87. *Phenylated Phthalic Acids and Anthracene Derivatives.*

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The reactions between arylmagnesium compounds and 3 : 6-*diphenylphthalic anhydride* and 3-*phenylphthalic anhydride*, leading to substituted *o*-benzoylbenzoic acids, have been studied.

Through the cyclic N-*hydroxyimide*, 3 : 6-diphenylphthalic anhydride was converted into the corresponding *anthranilic acid*, but from this the corresponding tetraphenylindigotin could not be prepared, probably for steric reasons. Other reactions of the anhydride are its cyclisation into 2-*phenylfluorenone*-1-*carboxylic acid* and 1′-*ketoindeno*(2′ : 3′ : 1 : 2)*fluorenone*.

1-Phenyl-, 1 : 4- and 1 : 5-*diphenyl*-, and 1 : 4 : 5 : 8-*tetraphenyl-anthraquinone* have been prepared, and their reactions studied. 1 : 4 : 9 : 10-Tetraphenylanthracene is of interest as a lower homologue of rubrene. An isomerisation of 1 : 4 : 9 : 10-*tetraphenylanthracene* throws some light on the formation of the so-called ψ-rubrene.

INCREASED interest in polycyclic substances has recently been aroused owing to the discovery of the carcinogenic or oestrogenic properties of members of this group, and this had led us to experiments in the series of anthracenes phenylated in the side rings, the only representatives known hitherto being 1-phenylanthraquinone (Diels and Alder, *Ber.*, 1929, **62**, 2339) and 2-phenylanthraquinone (Scholl and Neovius, *Ber.*, 1911, **44**, 1075; Groggins, *Ind. Eng. Chem.*, 1930, **22**, 620, 626). Two possible methods have been explored, namely, the route *via* substituted *o*-benzoylbenzoic acids and the diene synthesis, which was used by Diels and Alder for the preparation of 1-phenylanthraquinone.

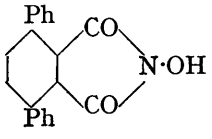
(1) The 3 : 6-diphenyltetrahydrophthalic anhydride accessible by the union of 1 : 4-diphenylbutadiene and maleic anhydride (Diels and Alder, *Ber.*, 1929, **62**, 2081; Kuhn and Wagner-Jauregg, *ibid.*, 1930, **63**, 2662) could be easily dehydrogenated by means of sulphur to form 3 : 6-*diphenylphthalic anhydride*, other methods of dehydrogenation being unsuccessful according to Kuhn and Wagner-Jauregg (*loc. cit.* For the analogous tetraphenylphthalic anhydride, see Dilthey, Thewalt, and Troesken, *Ber.*, 1934, **67**, 1959). The new anhydride showed most of the typical reactions of phthalic anhydrides, others being apparently hindered sterically. The interaction with Grignard reagents according to the method of Weizmann and co-workers (J., 1935, 1367; 1936, 567. Compare Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1937, **59**, 2331) gave the corresponding 2-aroyl-3 : 6-diphenylbenzoic acids; we thus prepared the *benzoyl*, 1′-*naphthoyl*, 4′-*methoxybenzoyl*, 4′-*bromobenzoyl*, and the 6′-*methoxy*-2′-*naphthoyl* derivatives. The sodium salts of most of these keto-acids were insoluble in water, but recrystallisable from boiling propyl alcohol; the free acids, therefore, were conveniently prepared by saturating propyl-alcoholic solutions of the sodium salts with hydrogen chloride. Cyclisation of the keto-acids proved very tedious; here apparently the presence of the voluminous ortho-substituents slows down the ring closure so that side reactions may prevail; *e.g.*, with sulphuric acid as cyclising agent, sulphonation readily takes place.

Other cases of this hindrance have been observed in the 3 : 6-diphenylanthranilic acid series. The preparation of 3 : 6-*diphenylphthalimide* could only be effected by heating a mixture of the anhydride and urea (compare, *inter al.*, Biedermann, *Ber.*, 1877, **10**, 1166; Tingle and Brenton, *J. Amer. Chem. Soc.*, 1910, **32**, 116) at 200°, but we were unable to degrade it into the amino-acid by means of sodium hypochlorite or hypobromite (Orthner-Reichel, "Organisch-chemisches Praktikum," Berlin, 1928, p. 181). The corresponding *hydroxyimide* (I) (compare Lassar-Cohn, *Annalen*, 1880, **205**, 295), on the other hand, could easily be prepared even at room temperature and was converted by alkali treatment into the sodium salt of the desired 3 : 6-*diphenylanthranilic* acid. This acid could not be coupled with chloro- or bromo-acetic acid (compare the similar case of 2-aminoveratric acid; Rodionov and Bogoslovskij, *Chem. Abstrs.*, 1938, **32**, 2939. It was resistant too against formaldehyde and potassium cyanide solution; Leonhardt, D.R.-P. 120,105), so that the synthesis of the tetraphenylindigotin could not be effected.

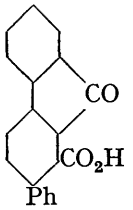
On heating with anhydrous aluminium chloride in benzene, 3 : 6-diphenylphthalic anhydride is cyclised with formation of 2-*phenylfluorenone*-1-*carboxylic acid* (II) (compare Schaarschmidt, *Ber.*, 1915, **48**, 1826; Weiss and Abeles, *Monatsh.*, 1932, **61**, 143, 162; Dilthey, *loc. cit.* and *J. pr. Chem.*, 1937, **148**, 53). This substance gives a well-defined *phenylhydrazone* and could be decarboxylated to 2-*phenylfluorenone*. On treatment with phenylmagnesium bromide, only one phenyl group enters the molecule (IV). On the other hand, reaction with phenyl-lithium leads to complete saturation with phenyl groups (V). When the keto-acid (II) is heated with thionyl chloride in carbon tetrachloride solution (compare Koelsch, *J. Amer. Chem. Soc.*, 1934, **56**, 480), cyclisation occurs again, giving the golden-red 1′-*ketoindeno*(2′ : 3′ : 1 : 2)*fluorenone* (III), which is also present in the uncrystallisable resins obtained in the preparation of the keto-acid (II). The diketone (III) gives a nearly black *bisphenylhydrazone* (a similar substance has been obtained by Dilthey *et al.*, *J. pr. Chem.*, 1937, **148**, 53; **149**, 85. These authors also observed very different ease of formation of the two five-membered rings).

In a similar way, by dehydrogenation of the adduct between phenylbutadiene and maleic anhydride (Diels and Alder, *Ber.*, 1929, **62**, 2081), 3-*phenylphthalic anhydride* was prepared (for another synthesis, see Butterworth, Heilbron, Hey, and Wilkinson, J., 1938, 1386). Interaction with phenylmagnesium bromide gave two isomeric *keto-acids* (VI, VII), in non-comparable yields. We suggest that the prevailing isomer (m. p. 163°) has formula (VI), its formation not being sterically hindered, and to the isomer, m. p. 172°, formula (VII) should be ascribed. A similar behaviour of 3-methylphthalic anhydride has been reported by Newman (*J. Amer. Chem Soc.*, 1937, **59**, 1003).

Attempts to condense maleic anhydride with 1 : 4-di-*p*-anisylbutadiene (E. Bergmann, unpublished) or 1 : 2 : 3 : 4-tetraphenylbutadiene (Bergmann, Winter, and Schreiber, *Annalen*, 1933, **500**, 122) failed.



(I.)



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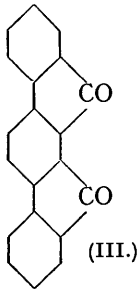

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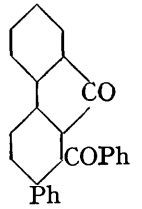
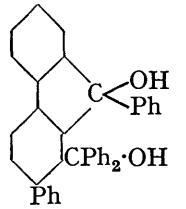
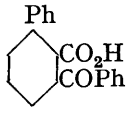


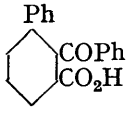
(IV.)



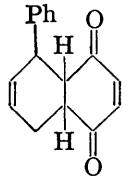
(V.)



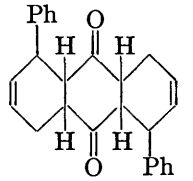
(VI.)



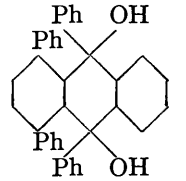
(VII.)



(VIII.)



(IX.)

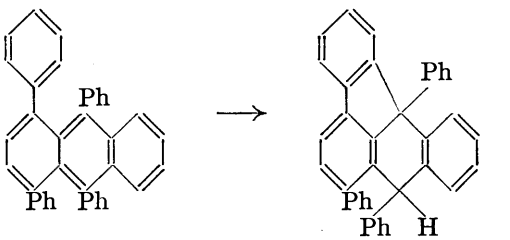


(X.)

(2) As mentioned above, 1-phenylanthraquinone can be obtained directly by coupling 1-phenylbutadiene and α-naphthaquinone according to Diels and Alder. The same procedure was applied to the coupling of 1 : 4-diphenylbutadiene with α-naphthaquinone and with benzoquinone, giving 1 : 4-*diphenyl-* and 1 : 4 : 5 : 8-*tetraphenyl-anthraquinone*, respectively, and of phenylbutadiene with benzoquinone, giving a diphenylanthraquinone which on account of its extremely high m. p. (355°) should be the centrosymmetrical 1 : 5-*diphenyl* compound, although the isomeric formula of a 1 : 8-diphenylanthraquinone is not excluded (1 : 5-dichloroanthraquinone, m. p. 251°; 1 : 8-isomer, m. p. 199°. Bromo-compounds, m. p.'s 292° and 232°, respectively. Nitro-compounds, m. p.'s 422° and 310°, respectively). When the last coupling was carried out in xylene solution, no dehydrogenation took place: the two *products* obtained have apparently the formulæ (VIII) and (IX). The latter substance could be dehydrogenated by air in presence of alkali to form the above quinone, m. p. 355°.

Treated with various reagents, 1 : 4-diphenylanthraquinone took up two substituent groups; a *dinitro-* and a *dibromo*-derivative and a disulphonic acid were thus obtained. The behaviour of the disulphonic acid indicates that disubstitution fails to attack the anthracene nucleus; we suggest that reaction takes place in the *p*-positions of the two phenyl groups. When heated with a large excess of bromine, 1 : 4-diphenylanthraquinone took up four bromine atoms. The structure of the intensely red product has not yet been determined.

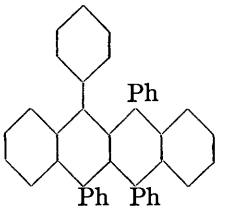
1-Phenyl- and 1 : 4-diphenyl-anthraquinone were reduced by the usual methods to the corresponding phenylated anthracenes, which showed no unusual properties. They behaved normally too with phenylmagnesium bromide, giving phenylated 9 : 10-dihydroxy-9 : 10-diphenyl-9 : 10-dihydroanthracenes (as X): in the case of 1 : 4 : 5 : 8-tetraphenyl-anthraquinone phenyl-lithium is to be preferred to phenylmagnesium bromide. Attempts to remove the hydroxyl groups from (X) gave results of more general interest. Boiling formic acid (Kovache, *Ann. Chim.*, 1918, **10**, 228; Schlenk and Bergmann, *Annalen*, 1928, **463**, 152) did not give the expected 1 : 4 : 9 : 10-*tetraphenylanthracene* (XI), but instead a colourless, non-fluorescent, isomeric *hydrocarbon*. That this was a secondary product was proved as follows: Reduction of the diol (X) with potassium iodide in presence of sodium hyposulphite (compare the analogous method of Haller and Guyot, *Bull. Soc. chim.*, 1904, **31**, 795; Dufraisse and Velluz, *ibid.*, 1936, **3**, 1905) gave—under certain conditions—the desired hydrocarbon (XI), a yellow, fluorescent substance. It could be converted into the colourless, non-fluorescent isomer by means of boiling formic acid. We suggest that this isomeric change takes place according to the scheme:

(XI.) 

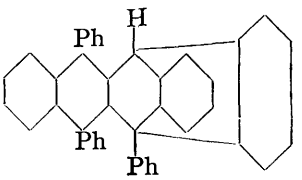
(XII.)

It involves a rearrangement completely analogous to the isomerisation of allylbenzenes into hydrindenes (Bergmann and Weiss, *Annalen*, 1930, **480**, 49. For further references, see Blum-Bergmann, *Ber.*, 1932, **65**, 109); as a matter of fact, the hydrocarbon (XI) contains an allybenzene system. A similar observation has been made by Moureu, Dufraisse, and Berchet (*Compt. rend.*, 1927, **185**, 1085; compare Moureu, Dufraisse, and Enderlin, *ibid.*, 1929, **188**, 673) in the rubrene series. In the preparation of this red hydrocarbon (XIII) a colourless ψ-rubrene also is formed; Dufraisse (*Bull. Soc. chim.*, 1936, **3**, 1855; compare Enderlin, *Ann. Chim.*, 1938, **10**, 5) has suggested for it the somewhat unusual formula (XIV), which he prefers to the second possibility (XV). The latter is, however, analogous to (XII) and seems to us by far the more probable (compare Haworth, *Ann. Reports*, 1937, **34**, 393). Our hydrocarbon (XI) is apparently a lower homologue of

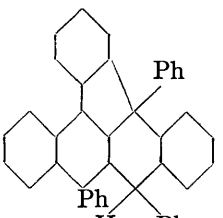
rubrene; in its colour, too, it is intermediate between rubrene and the almost colourless 9 : 10-diphenylanthracene (for references, see also Schlenk and Bergmann, *Annalen*, 1928,



(XIII.)



(XIV.)



(XV.)

463, 171. For a rearrangement which might be similar to the above, see Clar, *Ber.*, 1931, **64**, 2194).

Experimental.

3 : 6-*Diphenylphthalic Anhydride.*—A mixture of the tetrahydro-compound (30 g.) and sublimed sulphur (7 g.) was heated at 260—270° for 20 minutes; reaction started at 240°. The powdered mass was crystallised from methyl ethyl ketone or xylene, giving needles, m. p. 224°, of 3 : 6-*diphenylphthalic anhydride* in almost quantitative yield (Found: C, 79·9; H, 4·1. $C_{20}H_{12}O_3$ requires C, 80·0; H, 4·0%). The anhydride dissolved in boiling sodium carbonate solution. The sodium salt, which was only slightly soluble in water, formed leaflets. Its solution, on acidification at 0°, gave the free acid, m. p. 162° (decomp.) after crystallisation from alcohol. *Methyl* 3 : 6-*diphenylphthalate*, prepared from the silver salt and methyl iodide, formed needles, m. p. 188°, from acetone (Found: C, 75·4; H, 5·3. $C_{22}H_{18}O_4$ requires C, 76·3; H, 5·2%).

2-*Benzoyl*-3 : 6-*diphenylbenzoic Acid.*—Phenylmagnesium bromide (prepared from 0·48 g. of magnesium and 2·14 g. of bromobenzene) was added drop by drop to a boiling solution of the above anhydride (6 g.) in xylene (50 c.c.), the product separating immediately. The mixture was boiled for 15 minutes, decomposed with ice and dilute sulphuric acid, and treated with sodium carbonate solution. The sodium salt separating was collected—it formed silky needles, recrystallisable from propyl alcohol—and a propyl-alcoholic solution of it was treated with hydrogen chloride, filtered, and evaporated. The residual *acid* crystallised from benzene–light petroleum in clusters, m. p. 167°; yield, 50% (Found: C, 82·4; H, 5·1. $C_{26}H_{18}O_3$ requires C, 82·5; H, 4·8%). It gave a dark green colour in concentrated sulphuric acid.

2-α-*Naphthoyl*-3 : 6-*diphenylbenzoic Acid.*—The above procedure was carried out with α-bromonaphthalene (10·3 g.), magnesium (1·25 g.), and diphenylphthalic anhydride (15 g.). The product separated spontaneously; it was converted into its potassium salt by solution in boiling alcohol and addition of alcoholic potassium hydroxide. The *acid*, obtained as described above and crystallised successively from acetylene tetrachloride and benzene–light petroleum, formed prisms, m. p. 188°; yield, 50% (Found: C, 84·5; H, 4·7. $C_{30}H_{20}O_3$ requires C, 84·1; H, 4·7%).

2-p-*Methoxybenzoyl*-3 : 6-*diphenylbenzoic Acid.*—A solution of *p*-methoxyphenylmagnesium bromide (3·65 g. of magnesium; 28 g. of *p*-bromoanisole) was added as above to a boiling solution of 3 : 6-diphenylphthalic anhydride (15 g.) in xylene (300 c.c.). The acid separated as an oil, which solidified slowly on trituration with benzene. It crystallised from the same solvent in rhombohedra, which decomposed at 125°, resolidified, and then had m. p. 175°. It gave a brown-violet coloration with concentrated sulphuric acid. According to the analysis, the *keto-acid* contains 2 mols. of water, which could not be removed completely (Found: C, 72·4; 72·7; H, 4·5, 4·8. $C_{27}H_{20}O_4,2H_2O$ requires C, 73·0; H, 5·4%). The *methyl* ester, prepared by means of diazomethane and crystallised from glacial acetic acid or butyl alcohol, had m. p. 185° (Found: C, 79·4; H, 5·4. $C_{28}H_{22}O_4$ requires C, 79·6; H, 5·2%).

2-(6′-*Methoxy*-β-*naphthoyl*)-3 : 6-*diphenylbenzoic Acid.*—After the reaction between the anhydride (15 g.) and the Grignard solution prepared from magnesium (3·7 g.) and 2-bromo-6-methoxynaphthalene (35·6 g.), a semicrystalline sodium salt was obtained, an alcoholic solution of which was treated with hydrogen chloride. The precipitate, after drying, was triturated with benzene; the insoluble part, which consisted of the desired *keto-acid*, dissolved easily in glacial acetic acid and separated immediately afterwards. After precipitation from ethereal solution with light petroleum it had m. p. 220° after previous sintering (Found: C, 81·3; H, 4·8. $C_{31}H_{22}O_4$ requires C, 81·3; H, 4·8%). It gave a dark green colour with concentrated sulphuric acid. The *methyl* ester, prepared with diazomethane, had m. p. 220° (from glacial acetic acid) (Found: C, 82·3; H, 5·5. $C_{32}H_{24}O_4$ requires C, 81·2; H, 5·0%).

2-p-*Bromobenzoyl*-3 : 6-*diphenylbenzoic acid*, obtained similarly from *p*-bromophenylmagnesium bromide separated spontaneously on treatment of the Grignard product with ice-cold dilute sulphuric acid. It crystallised from glacial acetic acid or toluene in needles, m. p. 200°, and formed an intensely green solution in concentrated sulphuric acid (Found : C, 68·2; H, 3·8. $C_{26}H_{17}O_3Br$ requires C, 68·3; H, 3·7%).

3 : 6-*Diphenylphthalimide*.—The anhydride (10 g.) and urea (5 g.) were thoroughly mixed and heated at 200° for 2 hours. The light brown mass was powdered, washed with water, dried, and crystallised from 50% acetic acid, benzene, or butyl alcohol, yielding 8·2 g. of 3 : 6-*diphenylphthalimide*, m. p. 245° (Found : C, 79·7, 80·0; H, 4·8, 4·8. $C_{20}H_{13}O_2N$ requires C, 80·0; H, 4·3%).

N-*Hydroxy*-3 : 6-*diphenylphthalimide* (I).—A solution of hydroxylamine (6·6 g.) in absolute alcohol (400 c.c.) was shaken with finely powdered diphenylphthalic anhydride (15 g.) for 30 hours at room temperature. The *product* separated from glacial acetic acid or butyl alcohol in lancet-shaped crystals, m. p. 238°, insoluble in water, alcohol, and benzene (yield, quantitative) (Found : C, 75·7; H, 4·6; N, 4·5. $C_{20}H_{13}O_3N$ requires C, 76·2; H, 4·2; N, 4·4%).

3 : 6-*Diphenylanthranilic Acid*.—To a solution of sodium hydroxide (1·2 g.) in water (50 c.c.), the foregoing hydroxyimide (6·6 g.) was added and the dark red solution was heated for 12 hours on the water-bath. The solution, now colourless, was filtered hot; sodium 3 : 6-diphenylanthranilate separated on cooling. The *acid*, obtained on treatment with glacial acetic acid (yield, 96%), was insoluble in water and light petroleum, easily soluble in alcohol, acetone, and ether and was crystallised from benzene or glacial acetic acid; m. p. 200° (decomp.) (Found : C, 79·3; H, 5·6. $C_{19}H_{15}O_2N$ requires C, 78·9; H, 5·2%). The *methyl* ester, prepared by means of diazomethane in benzene solution, had m. p. 119—120°; its solutions exhibited a marked fluorescence (Found : C, 79·8; H, 5·7. $C_{20}H_{17}O_2N$ requires C, 79·3; H, 5·6%). The *acetyl* derivative, m. p. 215°, was prepared by means of acetic anhydride and sodium acetate, and recrystallised from alcohol (Found : C, 76·1; H, 5·1. $C_{21}H_{17}O_3N$ requires C, 76·1; H, 5·1%).

2-*Phenylfluorenone*-1-*carboxylic Acid* (II).—3 : 6-Diphenylphthalic anhydride (6 g.) was suspended in dry benzene (50 c.c.), aluminium chloride (10 g.) added during 30 minutes, and the mixture boiled for 2 hours, cooled, and decomposed with cold hydrochloric acid. An ethereal extract of the product was shaken with sodium carbonate solution. The sodium salt, which crystallised quickly, was acidified, and the *acid* crystallised from glacial acetic acid or xylene; m. p. 199—201° (yield, 4·5 g.). It gave a red colour with concentrated sulphuric acid (Found : C, 79·2; H, 4·1. $C_{20}H_{12}O_3$ requires C, 80·0; H, 4·0%). The *phenylhydrazone*, prepared in alcoholic solution, separated from ethyl acetate in yellowish crystals, m. p. 177° (Found : C, 79·6; H, 4·9. $C_{26}H_{18}O_2N_2$ requires C, 80·0; H, 4·6%). The *methyl* ester, prepared by means of diazomethane, crystallised from ligroin in yellow needles, m. p. 142° (Found : C, 80·5; H, 4·9. $C_{21}H_{14}O_3$ requires C, 80·3; H, 4·5%).

1-*Benzoyl*-2-*phenylfluorenone* (IV).—A benzene solution of the foregoing methyl ester (3·1 g.) was added to phenylmagnesium bromide (prepared from 2·4 g. of magnesium and 15·6 g. of bromobenzene). The *product*, isolated in the usual way, was an oil which solidified on trituration with methanol; it crystallised from glacial acetic acid or benzene in needles (1 g.), m. p. 236°, and gave a violet-red colour with sulphuric acid (Found : C, 86·9; H, 4·4. $C_{26}H_{16}O_2$ requires C, 86·7; H, 4·4%).

1-*Hydroxybenzhydryl*-2 : 9-*diphenylfluorenol* (V).—Methyl 2-phenylfluorenone-1-carboxylate (3·1 g.) was added to a solution of phenyl-lithium in ether (from 1·6 g. of lithium and 10·5 c.c. of bromobenzene; Ziegler and Colonius, *Annalen*, 1930, **479**, 135). After 24 hours, the mixture was worked up in the usual way. From the reddish resin obtained, on prolonged trituration with *iso*propyl alcohol at 0°, crystals (2 g.) separated. Recrystallised from propyl alcohol, these gave stout lancet-shaped crystals of the *fluorenol*, m. p. 123° (decomp.), which formed a brownish-red solution in concentrated sulphuric acid (Found : C, 87·7; H, 6·0. $C_{38}H_{28}O_2$ requires C, 88·3; H, 5·4%). The *iso*propyl-alcoholic mother-liquor was evaporated, and the residue treated with light petroleum–acetone; the white crystalline powder (1 g.) obtained was recrystallised from benzene and identified as 1-benzoyl-2-phenylfluorenone by its colour reaction and mixed m. p. 236°.

2-*Phenylfluorenone*.—2-Phenylfluorenone-1-carboxylic acid (0·5 g.) was heated with boiling quinoline (10 c.c.) and copper-bronze (0·5 g.) for 20 minutes, and the mass treated with dilute sulphuric acid and ether. The ethereal solution was washed with sodium carbonate solution, and evaporated; the residue crystallised from alcohol in golden needles (0·24 g.), m. p. 140—141°, which gave a deep red solution in concentrated sulphuric acid (Found : C, 89·2; H, 5·3. $C_{19}H_{12}O$ requires C, 89·1; H, 4·7%). The *phenylhydrazone* formed brownish needles, m. p. 168° (Found : C, 86·7; H, 6·0. $C_{25}H_{18}N_2$ requires C, 86·7; H, 5·2%).

1′-*Ketoindeno*(2′ : 3′ : 1 : 2)*fluorenone* (III).—2-Phenylfluorenone-1-carboxylic acid (1·5 g.) in carbon tetrachloride (2 c.c.) was boiled for 2 hours after addition of thionyl chloride (2 c.c.), and again for 2 hours after addition of a second portion (5 c.c. of thionyl chloride in 5 c.c. of carbon tetrachloride). The golden-red *diketone* separated spontaneously. It was collected when cold, washed with ethyl acetate (which removed traces of unchanged material), and recrystallised several times from bromobenzene; m. p. 298° (Found: C, 85·2; H, 4·0. $C_{20}H_{10}O_2$ requires C, 85·1; H, 3·5%). The diketone (0·28 g.) was dissolved in boiling glacial acetic acid (25 c.c.), and phenylhydrazine (0·2 g.) in butanol (3 c.c.) added. After 5 minutes' heating at 100°, brown prisms of the *bisphenylhydrazone* separated, m. p. 215° (decomp.) (Found: C, 82·4; H, 4·6. $C_{32}H_{22}N_4$ requires C, 83·1; H, 4·7%).

3-*Phenylphthalic Anhydride*.—A mixture of the tetrahydro-derivative (3 g.) and sulphur (0·7 g.) was heated at 280° for 3 hours, and the product distilled in a vacuum (b. p. 190°/2 mm.). The distillate crystallised, and on recrystallisation from benzene or glacial acetic acid formed needles, m. p. 143° (Found: C, 74·6; H, 3·7. $C_{14}H_8O_3$ requires C, 75·0; H, 3·6%).

6-*Benzoyl*-2-*phenyl*- (VI) *and* 2-*Benzoyl*-3-*phenyl-benzoic Acid* (VII).—A solution of 3-phenylphthalic anhydride (5 g.) in boiling benzene reacted violently with phenylmagnesium bromide solution (0·7 g. of magnesium; 2·6 c.c. of bromobenzene). After 1 hour's boiling and the usual treatment, the alkaline solution was acidified. The resinous products crystallised on trituration with 50% acetic acid and gave an orange-red colour reaction with concentrated sulphuric acid. Fractionation from 60% acetic acid gave a first crop of stout prisms (VII), m. p. 172° after recrystallisation from the same solvent, and a second one of white leaflets (VI), m. p. 163°. The latter substance crystallised with remarkable slowness, which facilitated separation of the isomers [Found: for (VII): C, 79·4, 79·0; H, 5·2, 4·7. Found for (VI): C, 78·8; H, 5·0. $C_{20}H_{14}O_3$ requires C, 79·3; H, 4·7%].

1-*Phenylanthraquinone*.—α-Naphthaquinone (5 g.) and 1-phenylbutadiene (5 g.) were brought into an oil-bath kept at 180°. When the violent reaction ceased, the heating was continued for another 5 minutes, the mass cooled, methyl alcohol (8 c.c.) added, and the product (3 g.), m. p. 177°, collected.

9 : 10-*Dihydroxy*-1 : 9 : 10-*triphenyl*-9 : 10-*dihydroanthracene*.—The foregoing quinone (2·4 g.) reacted with phenylmagnesium bromide (10 mols.). The oil produced crystallised on trituration with benzene–light petroleum. It had m. p. 238° and gave a dark blue colour reaction with concentrated sulphuric acid (Found: C, 87·3; H, 6·1. $C_{32}H_{24}O_2$ requires C, 87·3; H, 5·5%).

1-*Phenylanthracene*.—1-Phenylanthraquinone (3 g.) in alcohol (100 c.c.) was boiled for 8 hours with 30% sodium hydroxide solution (200 c.c.), aqueous ammonia (50 c.c., *d* 0·880), and zinc dust (15 g.). The alcohol was evaporated, and the solid collected and extracted with acetone. The acetone was distilled off, the residue dissolved in propyl alcohol, and, after addition of a few c.c. of alcoholic hydrochloric acid, the solution boiled for some minutes and filtered hot. On cooling, the fluorescent solution deposited yellow needles (2 g.), m. p. 123° (from alcohol) (Found: C, 93·8; H, 5·2. $C_{20}H_{14}$ requires C, 94·5; H, 5·5%).

1 : 5-*Diphenyl*-1 : 4 : 5 : 8 : 11 : 12 : 13 : 14-*octahydroanthraquinone* (IX).—1-Phenylbutadiene (13 g.) and benzoquinone (5·5 g.) were boiled for 6 hours in xylene solution (15 c.c.), the solvent evaporated in a vacuum, and the residue treated with glacial acetic acid. The insoluble *product* (IX) crystallised from butyl acetate or butanol in clusters of needles, m. p. 230° (Found: C, 84·6; H, 6·8. $C_{26}H_{24}O_2$ requires C, 84·8; H, 6·5%).

The glacial acetic acid mother-liquor was evaporated, and the residue distilled in a vacuum (b. p. 240°/0·2 mm.). The distillate partly crystallised on trituration with light petroleum (b. p. 80—100°). Recrystallisation from benzene furnished needles, m. p. 170°, of 5-*phenyl*-5 : 8 : 9 : 10-*tetrahydro*-α-*naphthaquinone* (VIII), which gave a blood-red colour reaction with concentrated sulphuric acid (Found: C, 80·9, 80·8; H, 6·1, 6·2. $C_{16}H_{14}O_2$ requires C, 80·7; H, 6·0%).

1 : 5-*Diphenylanthraquinone*.—Air was passed for 30 minutes through a boiling solution of the octahydro-derivative (IX) (0·3 g.) in 15% alcoholic potassium hydroxide (10 c.c.) (Diels and Alder, *Ber.*, 1929, **62**, 2337; Barnett and Lawrence, J., 1935, 1104), the colour becoming finally straw-yellow. The *product*, after being washed with alcohol and recrystallised from ethyl malonate, had m. p. 355° (Found: C, 86·3, 86·5; H, 4·7, 5·0. $C_{26}H_{16}O_2$ requires C, 86·7; H, 4·4%).

1 : 4 : 5 : 8-*Tetraphenylanthraquinone*.—1 : 4-Diphenylbutadiene (20 g.) and benzoquinone (5 g.) were slowly heated under slightly reduced pressure until a violent reaction set in; the mixture was then kept 5 hours at the same temperature. After cooling, the *product* was washed with cold glacial acetic acid (yield, 10 g.) and recrystallised from nitrobenzene or tetrahydronaphthalene; m. p. 355° (Found: C, 89·5; H, 4·9. $C_{38}H_{24}O_2$ requires C, 89·1; H, 4·7%).

9 : 10-*Dihydroxy*-1 : 4 : 5 : 8 : 9 : 10-*hexaphenyl*-9 : 10-*dihydroanthracene*.—1 : 4 : 5 : 8-Tetraphenylanthraquinone (2·5 g.) dissolved completely in ethereal phenyl-lithium solution (from 5·3 c.c. of bromobenzene and 0·8 g. of lithium turnings). After 24 hours, the black mixture was poured into water and acidified. The *dihydroxy*-compound was collected and recrystallised from a large amount of ethyl malonate; m. p. above 370°. It could not be converted into derivatives owing to its extremely sparing solubility (Found: C, 88·2; H, 5·6. $C_{50}H_{36}O_2$ requires C, 89·8; H, 5·4%).

1 : 4-*Diphenylanthraquinone* (III).—1 : 4-Diphenylbutadiene (5 g.) and α-naphthaquinone (2·2 g.) were heated at 160° for 10 hours and the black product was powdered, treated with hot glacial acetic acid (10 c.c.), and crystallised from benzene (charcoal), yellow needles, m. p. 212°, being obtained (Found: C, 86·5; H, 4·6. $C_{26}H_{16}O_2$ requires C, 86·7; H, 4·4%).

A solution of 1 : 4-diphenylanthraquinone in nitric acid (*d* 1·52) was poured after 30 minutes into ice-water; the *dinitro*-compound crystallised from glacial acetic acid in needles, m. p. 208° (not sharp) (Found: N, 6·2. $C_{26}H_{14}O_6N_2$ requires N, 6·2%). Heated with 10 parts of concentrated sulphuric acid for 1 hour at 100°, the quinone gave a disulphonic acid; the *sodium* salt crystallised as a trihydrate when an aqueous solution of the acid was treated with sodium chloride, and was recrystallised from water (Found: C, 50·6; H, 3·4. $C_{26}H_{14}O_8S_2Na_2,3H_2O$ requires C, 50·5; H, 3·2%). The quinone (3·6 g.) was kept in contact with liquid bromine (1 c.c.) for 48 hours, then triturated with water, and the reddish product washed with glacial acetic acid and sublimed at 0·1 mm.; the yellow sublimate formed needles of a *dibromo*-derivative, m. p. 295°, from glacial acetic acid (Found: C, 59·7; H, 2·4. $C_{26}H_{14}O_2Br_2$ requires C, 60·2; H, 2·7%). When the quinone (5 g.) was heated with liquid bromine (5 c.c.) at 60° for 12 hours, and the excess of bromine distilled in a vacuum, a brown-red *tetrabromo*-1 : 4-*diphenylanthraquinone* was obtained, which separated from nitrobenzene, on addition of alcohol, in red prisms, m. p. above 300° (Found: C, 45·5; H, 1·7. $C_{26}H_{12}O_2Br_4$ requires C, 46·1; H, 1·8%).

1 : 4-*Diphenylanthracene and* 9-*Hydroxy*-1 : 4-*diphenyl*-9 : 10-*dihydroanthracene*.—The foregoing quinone (1 g.) in alcohol (50 c.c.) was heated with 30% sodium hydroxide solution (10 c.c.), aqueous ammonia (25 c.c., *d* 0·880) and zinc dust (6 g.), which dissolved after 6 hours. The solid product crystallised from benzene in colourless rhombohedra and yellow needles; these were separated mechanically. The yellow needles, which gave an intense fluorescence in solution, were recrystallised several times from propyl alcohol or glacial acetic acid; 1 : 4-*diphenylanthracene* thus obtained had m. p. 170° (Found: C, 94·0; H, 5·6. $C_{26}H_{18}$ requires C, 94·5; H, 5·5%). The *picrate*, prepared in propyl-alcoholic solution and recrystallised from picric acid containing propyl alcohol, formed brown needles, m. p. 173° (Found: N, 7·5. $C_{26}H_{18},C_6H_3O_7N_3$ requires N, 7·5%).

The colourless rhombohedra, after recrystallisation from light petroleum (b. p. 80—100°), had m. p. 155° (Found: C, 89·2; H, 6·1. $C_{26}H_{20}O$ requires C, 89·7; H, 5·8%). Apart from the analysis, the structure of 9-*hydroxy*-1 : 4-*diphenyl*-9 : 10-*dihydroanthracene* follows from the observation that the crude product of the above reaction, on treatment with alcoholic hydrochloric acid, gave 1 : 4-diphenylanthracene exclusively, the colourless by-product being dehydrated under these conditions.

9 : 10-*Dihydroxy*-1 : 4 : 9 : 10-*tetraphenyl*-9 : 10-*dihydroanthracene* (X).—To phenylmagnesium bromide solution (from 2·4 g. of magnesium and 15·6 g. of bromobenzene), a hot benzene solution of 1 : 4-diphenylanthraquinone (3 g.) was added and the mixture was boiled for 2 hours. The crystalline *product*, isolated in the usual way, was washed with hot alcohol and recrystallised from benzene, forming needles (3 g.), m. p. 240°, which gave no colour reaction with concentrated sulphuric acid (Found: C, 88·3; H, 5·4. $C_{38}H_{28}O_2$ requires C, 88·4; H, 5·4%).

Hydrocarbon (XII).—The above dihydroxy-compound was boiled for 3 hours with ten times its weight of formic acid or acetyl chloride. The *product*, recrystallised from ligroin or acetic anhydride, had m. p. 322° (Found: C, 94·4; H, 5·3. $C_{38}H_{26}$ requires C, 94·6; H, 5·4%).

1 : 4 : 9 : 10-*Tetraphenylanthracene* (XI).—The diol (X) (0·5 g.) was heated at 80° for 2 hours with potassium iodide (0·5 g.) and sodium hyposulphite (1 g.) in glacial acetic acid (10 c.c.). The mixture was poured into water and the solid was washed with water and separated by fractional crystallisation from methyl ethyl ketone into the less soluble hydrocarbon (XII), m. p. 322°, and 1 : 4 : 9 : 10-*tetraphenylanthracene*, which formed yellow clusters of needles, m. p. 205° (Found: C, 94·5; H, 5·7. $C_{38}H_{26}$ requires C, 94·6; H, 5·4%). When the latter was boiled with ten times its weight of formic acid for 3 hours, it was converted into the high-melting isomer.

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