Synthesis of 2 : 3-6 : 7-*Dibenzofluoranthene.*

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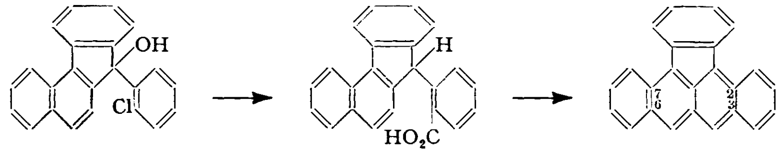
2 : 3-6 : 7-Dibenzofluoranthene has been synthesised and identified with the hydrocarbon obtained by Clar and Stewart (*J.*, 1952, **4783**).

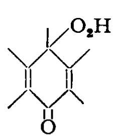
The synthesis of 2 : 3-6 : 7-dibenzofluoranthene (III) has been effected by condensing 3 : 4-benzofluorenone with the Grignard reagent prepared from *o*-bromochlorobenzene to give the alcohol (I). By standard methods this was converted into the carboxylic acid (II), the acid chloride of which on treatment with stannic chloride gave a mixture from which a very small yield of 2 : 3-6 : 7-dibenzofluoranthene (III) was obtained chromatographically. Dr. Clar kindly proved it to be identical with the hydrocarbon which he had obtained by different methods (Clar and Stewart, *loc. cit.*). The formation of the hydrocarbon rather than the anthrone was unexpected (see, *e.g.*, Campbell and Marks, *J.*, 1951, 2941). On another occasion the product was a peroxide, whose structure we were unable to investigate in detail, but which we regard as a hydroperoxide (IV) in view of the analogous hydroperoxide formation by the action of oxygen on 9-phenylanthranol or an alkaline solution of 9-phenylanthrone (Dufraisse, Etienne, and Rigaudy, *Bull. Soc. chim. France*, **1948**, 804).

It is to be noted that ring-closure (II ⟶ III) may take another course and a more detailed investigation may reveal some 2 : 3-10 : 11-dibenzofluoranthene or its derivatives among the products.

2 : 3-6 : 7-Benzofluoranthene forms an adduct with maleic anhydride and is rapidly oxidised on an alumina column to give a peroxide. From the parallelism between maleic anhydride adduct formation and the photo-oxidation of anthracene derivatives we suggest that the peroxide is the transannular photoxide of the benzofluoranthene and it is pertinent that 9 : 10-dimethyl-1 : 2-benzanthracene is rapidly oxidised chromatographically on alumina to give a photo-oxide (Sandin and Fieser, *J. Amer. Chem. Soc.*, 1940, **62**, 3098; Cook and Martin, *J.*, 1940, 1125; Cook, *Ann. Reports*, 1942, **39**, 189).



(I) (II) (III)



(IV)

In other attempts to synthesise the dibenzofluoranthene, 1-benzoyl-9-phenyl-3 : 4-benzofluoren-9-ol and 3 : 4-benzofluorene-1-carboxylic acid were prepared.

EXPERIMENTAL

M. p.s were determined on the Kofler block; chromatographic purification was effected on alumina; and fluorescence observations were made under a Hanovia ultraviolet lamp.

9-o-*Chlorophenyl*-3 : 4-*benzofluorene*-9-*ol*.—Boiling phenylpropiolic acid with acetic anhydride for 5—6 hr. or acetic acid–acetic anhydride (4 : 1) for 2—3 hr. gave consistent 55—60% yields of 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride. Schaarschmidt's 78% yield (*Ber.*, 1915, **48**, 1826) could not be repeated. Ring-closure gave 3 : 4-benzofluorenone-1-carboxylic acid, which was best decarboxylated in boiling quinoline with copper. Chromatographing the product gave 3 : 4-benzofluorenone (70—80%), m. p. 159—160°, giving a green colour with concentrated sulphuric acid.

3 : 4-Benzofluorenone (11·5 g.) in dry benzene (250 ml.) was added to the Grignard reagent (4 mol.) prepared from *o*-bromochlorobenzene (24 ml.) and magnesium (4·7 g.) in ether (700 ml.), the solution then being boiled for 12—15 hr. After decomposition with ice and hydrochloric acid, the organic layer was separated and on evaporation yielded an oil. Trituration with light petroleum gave 9-o-*chlorophenyl*-3 : 4-*benzofluoren*-9-*ol* (65%) as a solid, prisms (from ethanol), m. p. 100° (decomp.) followed by solidification, the anhydrous substance melting at 170° (Found : C, 76·4; H, 5·0; Cl, 9·6. $C_{23}H_{15}OCl,H_2O$ requires C, 76·4; H, 4·7; Cl, 9·7%). The anhydrous *compound* was obtained by drying at 80° (Found : C, 80·2; H, 4·1; Cl, 10·6. $C_{23}H_{15}OCl$ requires C, 80·6; H, 4·3; Cl, 10·3%). It gives a red colour with concentrated sulphuric acid.

2 : 3-6 : 7-*Dibenzofluoranthene*.—The above alcohol (11·9 g.) was boiled for 3 hr. with amalgamated zinc (10 g.), zinc dust (5 g.), and concentrated hydrochloric acid. Zinc dust (2 g.) was added and boiling continued for a further 1 hr. The solution was poured into water, and the precipitate, dissolved in benzene, was chromatographed. A strong blue fluorescent zone developed and yielded an oil which solidified on trituration with light petroleum. 9-o-*Chlorophenyl*-3 : 4-*benzofluorene* (82%), prisms (from light petroleum), had m. p. 106—107° (Found : Cl, 11·5. $C_{23}H_{15}Cl$ requires Cl, 10·8%). This substance (8·6 g.), cuprous cyanide (3·6 g.), pyridine (20 ml.), and acetonitrile (2 ml.) were heated in a sealed tube for 24 hr. at 240°. The mixture was poured into dilute hydrochloric acid and extracted with benzene, and the benzene washed with aqueous ammonia, water, acid, and water, and dried. The solution was passed down a column and when developed with benzene yielded a pale yellow band from which 9-o-*cyanophenyl*-3 : 4-*dibenzofluorene* (74%) was obtained as an oil which solidified when triturated with light petroleum and crystallised from benzene–light petroleum in prisms, m. p. 140° (Found : N, 4·1. $C_{24}H_{15}N$ requires N, 4·4%).

The cyano-compound (2·0 g.) in acetic acid (18 ml.), concentrated sulphuric acid (9 ml.), and water (18 ml.) was boiled for 18 hr. and the whole poured into water. 9-o-*Carboxyphenyl*-3 : 4-*benzofluorene* separated and was extracted with warm aqueous sodium carbonate. Acidification and crystallisation from acetic acid (charcoal) gave needles (0·9 g.), m. p. 200° (clear only at 225°) (Found : C, 85·0; H, 5·3. $C_{24}H_{16}O_2$ requires C, 85·7; H, 4·8%). A quantitative hydrolysis was effected by boiling (24 hr.) the cyano-compound (3·5 g.), sodium hydroxide (1·4 g.), water (3·5 ml.), and ethylene glycol (17·5 ml.). Pouring the mixture into acidified water gave the acid. It formed a *methyl ester*, nodules (from light petroleum), m. p. 110—111° (Found : C, 85·2; H, 5·3. $C_{25}H_{18}O_2$ requires C, 85·7; H, 5·2%). The m. p. of the acid obtained by hydrolysis was as described above.

9-*o*-Carboxyphenyl-3 : 4-benzofluorene (0·34 g.) was kept overnight in dry benzene (5 ml.) with phosphorus pentachloride (0·35 g.). A deep red solution resulted to which stannic chloride (0·2 ml.) in dry benzene (3 ml.) was added. Vigorous shaking for a few minutes afforded a dark brown complex, which after 30 min. was decomposed by ice and hydrochloric acid. Benzene (25 ml.) was added, and the organic layer was separated, washed with dilute aqueous sodium carbonate, dried (Na_2SO_4), and concentrated. The wine-red concentrate was chromatographed. The column was developed with benzene, then sealed off overnight, and a bluish-green band at the top with a greenish-yellow fluorescence was extracted with acetone, which on evaporation yielded a product whose analysis and properties indicated that it was the *hydroperoxide* of 1 : 9-*o*-phenylene-2 : 3-benzanthrone, needles (by sublimation at 210°), m. p. 235—239° (decomp.) (Found : C, 82·3; H, 4·4. $C_{24}H_{14}O_3$ requires C, 82·3; H, 4·0%). It gave a positive oxidation test with ammonium thiocyanate and ferrous ammonium sulphate in acetone and concentrated sulphuric acid.

9-*o*-Carboxyphenyl-3 : 4-benzofluorene (1 g.) was suspended in dry benzene (10 ml.), and phosphorus pentachloride (0·9 g.) was added. The suspension was gently warmed and after the solid acid had disappeared (15 min.) stannic chloride (0·4 ml.) in dry benzene (6 ml.) was added. The solution overnight deposited a dark-brown complex which was decomposed and worked up as above. A wine-red band with a vermilion fluorescence separated on the column and on extraction yielded 2 : 3-6 : 7-dibenzofluoranthene (0·06 g.), purple needles (from acetic acid), m. p. or mixed m. p. 215—218° (Found : C, 94·5; H, 4·9. Calc. for $C_{24}H_{14}$: C, 95·3; H, 4·7%).

In another experiment, carried out as above except that after addition of the stannic chloride the mixture was kept for 20 hr. before being decomposed, the product was chromatographed, giving two zones from the lower of which some dibenzofluoranthene was obtained. The upper green zone with a greenish-yellow fluorescence gave a yellow powder, which was again chromatographed. The prominent yellow zone (green on the side exposed to light) was extracted with benzene–chloroform, evaporation of which yielded the *photo-oxide* of 2 : 3-6 : 7-dibenzofluoranthene, colourless needles (from toluene), decomp. 260° (Found : C, 85·6; H, 4·3. $C_{24}H_{14}O_2$ requires C, 86·2; H, 4·2%). It gave positive tests for an oxidising agent.

Attempted Preparation of Methyl 9-*Hydroxy*-9-*phenyl*-3 : 4-*benzofluorene*-1-*carboxylate*.—The action of phenylmagnesium bromide on methyl 3 : 4-benzofluorenone-1-carboxylate was studied under various conditions, but only one experiment gave a pure product. The ester (0·78 g.) in dry benzene (30 ml.) was added to excess of Grignard reagent prepared from bromobenzene (2·35 ml.) and magnesium (0·55 g.) in anhydrous ether (100 ml.), and the whole was boiled for 10 hr. Decomposition of the product with ice and hydrochloric acid followed by evaporation of the ether gave an oil (0·55 g.), which when triturated with light petroleum gave 1-*benzoyl*-9-*phenyl*-3 : 4-*benzofluoren*-9-*ol*, colourless prisms (from ethanol–benzene), m. p. 243—245° (Found : C, 86·8; H, 4·9. $C_{30}H_{20}O_2$ requires C, 87·4; H, 4·9%). It gives a wine-red colour with concentrated sulphuric acid.

3 : 4-*Benzofluorene*-1-*carboxylic Acid*.—Methyl 3 : 4-benzofluorenone-1-carboxylate (0·5 g.) was boiled for 4½ hr. with lightly amalgamated zinc (0·6 g. of metal; 0·6 g. of dust), toluene (15 ml.), acetic acid (50 ml.), and hydrochloric acid (10 ml.), toluene being added to dissolve crystals which separated. The organic layer was separated, dried (Na_2SO_4), and reduced to half volume. On cooling, 3 : 4-*benzofluorene*-1-*carboxylic acid* (0·27 g.) separated; it formed colourless needles (from toluene), m. p. 322—325° (rapid heating) (Found : C, 82·8; H, 4·6. $C_{18}H_{12}O_2$ requires C, 83·1; H, 4·6%).

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