CCCCXIII.—*The Structure of the Benzene Nucleus. Part V. Some meso-Derivatives of Anthracene.*

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THE suggestion underlying the preceding parts of this series (J., 1922, **121**, 1133, 1143; 1923, **123**, 2066, 2081) that the propagation of reactivity from a substituent to the para-position of an aromatic ring occurs by direct affinity exchange in the Dewar form, regarded as one of the intra-annular phases to which the reactivity of the nucleus is due,* has been supplemented by numerous analogies with the *cyclo*pentadienes in which the evidence of trans-annular affinity exchange is particularly strong.
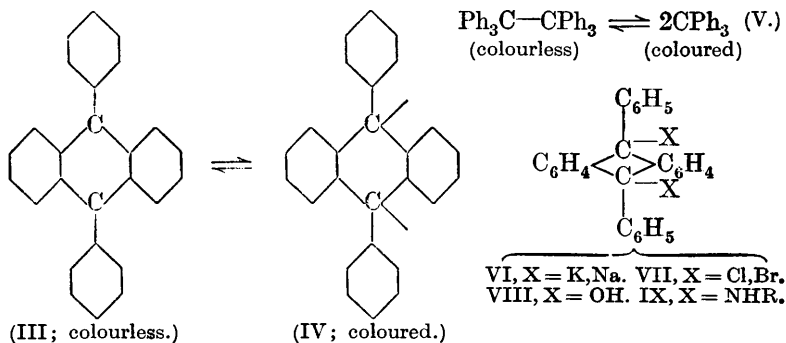
In the benzene series, however, it frequently happens that two views (neither necessarily excluding the other), namely, propagation round the ring in the Kekulé form, and by direct affinity exchange across it in the Dewar form, are equally applicable. Therefore, illustrated by any *op*-substitution of the ordinary type, the theory that the antecedent activation of the nucleus occurs by " Lewis displacement " in the intra-annular forms
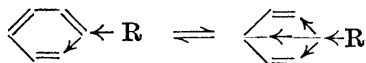
is an obvious variant of the electronic strain-propagation scheme given by Ingold and Ingold (this vol., p. 1312, fig. C_1); whilst the corresponding view of *op*-deactivation (Holleman) during *m*-substitution (same formulæ with arrows reversed) avoids the difficulty encountered by a conjugation mechanism in explaining the practically exclusive *op*-substitution of such fully conjugated compounds as ω-nitrostyrene and cinnamic acid; it has also other advantages.

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* The authors accept Bamberger's theory of the aromatic sextuple valency-group (*Ber.*, 1891, **24**, 1758; 1893, **26**, 1946; *Annalen*, 1893, **273**, 373) as representing the resting condition of the nucleus, but regard the sextuple association as peripheral (Thiele) rather than centric.

The problem of distinguishing between these two views is a difficult one and requires a separate solution for each group of aromatic phenomena. This paper records the results of an attempt to make the decision for the dissociation of the carbon–carbon bond, and the principle employed is as follows. The reactivity of the *meso*-carbon atoms of anthracene is well known and has recently been profusely illustrated (Barnett, Cook). The question to be answered is : Does this activity arise solely from the disturbance by the lateral rings of the equal distribution of valency *around* the central ring; or is it to be attributed to a phase in which there exists direct affinity exchange *across* the ring, that is, to a dissociable para-bond ? According to the former alternative, the attachment of two phenyl nuclei to the 9- and 10-positions should, by con-jugation, absorb this free affinity and 9 : 10-diphenylanthracene should exhibit less *meso*-reactivity than anthracene itself.* Accord-ing to the latter view, however, the reverse *might* hold, since in this case there will be *one* phase in which the condition of the *meso*-carbon atoms is comparable with the condition of the ethane carbon atoms in a hexa-arylethane : each is joined to three benzene rings and to another carbon atom exactly like itself (III); and just as hexaphenylethane reversibly dissociates (V), so diphenyl-anthracene, and diarylanthracenes generally, should *internally* dissociate (IV), and should exhibit (doubtless in a subdued form, for this condition applies to only one of the intra-annular phases) those properties indicative of free affinity which are so strikingly displayed by the typical tervalent carbon radicals.

$$Ph_3C\text{—}CPh_3 \rightleftharpoons 2CPh_3 \quad (V.)$$

(colourless)   (coloured)

$$C_6H_4 \begin{matrix} C_6H_5 \\ | \\ C\text{—}X \\ C \end{matrix} > C_6H_4$$
$$\begin{matrix} \\ | \\ C_6H_5 \end{matrix}$$

VI, X = K, Na. VII, X = Cl, Br.
VIII, X = OH. IX, X = NHR.

(III; colourless.)   (IV; coloured.)

Actually, the 9 : 10-diarylanthracenes and substituted 9 : 10-diarylanthracenes which we have prepared exhibit characteristics corresponding to those of the hexa-arylethanes; *e.g.*, they are colour-less or nearly so, in the solid state, but form coloured solutions (*e.g.*, in xylene) the colour of which (indicating dissociation) increases in
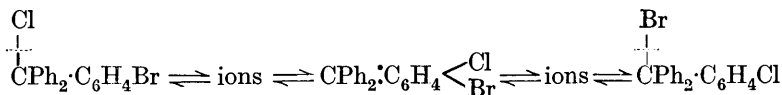
* Steric hindrance would work in the same way.

intensity with increase of temperature, and fades to its original depth on cooling; they form derivatives of type (VI) with the alkali metals in liquid ammonia, are readily oxidised and reduced in the 9- and 10-positions and add on halogens reversibly in these positions; the halogen compounds (Type VII), like triarylmethyl halides, are sensitive to water, giving carbinols (Type VIII), and to bases, giving amines of type (IX). All the reactions, however, except the rapid development of colour in solution, are noticeably less facile than the corresponding reactions of triphenylmethyl. Three points require elaboration :

(i) In electrolytically dissociating solvents the dissociation of triarylmethyls is, at least partly, ionic, and Gomberg's experiments have shown (compare Flürscheim, J., 1910, **97**, 92) that the positive triarylmethyl ion is tautomeric with its semi-quinonoid isomeride :

$$\mathrm{Ph_2\overset{\oplus}{C}}\!\!-\!\!\diagdown\!\!=\!\!\diagup\!\!-\mathrm{H} \;\rightleftharpoons\; \mathrm{Ph_2C}\!\!=\!\!\diagdown\!\!=\!\!\diagup\!\!\overset{\oplus}{\diagdown}_{\mathrm{H}}$$

The proof of this is that p-bromotriphenylmethyl chloride and p-chlorotriphenylmethyl bromide, which are stable isomerides in non-ionising solvents, at once come into equilibrium when dissolved in an ionising solvent such as sulphur dioxide :

$$\overset{\mathrm{Cl}}{\underset{|}{\mathrm{CPh_2 \cdot C_6H_4Br}}} \rightleftharpoons \text{ions} \rightleftharpoons \mathrm{CPh_2 \cdot C_6H_4}\!\!<^{\mathrm{Cl}}_{\mathrm{Br}} \rightleftharpoons \text{ions} \rightleftharpoons \overset{\mathrm{Br}}{\underset{|}{\mathrm{CPh_2 \cdot C_6H_4Cl}}}$$

We have obtained evidence of an analogous condition of tautomerism both in the 9- and 10-phenyl rings, and in the lateral anthracene rings of our 9 : 10-diarylanthracene derivatives, using glacial acetic acid as the ionising solvent.

(ii) The tendency of the hexa-arylethanes and tetra-arylhydrazines towards dissociation into free radicals is known to be influenced by p-substituents, the effect of these in augmenting dissociation running roughly parallel with their op-directive power in aromatic substitution. To test this point for the diarylanthracenes, we have prepared a series of comparable pp'-disubstituted 9 : 10-diarylanthracenes, and, judging from the colour-intensities at equal molecular dilutions, we find for the order of the effect on dissociation : MeO > Me > Cl > H; the effects due to Me and Cl are, however, very close together and the errors inherent in the method are such that their order cannot be guaranteed.

(iii) We have carried out a series of colorimetric measurements at different temperatures and concentrations in order to ascertain whether the relation between the colour depth, temperature, and

dilution corresponds with the requirements of a reversible unimolecular change of the type (III) $\rightleftharpoons$ (IV). The numerical results are consistent with this theory, although they are not sufficiently exact to establish it unequivocally, and the question whether the "degree of dissociation" should be taken in these cases to connote merely the proportion of fully dissociated isomeride, or whether mathematical recognition should be given to the continuous series of possible intermediate states (as in Debye's theory of electrolytic dissociation), is one which must await further evidence.

<h2 style="text-align:center">EXPERIMENTAL.</h2>

9 : 10-*Dichloro*- and 9 : 10-*Dianilino*-9 : 10-*diphenyl*-9 : 10-*dihydroanthracene*.—9 : 10-Dihydroxy-9 : 10-diphenyldihydroanthracene was prepared by Haller and Guyot's process (*Compt. rend.*, 1904, **138**, 327), modified with the object of improving the yield. The reaction product, which contained much unaltered anthraquinone, was decomposed with water, and the solid obtained was twice boiled with 500 c.c. of ethyl acetate. The combined, cooled, and filtered solutions, on concentration to a small bulk, deposited the dihydroxy-compound, which, after being washed with ligroin and crystallised from acetone, was obtained in 34% yield, m. p. 252—254° (Haller and Guyot record yield 10% and m. p. 242°).

A hot chloroform solution of the dihydroxy-compound, on saturation with hydrogen chloride, became turbid owing to separation of water; addition of acetic acid (2—3 vols.) then gave 9 : 10-dichloro-9 : 10-diphenyl - 9 : 10 - dihydroanthracene in colourless needles, m. p. 170° (decomp.), which were washed with acetic acid, water, and alcohol. This compound gave a deep yellow colour in liquid sulphur dioxide. When it was boiled with water, hydrochloric acid was gradually liberated and the dihydroxy-compound formed.

A solution of the dichloro-compound in hot benzene reacted very readily with aniline (4 mols.), aniline hydrochloride being precipitated (yield, 1·7 mols.; theoretical, 2·0 mols.). 9 : 10-*Dianilino*-9 : 10-*diphenyl*-9 : 10-*dihydroanthracene* crystallised when the filtrate was concentrated to a small bulk; it was washed with warm water to remove adhering aniline hydrochloride and recrystallised from benzene–ligroin, from which it separated in minute, colourless needles, m. p. 232—234° (Found : C, 88·8; H, 6·0. $C_{38}H_{30}N_2$ requires C, 88·7; H, 5·8%). It formed an orange solution in liquid sulphur dioxide and a blue solution in sulphuric acid.

9 : 10-Diphenylanthracene was obtained by treating the dihydroxy- or the dichloro-derivative with zinc dust and acetic acid, and from the latter by treatment with an aqueous solution of potassium iodide or carbamide. On chlorination in chloroform solution the dichloro-

derivative was re-formed, but the dibromo-derivative could not be produced in a similar way. An attempt to prepare the dibromo-compound by saturating an acetic acid solution of the dihydroxy-derivative with hydrogen bromide at 60° yielded only diphenyl-anthracene; from which it seems clear that the conversion of this substance into its 9 : 10-dihalogen addition products is reversible, and that whereas the dichloride is moderately stable, the dibromide and di-iodide lose their halogen with much greater ease (compare triarylmethyl halides). The hydrocarbon prepared by any of these methods separated from acetic acid or benzene in very pale yellow prisms, m. p. 249—250° (Found : C, 94·4; H, 5·4. Calc. : C, 94·5; H, 5·5%). It gave a deep yellow solution in liquid sulphur dioxide and yellow, fluorescent solutions in the ordinary organic solvents (p. 3089). It was stable in air at the ordinary temperature, but on heating was converted into a product which gave the colour reactions of the dihydroxy-compound; this could be obtained from the hydrocarbon by successive treatment with silver oxide in xylene and with water.

When sodium or potassium was added to a solution of 9 : 10-diphenylanthracene in anhydrous liquid ammonia, a bright cherry-red solution was formed which soon deposited a brick-red, amorphous precipitate. These precipitates apparently consisted of the 9 : 10-*disodio*- and 9 : 10-*dipotassio*-derivatives of 9 : 10-diphenyl-9 : 10-dihydroanthracene. They were less stable than the corresponding compounds prepared from triphenylmethyl (Kraus and Kawamura, *J. Amer. Chem. Soc.*, 1923, **45**, 2756), and were not purified owing to their instability in moist air. By taking advantage of the intense colour of the solutions of the alkali metals in ammonia, however, indirect analyses were carried out : a known weight of the hydrocarbon dissolved in liquid ammonia was titrated with a solution of potassium or sodium in the same solvent until one more drop gave a maroon or purple end-point; the ammonia was then evaporated and the residue was dried over sulphuric acid, decomposed with water, and titrated with standard hydrochloric acid* (Found : K, 19·8. Na, 13·8. $C_{26}H_{18}K_2$ requires K, 19·1%. $C_{26}H_{18}Na_2$ requires Na, 12·2%). When water was added during these estimations, a small amount of a gas (presumably hydrogen) was evolved; the residue contained 9 : 10-*diphenyl*-9 : 10-*dihydroanthracene*, colourless needles with a bluish-violet sheen, m. p. 222—225° after crystallisation from acetone (Found : C, 93·9; H, 6·2. $C_{26}H_{20}$ requires

* To correct for the water content of the ammonia, a small quantity of sodium or potassium was dissolved in ammonia, and the solution diluted from the main stock until the colour vanished. The volume was then noted, and the alkali hydroxide remaining after evaporation estimated.

C, 94·0; H, 6·0%), but also gave, before purification, the colour reactions of 9 : 10-diphenylanthracene.

9 : 10-*Dihydroxy*-9 : 10-*di* - p - *tolyl* - 9 : 10 - *dihydroanthracene.* — A suspension of anthraquinone (45·5 g.) in 300 c.c. of dry ether was gradually added to the Grignard solution prepared from *p*-iodotoluene (100 g.), magnesium (10·8 g.), ether (220 c.c.), and a trace of iodine. After the mixture had been boiled under reflux for 4 hours, the solid product was collected and decomposed with very dilute hydrochloric acid. The material thus obtained was twice extracted with 500 c.c. of boiling ethyl acetate, and the combined filtrates were concentrated and mixed with ligroin. The crystalline product was collected, washed with ligroin, and crystallised from toluene, from which colourless needles, m. p. 267—270°, separated. A further crystallisation from acetone, alcohol, or pyridine raised this m. p. to 275°, perceptible softening taking place at 270° (yield, 18%) (Found : C, 85·9; H, 6·2. $C_{28}H_{24}O_2$ requires C, 85·7; H, 6·2%). The compound gave a yellow solution in liquid sulphur dioxide and a deep blue solution in sulphuric acid.

9 : 10-*Di*-p-*tolylanthracene.*—Zinc dust was added at intervals during 1 hour to a boiling solution of the dihydroxy-compound (5 g.) in glacial acetic acid (50 c.c.). The solution (final volume, 30 c.c.) was well cooled and filtered, and the hydrocarbon extracted from the residue with boiling toluene. The product, obtained by concentrating the extract, was again crystallised from toluene; very pale yellow prisms were then obtained, m. p. 278—279° (Found : C, 93·7; H, 6·3. $C_{28}H_{22}$ requires C, 93·8; H, 6·2%). This substance closely resembles the diphenyl analogue (see, however, p. 3089). Yield 63%. The *dipotassio*- and *disodio*-derivatives were obtained as in the case of the diphenyl derivatives (Found : K, 18·9. Na, 10·7. $C_{28}H_{22}K_2$ requires K, 17·9%. $C_{28}H_{22}Na_2$ requires Na, 11·4%).

9 : 10-*Dihydroxy*-9 : 10-*di* -p-*chlorophenyl*-9 : 10-*dihydroanthracene.* —A suspension of anthraquinone (30 g.) in ether (250 c.c.) was added gradually to a Grignard solution prepared from *p*-chloroiodobenzene (95 g.), magnesium (9·5 g.), and 250 c.c. of ether; the product was isolated like the dihydroxyditolyl compound and obtained in colourless, prismatic needles, m. p. 267° (decomp.). It is similar in all respects to the ditolyl analogue (Found : C, 72·3; H, 4·3. $C_{26}H_{18}O_2Cl_2$ requires C, 72·1; H, 4·2%). This analysis and qualitative tests showed that the product contained no di-iodophenyl derivatives.

9 : 10-*Di*-p-*chlorophenylanthracene* was prepared in the same way as ditolylanthracene, except that xylene was used for the extraction and crystallisation of the product, m. p. 306—307·5° (Found : C, 78·3; H, 4·3. $C_{26}H_{16}Cl_2$ requires C, 78·2; H, 4·0%), which had

properties closely similar to those of the tolyl compound (compare, however, p. 3089). Yield, 60%.

In an unsuccessful attempt to synthesise 9 : 10-dibromo-9 : 10-di-*p*-chlorophenyl-9 : 10-dihydroanthracene, the above dichlorohydrocarbon was reduced to 9 : 10-*di*-p-*chlorophenyl*-9 : 10-*dihydroanthracene* by adding sodium amalgam to a boiling alcoholic suspension until the fluorescence had almost disappeared. The mercury was removed, the suspension mixed with water, and the solid material collected. A filtered solution of this in hot toluene, after admixture with absolute alcohol (2 vols.), gave colourless needles, m. p. about 206°. The filtrate from this, on being concentrated and mixed with a further quantity of alcohol, yielded colourless needles, m. p. about 165° (Found : C, 77·7; H, 4·7. $C_{26}H_{18}Cl_2$ requires C, 77·8; H, 4·5%). A mixture of *cis*- and *trans*-isomerides would be expected.

9 : 10-*Dihydroxy*-9 : 10-*di*-p-*bromophenyl*-9 : 10 - *dihydroanthracene* was prepared in the usual way, 25 g. of anthraquinone suspended in 250 c.c. of ether, and a Grignard solution prepared from 90 g. of *p*-bromoiodobenzene, 7·56 g. of magnesium, and 200 c.c. of ether being used. The product separated from xylene or ethyl acetate–ligroin in colourless, prismatic needles, m. p. 273—274° (Found : C, 60·0; H, 3·4. $C_{26}H_{18}O_2Br_2$ requires C, 59·8; H, 3·4%). Its properties are similar to those of the chloro-compound.

9 : 10-*Di*-p-*bromophenylanthracene* was prepared in the same way as the chloro-analogue; it shrank at 315° and melted at 326—327° (Found : C, 63·9; H, 3·4. $C_{26}H_{16}Br_2$ requires C, 63·9; H, 3·3%).

9 : 10-*Dihydroxy*-9 : 10-*di*-p-*anisyl*-9 : 10-*dihydroanthracene* was obtained from 40 g. of anthraquinone, suspended in ether (250 c.c.), and a Grignard solution prepared from *p*-bromoanisole (93·5 g.), magnesium (12·0 g.), and ether (250 c.c.). After the product had been decomposed with dilute hydrochloric acid, the dianisyl compound was extracted by boiling the solid material three times with 400 c.c. of ethyl acetate. The concentrated extracts were allowed to cool and the crystalline product was freed from gummy impurities by washing with alcohol and from anthraquinone by filtering its solution in boiling acetone. A further crystallisation from acetone yielded colourless needles, m. p. 258—262° (yield, 31 g.). This compound gives a brilliant cherry-red solution in sulphuric acid (Found : C, 79·3; H, 5·7. $C_{28}H_{24}O_4$ requires C, 79·2; H, 5·7%).*

9 : 10-*Di*-p-*anisylanthracene*, prepared in the usual way and crystal-

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* On heating with phosphorus and hydriodic acid at 150°, this substance yielded a hydrocarbon, m. p. 105—108°, forming colourless leaflets when crystallised from ligroin. Analysis (Found : C, 92·7; H, 7·5. $C_{26}H_{26}$ requires C, 92·3; H, 7·7%) indicated that it is *octahydro*-9 : 10-*diphenylanthracene*.

lised from toluene containing a little ligroin, was obtained in very pale yellow prisms, m. p. 282° (Found : C, 85·7; H, 5·7. $C_{23}H_{22}O_2$ requires C, 86·2; H, 5·9%). It gives an olive solution in sulphuric acid, and otherwise resembles its analogues (compare, however, p. 3089).

2-*Chloro*-9 : 10-*dihydroxy*-9 : 10-*diphenyl*- 9 : 10 - *dihydroanthracene* was prepared from 2-chloroanthraquinone (42·5 g., suspended in ether, 250 c.c.) and the Grignard derivative obtained from bromobenzene (60 g.), magnesium (8·72 g.), and ether (150 c.c.), and was crystallised from toluene–ligroin (4 : 1); m. p. 220—221° (Found : C, 78·7; H, 5·1. $C_{26}H_{19}O_2Cl$ requires C, 78·3; H, 4·8%). Its solution in concentrated sulphuric acid is indigo-blue.

2-*Chloro*-9 : 10-*diphenylanthracene*, prepared in the usual way by reduction of the dihydroxy-compound, and extracted from the zinc, etc., with ligroin, formed small, pale yellow crystals, m. p. 193°. It is much more soluble in the usual solvents than 9 : 10-diphenyl-anthracene, which it otherwise resembles (Found : C, 86·0; H, 5·0. $C_{26}H_{17}Cl$ requires C, 85·6; H, 4·7%).

2-*Bromo*-9 : 10-*dihydroxy*-9 : 10-*diphenyl*-9 : 10 - *dihydroanthracene*, prepared from 2-bromoanthraquinone (78 g., suspended in ether, 250 c.c.) and the Grignard compound from bromobenzene (120 g.), magnesium (17·4 g.), and ether (300 c.c.), separated from acetone in colourless needles, m. p. 206—209° (Found : C, 70·8; H, 4·3. $C_{26}H_{19}O_2Br$ requires C, 70·4; H, 4·3%). It resembles the 2-chloro-compound.

2-*Bromo*-9 : 10-*diphenylanthracene* was prepared in the same way as its chloro-analogue, except that acetone was used in place of ligroin for the extraction. Crystallised from acetone–ligroin, it formed very pale greenish-yellow needles, m. p. 185—187° (Found : C, 76·5; H, 4·3. $C_{26}H_{17}Br$ requires C, 76·3; H, 4·1%).

9-*Hydroxy*-9-*triphenylmethylanthrone* was obtained during some unsuccessful attempts to synthesise 9 : 10-bistriphenylmethylanthra-cene. The Grignard compound prepared from triphenylchloro-methane (36 g.), magnesium (3·1 g.), and ether (100 c.c.) was treated with anthraquinone (11 g.) suspended in ether (80 c.c.); the product was worked up as usual. After several crystallisations from toluene, colourless prisms, m. p. 183—190°, were obtained (Found : C, 87·6; H, 5·7. $C_{33}H_{24}O_2$ requires C, 87·6; H, 5·3%). It gives a yellow solution in sulphuric acid.

Action of Hydrogen Chloride on 9 : 10-*Dihydroxy*-9 : 10-*di*-p-*bromo-phenyl*-9 : 10-*dihydroanthracene and of Chlorine on* 9 : 10-*Di*-p-*bromo-phenylanthracene* : *Formation of* 9 : 10-*Dichloro*-9 10-*di*-p-*bromo-phenyl*-9 : 10-*dihydroanthracene and* 9 : 10-*Di*-p-*chloroanthracene.*— The dihydroxy-compound (1 g.) dissolved in hot glacial acetic acid

was treated with a stream of hydrogen chloride for 5 minutes. After cooling, the crystals were collected, washed with acetic acid, and crystallised from benzene, almost colourless needles, m. p. 218°, being obtained. 9 : 10-*Dichloro*-9 : 10-*di*-p-*bromophenyl*-9 : 10-*dihydroanthracene* gives a deep blue colour with concentrated sulphuric acid and an orange-yellow solution in liquid sulphur dioxide (Found : C, 55·7 ; H, 3·0. $C_{26}H_{16}Cl_2Br_2$ requires C, 55·8 ; H, 2·9%). The same substance is formed when chlorine is passed into a solution of 9 : 10-di-p-bromophenylanthracene in chloroform. It does not appear to undergo rearrangement (except possibly to a small extent) in liquid sulphur dioxide : whether this is due to slow reaction at the low temperature or to an unfavourable equilibrium we have not been able to determine, since the 9 : 10-dibromo-9 : 10-di-*p*-chlorophenyl-9 : 10-dihydroanthracene required to investigate the reverse change could not be prepared (pp. 3084, 3086). Evidence of the occurrence of the rearrangement in hot glacial acetic acid was, however, obtained by the isolation of 9 : 10-di-*p*-chlorophenyl-anthracene from the product formed by treating the dihydroxydi-*p*-bromophenyl compound for $\frac{1}{2}$ hour with hydrogen chloride in hot glacial acetic acid. In another experiment, the treatment with hydrogen chloride was continued for 15 minutes, and the solution boiled for 15 minutes. The product, crystallised repeatedly from toluene and then from toluene–alcohol, gave (*a*) a sparingly soluble product, m. p. 290—320°, containing chlorine and bromine, which was not further investigated, (*b*) di-*p*-chlorophenylanthracene (m. p. 304—306° ; mixed m. p. 305—307°) (Found : C, 78·0 ; H, 4·3. Calc. : C, 78·2 ; H, 4·0%), (*c*) a product, m. p. 209—214° (mixed m. p. with 9 : 10-dichloro-9 : 10-di-*p*-bromophenyl-9 : 10-dihydroanthracene, 212—215°), containing both chlorine and bromine, which, however, could not be completely purified. Since 9 : 10-dibromo-9 : 10-di-*p*-chlorophenyl-9 : 10-dihydroanthracene would lose bromine spontaneously, giving 9 : 10-di-*p*-chlorophenylanthracene under the conditions employed, we regard these observations as establishing the series of reactions referred to on p. 3082.

Action of Hydrogen Chloride on 2-Bromo-9 : 10-*dihydroxy*-9 : 10-*diphenyl*-9 : 10-*dihydroanthracene*.—The bromodihydroxy-compound was treated in boiling glacial acetic acid solution with hydrogen chloride for 1·5 hours. After cooling, the yellow product was collected and separated into two portions by filtering its suspension in boiling acetone. The undissolved portion, after crystallising three times from toluene and twice from pyridine, formed very pale greenish-yellow needles, m. p. 294—295°, which contained chlorine but no bromine (Found : C, 73·3, 73·4 ; H, 3·8, 3·9 ; Cl, 23·8. $C_{26}H_{15}Cl_2$ requires C, 72·0 ; H, 3·5 ; Cl, 24·5%). This compound,

which was obviously of the 9 : 10-diarylanthracene type and gave with cold xylene a yellow solution which became intensely orange-yellow at the boiling point, appears to contain one atom of chlorine more than 2 : 3-dichloro- or 2 : 6-dichloro-9 : 10-diphenylanthracene, the highest-chlorinated bromine-free derivatives we expected to obtain, and there are many conceivable ways in which this result may have been brought about. The product soluble in acetone, after further crystallisation from acetone and toluene–ligroin, had m. p. about 175° and obviously consisted largely of 2-chloro-9 : 10-diphenylanthracene (mixed m. p. 187—192°), although it could not be entirely freed from a bromine-containing impurity. Since its reactions were exclusively those of a diarylanthracene, we conclude that the persistent impurity was probably 2-bromo-9 : 10-diphenylanthracene.

Colorimetric Determinations.—The following table records the length of the column of a colour-standard against which solutions of 9 : 10-di-*p*-anisylanthracene were matched at different temperatures. These solutions each contained 0·5 g. in 100 c.c.; the measurements refer to solutions in (*a*) mesitylene, (*b*) benzylidene-methylamine, and (*c*) bromonaphthalene. Series of readings were taken,* with rising temperatures, † with falling temperatures.

	†	†	†	*	†	*	†
Solvent	*a*	*b*	*a*	*a*	*b*	*a*	*c*
Temp.	20°	40°	50°	85°	93°	120°	120°
Length (mm.)	2·5	3·0	4·0	9·5	12·0	19·5	18·5
	*	*	*	*	*	*	*
Solvent	*b*	*a*	*b*	*c*	*b*	*c*	*c*
Temp.	135°	140°	150°	158°	172°	220°	265°
Length (mm.)	20·5	25·0	27·5	30·0	36·0	50·5	57·0

Solutions of diphenylanthracene, di-*p*-tolylanthracene, di-*p*-chlorophenylanthracene, and di-*p*-anisylanthracene in benzylidene-methylamine were compared with the same colour-standard at 150°, and the following relative colour intensities obtained : 1·0, 1·4, 1·5, 2·7, respectively.

An approximately decimolecular solution of trichlorodiphenyl-anthracene (see above) in xylene was matched against a colour-standard and then diluted. The following colour intensities refer to the temperature 25°, for the relative dilutions 1·0, 2·4, 5·1 and 8·1, respectively : 7·7, 7·4, 7·8 and 7·9.

Similar results were obtained at 100°, indicating that the intensity of colour is substantially independent of concentration.