680. *The Preparation of Some Naphthofluoranthenes and their Quinones.*

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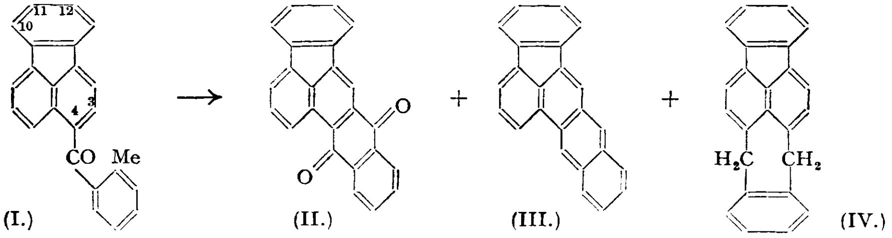
The syntheses of naphtho(2' : 3'-3 : 4)-, naphtho(2' : 3'-10 : 11)-, and naphtho(2' : 3'-11 : 12)-fluoranthenes and their quinones and of 4 : 5-phthaloylfluoranthene are described.

o-Toluoyl chloride and fluoranthene with aluminium chloride yield a mixture of 4- and 11-*o*-toluoylfluoranthene, m. p. 115—116·5° and 148·5—150°, respectively (I and VII), each of which was subjected to the Elbs reaction. The first ketone gave three products: (1) an orange-coloured quinone which proved to be naphtho(2' : 3'-3 : 4)fluoranthene-1' : 4'-quinone (3 : 4-phthaloylfluoranthene) (II) since it gave no m. p. depression with an authentic sample (Campbell and Wang, *J.*, **1949**, 1513); (2) a yellow hydrocarbon, m. p. 229—230°, which was shown to be naphtho(2′ : 3′-3 : 4)fluoranthene (III) since on oxidation it yielded the quinone (II); (3) a colourless hydrocarbon, m. p. 208—210°, which is presumably 4 : 5-*o*-xylylenefluoranthene (IV)

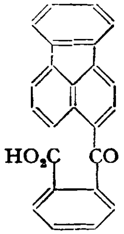


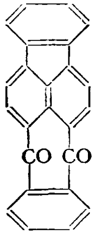
and whose skeleton structure follows from its oxidation to 4 : 5-phthaloylfluoranthene (VI). The isolation of the hydrocarbon (IV) and the quinone (II) serves to orientate the original ketone.

1 : 2-Benzanthracene and its quinone, but no 1 : 8-phthaloylnaphthalene derivatives, were isolated from the pyrolysis of 1-*o*-toluoylnaphthalene.

11-*o*-Toluoylfluoranthene (VII) on pyrolysis gave two isomeric hydrocarbons : (1) a yellow hydrocarbon, m. p. 301—303°, which was oxidised to the known naphtho(2′ : 3′-11 : 12)fluoranthene-1′ : 4′-quinone (IX) (Campbell and Gow, *J.*, 1949, 1555) and is therefore naphtho(2′ : 3′-11 : 12)fluoranthene (VIII)—the structure of the original ketone follows from this identification; (2) a red hydrocarbon, m. p. 225·5—227°, which must by elimination be naphtho(2′ : 3′-10 : 11)-fluoranthene (X) and whose structure was confirmed by oxidation to the quinone (XI) (for preparation, see below).

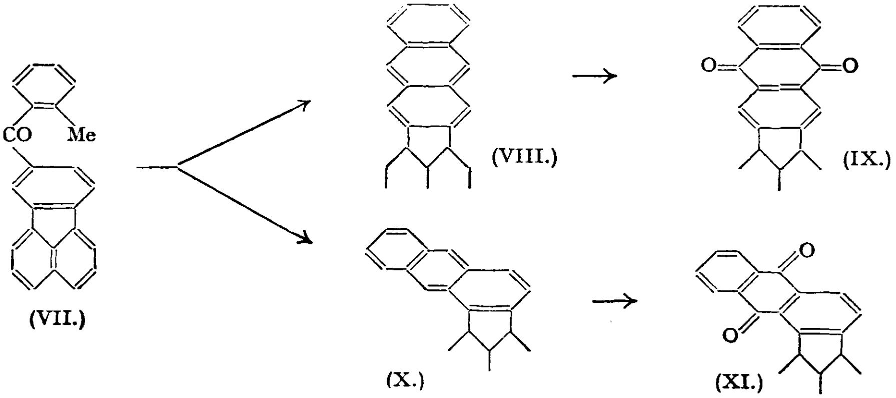
(V.)





(VI.)

4-Benzoylfluoranthene-2′-carboxylic acid (V) did not undergo ring-closure when heated in trichlorobenzene with toluene-*p*-sulphonyl chloride (cf. the 11-isomer described below), but did so when fused with aluminium chloride and sodium chloride and yielded two products : (1) naphtho(2′ : 3′-3 : 4)fluoranthene-1′ : 4′-quinone (II) and (2) an isomeric compound, m. p. 296°, which gave a cherry-red colour with concentrated sulphuric acid and no vat with sodium dithionite. These facts are evidence that the substance is 4 : 5-phthaloylfluoranthene (VI).



Now von Braun and Manz (*Annalen*, 1932, **496**, 170) by the ring closure of the above acid obtained a substance, m. p. 328—331°, which they claimed to be the quinone (II), but which Campbell and

Wang (*loc. cit.*) showed must have some other structure, and might be the 4 : 5-phthaloyl compound. This is now excluded by the preparation of this substance. It is impossible to say what von Braun and Manz's substance was, but they did not have the advantage of chromatography to aid them in their separations and purifications. As a result their 11-acid, for example, was impure with a m. p. 212° as compared to our product, m. p. 234°.

Pure 11-*o*-carboxybenzoylfluoranthene (cf. von Braun and Manz, *loc. cit.*; Campbell and Easton, *J.*, 1949, 340) was cyclised by boiling it with toluene-*p*-sulphonyl chloride in trichlorobenzene to give the two expected quinones : (1) a yellow-orange quinone, m. p. >335°, found to be identical with naphtho(2′ : 3′-11 : 12)fluoranthene-1′ : 4′-quinone (IX), and (2) a yellow isomer, m. p. 316°, which must be naphtho(2′ : 3′-10 : 11)fluoranthene-1′ : 4′quinone (XI). We could detect no sign of the red substance, m. p. 228°, claimed by von Braun and Manz (*loc. cit.*) to be this quinone (cf. also G.P. 624,918; Friedländer, 1937, **21**, 1189; Czech.P., 56,604; *Centr.*, 1937, II, 2597).

It is unlikely that the quinones isolated from the Elbs products were formed during the pyrolysis for so far as we are aware quinones have not been thus obtained. They probably resulted from the oxidation of anthrones on the chromatographic columns used to purify the products. Control experiments showed that they were not produced by oxidation of the corresponding hydrocarbons on the column (cf. Levy and Campbell, *J.*, 1939, 1442).

Attempts to cyclise 4- and 11-benzoylfluoranthene-2′-carboxylic acids and 5-benzoylacenaphthene-2′-carboxylic acid by heating with potassium iodide and hydrogen iodide (Miescher and Billeter, *Helv. Chim. Acta*, 1939, **22**, 601) failed, although 1-benzoylnaphthalene-2′-carboxylic acid yielded a hydrogenated product, which on chloranil dehydrogenation furnished 1 : 2-benzanthracene.

5-Benzoylacenaphthene-2′-carboxylic acid when fused with aluminium chloride gave 3 : 4-phthaloylacenaphthene whose structure was proved by oxidation to 4 : 5-phthaloylnaphthalic anhydride, decarboxylation of which afforded 1 : 8-phthaloylnaphthalene. We have thereby confirmed the structure of 3 : 4-phthaloylacenaphthene which Peters and Rowe (*J. Soc. Dyers Col.*, 1943, **59**, 52) had advanced from a consideration of its synthesis and properties.

EXPERIMENTAL.

M. p.s were determined on the Kofler heating-stage microscope, and unless otherwise stated the fluorescence observations were made in the ultra-violet light of a Hanovia lamp. All chromatographic purifications were effected on alumina (Brockmann).

4- *and* 11-o-*Toluoylfluoranthenes*.—Fluoranthene and *o*-toluoyl chloride in carbon disulphide with aluminium chloride gave by the method of von Braun and Manz (*loc. cit.*) a 91% yield of mixed toluoylfluoranthenes. Partial separation was effected by passing a benzene solution through a column (40 g. of alumina per 1 g. of material) and development with benzene–light petroleum. Three lots of crystals were obtained, m. p.s 100—130°, 130—140°, and 140—155°. The first fraction on further chromatographic purification gave complete separation into a lower and an upper yellow zone. The lower zone on elution with ethanol gave 4-*toluoylfluoranthene*, which was crystallised first from ethanol and then from benzene–light petroleum (b. p. 60—80°), forming yellow crystals, m. p. 115—116·5° (Found : C, 90·3; H, 5·1. $C_{24}H_{16}O$ requires C, 90·0; H, 5·0%). The third fraction, m. p. 140—155°, on repeated crystallisation from ethanol or benzene–light petroleum afforded 11-*toluoylfluoranthene*, m. p. 148·5—150° (Found : C, 89·4; H, 5·0%). Both isomers gave with concentrated sulphuric acid an orange-green coloration in reflected and an orange colour in transmitted ultra-violet light.

Elbs Pyrolysis of 11-o-*Toluoylfluoranthene*.—The ketone (1·30 g.) was pyrolysed in an atmosphere of carbon dioxide at 440° as described by Fieser (" Organic Reactions," Vol. I, p. 129). The dark red product was dissolved in the minimum volume of benzene and passed through a column 40 × 1·3 cm. Development with benzene gave a lower yellow zone, an intermediate orange zone, and a top dark band. The orange zone gave a product, m. p. 190—220° (0·46 g.), which on crystallisation from benzene and then glacial acetic acid furnished compact red prisms of *naphtho*(2′ : 3′-10 : 11)*fluoranthene*, m. p. 225·5—227·5° (0·18 g., 15%) (Found : C, 95·4; H, 4·7. $C_{24}H_{14}$ requires C, 95·3; H, 4·7%), which has an orange fluorescence and gives a purplish-blue colour with concentrated sulphuric acid which becomes crimson when kept. Continued development of the column gave a buff-coloured band which was extracted with acetone. The top dark band was extracted with cold glacial acetic acid and the combined extracts gave naphtho(2′ : 3′-11 : 12)fluoranthene, which separated as a yellow powder from benzene–acetic acid, m. p. 301—303° (0·25 g., 20%) (Found : C, 95·1; H, 4·8%). The m. p. differs from those previously recorded, namely, 290—291° (von Braun and Manz, *loc. cit.*) and >310° (Campbell and Gow, *loc. cit.*). The hydrocarbon sublimes in yellow needles, fluoresces with a bright yellow colour, and in benzene or acetic acid has a strong bluish-green fluorescence in daylight. When heated with sulphuric acid it gives a pink colour, changing successively to brown, green, and brown. The hydrocarbon (50 mg.) in boiling acetic acid (10 c.c.) was oxidised by " AnalaR " chromic anhydride (70 mg.) in acetic acid (1 c.c.). The cooled solution deposited an orange-brown substance which was dissolved in chlorobenzene and passed through a column (20 × 1·2 cm.). Development with the same solvent gave an orange band, which was cut and extracted with chloroform. The extract yielded naphtho(2′ : 3′-11 : 12)fluoranthene-1′ : 4′-quinone (33 mg.), which crystallised in yellow needles from chlorobenzene, m. p. 338—340°, showing no depression when admixed with a sample prepared as below. It sublimes, gives a blue vat with sodium dithionite, and a blue colour with concentrated sulphuric acid, and has a dull golden-yellow fluorescence. The isomeric naphthofluoranthene (0·07 g.), m. p. 225·5—227·5°, when similarly oxidised, gave naphtho-(2′ : 3′-10 : 11)fluoranthene-1′ : 4′-quinone (34 mg.), yellow needles (chlorobenzene), m. p. 316—318°, giving no depression with the quinone prepared as below. It sublimes, gives a purple coloration with sulphuric acid, gives no vat with sodium dithionite, and has a bright greenish-yellow fluorescence.

Pyrolyses of 4-o-*Toluoylfluoranthene.*—The ketone (1·00 g.) was pyrolysed for 30 minutes at 450° in carbon dioxide and the resulting solid was dissolved in benzene and passed through a column, 40 × 1·9 cm. Development with light petroleum–benzene (2 : 3 by vol.) gave (*a*) a bottom, colourless zone with a bright blue fluorescence, (*b*) a yellow zone, (*c*) an orange-pink zone with a green fluorescence, and (*d*) a top, reddish-black band. (*a*) This band gave a pale yellow solid, m. p. 80—150°, which was passed in benzene through a column, 25 × 1·3 cm., and was developed as above. When the whole column showed a blue fluorescence, it was cut, and the lower half extracted with acetone. Evaporation gave 4 : 5-o-*xylylenefluoranthene* (0·03 g.), colourless crystals (light petroleum, b. p. 80—100°), m. p. 208—210° (Found : C, 94·3; H, 5·2. $C_{24}H_{16}$ requires C, 94·7; H, 5·3%). The hydrocarbon has a pale greenish-yellow fluorescence, and when heated with concentrated sulphuric acid gives a pink colour turning to brown. The hydrocarbon (30 mg.) was oxidised with chromic acid (60 mg.) in glacial acetic acid to 4 : 5-phthaloylfluoranthene, m. p. 285—287°, undepressed when mixed with the substance prepared as below. (*b*) The yellow band on elution gave a yellow solution with a strong blue fluorescence, and concentration of the solution afforded *naphtho*(2′ : 3′-3 : 4)*fluoranthene* (0·16 g.), m. p. 229—230° (Found : C, 94·9; H, 4·9%). It sublimes in yellow needles, and has a blue fluorescence in solution and a greenish-yellow fluorescence in the solid state. On oxidation with chromic anhydride in glacial acetic acid it gave the quinone, m. p. 250—253°, not depressed when admixed with Campbell and Wang's quinone (*loc. cit.*). (*c* and *d*) Continued development brought through a filtrate with a greenish-yellow fluorescence in daylight, from which nothing could be isolated, and then an orange-coloured filtrate. This was combined with the acetone eluate of the column and on evaporation gave naphtho(2′ : 3′-3 : 4)fluoranthene-1′ : 4′-quinone (3 : 4-phthaloylfluoranthene), orange crystals (benzene), m. p. 250—253°, undepressed with the above quinone; yield 0·025 g. It gave a blue vat with sodium dithionite and a green colour with concentrated sulphuric acid.

Pyrolysis of 1-o-*Toluoylnaphthalene.*—1-*o*-Toluoylnaphthalene (5 g.) was pyrolysed with zinc dust (1·4 g.) in carbon dioxide at 415° for 3 hours. The product was dissolved in benzene, and the filtered solution passed through a column, 50 × 2·3 cm. Development with benzene–light petroleum (b. p. 80—100°) (1 : 2 by vol.) gave a colourless bottom zone with a purple fluorescence, and an upper yellow layer with a blue fluorescence. Washing through the filtrates from both layers yielded 1 : 2-benzanthracene (1·98 g.), m. p. and mixed m. p. 160—161°. Development was continued with benzene and gave first a yellow filtrate with a strong yellowish-green fluorescence in daylight which deposited a small quantity of impure 1 : 2-benzanthraquinone. Finally, a deep golden-yellow filtrate without fluorescence in daylight was collected; it deposited on evaporation 1 : 2-benzanthraquinone (0·38 g.), m. p. 168—169°. It gave a green colour with concentrated sulphuric acid and an orange-red vat with sodium dithionite. The solid fluoresced with a dull scarlet-red colour. The pyrolysis was repeated at 440° without zinc dust and gave similar products but in different quantities, *i. e.*, 36% of hydrocarbon and 13% of quinone. No xylylenenaphthalene or derivative was detected in either experiment.

Ring-closure of 4- *and* 11-*Benzoylfluoranthene-2′-carboxylic Acids.*—Phthaloylation was best effected as follows. Fluoranthene (20 g.) in methylene chloride was added with stirring at room temperature to phthalic anhydride (16·3 g.) and aluminium chloride (33·4 g.) in methylene chloride (75 c.c.). Stirring was continued overnight and the mixture was then decomposed with hydrochloric acid and ice. The solvent was removed by steam and the residue was extracted with potassium carbonate. Acidification yielded a mixture of acids (35 g.). The acids (25 g.) were dissolved in chloroform, concentration of which gave 11-benzoylfluoranthene-2′-carboxylic acid (13 g.), m. p. 234°, showing no depression when mixed with an authentic sample. Complete evaporation of the chloroform gave a residue which was esterified with methanol and sulphuric acid, and the esters separated chromatographically. The 4-ester (2·5 g.) thus obtained on hydrolysis gave the 4-acid, m. p. 230°, giving a m. p. depression when mixed with the 11-acid.

Pure 11-acid (3 g.) and toluene-*p*-sulphonyl chloride (1·65 g.) were boiled in trichlorobenzene (15 c.c.) for 1 hour. The cold solution deposited a solid which when washed with acetone afforded a mixture (1·7 g.) of yellowish-orange plates and yellow needles. The mixture (0·6 g.) was dissolved in chlorobenzene (400 ml.) and chromatographed on a column, 18 × ⅞ in. Development with the same solvent gave a strongly orange adsorbed zone and a lower, yellow band. The orange zone on extraction gave naphtho-(2′ : 3′-11 : 12)fluoranthene-1′ : 4′-quinone, m. p. >335°, which gave a blue colour with concentrated sulphuric acid and a blue vat with sodium dithionite. The yellow band gave *naphtho*(2′ : 3′-10 : 11)-*fluoranthene*-1′ : 4′-*quinone* (10 : 11-*phthaloylfluoranthene*) (0·1 g.), yellow elongated plates, m. p. 319—320° (Found : C, 85·8; H, 3·7. $C_{24}H_{12}O_2$ requires C, 86·7; H, 3·6%). It gave a red colour with concentrated sulphuric acid and no vat with sodium dithionite. A mixture of the two quinones was separated by sodium dithionite and indicated that the 11 : 12-quinone and the 10 : 11-quinone are formed approximately in the ratio 5 : 1.

Pure 4-benzoylfluoranthene-2′-carboxylic acid (1·1 g.), aluminium chloride (3·3 g.), and sodium chloride (2·75 g.) were intimately mixed and heated in an oil-bath the temperature of which was raised to 140° during 30 minutes. Nitrogen was passed through at this temperature for 3 hours. The product was decomposed with ice and hydrochloric acid and the black solid was then extracted with 5% sodium carbonate and dried. The dry product was extracted with benzene, and the benzene concentrate chromatographed on a column 12 × ¾ in. Development with benzene gave a yellow zone which quickly passed down the column. The filtrate on evaporation furnished a solid (20 mg.) which crystallised from chlorobenzene in yellow-orange prisms, m. p. 252—253° with sublimation, and was proved to be naphtho-(2′ : 3′-3 : 4)fluoranthene-1′ : 4′-quinone (Campbell and Wang, *loc. cit.*). It gave a bluish-green colour with concentrated sulphuric acid and a bluish-violet vat with alkaline sodium dithionite. Further development of the column gave a deep yellow zone below the top dark band. The column was cut and the yellow zone eluted with chloroform which on evaporation gave 4 : 5-*phthaloylfluoranthene*, yellow elongated prisms (chlorobenzene), m. p. 296—297° (Found : C, 86·3; H, 3·6. $C_{24}H_{12}O_2$ requires C, 86·7; H, 3·6%). It gave a red colour with concentrated sulphuric acid and no vat with alkaline dithionite.

3 : 4-*Phthaloylacenaphthene.*—Crude 3 : 4-phthaloylacenaphthene (Peters and Rowe, *loc. cit.*) (3·5 g.) was purified by passing a benzene solution down a column, 17 × ¾ in., and development with benzene–light petroleum (b. p. 60—80°) (4 : 1 by vol.). A yellow zone separated and afforded on elution 3 : 4-phthaloylacenaphthene (1·3 g.), yellow elongated prisms (ethanol), m. p. 196—197° (lit., 194—195°) (Found : C, 84·5; H, 4·5. Calc. for $C_{20}H_{12}O_2$: C, 84·5; H, 4·2%). The phthaloylacenaphthene was oxidised by chromic anhydride ("AnalaR") and glacial acetic acid to 4 : 5-phthaloyl-1 : 8-naphthalic anhydride which, after purification by being washed successively with ethanol, water, and glacial acetic acid, was isolated as bright yellow needles, m. p. >310° (lit., 368°) (Found : C, 73·2; H, 2·4. Calc. for $C_{20}H_8O_5$: C, 73·2; H, 2·3%). The anhydride (0·75 g.), water (20 c.c.), and mercuric oxide, freshly prepared from mercuric acetate (1·5 g.), were heated in a sealed tube at 250° for 4 hours. The product was refluxed with concentrated hydrochloric acid for 2 hours, washed with water, and dried. The dry material (1·1 g.) was extracted with benzene, and the benzene extract passed through a column, 6 × ½ in. A pale yellow zone separated, below which was a band with a bright yellow fluorescence. Both zones yielded 1 : 8-phthaloylnaphthalene, colourless needles (ethanol–acetic acid), m. p. 176—177° (lit., 178°), yield 0·30 g. (Found : C, 83·6; H, 4·1. Calc. for $C_{18}H_{10}O_2$: C, 83·7; H, 3·9%). In concentrated sulphuric acid it gave a yellow solution with a green fluorescence. No colours were obtained with zinc and ammonia or alkaline sodium dithionite.

Ring-closure of 1-*Benzoylnaphthalene*-2′-*carboxylic Acid.*—The acid (4·6 g.), potassium iodide (5·5 g.), red phosphorus (1·5 g.), and phosphoric acid (20 ml.) were refluxed for 4 hours. Water was added, and the residue extracted with ethanol. Evaporation gave a solid (2·0 g.), which was dissolved in the minimum volume of benzene and passed through a column, 14 × 0·75 in. Development with the same solvent gave a bottom zone with a bright purple fluorescence which gave 0·6 g. of a solid, m. p. 112—120° after crystallisation from glacial acetic acid, and a yellow zone which afforded a solid, m. p. 138—145° (0·9 g.) after crystallisation from acetic acid. The second substance (0·75 g.) in benzene was passed through a column, 9·5 × 0·45 in., and a yellow zone which separated yielded a substance, m. p. 146—150° (0·65 g.) after crystallisation from acetic acid. Dehydrogenation with chloranil in xylene (3 hours) gave 1 : 2-benzanthracene, m. p. and mixed m. p. 156° (lit., 158°) (Found : C, 94·2; H, 5·3. Calc. for $C_{18}H_{12}$: C, 94·7; H, 5·3%).

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