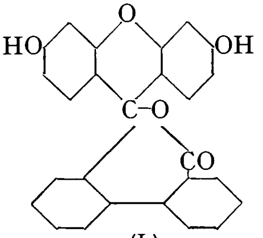
292. *The Interaction of Diphenic Anhydride with Phenols and Hydrocarbons.*

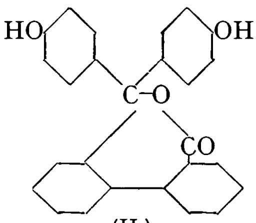
By FRANK BELL and FRED BRIGGS.

Diphenic anhydride reacts with hydrocarbons, phenols, and phenolic ethers to give derivatives of 2-benzoyldiphenyl-2′-carboxylic acid and 2 : 2′-dibenzoyldiphenyl. In spite of statements to the contrary in the literature, evidence for the production of compounds analogous to phenolphthalein and fluorescein is lacking.

ALTHOUGH diphenic anhydride might be expected to resemble phthalic anhydride closely in its reactions, comparatively little work has been done on its condensation with phenols and hydrocarbons. Bischoff and Adkins (*J. Amer. Chem. Soc.*, 1923, **45**, 1030) heated together diphenic anhydride, resorcinol, and zinc chloride and obtained a product which could not be crystallised from any of the common solvents. However, analysis of the impure sodium salt derived from it was held to favour a formula (I) analogous to that of fluorescein. Dutt (J., 1923, **123**, 225), using similar conditions, isolated resorcinol-diphenein, $C_{26}H_{16}O_5$ (I), as prisms, m. p. 172°, showing a brilliant green fluorescence in alkalis, but Underwood and Kochmann (*J. Amer. Chem. Soc.*, 1923, **45**, 3071) ascribed to it the m. p. 178—179° and the formula $C_{26}H_{18}O_6$, and stated that it dissolves in alkalis without fluorescence. Underwood and Clough (*ibid.*, 1929, **51**, 583) state that resorcinoldiphenein may have the m. p. 249° but leave unsettled the relationship of the two forms.



(I.)



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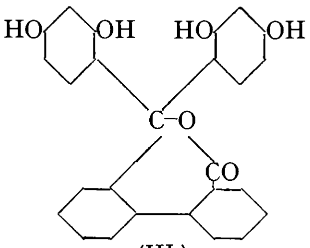


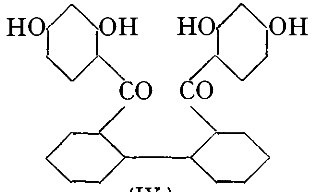
(III.)

The tetrabromo-derivative has been variously described as a pinkish-yellow precipitate, as a product $C_{26}H_{12}O_5Br_4$, which could not be crystallised but dissolved in alkali with a blood-red colour, and as yellow crystals, $C_{26}H_{14}O_6Br_4$, m. p. 273°, soluble in alkali with a yellow colour.

Phenoldiphenein (II) has been obtained by the condensation of phenol and diphenic anhydride in the presence of stannic chloride. Dutt states that it crystallises in needles, m. p. 134°, and dissolves in alkali with a pink colour; Underwood and Kochmann on the other hand describe it as rhombs, m. p. 250—251°, yielding a pale yellow solution in alkali.

In addition, the condensations of diphenic anhydride with phloroglucinol (Dutt, *loc. cit.*), with pyrogallol (Underwood and Kochmann, *loc. cit.*), with anisole (Underwood and Barker, *ibid.*, 1930, **52**, 4082) and with *o*-cresol (*idem, ibid.*, 1936, **58**, 642) have been described. It will be seen that the literature contains obvious discrepancies and it is the object of the present communication to clear the points at issue and to extend the work to include condensations with hydrocarbons.

The condensation of resorcinol with diphenic anhydride under the action of zinc chloride is not a simple reaction. The resinous product dissolves in sodium hydroxide to yield a strongly fluorescent solution. Submitted to the process of purification advocated by Dutt and by Underwood and Kochmann, it gives a poor yield of an almost colourless, highly crystalline compound, m. p. 180° (decomp.), which dissolves in sodium hydroxide to yield a non-fluorescent solution. It suffers loss of alcohol above 180° and then melts at 256—257° and corresponds to the formula $C_{26}H_{18}O_6$. This compound is more advantageously prepared from resorcinol and diphenic anhydride by use of stannic chloride as a condensing agent. No compound of formula $C_{26}H_{16}O_5$ was encountered. Bromination of this substance gave results in accord with those of Underwood and Kochmann. The product is therefore $C_{26}H_{14}O_6Br_4$ and not $C_{26}H_{12}O_5Br_4$. Moreover, since the sodium salt isolated by Bischoff and Adkins had the formula $C_{26}H_{14}O_6Na_4$ and not $C_{26}H_{14}O_5Na_2$, there is, neglecting the analysis of Dutt, no evidence for a structure of type (I). Formula (III), advocated by Underwood and Kochmann, meets all the analytical data, as does (II) for the compound obtained by condensation of phenol and diphenic anhydride. However (IV) and (V) also meet the analytical requirements and appear preferable for the following reasons.



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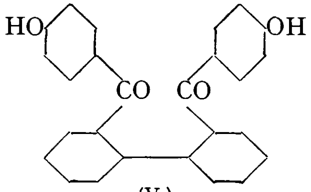

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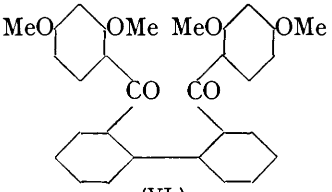


(VI.)

(i) The colour reactions and absorption spectra of the " dipheneins " (Underwood, Harris, and Barker, *J. Amer. Chem. Soc.*, 1936, **58**, 643) are completely different from those of the phthaleins.

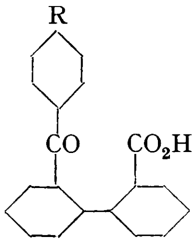
(ii) There is no evidence for a lactone ring in the molecule. Unless hydroxyl groups are present, as in (IV) and (V), the compounds, *e.g.* (VI), are insoluble under all conditions in sodium hydroxide solution.

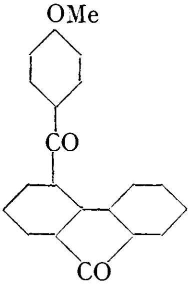
(iii) Methylation of " resorcinoldiphenein " gives a compound identical with that obtained by interaction of resorcinol dimethyl ether and diphenic acid chloride in presence of alumininm chloride. The latter must almost certainly be (VI).

(iv) Methylation of " phenoldiphenein " gives a compound identical with that obtained by interaction of anisole with diphenic acid chloride.

The condensation of phenols with diphenic anhydride by means of stannic chloride has been examined in some detail. In most cases there was obtained a mixture of the appropriate diketone (V with various substitutents and with the hydroxyl groups ortho to the carbonyl groups in the case of *p*-substituted phenols) and the ketonic carboxylic acid (VII). The acids were colourless compounds, yielding pale yellow solutions with sodium hydroxide. The diketones with hydroxyl groups para to carbonyl were colourless solids, yielding deep yellow solutions with sodium hydroxide; those with *o*-hydroxyl groups were yellow and gave deep yellow, sparingly soluble sodium salts. *p*-Chlorophenol and *p*-bromophenol behaved quite differently and gave the corresponding esters, *viz.*, p-*chlorophenyl* and p-*bromophenyl diphenates.*

(VII.)





(VIII.)

Next, it was found that phenolic ethers such as anisole and phenetole condense with diphenic anhydride in a similar manner to phenols. The 2-*anisoyldiphenyl*-2'-*carboxylic acid* so obtained reacted with sulphuric acid to give 4-*anisoylfluorenone* (VIII), alternatively prepared by condensation of fluorenone-4-carboxylic chloride with anisole. On the other hand, 2-p-*ethoxybenzoyldiphenyl*-2'-*carboxylic acid* with sulphuric acid gave progressively 2-p-*hydroxybenzoyldiphenyl*-2'-*carboxylic acid* and then fluorenone-4-carboxylic acid. 2 : 2'-Dianisoyldiphenyl did not react with phenylhydrazine, semicarbazide or hydroxylamine under various conditions. This is probably due to steric factors.

Treatment of hydrocarbons with diphenic anhydride in the presence of aluminium chloride gave the following results: (1) Benzene, toluene, and ethylbenzene underwent no reaction. The diphenic anhydride was recovered as diphenic acid and as fluorenone-4-carboxylic acid. (2) Diphenyl gave non-crystallisable material. (3) *o*-, *m*-, and *p*-Xylenes, mesitylene, and naphthalene gave derivatives of 2-benzoyldiphenyl-2'-carboxylic acid. *p*-Xylene in addition furnished 2 : 2'-*bis*-2'' : 5''-*dimethylbenzoyldiphenyl*, readily prepared by interaction of *p*-xylene with diphenic acid chloride.

2-3'' : 4''- and 2-2'' : 5''-*Dimethylbenzoyldiphenyl*-2'-*carboxylic acids* with sulphuric acid gave the corresponding 4-*dimethylbenzoylfluorenones*; on the other hand, 2-2'' : 4'' : 6''-*trimethylbenzoyl*- and 2-2'' : 4''-*dimethylbenzoyl-diphenyl*-2'-*carboxylic acids* gave fluorenone-4-carboxylic acid (cf. Klages, *Ber.*, 1899, **32**, 1565; Weiler, *ibid.*, 1908, on the splitting of substituted benzophenones).

EXPERIMENTAL.

An asterisk indicates microanalysis by Dr. G. Weiler of Oxford.

Diphenic Acid.—Phenanthrene (Light's 90—95%) was oxidised by the method of Underwood and Kochmann (*J. Amer. Chem. Soc.*, 1924, **46**, 2073), and the resultant phenanthraquinone, without purification by the troublesome bisulphite process, converted into diphenic acid, which was crystallised from acetic acid (yield, 484 g., m. p. 227—229°, from 1 kg. of phenanthrene).

Reaction of Diphenic Anhydride with Hydrocarbons.—Naphthalene. Diphenic anhydride (7 g.) was suspended in naphthalene (10 g.) dissolved in a little benzene, and aluminium chloride (10 g.) added ; after 12 hours the deep red solution was decomposed with water, and the excess of naphthalene removed with steam. The residue was extracted with aqueous ammonia, the extract filtered from a considerable plastic residue and acidified with hydrochloric acid, and the precipitate dissolved in warm sodium bicarbonate solution. The sodium salt which separated in plates on cooling was filtered off, redissolved in hot water, and decomposed with hydrochloric acid. The precipitate was repeatedly crystallised from acetic acid and gave 2-*naphthoyldiphenyl*-2′-*carboxylic acid* in needles, m. p. 180°, unchanged by recrystallisation from benzene (Found : equiv., 356. $C_{24}H_{16}O_3$ requires equiv., 352).

m-*Xylene.* Aluminium chloride (20 g.) was added to a suspension of diphenic anhydride (20 g.) in dry *m*-xylene (about 50 c.c.) ; there was a brisk reaction with considerable evolution of hydrogen chloride. After 4 hours the deep red solution was decomposed with hydrochloric acid, and the excess of xylene removed in steam. The residual solid was filtered off, freed from diphenic acid (7 g.) by extraction with dilute aqueous ammonia, and crystallised from acetic acid. It furnished 2-2′′ : 4′′-*dimethylbenzoyldiphenyl*-2′-*carboxylic acid* in prisms, m. p. 194°, unchanged by recrystallisation from benzene (Found * : C, 80·6 ; H, 5·3. $C_{22}H_{18}O_3$ requires C, 80·0 ; H, 5·4%). This substance was soluble in hot sodium hydroxide solution ; on addition of hydrochloric acid it separated as an oil which almost immediately solidified. It dissolved in cold sulphuric acid to form a bright yellow solution, from which it was precipitated unchanged by water. If the solution was heated at 150° for ¼ hour, decomposition occurred to give fluorenone-4-carboxylic acid.

o-*Xylene.* The procedure was that described for *m*-xylene. After removal of the excess of xylene the residual plastic mass was soluble in dilute aqueous ammonia. It was reprecipitated with hydrochloric acid and separated into diphenic acid (insoluble in cold benzene) and 2-3′′ : 4′′-*dimethylbenzoyldiphenyl*-2′-*carboxylic acid* (easily soluble in benzene). After crystallisation from aqueous alcohol the latter formed needles, m. p. 114—117° (Found : equiv., 329. $C_{29}H_{18}O_3$ requires equiv., 330) ; from acetic acid it crystallised in needles, m. p. 93—95°, which regained the original m. p. on recrystallisation from aqueous alcohol. 1 G. was heated with sulphuric acid (2 c.c.) at 120° for ¼ hour, and the solution poured into water. The precipitate, recrystallised from alcohol, gave 4-3′ : 4′-*dimethylbenzoylfluorenone* in yellow plates, m. p., 144° (Found * : C, 83·9 ; H, 5·1. $C_{22}H_{16}O_2$ requires C, 84·6 ; H, 5·1%), alternatively prepared in almost quantitative yield by the interaction of fluorenone-4-carboxylic chloride and *o*-xylene in the presence of aluminium chloride.

p-*Xylene.* As for *m*-xylene. The product was readily separated into 2 : 2′-*bis*-2′′ : 5′′-*dimethylbenzoyldiphenyl* (insoluble in aqueous ammonia), 2-2′′ : 5′′-*dimethylbenzoyldiphenyl*-2′-*carboxylic acid* (soluble in aqueous ammonia and benzene), and diphenic acid (soluble in aqueous ammonia but insoluble in cold benzene). The first crystallised from acetic acid in colourless prisms, m. p. 148° (Found * : C, 85·5 ; H, 6·2. $C_{30}H_{26}O_2$ requires C, 86·1 ; H, 6·2%), and was alternatively prepared as follows : Aluminium chloride (10 g.) was added slowly to a solution of diphenic acid dichloride (6 g.) in *p*-xylene (12 c.c.), water added after 1 hour, and the excess of *p*-xylene removed with steam. The residue, after solidification, was filtered off, powdered, extracted with aqueous ammonia to remove diphenic acid and crystallised from acetic acid.

2-2′′ : 5′′-Dimethylbenzoyldiphenyl-2′-carboxylic acid crystallised from aqueous alcohol in needles, m. p. 163—165° (Found : equiv. 326). With sulphuric acid at 120° it gave 4-2′ : 5′-*dimethylbenzoylfluorenone*, which formed yellow needles, m. p. 143° (Found * : C, 83·8 ; H, 4·9%).

Mesitylene. As for *m*-xylene. 2-2′′ : 4′′ : 6′′-*Trimethylbenzoyldiphenyl*-2′-*carboxylic acid* crystallised from acetic acid in plates or from benzene as a white powder, m. p. 213° (Found * : C, 80·5 ; H, 5·6. $C_{23}H_{20}O_3$ requires C, 80·2 ; H, 5·8%). It was very sparingly soluble in aqueous ammonia, but dissolved in hot dilute sodium hydroxide solution ; it could be recovered unchanged from potassium hydroxide at 220° or after boiling with stannic chloride for 1 hour, but with sulphuric acid at 100° it gave fluorenone-4-carboxylic acid.

Benzene, toluene, ethylbenzene. As for *m*-xylene. The end product consisted of diphenic acid together with fluorenone-4-carboxylic acid. Diphenic acid was recovered unchanged after heating with aluminium chloride at 150° for 5 hours.

Diphenyl. As for naphthalene. The end product consisted of diphenic acid and much resinous material.

Reaction of Diphenic Anhydride with Phenolic Ethers.—Anisole. The procedure was that described for *m*-xylene. The resinous product was extracted with dilute aqueous ammonia, only a small residue (1 g.) of 2 : 2′-dianisoyldiphenyl remaining. The extract on acidification gave a viscous mass, which crystallised from acetic acid in needles, m. p. 115°; these slowly lost acetic acid at 100°. On recrystallisation from alcohol, acetic acid was removed and 2-*anisoyldiphenyl*-2′-*carboxylic acid* was obtained in white prisms, m. p. 155° (Found: equiv., 330. $C_{21}H_{16}O_4$ requires equiv., 332). 5 G. were heated with sulphuric acid (10 c.c.) at 120° for $\frac{1}{4}$ hour, and the dark coloured solution poured into water. The semi-solid material was extracted with aqueous ammonia, which removed fluorenone-4-carboxylic acid, and the residue repeatedly crystallised from acetic acid to yield 4-*anisoylfluorenone* in yellow prisms (0·5 g.), m. p. 115° (Found *: C, 80·2; H, 4·3. $C_{21}H_{14}O_3$ requires C, 80·3; H, 4·5%). After diphenic anhydride (5 g.), anisole (10 c.c.), and sulphuric acid (2 c.c.) had been heated at 120° for 7 hours, no compound other than diphenic acid was isolated from the product.

2 : 2′-Dianisoyldiphenyl was alternatively prepared by interaction of diphenic acid chloride and anisole (cf. preparation of 2 : 2′-bis-2″ : 5″-dimethylbenzoyldiphenyl). 2-Anisoyldiphenyl-2′-carboxylic acid was obtained as a by-product.

Phenetole. As for anisole. 9·2 G. of diphenic anhydride gave as the only isolated product 11 g. of purified 2-p-*ethoxybenzoyldiphenyl*-2′-*carboxylic acid*. This crystallised from alcohol in prisms, m. p. 178—180° (Found: equiv., 343. $C_{22}H_{18}O_4$ requires equiv., 346). 5 G. in sulphuric acid (10 c.c.) were heated at 120° for $\frac{1}{4}$ hour, and the solution poured into water; the resultant gum on repeated crystallisation from acetic acid was separated into unchanged substance, fluorenone-4-carboxylic acid, and 2-p-*hydroxybenzoyldiphenyl*-2′-*carboxylic acid*. The last crystallised in needles, m. p. 223° (Found *: C, 74·6; H, 4·5. $C_{20}H_{14}O_4$ requires C, 75·4; H, 4·4%); it was converted into fluorenone-4-carboxylic acid on heating with sulphuric acid at 150° for $\frac{1}{4}$ hour. 2-*p*-Ethoxybenzoyldiphenyl-2′-carboxylic acid was recovered unchanged after heating with thionyl chloride or stannic chloride for 1 hour (both reaction mixtures were decomposed with water before being worked up).

Reaction of Diphenic Anhydride with Phenols.—General process. The phenol (10 g.), diphenic anhydride (5 g.), and stannic chloride (5 c.c.) were heated in an oil-bath at 120° for 5—6 hours. The excess of phenol was removed in steam, and the residue (usually a plastic mass) allowed to harden, separated by decantation or filtration, and treated as described under the individual phenols.

p-*Chlorophenol.* The product was insoluble in hot sodium hydroxide solution. It crystallised from alcohol, yielding p-*chlorophenyl diphenate* in colourless plates, m. p. 89° (Found *: C, 67·2; H, 3·6; Cl, 15·3. $C_{26}H_{16}O_4Cl_2$ requires C, 67·4; H, 3·5; Cl, 15·3%), readily hydrolysed by alcoholic potash to yield diphenic acid.

p-*Bromophenol.* The product consisted of diphenic acid and p-*bromophenyl diphenate*, which were readily separated by means of sodium hydroxide. The diphenate crystallised from alcohol in colourless plates, m. p. 100° (Found *: Br, 28·9. $C_{26}H_{16}O_4Br_2$ requires Br, 29·0%).

Phenol. (a) The residual brown solid obtained by the general process was dissolved in warm dilute sodium hydroxide solution and, after filtration, reprecipitated with hydrochloric acid. The precipitate was readily soluble in cold acetic acid, but the solution soon began to deposit crystals. After some hours the crop was filtered off and recrystallised from acetic acid (100 c.c. of boiling acid required), 2 : 2′-bis-4″-hydroxybenzoyldiphenyl being obtained in prisms, m. p. 245°. From the mother-liquor a small yield of 2-*p*-hydroxybenzoyldiphenyl-2′-carboxylic acid (above) was isolated. 0·75 G. of this was heated with phenol (1·5 g.) and stannic chloride (1 c.c.) for 5 hours at 120°; 0·2 g. of purified 2 : 2′-bis-4″-hydroxybenzoyldiphenyl was isolated from the product.

A solution of 2 : 2′-bis-4″-hydroxybenzoyldiphenyl in aqueous sodium hydroxide (pale yellow: no trace of pink) was shaken with methyl sulphate. The liquid soon filled with a precipitate, which on crystallisation from alcohol furnished 2 : 2′-dianisoyldiphenyl in lustrous plates, m. p. 155°, insoluble in even boiling sodium hydroxide solution. Underwood and Barker (*J. Amer. Chem. Soc.*, 1930, **52**, 4084) effected this conversion by means of methyl iodide.

(b) Diphenic anhydride (5 g.) and phenol (10 g.) were heated together at 125° for 5 hours, and the excess of phenol removed in steam. The residual *phenyl hydrogen diphenate* crystallised from acetic acid or benzene–light petroleum in prisms, m. p. 139° (Found *: C, 75·2; H, 4·4. $C_{20}H_{14}O_4$ requires C, 75·4; H, 4·4%). This ester could be reprecipitated unchanged from solution in aqueous ammonia, but was rapidly hydrolysed by sodium hydroxide solution (equiv., 280—159 depending on the conditions of titration). 5 G. in tetrachloroethane (15 c.c.) were treated with aluminium chloride (5 g.), and the mixture heated at 120° for 1 hour; the products isolated were fluorenone-4-carboxylic acid (0·5 g.), diphenic acid, and gummy material. By heating phenyl hydrogen diphenate in sulphuric acid solution at 100° for ¼ hour, fluorenone-4-carboxylic acid was obtained in good yield.

(c) Aluminium chloride (15 g.) was added to a suspension of diphenic anhydride (8 g.) in a solution of phenol (15 g.), in benzene (15 c.c.), a brisk reaction ensuing. The mixture was left overnight and decomposed with hydrochloric acid, and the benzene and the excess of phenol removed in steam. The residue was almost pure phenyl hydrogen diphenate.

(d) A mixture of diphenic anhydride (7 g.), phenol (14 g.), and sulphuric acid (2 c.c.) was maintained at 115° for 5 hours, then poured into water, and the excess of phenol removed by evaporation. The residual solid was filtered off, dissolved in aqueous ammonia, and reprecipitated by hydrochloric acid. The oil which separated slowly solidified to a plastic mass, which was fractionally crystallised from acetic acid. 2-*p*-Hydroxybenzoyldiphenyl-2′-carboxylic acid (1·5 g.) was obtained.

o-*Cresol.* (a) As for phenol (a). The product consisted of 2 : 2′-bis-6″-hydroxy-*m*-toluoyldiphenyl (Underwood and Barker, *loc. cit.*), with some 2-6″-*hydroxy*-m-*toluoyldiphenyl*-2′-*carboxylic acid* (Found *: C, 75·8; H, 4·9. $C_{21}H_{16}O_4$ requires C, 75·9; H, 4·8%), which crystallised from acetic acid in needles, m. p. 207°. When heated in sulphuric acid solution at 120° for ½ hour, the latter compound gave fluorenone-4-carboxylic acid, whereas the former gave only water-soluble compounds.

(b) As for phenol (d). 2-6″-Hydroxy-*m*-toluoyldiphenyl-2′-carboxylic acid was obtained in small yield.

m-*Cresol.* Treatment of the condensation product with dilute aqueous sodium hydroxide gave a yellow residue (A) and a solution, which on acidification gave a black tar (B). The residue A was decomposed with hydrochloric acid and then on crystallisation from alcohol or acetic acid gave 2 : 2′-*bis*-5″-*hydroxy*-o-*toluoyldiphenyl* in prisms, m. p. 147° (Found *: C, 78·7; H, 5·5. $C_{28}H_{22}O_4$ requires C, 79·6; H, 5·2%). B was dissolved in hot alcohol and the solution on cooling deposited prisms, m. p. 120° (decomp.); recrystallisation raised the decomposition point to 123—125°, at which temperature about 8% of ethyl alcohol was evolved. The residual glassy mass was very soluble in acetic acid, benzene, and chloroform and was not rendered crystalline by light petroleum. It readily crystallised from alcohol and appeared to be an isomeric *bishydroxytoluoyldiphenyl* (Found *: C, 77·1; H, 6·1. $C_{28}H_{22}O_4,C_2H_5{\cdot}OH$ requires C, 76·9; H, 6·0%). It was insoluble in sodium carbonate solution.

p-*Cresol.* The condensation product was separated into 2 : 2′-*bis*-4″-*hydroxy*-m-*toluoyldiphenyl*, insoluble in sodium hydroxide solution, and 2-4″-*hydroxy*-m-*toluoyldiphenyl*-2′-*carboxylic acid*, soluble in that solvent. The former crystallised from alcohol or acetic acid in pale yellow prisms, m. p. 205° (Found *: C, 79·0; H, 5·2%), coloured bright yellow by sodium hydroxide solution, and the latter from alcohol in pale yellow prisms, m. p. 190—194° (Found *: C, 75·3; H, 4·9. $C_{21}H_{16}O_4$ requires C, 75·9; H, 4·8%), easily soluble in aqueous sodium hydroxide to yield a bright yellow solution.

m-4-*Xylenol.* The product was boiled with sodium hydroxide solution and filtered hot. The residue was boiled with hydrochloric acid and then repeatedly crystallised from acetic acid, 2 : 2′-*bis*-2″-*hydroxy*-3″ : 5″-*dimethylbenzoyldiphenyl* being obtained in bright yellow needles, m. p. 168° (Found *: C, 79·3; H, 5·7. $C_{30}H_{26}O_4$ requires C, 80·0; H, 5·8%).

p-*Xylenol.* The product was extracted with dilute aqueous ammonia, the residue dissolved in sodium hydroxide solution, and the filtered solution acidified with hydrochloric acid. The precipitate, crystallised from acetic acid, gave 2 : 2′-*bis*-4″-*hydroxy*-2″ : 5″-*dimethylbenzoyldiphenyl* in colourless needles, m. p. 252° (Found *: C, 79·2; H, 5·8%).

The ammoniacal extract was treated with hydrochloric acid, and the precipitate crystallised from acetic acid. It gave 2-4″-*hydroxy*-2″ : 5″-*dimethylbenzoyldiphenyl*-2′-*carboxylic acid* in prisms, m. p. 245° (Found *: C, 75·7; H, 5·1. $C_{22}H_{18}O_4$ requires C, 76·3; H, 5·2%).

o-4-*Xylenol.* The product became bright yellow on heating with sodium hydroxide solution. After cooling, the solid was filtered off, warmed with hydrochloric acid, most of the colour being discharged, and crystallised from acetic acid. 2 : 2′-*Bis*-2″-*hydroxy*-4″ : 5″-*dimethylbenzoyldiphenyl* was obtained in pale yellow prisms, m. p. 163° (Found *: C, 79·3; H, 5·7%). The material soluble in sodium hydroxide solution was reprecipitated with hydrochloric acid and then repeatedly crystallised from acetic acid, 2-2″-*hydroxy*-4″ : 5″-*dimethylbenzoyldiphenyl*-2′-*carboxylic acid* being obtained in colourless prisms, m. p. 177° (Found *: C, 76·1; H, 5·5%).

Thymol. The product was separated into 2 : 2′-*bis*-4″-*hydroxy*-2″-*methyl*-5″-iso*propylbenzoyldiphenyl*, insoluble in aqueous ammonia, and 2-4″-*hydroxy*-2″-*methyl*-5″-iso*propylbenzoyldiphenyl*-2′-*carboxylic acid*. The former crystallised from acetic acid in colourless needles,

m. p. 258° (Found * : C, 80·1; H, 6·6. $C_{34}H_{34}O_4$ requires C, 80·6; H, 6·7%), and the latter from acetic acid in colourless prisms, m. p. 245°, soluble in warm sodium bicarbonate solution with a pale yellow colour (Found * : C, 76·2; H, 5·9. $C_{24}H_{22}O_4$ requires C, 77·0; H, 5·9%).

Quinol. Condensation with diphenic anhydride was attempted, sulphuric acid or stannic chloride being used as condensing agent, but no crystallisable product was isolated.

Resorcinol. (a) " Resorcinoldiphenein," prepared and purified by the method of Underwood and Kochmann (*loc. cit.*), formed almost colourless prisms, m. p. 180° (decomp.). It was soluble in dilute aqueous sodium hydroxide to give a pale yellow solution devoid of fluorescence. (b) Diphenic anhydride (5 g.), resorcinol (10 g.), and stannic chloride (5 c.c.) were heated together at 120° for 6 hours. The product was repeatedly boiled with water to free it from the excess of resorcinol and the residual black tar was then extracted with boiling dilute sodium hydroxide solution. The extract, filtered from slimy material, was acidified with hydrochloric acid, and the precipitated black tar separated by decantation and boiled with alcohol. On cooling, the alcohol deposited 2 : 2'-*bis*-2'' : 4''-*dihydroxybenzoyldiphenyl* (IV), m. p. 180° (decomp.) (6 g.). 3·493 G., kept at 200° for $\frac{1}{4}$ hour, evolved alcohol and gave 3·136 g. of solvent-free substance, m. p. 256°, unchanged by crystallisation from acetic acid, benzene–light petroleum, or by solution in aqueous sodium hydroxide or sodium bicarbonate, followed by reprecipitation with hydrochloric acid. It did not again take up alcohol of crystallisation when recrystallised from alcohol [Found * for material of m. p. 256° : C, 72·8; H, 4·2. $C_{26}H_{18}O_6$ requires C, 73·2; H, 4·3%. Found for material of m. p. 180° (decomp.) : $C_2H_5{\cdot}OH$, 10·2. $C_{26}H_{18}O_6,C_2H_5{\cdot}OH$ requires $C_2H_5{\cdot}OH$, 9·75%].

A solution of 2 : 2'-bis-2'' : 4''-dihydroxybenzoyldiphenyl in sodium hydroxide was shaken with methyl sulphate. The pale yellow, resinous precipitate was filtered off, dried, and extracted with a small bulk of benzene. The filtered extract was treated with light petroleum, and the resultant viscous oil separated by decantation and dissolved in alcohol. Crystals slowly separated in the course of a day; six recrystallisations from alcohol raised the m. p. to 132°. It was then found that the troublesome impurity was best eliminated by crystallisation from carbon tetrachloride. After two crystallisations the highly crystalline product had m. p. 137—140°. The appearance under the microscope was identical with that of 2 : 2'-*bis*-2'' : 4''-*dimethoxybenzoyldiphenyl*, obtained in large prisms, m. p. 140—142° (Found * : OMe, 26·4. $C_{30}H_{26}O_6$ requires OMe, 25·7%), by the process outlined below; a mixed m. p. with it gave 138—141°.

Aluminium chloride (5 g.) was added to a cooled solution of diphenic acid chloride (5 g.) in resorcinol dimethyl ether (10 c.c.). The mixture gradually became black; after standing overnight, it was decomposed with ice, and the excess of resorcinol dimethyl ether removed in steam. The pitch-like residue was heated with dilute sodium hydroxide solution, becoming harder and light yellow in colour. It was dissolved in alcohol and poured into boiling sodium hydroxide solution to free it from the last traces of sodium hydroxide-soluble material. The residue was dissolved in hot alcohol. On cooling, there separated a crop of very indefinite m. p.; the mother-liquor deposited a small quantity of prisms, m. p. 208—213°. The main crop was repeatedly crystallised from alcohol, whereby 2 : 2'-bis-2'' : 4''-dimethoxybenzoyldiphenyl, m. p. 140—142°, was freed from a small amount of less soluble material, m. p. 195—201°. The m. p. was not changed by recrystallisation from carbon tetrachloride or ethyl acetate. The substance separated from acetic acid in needles of indefinite m. p.; in acetone, acetic anhydride, and chloroform it was very soluble.

Phloroglucinol. No pure compound could be isolated.

Pyrogallol. The result was in agreement with that of Underwood and Kochmann (*loc. cit.*). The black amorphous product could not be obtained pure.

Reactions of Fluorenone-4-carboxylic Acid.—(a) 3 G. of the acid were added slowly to potassium hydroxide (10 g.) at 200—220°. After cooling, the product was dissolved in water, and the boiling solution treated with excess of hydrochloric acid. The precipitate on fractional crystallisation from acetic acid yielded diphenic acid, unchanged material, and *diphenyl-*2 : 6-*dicarboxylic acid* (Found : equiv., 121. $C_{14}H_{10}O_4$ requires equiv., 121). The last formed needle crystals, m. p. 282°, and dissolved in warm sulphuric acid to yield a deep red solution, from which water precipitated fluorenone-4-carboxylic acid in quantitative yield.

(b) A mixture of the acid (6 g.), phenol (12 g.), and sulphuric acid (2 c.c.) was maintained at 115° for 8 hours. The product was diluted with water, the excess of phenol removed by evaporation, and the resultant solid filtered off. This was dissolved in dilute aqueous ammonia and reprecipitated by hydrochloric acid. The sticky product was very soluble in acetic acid and ethyl alcohol, but insoluble in benzene. Repeated crystallisation from ether gave

9 : 9-*di*-p-*hydroxyphenylfluorene*-4-*carboxylic acid* in flat needles, m. p. 276—279° (decomp.) (Found *: C, 79·1; H, 4·7. $C_{26}H_{18}O_4$ requires C, 79·1; H, 4·6%). This compound appears to have been previously obtained in an impure condition by Graebe and Aubin (*Annalen*, 1888, **247**, 286) and by Underwood and Kochmann (*loc. cit.*).

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