Structural Problems in the Indole Group. Part V. Some Derivatives of 2 : 3-Diphenylindole.*

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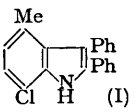
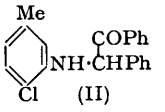
Both 4- and 6-methyl-2 : 3-diphenylindole have been obtained by a Fischer reaction from deoxybenzoin *m*-tolylhydrazone and from the action of *m*-toluidine on benzoin. The former has been unambiguously synthesised by decarboxylation of 4-methyl-2 : 3-diphenylindole-7-carboxylic acid. The possibility of synthesising 1 : 2 : 3 : 4-tetrahydro-5-methylcarbazole similarly from the corresponding carboxylic acid has also been investigated. 2 : 3-Diphenylindole-4-, -5-, -6-, and -7-carboxylic acids have been prepared by the Fischer reaction. The 4- and the 6-carboxylic acid were obtained as a mixture from deoxybenzoin *m*-carboxyphenylhydrazone and identified by conversion of the latter acid into the known fluorenone-3-carboxylic acid.

Since the cyclisation process can proceed in two directions, ambiguity attaches to the structure of the products obtained by an extension to *meta*-substituted anilines of the reaction by which Japp and Murray (*J.*, 1894, **65**, 889) prepared 2 : 3-diphenylindole from aniline and benzoin. Ritchie (*J. Proc. Roy. Soc., N.S.W.*, 1946, **80**, 33) found that only one of the two possible products, proved to be 6-methyl-2 : 3-diphenylindole, was formed from *m*-toluidine. Similar ambiguity is associated with the application of the Fischer reaction to *meta*-substituted phenylhydrazines, and, since preliminary experiments showed that a mixture, the separation of which proved to be difficult, resulted from deoxybenzoin *m*-tolylhydrazone, it seemed desirable to obtain and examine an authentic sample of 4-methyl-2 : 3-diphenylindole. For this purpose 7-chloro-4-methyl-2 : 3-diphenylindole (I) was prepared from 2-chloro-5-methylaniline by the Japp–Murray reaction in the presence of zinc chloride. The use of toluene-*p*-sulphonic acid as catalyst (cf. Ritchie, *loc. cit.*) gave a trace of the same product, but with concentrated hydrochloric acid the reaction stopped at the



(I)



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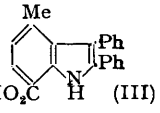


(III)

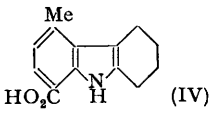
intermediate stage (II). The yields of the indole were, however, small, and it was more conveniently obtained by the Fischer reaction from 2-chloro-5-methylphenylhydrazine. Although hydrogen chloride was evolved in attempts to obtain 4-methyl-2 : 3-diphenylindole from this substance by heating it with palladium–charcoal in hydrogen, nothing pure could be isolated from the product. This was surprising in view of the fact that 2 : 3-diphenylindole was satisfactorily obtained from its 7-chloro-derivative under similar conditions, which had no effect on 2 : 3-diphenylindole itself and the 6-methyl compound. The 7-chloro-2 : 3-diphenylindole was prepared by the Fischer route; attempts to make it by the Japp–Murray process with *o*-chloroaniline under various conditions gave products from which nothing crystalline could be obtained.

* Part IV, *J.*, 1940, 283.

2 : 3-Diphenylindole-7-carboxylic acid was conveniently prepared in small amounts from benzoin in reaction with anthranilic acid and its hydrochloride, by taking advantage of the sparingly soluble character of its sodium salt, but the process was wasteful because the yields were small and much 2 : 3-diphenylindole was obtained from the product. Attempts to obtain the methyl ester similarly from methyl anthranilate failed. Larger quantities of the acid were therefore made by the Fischer reaction with *o*-hydrazinobenzoic acid and deoxybenzoin. Decarboxylation of 2 : 3-diphenylindole-7-carboxylic acid with copper oxide in boiling quinoline gave an unsatisfactory product, but the process was effected by heating the acid with soda-lime. 4-Methyl-2 : 3-diphenylindole-7-carboxylic acid (III) was accordingly prepared from the less readily available 2-amino-4-methylbenzoic acid through the corresponding hydrazine and a Fischer reaction, and converted into 4-methyl-2 : 3-diphenylindole by distillation of its sodium salt with soda-lime.

Ritchie's method for the preparation of 6-methyl-2 : 3-diphenylindole gave products from which, in addition to this substance, very small quantities of the 4-methyl compound were isolated chromatographically with alumina, but greater amounts of the new isomer were extracted from the mixture obtained from a Fischer reaction with deoxybenzoin *m*-tolylhydrazone. Substantial proportions of both isomers were ultimately isolated from the latter reaction by separation with the aid of picric acid.

Decarboxylation of 1 : 2 : 3 : 4-tetrahydrocarbazole-8-carboxylic acid by distillation with soda-lime (cf. Collar and Plant, *J.*, 1926, 808), even in nitrogen, was found to be accompanied by some dehydrogenation, and the presence of carbazole in the distillate was detected by its colour reaction in concentrated sulphuric acid with sodium nitrite. Decarboxylation of 1 : 2 : 3 : 4-tetrahydro-5-methylcarbazole-8-carboxylic acid (IV), from



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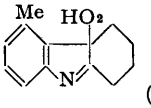

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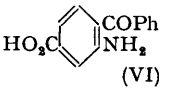

(VI)

2-hydrazino-4-methylbenzoic acid and *cyclo*hexanone, which it was hoped would give authentic 1 : 2 : 3 : 4-tetrahydro-5-methylcarbazole, was, however, accompanied by another difficulty which arose through the formation of the hydroperoxide (V) during working up of the product. The tendency of tetrahydrocarbazoles to form peroxides (Beer, McGrath, and Robertson, *J.*, 1950, 2118) is known to be well developed in the methyl derivatives (Campbell and McCall, *J.*, 1950, 2870; Jones and Tomlinson, *J.*, 1953, 4114). Both the Fischer reaction with *cyclo*hexanone *m*-tolylhydrazone and the action of *m*-toluidine on 2-chloro*cyclo*hexanone (Campbell and McCall, *loc. cit.*) should give mixtures of 1 : 2 : 3 : 4-tetrahydro-5- and -7-methylcarbazole, but it has not been possible to obtain the components in a pure condition.

Although 2 : 3-diphenylindole-5-carboxylic acid was obtained unambiguously from deoxybenzoin *p*-carboxyphenylhydrazone, two acids, m. p. 211—213° and 223—225° respectively, were isolated through their methyl esters from the product of a Fischer reaction with the corresponding *m*-carboxy-compound. The former, on oxidation and hydrolysis, gave 3-amino-4-benzoylbenzoic acid (VI), m. p. 217—218°, which was converted into the known fluorenone-3-carboxylic acid, m. p. 302—303° (Campbell and Stafford, *J.*, 1952, 299, give m. p. 304°). This proved it to be 2 : 3-diphenylindole-6-carboxylic acid, for the alternative would have given 3-amino-2-benzoylbenzoic acid, which is known to melt at 193—194° (Lawrance, *J. Amer. Chem. Soc.*, 1920, **42**, 1877), and fluorenone-1-carboxylic acid, m. p. 192—193°.

Experimental

Condensation of 2-Chloro-5-methylaniline with Benzoin.—(*a*) The amine (1·8 g.), benzoin (0·75 g.), and concentrated hydrochloric acid (0·2 c.c.) were refluxed for 1 hr. and then extracted with ether. When the extract was shaken with very dilute hydrochloric acid until free from unchanged amine, dried ($MgSO_4$), and evaporated, and the residue crystallised from ethanol, α-(*2-chloro-5-methylanilino*)*deoxybenzoin* (0·37 g.), yellow prisms, m. p. 101° (from acetic acid), was obtained (Found : C, 75·2; H, 5·2. $C_{21}H_{18}ONCl$ requires C, 75·1; H, 5·4%).

(*b*) After a mixture of the amine (1·41 g.), benzoin (1·06), and powdered zinc chloride (0·68 g.) had been heated under a reflux condenser at 180° for 1 hr. and then treated as above, the residue was adsorbed on alumina from benzene–light petroleum. Elution with the same solvent removed first *7-chloro-4-methyl-2 : 3-diphenylindole* (0·3 g.), pale yellow prisms, m. p. 128° (from ethanol) (Found : C, 79·6; H, 4·5. $C_{21}H_{16}NCl$ requires C, 79·4; H, 5·0%), and then small amounts of α-(2-chloro-5-methylanilino)deoxybenzoin and 6-methyl-2 : 3-diphenylindole, identified by mixed m. p.s.

Deoxybenzoin 2-Chloro-5-methylphenylhydrazone (4·3 g.), which separated in needles, m. p. 108°, after an ethanolic solution of molecular proportions of the ketone and hydrazine had been boiled for 10 min. (Found : C, 74·9; H, 5·8. $C_{21}H_{19}N_2Cl$ requires C, 75·3; H, 5·7%), was refluxed for a few hr. in acetic acid (54 c.c.) containing concentrated hydrochloric acid (32 c.c.), and, when cold, the solid was collected and crystallised from acetic acid; 7-chloro-4-methyl-2 : 3-diphenylindole, m. p. 127—128°, identical (mixed m. p.) with the above product, was obtained in 29% yield.

7-Chloro-2 : 3-diphenylindole.—A mixture of *o*-chlorophenylhydrazine (6 g.) and deoxybenzoin (8·25 g.), which had been heated on a steam-bath until clear, solidified on cooling and gave the *o-chlorophenylhydrazone* in plates (91%), m. p. 80—81°, on recrystallisation from acetic acid (Found : C, 74·9; H, 5·9. $C_{20}H_{17}N_2Cl$ requires C, 74·9; H, 5·3%). After the hydrazone (16 g.) had been refluxed for 3½ hr. with acetic acid (300 c.c.) and concentrated hydrochloric acid (120 c.c.), and the whole poured into water, the product, when solid, was collected and crystallised from acetic acid; *7-chloro-2 : 3-diphenylindole* was obtained in plates (51%), m. p. 96—97° (Found : C, 79·2; H, 4·7. $C_{20}H_{14}NCl$ requires C, 79·1; H, 4·6%). When this substance was heated with 25% of its weight of palladium–charcoal (10%) in hydrogen at 280—300° for 9½ hr., and then at 320° for ½ hr., the product extracted with boiling acetone, and the extract diluted with water, almost pure 2 : 3-diphenylindole (57%), identified by mixed m. p. with an authentic sample, was precipitated.

1-Acetyl-7-chloro-2 : 3-diphenylindole.—Acetyl chloride (1·74 c.c.) was gradually added, with vigorous shaking, to 7-chloro-2 : 3-diphenylindole (7·15 g.) in acetone (70 c.c.) containing potassium hydroxide (1·98 g.) in water (1 c.c.), and the whole was poured into water. When the solid was crystallised from methanol, *1-acetyl-7-chloro-2 : 3-diphenylindole* was obtained in needles (4·04 g.), m. p. 116° (Found : C, 76·1; H, 4·8. $C_{22}H_{16}ONCl$ requires C, 76·4; H, 4·6%). After a solution of this substance in aqueous-ethanolic potassium hydroxide had been refluxed for 1 hr., addition of water precipitated 7-chloro-2 : 3-diphenylindole, identified by mixed m. p.

Chromic anhydride (2·13 g.) in a little water was added to the acetyl compound (5·44 g.) in acetic acid (80 c.c.), and the whole kept at room temperature for 3 hr., then at 70° for 10 min., and poured into water. After the solid had been refluxed for 1 hr. with ethanol (40 c.c.) and concentrated hydrochloric acid (20 c.c.), dilution with water precipitated *2-benzamido-3-chlorobenzophenone*, needles (58%), m. p. 141° (from ethanol) (Found : C, 71·0; H, 4·2. $C_{20}H_{14}O_2NCl$ requires C, 71·5; H, 4·2%). A mixture of this substance with 15 parts of sulphuric acid (65%) was refluxed for 4 hr., poured into water, and made alkaline with ammonia. The precipitated *2-amino-3-chlorobenzophenone* (89%) separated from aqueous ethanol in yellow needles, m. p. 56—57° (Found : C, 67·7; H, 4·4. $C_{13}H_{10}ONCl$ requires C, 67·4; H, 4·3%).

2 : 3-*Diphenylindole-7-carboxylic Acid.*—(*a*) Benzoin (3·6 g.), anthranilic acid hydrochloride (3 g.), and anthranilic acid (8·05 g.) were heated at 135—140° for 1 hr. and then at 140—150° until, after vigorous frothing, it became a viscous brown liquid. The whole was extracted with ether, and the extract repeatedly washed with very dilute hydrochloric acid, and then shaken vigorously with dilute aqueous sodium hydroxide. The sparingly soluble sodium salt was filtered off, and acidification (HCl) of its filtered solution in boiling water precipitated 2 : 3-*diphenylindole-7-carboxylic acid* (12·4% based on the benzoin), needles, m. p. 256° (from acetic acid) (Found : C, 80·0; H, 4·9. $C_{21}H_{15}O_2N$ requires C, 80·5; H, 4·8%). The ethereal part of the filtrate, on being dried and evaporated, gave 2 : 3-diphenylindole (about 30% based on the benzoin).

(*b*) After a mixture of deoxybenzoin (0·64 g.) and *o*-hydrazinobenzoic acid (0·5 g.) had been gradually heated to 180° and the product crystallised from acetic acid, *deoxybenzoin o-carboxyphenylhydrazone* was obtained in yellow needles (93%), m. p. 232° (decomp.) (Found : C, 76·6; H, 5·3. $C_{21}H_{18}O_2N_2$ requires C, 76·4; H, 5·5%). After a solution of this hydrazone (2 g.) in acetic acid (80 c.c.) containing concentrated hydrochloric acid (25 c.c.) had been refluxed for 4 hr., 2 : 3-diphenylindole-7-carboxylic acid (0·75 g.), m. p. 254—256°, identical (mixed m. p.) with the above product, separated on cooling. Its *methyl* ester separated in plates (0·25 g.), m. p. 123°, after a solution of the acid (0·5 g.) in methanol (50 c.c.) containing concentrated sulphuric

acid (1 c.c.) had been refluxed for 5 hr. (Found : C, 80·6; H, 5·2. $C_{22}H_{17}O_2N$ requires C, 80·7; H, 5·2%).

Decarboxylation of 2 : 3-diphenylindole-7-carboxylic acid (0·6 g.) was effected by heating it with soda-lime (2·3 g.) in a distilling flask. Some of the product distilled over and the rest was extracted from the residue with acetone, the total yield of 2 : 3-diphenylindole being 58%.

When 2 : 3-diphenylindole-7-carboxylic acid was oxidised as described for 1-acetyl-7-chloro-2 : 3-diphenylindole, *2-benzamido-3-benzoylbenzoic acid*, needles (50%), m. p. 218° (decomp.) (from acetic acid), was obtained (Found : C, 73·6; H, 4·4. $C_{21}H_{15}O_4N$ requires C, 73·0; H, 4·3%).

4-Methyl-2 : 3-diphenylindole-7-carboxylic Acid.—The crude hydrochloride of 2-hydrazino-4-methylbenzoic acid was prepared from the corresponding amine in 68% yield by a method similar to that described in *Org. Synth.*, 1949, **29**, 54, for *o*-hydrazinobenzoic acid hydrochloride. The solid (1·5 g., dried at room temperature) obtained by grinding this hydrochloride with aqueous sodium acetate was heated with deoxybenzoin (1·95 g.) gradually to 140°. After the product had been crystallised from ethanol, *deoxybenzoin 2-carboxy-5-methylphenylhydrazone* was obtained in pale yellow needles (58%), m. p. 226° (Found : C, 76·4; H, 5·8. $C_{22}H_{20}O_2N_2$ requires C, 76·7; H, 5·8%). When the hydrazone (3·17 g.) had been refluxed with acetic acid (120 c.c.) and concentrated hydrochloric acid (30 c.c.) for 4 hr., 4-methyl-2 : 3-diphenylindole-7-carboxylic acid separated, on cooling, in prisms (40%), m. p. 244—245°. It was characterised as its *methyl* ester, prisms, m. p. 136° (from methanol) (Found : C, 80·9; H, 5·8. $C_{23}H_{19}O_2N$ requires C, 80·9; H, 5·6%).

4-Methyl-2 : 3-diphenylindole.—The sodium salt which separated on cooling from a filtered solution of 4-methyl-2 : 3-diphenylindole-7-carboxylic acid (2 g.) in boiling aqueous sodium hydroxide (15 c.c. of 2·5%) was dried and distilled with crushed soda-lime (6·6 g.). When the distillate was crystallised from ethanol, *4-methyl-2 : 3-diphenylindole* was obtained in prisms (0·42 g.), m. p. 135° (Found : C, 89·1; H, 6·3. $C_{21}H_{17}N$ requires C, 89·0; H, 6·0%).

After a mixture of this substance (0·3 g.), acetic anhydride (2 c.c.), and dry potassium acetate (0·3 g.) had been refluxed for 4 hr. and poured into water, crystallisation of the sticky product from ethanol gave *1-acetyl-4-methyl-2 : 3-diphenylindole* in pale brown needles (0·12 g.), m. p. 181° (Found : C, 85·0; H, 6·1. $C_{23}H_{19}ON$ requires C, 84·9; H, 5·8%).

The Fischer Reaction with Deoxybenzoin m-Tolylhydrazone.—A mixture of deoxybenzoin (20·9 g.) and *m*-tolylhydrazine (13·05 g.) was heated in a Claisen flask for 1 hr. at 100° and then for a short time at 120—130°. After the addition of powdered, anhydrous zinc chloride (29 g.), the temperature was gradually raised during 1 hr. to 230° and a mixture of 4- and 6-methyl-2 : 3-diphenylindole (87% yield) was then distilled off at 200—250°/30 mm. and collected as a pale brown syrup. When some of this syrup (11·6 g.) was mixed with picric acid (9·4 g.) in hot ethanol (75 c.c.), the fairly pure picrate of 6-methyl-2 : 3-diphenylindole, from which the free indole was obtained on treatment with alkali, separated on cooling in dark red needles (9·9 g.), m. p. 158—163° (Ritchie, *loc. cit.*, gives m. p. 166°), identified by mixed m. p. The mother-liquor, mixed with ether, was shaken with dilute aqueous sodium hydroxide until the picric acid had been removed, the ethereal layer dried (Na_2SO_4) and evaporated, and the residue crystallised from acetic acid; 4-methyl-2 : 3-diphenylindole was obtained in prisms (2·3 g.), m. p. 134—135°, identical (mixed m. p.) with the substance described above.

1 : 2 : 3 : 4-Tetrahydro-5-methylcarbazole-8-carboxylic Acid.—After crude 2-hydrazino-4-methylbenzoic acid hydrochloride (5 g.) and *cyclo*hexanone (2·8 g.) had been shaken with aqueous-ethanolic sodium acetate for 10 min. at 70°, and the product crystallised from ethanol, the *hydrazone* was obtained in almost colourless needles (4 g.), m. p. 198—200° (decomp.) (Found : C, 68·4; H, 7·5. $C_{14}H_{18}O_2N_2$ requires C, 68·3; H, 7·3%). When this was heated with water (80 c.c.) and concentrated sulphuric acid (20 c.c.) at 100° for 15 min. and the solid crystallised from methanol, *1 : 2 : 3 : 4-tetrahydro-5-methylcarbazole-8-carboxylic acid* separated in pale yellow prisms (1·95 g.), m. p. 244° (Found : C, 73·0; H, 6·7. $C_{14}H_{15}O_2N$ requires C, 73·4; H, 6·6%).

After the acid (1·2 g.) had been distilled with soda-lime (5 g.) in nitrogen and the distillate (0·65 g., m. p. 137—145°) crystallised from ethanol, needles, m. p. 140—146°, were obtained, but an attempt to effect further purification by recrystallisation from the same solvent was unsuccessful; dilution of the solution with water gave a red gum which liberated iodine from acidified potassium iodide. When the distillate was crystallised first from benzene and then from light petroleum, the whole being left overnight, *1 : 2 : 3 : 4-tetrahydro-5-methyl-11-carbazolyl hydroperoxide* was obtained in prisms, m. p. 125° (decomp.), which liberated iodine from acidified potassium iodide (Found : C, 71·5; H, 7·0. $C_{13}H_{15}O_2N$ requires C, 71·9; H, 6·9%).

2 : 3-*Diphenylindole*-5-*carboxylic Acid*.—*Deoxybenzoin* p-*carboxyphenylhydrazone*, orange plates, m. p. 217—218° (from amyl alcohol) (Found : C 76·7; H 6·0%), prepared by heating deoxybenzoin (15 g.) with *p*-hydrazinobenzoic acid (11·7 g.; cf. *Org. Synth.*, *loc. cit.*) at 160° for 10 min., was refluxed without purification with acetic acid (800 c.c.) and concentrated hydrochloric acid (250 c.c.) for 4 hr. Part of the 2 : 3-*diphenylindole*-5-*carboxylic acid*, prisms (44%), m. p. 272° [from acetic acid (charcoal)], separated from the solution on cooling and the rest was obtained by precipitation with water (Found : C, 80·2; H, 4·9; N, 4·5. $C_{21}H_{15}O_2N$ requires C, 80·5; H, 4·8; N, 4·5%). The *methyl* ester separated from methanol in needles, m. p. 248° (Found : C, 80·6; H, 5·3%), and the *ethyl* ester from ethanol in needles, m. p. 223° (Found : C, 81·1; H, 5·6. $C_{23}H_{19}O_2N$ requires C, 80·9; H, 5·6%).

After 2 : 3-diphenylindole-5-carboxylic acid (10 g.) and chromic anhydride (6 g. in a little water) in glacial acetic acid (900 c.c.) had been left overnight at room temperature and then heated at 70° for 10 min., 4-*benzamido*-3-*benzoylbenzoic acid* (6·7 g.), needles, m. p. 268° (from *cyclo*hexanone and then anisole), separated (Found : C, 72·9; H, 4·3%). When the latter (5·7 g.), acetic acid (330 c.c.), and concentrated hydrochloric acid (300 c.c.) were refluxed for 5 hr., poured into water, and neutralised with aqueous sodium hydroxide, 4-*amino*-3-*benzoylbenzoic acid* (3·1 g.), pale yellow needles, m. p. 267° (from anisole), was obtained (Found : C, 69·5; H, 4·5. $C_{14}H_{11}O_3N$ requires C, 69·7; H, 4·6%). After sodium nitrite (0·2 g.) in water (2 c.c.) had been added to the amine (0·4 g.) in hydrochloric acid (20 c.c. of 18%), the whole was well shaken and heated on a steam-bath for 10 min. When the solid was crystallised from ethanol, fluorenone-2-carboxylic acid was obtained in golden-yellow needles (0·2 g.) which sublimed above 300° without melting (Found : C, 74·5; H, 3·6. Calc. for $C_{14}H_8O_3$: C, 75·0; H, 3·6%).

2 : 3-*Diphenylindole*-4- *and* -6-*carboxylic Acid*.—*Deoxybenzoin* m-*carboxyphenylhydrazone*, prisms, m. p. 170—172° (from ethanol), was obtained by slowly heating molecular proportions of the ketone and hydrazine (prepared like its isomers referred to above) together to 110°, the mixture being kept at that temperature for 10 min. (Found : N, 8·5. $C_{21}H_{16}O_2N_2$ requires N, 8·5%). When the crude hydrazone (41 g.) had been refluxed for 5 hr. with glacial acetic acid (800 c.c.) and concentrated hydrochloric acid (180 c.c.), the whole was poured into water, and the precipitate (34 g.) was dried on a steam-bath and refluxed with methanol (600 c.c.) containing concentrated sulphuric acid (70 c.c.). After 1 hr. the solution was cooled and the solid (10·9 g., m. p. 226—230°) collected. This was reasonably pure *methyl* 2 : 3-*diphenylindole*-6-*carboxylate*, needles, m. p. 232—234° (after successive recrystallisations from methanol and benzene) (Found : C, 80·6; H, 5·1%). The filtrate was refluxed for a further 8 hr., then poured into water, and the solid dissolved in ether. After the ethereal solution had been dried ($MgSO_4$) and evaporated, the residue was triturated with a mixture of ethyl acetate (2 vols.) and light petroleum (1 vol.). The residual solid was washed with a little ethyl acetate and crystallised from benzene, from which *methyl* 2 : 3-*diphenylindole*-4-*carboxylate* (5·6 g.; m. p. 164—167°) was obtained; recrystallisation from benzene gave prisms, m. p. 168—170° (Found : C, 80·4; H, 5·3%).

After the ester (5·25 g., m. p. 232—234°) had been refluxed for 1½ hr. with potassium hydroxide (10 g.) in water (40 c.c.) and ethanol (100 c.c.), the whole was diluted with water (200 c.c.) and acidified with concentrated hydrochloric acid. When the solid was dried and crystallised from benzene, 2 : 3-*diphenylindole*-6-*carboxylic acid* was obtained in needles, m. p. 211—213° (after being heated under reduced pressure at 100° for 5 hr.) (Found : C, 80·3; H, 5·0%). Obtained similarly from the ester, m. p. 168—170°, 2 : 3-*diphenylindole*-4-*carboxylic acid* separated from acetic acid in prisms, m. p. 223—225° (Found : C, 80·3; H, 4·7%). Re-esterification of these purified acids gave methyl esters of m. p. 232° and 168° respectively.

2 : 3-Diphenylindole-6-carboxylic acid (3·5 g.) was oxidised as described above for the 5-carboxylic acid except that the product was isolated by pouring the reaction mixture into water, and 3-*benzamido*-4-*benzoylbenzoic acid* was obtained from acetic acid in almost colourless needles (1·4 g.), m. p. 233° (Found : C, 72·8; H, 4·5%). Prepared like the corresponding derivatives from 4-benzamido-3-benzoylbenzoic acid, 3-*amino*-4-*benzoylbenzoic acid* separated from ethanol in yellow needles (60%), m. p. 217—218° (Found : C, 69·9; H, 4·6%), and fluorenone-3-carboxylic acid from acetic acid in yellow needles (40%), m. p. 302—303° (Found : C, 75·1; H, 3·5%).

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