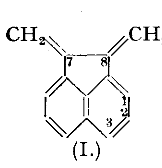
332. *Syntheses of Fluoranthene and its Derivatives from* 7 : 8-*Dialkylacenaphthene*-7 : 8-*diols.*

By Neil Campbell and R. S. Gow.

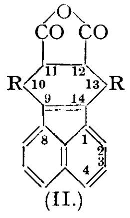
7 : 8-Dialkylacenaphthene-7 : 8-diols, when heated with dienophiles in dehydrating solvents, condense readily to give fluoranthene derivatives which on appropriate treatment yield substituted fluoranthenes. In this way fluoranthene, 4-bromofluoranthene, 10 : 13-*dimethylfluoranthene, fluorantheno*(11′ : 12′-2 : 3)-p-*benzoquinone, fluorantheno*(11′ : 12′-2 : 3)*naphtha*-1 : 4-*quinone, naphtho*(2′ : 3′-11 : 12)*fluoranthene,* 11 : 12-*di*-p-*toluoylfluoranthene,* and 1′ : 4′-*di*-p-*tolyl*-11 : 12-*benzfluoranthene* have been synthesised. Certain statements in the literature have been corrected.

ACENAPHTHENE-7 : 8-QUINONE reacts easily with Grignard reagents to give 7 : 8-dialkylacenaphthene-7 : 8-diols (Maxim, *Bull. Soc. chim.*, 1928, **43**, 769; 1929, **45**, 1137). Theoretically a mixture of *cis*- and *trans*-forms may result, but Maxim found that this holds only for the dimethylglycol; the diethyl and dibenzyl compounds, for instance, were obtained in one form only, and this is in agreement with the results of Bachmann and Chu (*J. Amer. Chem. Soc.*, 1936, **58**, 1118) on the formation of 7 : 8-diarylacenaphthene-7 : 8-diols.

Criegee *et al.* (*Annalen*, 1933, **507**, 176) improved Maxim's method for separating the two 7 : 8-dimethylacenaphthene-7 : 8-diols and proved the isomers, m. p. 187—189° and 182—183°, to be the *cis*- and *trans*-compounds respectively. On treating the former substance with glacial acetic acid, Maxim (*loc. cit.*) isolated a hydrocarbon which he claimed to be 7 : 8-dimethyleneacenaphthene (I). This substance has a high m. p. and is almost insoluble in organic solvents, in contrast to the other 7 : 8-dialkylideneacenaphthenes, and is probably a polymer of dimethyleneacenaphthene. It was, therefore, decided to generate the diene by dehydrating the glycol



(I.)



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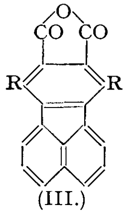


(III.)

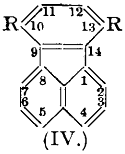
and simultaneously to condense it with a dienophile. This proved to be successful and *trans*-7 : 8-dimethylacenaphthene-7 : 8-diol, when heated under reflux in acetic anhydride with maleic anhydride for 15 minutes, smoothly yielded 10 : 11 : 12 : 13-*tetrahydrofluoranthene*-11 : 12-*dicarboxylic anhydride* (II; R = H) which was dehydrogenated by chloranil to *fluoranthene*-11 : 12-*dicarboxylic anhydride* (III; R = H). Decarboxylation was difficult, but, when the tetrahydro-compound (II) was heated with alkaline potassium ferricyanide (cf. Wagner-Jauregg, *Annalen*, 1931, **491**, 1), dehydrogenation and decarboxylation proceeded simultaneously to give a 50% yield of fluoranthene (IV; R = H).

Use of *cis*-7: 8-dimethylacenaphthene-7 : 8-diol in the diene reaction gave only a red polymer.

Acenaphthenequinone and ethylmagnesium iodide gave only one isomer of 7 : 8-diethylacenaphthene-7 : 8-diol, presumably the *trans*-form as it afforded with maleic anhydride in acetic anhydride a 33% yield of 10 : 13-*dimethyl*-10 : 11 : 12 : 13-*tetrahydrofluoranthene*-11 : 12-*dicarboxylic anhydride* (II; R = Me), which on dehydrogenation by chloranil gave 10 : 13-*dimethylfluoranthene*-11 : 12-*dicarboxylic anhydride* (III; R = Me). Decarboxylation yielded 10 : 13-*dimethylfluoranthene* (IV; R = Me).

3-Bromoacenaphthenequinone with methylmagnesium iodide gave 3-*bromo*-7 : 8-*dimethylacenaphthene*-7 : 8-*diol*, probably a mixture of the *cis*- and *trans*-isomers since it melted over a range of 10° and did not react satisfactorily with maleic anhydride in acetic anhydride. Repeated crystallisation from benzene gave, presumably, the *trans*-form, m. p. 167—168°, which reacted easily with maleic anhydride in acetic anhydride to give 4-*bromo*-10 : 11 : 12 : 13-*tetrahydrofluoranthene*-11 : 12-*dicarboxylic anhydride*, which was dehydrogenated by chloranil to 4-*bromofluoranthene*-11 : 12-*dicarboxylic anhydride*. Decarboxylation was troublesome and the end product, 4-bromofluoranthene, was best obtained by treatment of the tetrahydro-anhydride with alkaline potassium ferricyanide. 4-Bromofluoroanthene thus synthesised was identical with the main substitution product of fluoranthene and so confirms the orientation studies of von Braun and Manz (*Annalen*, 1931, **488**, 111).

trans-7 : 8-Dimethylacenaphthene-7 : 8-diol with *p*-benzoquinone gave *fluorantheno*-(11′ : 12′-2 : 3)-p-*benzoquinone* (V), the intermediate tetrahydro-derivative apparently being dehydrogenated by excess of benzoquinone. The dienophilic character of the product is shown by its ability to react with a second molecule of the *trans*-diol to give *difluorantheno*(11′ : 12′-2 : 3)(11″ : 12″-5 : 6)-p-*benzoquinone* (VI), again no tetrahydro-intermediate being isolated. All attempts, including zinc-dust distillation and Clar's zinc–zinc chloride melt, failed to reduce the quinone (V) to the corresponding hydrocarbon. The quinone, it may be noted, differs from that obtained by Moureu *et al.* (*Bull. Soc. chim.*, 1948, 99) by the oxidation of 11 : 12-benzfluoranthene, and thus confirms the constitution assigned without proof by Moureu to his product.



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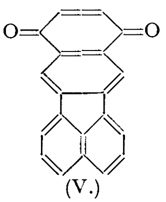

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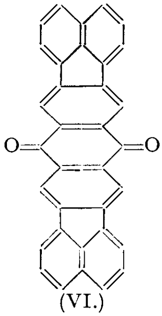

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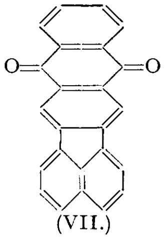

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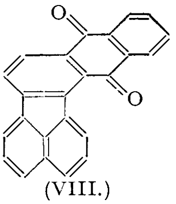

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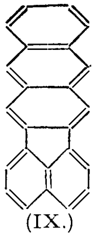
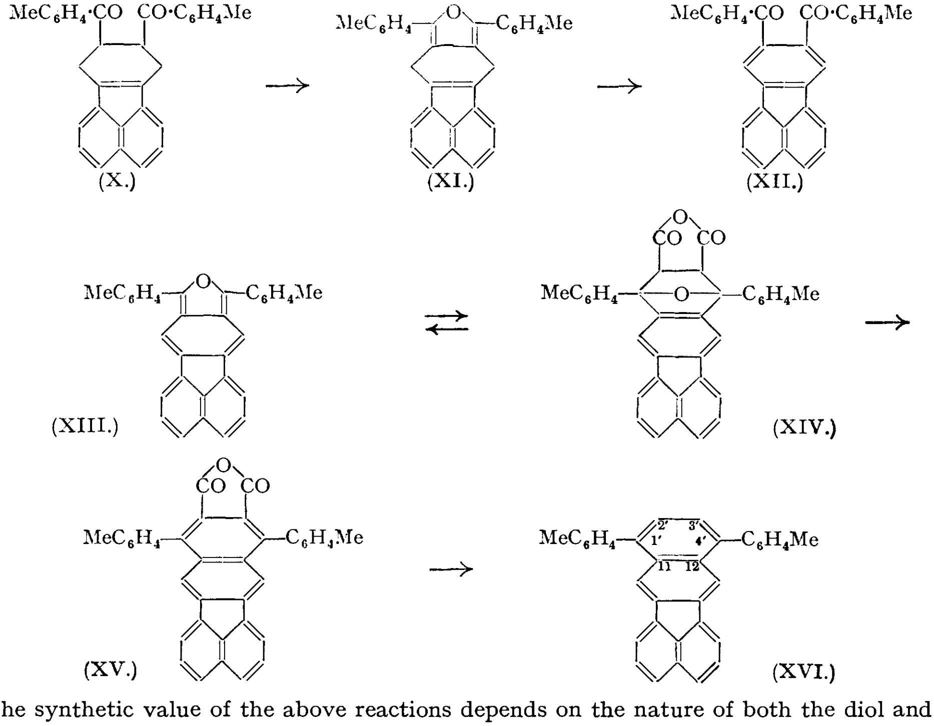

(IX.)

With 1 : 4-naphthaquinone *trans*-7 : 8-dimethylacenaphthene-7 : 8-diol in acetic anhydride gave a good yield of fluorantheno(11′ : 12′-2 : 3)naphtha-1 : 4-quinone (VII), a yellow compound, m. p. > 310°, the constitution of which follows indisputably from this synthesis. Now, von Braun and Manz (*Annalen*, 1932, **496**, 170) by the ring-closure of 11-*o*-carboxybenzoylfluoranthene obtained two isomeric quinones, one red, m. p. 228°, and the other yellow, m. p. 332—333°, to which were assigned respectively the structures (VII) and (VIII). These, however, must be reversed since the properties of our quinone are identical with those of the higher-melting quinone. The conclusions of von Braun and Manz were based on oxidation studies which are incomplete and unreliable since, of the three expected oxidation products from the two quinones, they isolated only one in anything approaching the pure condition and this they failed to identify by mixed-m.p. determination with an authentic sample.

The quinone (VII) was converted into naphtho(2′ : 3′-11 : 12)fluoranthene (IX) by fusion with zinc and zinc chloride (Clar, *Ber.*, 1939, **72**, 1645), m. p. > 310°. von Braun and Manz's compound (*loc. cit.*), obtained by zinc-dust distillation and by implication erroneously regarded as the 10 : 11-fluoranthene derivative, had m. p. 290—291° and must have been impure.

Clar (" Aromatische Kohlenwasserstoffe," p. 18) correlated the oxidation–reduction potential of quinones with their ability to give vats, and it is therefore of interest to compare the quinones (V), (VII), and (VI). (V) gave a wine-red vat, discharged overnight by alkaline dithionite, zinc dust and ammonia, or sodium hydroxide; (VII) gave, only with dithionite, a vat which was stable for a few hours; and (VI), only with dithionite, gave a pale blue vat, stable for a few seconds. The stability of the vats is clearly in the order, (V) > (VII) > (VI).

trans-Di-*p*-toluoylethylene and the dimethylacenaphthenediol in acetic anhydride yielded the *iso*benzfuran derivative (XI), presumably through the intermediate (X) which enolises and then loses a molecule of water. On hydrolysis with 50% sulphuric acid, (XI) underwent both ring-fission and dehydrogenation to give 11 : 12-*di*-p-*toluoylfluoranthene* (XII), the full aromaticity of which was shown by its failure to give tetrachloroquinol when heated in xylene with chloranil. (XI) was dehydrogenated to 2 : 5-*di*-p-*tolylfluorantheno*(11′ : 12′-3 : 4)*furan* (XIII), the orange colour of which is due to its conjugation. With 50% sulphuric acid, (XIII) gave (XII), hydrolysis again being accompanied by dehydrogenation. The constitution of the furan derivative (XIII) was proved by its combination with maleic anhydride to give the *adduct* (XIV). This addition is characterised by its occurrence in a few seconds at room temperature and the disappearance of all colour; when the mixture is warmed, the yellow colour and characteristic yellowish-orange fluorescence of the furan (XIII) reappear, thus showing the dissociation of the adduct into its generators. Such dissociation of Diels–Alder adducts is not unknown (*e.g.*, Bachmann, *J. Amer. Chem. Soc.*, 1938, **60**, 481) and has been observed with *iso*benzfuran derivatives by Barnett (*J.*, 1935, 1326). The adduct (XIV), on treatment with hydrobromic acid, lost water to give the *substance* (XV) which yielded on decarboxylation 1′ : 4′-*di*-p-*tolyl*-11 : 12-*benzfluoranthene* (XVI).



(X.) (XI.) (XII.) (XIII.) (XIV.) (XV.) (XVI.)

The synthetic value of the above reactions depends on the nature of both the diol and the dienophile. For example, maleic anhydride reacts in acetic anhydride with the dimethyl-diol in 15 minutes giving a 70% yield of the adduct, and with the diethyl diol in 5 hours to give a

33% yield, but with the dibenzyl diol no reaction occurred. Highly reactive dienophiles such as maleic anhydride or benzoquinone are required, since other substances such as vinyl cyanide and crotonic acid give only polymeric products.

EXPERIMENTAL.

All analyses were done by Drs. Weiler and Strauss, Oxford.

Synthesis of Fluoranthene.—*trans*-7 : 8-Dimethylacenaphthene-7 : 8-diol (1·0 g.), maleic anhydride (4 g.), and acetic anhydride (30 c.c.) were heated under reflux for 15 minutes. The cooled solution deposited 10 : 11 : 12 : 13-*tetrahydrofluoranthene*-11 : 12-*dicarboxylic anhydride*, yellow elongated prisms (from ethanol–acetic acid), m. p. 209—210° (yield, 0·9 g., 70%) (Found : C, 77·6; H, 4·9. $C_{18}H_{12}O_3$ requires C, 78·25; H, 4·4%). The *dimethyl* ester crystallised from ethanol in yellow prisms, m. p. 153° (Found : C, 73·8; H, 5·8. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6%). The anhydride (1·15 g.), chloranil (2·05 g.), and sulphur-free xylene (30 c.c.) were boiled under reflux for 24 hours, and the adduct which separated on cooling was purified by trituration with 5% aqueous sodium hydroxide and crystallisation from acetic acid. *Fluoranthene*-11 : 12-*dicarboxylic anhydride* was thus obtained as needles, m. p. 299—300°, with a faint orange fluorescence and a blue fluorescence in acetic acid (yield, 1·0 g., 95%) (Found : C, 79·0; H, 3·1. $C_{18}H_8O_3$ requires C, 79·4; H, 3·0%). The *dimethyl* ester was obtained by boiling the anhydride under reflux with sulphuric acid in methanol for 11 hours and crystallised from ethanol in large plates, m. p. 127—128° (Found : C, 75·5; H, 4·6. $C_{20}H_{14}O_4$ requires C, 75·5; H, 4·4%). The anhydride, when heated with calcium oxide, gave a 50% yield of fluoranthene, identified by its m. p. and mixed m. p. with an authentic coal-tar sample and by the m. p. of the picrate.

The anhydride was not readily decarboxylated, heating with copper and quinoline or with mercuric oxide at 250° in a sealed tube (Dziewonski and Kahl, *Chem. Abs.*, 1935, **29**, 2941) proving unsuccessful and heating with calcium oxide wasteful. With naphthalic anhydride the second method gave 80% of naphthalene. Tetrahydrofluoranthene-11 : 12-dicarboxylic anhydride (0·5 g.) in hot 10% sodium hydroxide (40 c.c.) was added to potassium ferricyanide (4·5 g.) in water (20 c.c.) and heated for 3 hours; the solution deposited fluoranthene in 50% yield.

Synthesis of 10 : 13-*Dimethylfluoranthene.*—7 : 8-Diethylacenaphthene-7 : 8-diol (0·5 g.), maleic anhydride (2 g.), and acetic anhydride (15 c.c.) were boiled under reflux for 5 hours. 10 : 13-*Dimethyl*-10 : 11 : 12 : 13-*tetrahydrofluoranthene*-11 : 12-*dicarboxylic anhydride* separated and crystallised from acetic acid in yellow cubic crystals, m. p. approx. 260° depending on the rate of heating (yield, 0·2 g., 33%) (Found : C, 78·5; H, 5·2. $C_{20}H_{16}O_3$ requires C, 78·9; H, 5·3%). The anhydride dissolved in hot sodium hydroxide to give with hydrochloric acid the *acid*, m. p. 218°, which did not crystallise well from ethanol or acetic acid (Found : C, 73·65; H, 5·7. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6%). The adduct (0·1 g.), when boiled under reflux for 9 hours with 10 c.c. of methanol containing 1 c.c. of sulphuric acid gave the *dimethyl* ester, yellow needles (from ethanol), m. p. 173—174° (Found : C, 75·3; H, 6·5. $C_{22}H_{22}O_4$ requires C, 75·4; H, 6·3%). The adduct (0·28 g.), chloranil (0·45 g.), and xylene (10 c.c.) were heated under reflux for 24 hours. 10 : 13-*Dimethylfluoranthene*-11 : 12-*dicarboxylic anhydride* separated and was washed out with sodium hydroxide and then crystallised from xylene; yellow plates, m. p. > 300°; yield, 50% (Found : C, 79·8; H, 4·3. $C_{20}H_{12}O_3$ requires C, 80·0; H, 4·0%). Solutions of the anhydride, especially in acetone, show a bright blue fluorescence. Attempts to prepare the dimethyl ester by the method given above failed. The anhydride (0·5 g.) when heated to dull redness with calcium oxide (50 g.) gave a sublimate of 10 : 13-*dimethylfluoranthene* which crystallised from acetic acid in plates, m. p. 210—211° (yield, 25%) (Found : C, 93·6; H, 6·1. $C_{18}H_{14}$ requires C, 93·9; H, 6·1%). The solid has a yellow fluorescence and in solution a bright greenish-blue fluorescence.

Synthesis of 4-*Bromofluoranthene.*—To the Grignard reagent from methyl iodide (11·1 g.), magnesium (1·9 g.), and ether (50 c.c.) 3-bromoacenaphthenequinone (Rule and Thomson, *J.*, 1937, 1761) (10·2 g.) was added in portions during ½ hour, and the mixture was boiled under reflux for 2 hours, and set aside overnight. Decomposition with 4N-sulphuric acid gave a product, m. p. 150—160°, which was obtained by evaporation of the ethereal layer. trans-3-*Bromo*-7 : 8-*dimethylacenaphthene*-7 : 8-*diol* has m. p. 167—168° after four crystallisations from benzene; yield, 5·0 g. (50%) (Found : C, 56·9; H, 4·6; Br, 27·2. $C_{14}H_{13}O_2Br$ requires C, 57·35 ; H, 4·5 ; Br, 27·3%). The glycol (1·0 g.), maleic anhydride (5 g.), quinol (0·001 g.), and acetic anhydride (15 c.c.) were boiled under reflux for 1 hour. 4-*Bromo*-10 : 11 : 12 : 13-*tetrahydrofluoranthene*-11 : 12-*dicarboxylic acid anhydride* separated from the cold mixture and crystallised from acetic acid in yellow plates, m. p. 213—216° (yield, 0·51 g., 43%) (Found : C, 60·2; H, 3·45. $C_{18}H_{11}O_3Br$ requires C, 60·9; H, 3·1%). The adduct gave the *dimethyl* ester, yellow needles (from ethanol), m. p. 152—154° (Found : Br, 19·3. $C_{20}H_{17}O_4Br$ requires Br, 19·9%). The adduct (0·40 g.) was dissolved in hot saturated sodium carbonate solution (30 c.c.), potassium ferricyanide (4 g.) in water (20 c.c.) added, and the solution warmed on a steam-bath. The precipitate which separated after 2 hours was dissolved in ethanol, to which picric acid was then added. 4-Bromofluoranthene picrate, yellow needles (from ethanol), m. p. 130—131° (lit., 129—130°), separated and gave with warm dilute ammonia 4-bromofluoranthene, m. p. 103—105°, not depressed when mixed with a sample obtained by the bromination of fluoranthene; yield, 0·06 g. (25%).

The adduct (0·95 g.), chloranil (1·32 g.), and xylene (12 c.c.) were boiled under reflux for 3 hours. When the mixture cooled, 4-*bromofluoranthene*-11 : 12-*dicarboxylic anhydride* separated and was purified by washing with 5% sodium hydroxide and crystallisation from chlorobenzene; yellow needles, m. p. > 310°; yield, 0·40 g. (42%) (Found : C, 61·4; H, 2·0; Br, 22·5. $C_{18}H_7O_3Br$ requires C, 61·6; H, 2·0; Br, 22·75%). Unsuccessful attempts were made to convert this anhydride into 4-bromofluoranthene.

Fluorantheno(11′ : 12′-2 : 3)-p-*benzoquinone.*—*trans*-7 : 8-Dimethylacenaphthene-7 : 8-diol (4·0 g.), benzoquinone (16 g.), quinol (0·001 g.), and acetic anhydride (25 c.c.) were heated under reflux for 1½ hours and deposited, on cooling, *fluorantheno*(11′ : 12′-2 : 3)-p-*benzoquinone* which was boiled with water and then crystallised from xylene (charcoal) : yellow prisms, m. p. 265° (decomp.), depends on rate of heating; yield, 1·7 g. (30%) (Found : C, 84·7; H, 3·6. $C_{20}H_{10}O_2$ requires C, 85·05; H, 3·6%). The quinone gives a blue colour with concentrated sulphuric acid, and a yellow fluorescence either in the solid state or in solution.

Difluorantheno(11′ : 12′-2 : 3)(11″ : 12″-5 : 6)-p-*benzoquinone*.—A mixture of the above quinone (0·5 g.), *trans*-7 : 8-dimethylacenaphthene-7 : 8-diol (0·25 g.), quinol (0·001 g.), and acetic anhydride (200 c.c.) was heated under reflux for 12 hours. *Difluorantheno*(11′ : 12′-2 : 3)(11″ : 12″-5 : 6)-p-*benzoquinone* slowly formed and crystallised from *o*-dichlorobenzene in brown prisms, m. p. > 300° (yield, 0·1 g., 8%) (Found : C, 88·2; H, 3·5. $C_{34}H_{16}O_2$ requires C, 89·5; H, 3·5%). The quinone gives a blue colour with concentrated sulphuric acid.

Naphtho(2′ : 3′-11 : 12)*fluoranthene*.—*trans*-7 : 8-Dimethylacenaphthene-7 : 8-diol (2·0 g.), 1 : 4-naphthaquinone (6·0 g.), quinol (0·001 g.), and acetic anhydride (35 c.c.) were boiled under reflux for 1½ hours, and the precipitated fluorantheno(11′ : 12′-2 : 3)naphtha-1 : 4-quinone was washed with ether and crystallised from *o*-dichlorobenzene; yellow needles, m. p. > 310°; yield, 1·80 g. (54%) (Found : C, 86·1; H, 4·1. Calc. for $C_{24}H_{12}O_2$: C, 86·7; H, 3·65%). This gives a blue colour with concentrated sulphuric acid. This quinone (0·2 g.), zinc dust (0·2 g.), sodium chloride (0·2 g.), and zinc chloride (1·0 g.) were thoroughly mixed, a drop of water was added, and the mixture fused at 210°. The temperature was raised during 6 minutes to 290°, and the product was then cooled and boiled with dilute hydrochloric acid. The precipitate was chromatographed in benzene on a column of alumina (8 × 1 in.) and a yellow band was eluted with benzene to give naphtho(2′ : 3′-11 : 12)fluoranthene, yellow crystals, m. p. > 310° (yield, 0·02 g., 10%) (Found : C, 95·25; H, 5·2. Calc. for $C_{24}H_{14}$: C, 95·3; H, 4·7%). The hydrocarbon shows a yellowish-blue fluorescence in benzene.

11 : 12-*Di*-p-*toluoylfluoranthene*.—*trans*-7 : 8-Dimethylacenaphthene-7 : 8-diol (4·3 g.), *trans*-di-*p*-toluoylethylene (5·3 g.), quinol (0·001 g.), and acetic anhydride (40 c.c.) were heated under reflux for 1½ hours. The *furan* derivative (XI) separated and crystallised from chlorobenzene in yellow prisms, m. p. 301—302° (yield, 2·6 g., 30%) (Found : C, 90·3; H, 5·5. $C_{32}H_{24}O$ requires C, 90·5; H, 5·7%). The furan derivative (0·1 g.) was boiled under reflux in 50% aqueous sulphuric acid (6 c.c.) and acetic acid (50 c.c.) for 2 hours. The solution on cooling deposited 11 : 12-*di*-p-*toluoylfluoranthene*, which separated from acetic acid in needles, m. p. 260—261°; yield, 0·085 g. (84%) (Found : C, 87·2; H, 5·3. $C_{32}H_{22}O_2$ requires C, 87·6; H, 5·1%). The furan derivative (XI) (1·26 g.), chloranil (0·75 g.), and sulphur-free xylene (130 c.c.) were boiled under reflux for 16 hours. When the mixture cooled, 2 : 5-*di*-p-*tolylfluorantheno*(11′ : 12′-3 : 4)*furan* separated and crystallised from chlorobenzene in orange-red prisms, m. p. 289—290° (yield, 0·90 g., 71%) (Found : C, 90·7; H, 5·6. $C_{32}H_{22}O$ requires C, 90·95; H, 5·3%). Unlike the dihydro-compound it is soluble in benzene in which it displays a magnificent yellowish-orange fluorescence. The furan (0·1 g.) was heated under reflux for 2 hours in 50% sulphuric acid (5 c.c.) and acetic acid (35 c.c.). 11 : 12-Di-*p*-toluoylfluoranthene separated and after crystallisation from acetic acid had m. p. 260—262° (yield, 0·05 g., 49%), and showed no m. p. depression when mixed with a sample obtained as above.

1′ : 4′-*Di*-p-*tolyl*-11 : 12-*benzfluoranthene*.—When molar quantities of maleic anhydride and fluoranthenofuran were dissolved in benzene, the orange colour and orange-yellow fluorescence of the furan disappeared and prisms of the *adduct* (XIV) separated. When, however, the solution was warmed, the colour and fluorescence reappeared. Displacement of the equilibrium to the adduct side was effected by cooling or by adding excess of maleic anhydride to the hot solution. The adduct was best prepared as follows. Maleic anhydride (0·6 g.) was added to the furan (0·1 g.) suspended in ethanol (8 c.c.), and the mixture heated under reflux. After 20 minutes separation of the adduct was complete. The adduct was washed with ether, but could not be crystallised from acetic acid since dissociation occurred; m. p. 220—264° (varies with rate of heating) (Found : C, 83·3; H, 4·75. $C_{36}H_{24}O_4$ requires C, 83·05; H, 4·65%). (XIV) (0·4 g.), maleic anhydride (0·4 g.), and ethanol (50 c.c.) were heated under reflux, and hydrogen bromide passed through the mixture. Dissolution soon occurred and a faint purple fluorescence appeared. After 1 hour the solution was evaporated to about 15 c.c. and on cooling deposited 1′ : 4′-*di*-p-*tolyl*-11 : 12-*benzfluoranthene*-2′ : 3′-*dicarboxylic anhydride*, which separated from chlorobenzene in yellow needles, showing in solution, and especially in acetone, a bright blue fluorescence; m. p. > 310°; yield, 0·2 g. (40%) (Found : C, 85·2; H, 4·5. $C_{36}H_{22}O_3$ requires C, 86·05; H, 4·4%). The yellow sublimate obtained by heating the anhydride (1·0 g.) at red heat with calcium oxide (50 g.) was dissolved in toluene (100 c.c.) and chromatographed on alumina (12 × 1 in.). Development with toluene gave a yellow zone which was eluted with the same solvent. Evaporation afforded 1′ : 4′-*di*-p-*tolyl*-11 : 12-*benzfluoranthene*, which crystallised from acetic acid in yellow needles with a blue fluorescence in toluene; m. p. 289°; yield, 0·10 g. (12%) (Found : C, 93·6; H, 5·7. $C_{34}H_{24}$ requires C, 94·4; H, 5·6%).

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