulphuric acids, the red resin, when treated as described above, yielded a small amount of a yellow, strongly fluorescent substance which, after being washed with boiling methyl alcohol and recrystallised from ethyl acetate, melted at 196°. This product was almost certainly 1 : 5-*dichloro-9-phenyl*-10-n-*propyl-anthracene* (VIII; R = Et), but the yield was less than 0·1 g. from 7 g. of phenyldichloroanthrone (Found : C, 75·8; H, 5·6. $C_{23}H_{18}Cl_2$ requires C, 75·6; H, 4·9%).

iso*Propyl derivative*. Treatment of the crude dihydroanthranol with acetic and either sulphuric or hydrochloric acids yielded a red resin from which, by treatment with ethyl acetate as described above, about 0·2 g. of a yellow, strongly fluorescent, crystalline powder, m. p. 195° (to a red liquid), was isolated which analysis indicated to be 1 : 5-*dichloro-9-phenyl*-10-iso*propylanthracene* (Found : C, 75·0; H, 5·1. $C_{23}H_{18}Cl_2$ requires C, 75·6; H, 4·9%).

n- *and* iso-*Butyl derivatives*. In neither case was it found possible to isolate sufficient pure material from the red resin for analysis, but from the n-butyl product a minute amount of a yellow, fluorescent, crystalline powder, m. p. 186° (to a red liquid), was obtained.

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1 : 5-*Dichloro-9-phenyl-*10-*benzyl-*9 : 10-*dihydroanthranol* (X).—
The reaction between phenyldichloroanthrone and magnesium benzyl chloride was carried out as with other magnesium alkyl halides. After the mixture had been poured on ice and ammonium chloride, the colourless solid which was insoluble in ether was collected, washed with ether, and recrystallised from alcohol; m. p. 173° (yield, 3·5 g. from 7 g. of phenyldichloroanthrone) (Found : Cl, 16·5. $C_{27}H_{20}OCl_2$ requires Cl, 16·5%). This product was much more stable to acids than most dihydroanthranols; when boiled under reflux with glacial acetic acid and either hydrochloric or sulphuric acid, or with acetic anhydride, or when heated alone to 300°, it underwent some change, but repeated crystallisation of the product from various solvents failed to yield any substance of constant melting point.

1 : 5-*Dichloro-9-phenyl-*10-*benzylanthracene* (XII).—When the ethereal solution from the above preparation was evaporated to dryness, an oil was left which rapidly passed into a crystalline solid when heated on the water-bath with glacial acetic acid containing a little hydrochloric acid. After boiling with animal charcoal in acetone–aqueous alcohol solution and recrystallisation from benzene, this was obtained as a yellow, crystalline powder, m. p. 209°. The solution showed a strong blue fluorescence (Found : C, 78·4; H, 4·8. $C_{27}H_{18}Cl_2$ requires C, 78·4; H, 4·6%).

1 : 5-*Dichloro-*9 : 10-*diphenyl-*9 : 10-*dihydroanthranol* was obtained in good yield from phenyldichloroanthrone and magnesium phenyl bromide and after recrystallisation from alcohol melted and evolved gas at 201° (Found : Cl, 17·2. $C_{26}H_{18}OCl_2$ requires Cl, 17·0%).

Attempts to prepare the corresponding α-naphthyl compound led only to the isolation of unchanged phenyldichloroanthrone.

1 : 5-*Dichloro-*9 : 10-*diphenylanthracene.*—The above dihydroanthranol was boiled with glacial acetic acid containing a little hydrochloric acid, and the product recrystallised several times from amyl alcohol and from benzene–light petroleum. It then formed a yellow, crystalline powder, m. p. 236° after previous sintering (Found : Cl, 17·9. $C_{26}H_{16}Cl_2$ requires Cl, 17·8%). On oxidation with sodium dichromate in boiling glacial acetic acid, it passed into the same dihydroanthraquinol that was obtained by the action of magnesium phenyl bromide on 1 : 5-dichloroanthraquinone.