STUDIES IN THE FLUORANTHENE SERIES

by

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A THESIS submitted for the degree of

DOCTOR of PHILOSOPHY

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INDEX

INTRODUCTION

This thesis is divided into three main sections which, while each complete in itself, are related. These are:-

SECTION A. ORIENTATIONS AND TRANSFORMATIONS OF DI- AND TRI-BROMOFLUORANTHENES.

SECTION B. THE NITRATION OF 1:2:3:4-TETRAHYDROFLUOR-ANTHENE.

SECTION C. THE SYNTHESIS OF 1:2-BENZFLUORENE.

Section A consists of oxidation experiments proving the structure of 4:11-dibromo- and 4:11:12-tribromo-fluoranthene and also reports the unequivocal synthesis of the latter. In addition the reduction of 4:11-dibromofluoranthene and its conversion to 4:11-dicarboxy-fluoranthene are reported.

In order to obtain more information about disub-stitution in the fluoranthene series the preparation of a dinitrofluoranthene was attempted. Early experiments with fluoranthene itself proved unpromising and so the nitration of 1:2:3:4-tetrahydrofluoranthene was investigated in the hope of obtaining a dinitrotetrahydro-fluoranthene which could then be dehydrogenated to a dinitrofluoranthene. The unusual course of this reaction and the nature of the resulting products is discussed in Section B.

During the investigations reported in Section B it was found necessary to prepare β-1-fluorenonepropionic acid/

acid and the ease with which it was obtained in fair yield by the oxidation of 1:2:3:4-tetrahydrofluoranthene suggested that it might be a suitable starting-point in the synthesis of 1:2-benzfluorene, an aromatic hydrocarbon which is related to fluoranthene. This synthesis was accomplished and is reported in Section C.

Preprinted from the Journal of the Chemical Society,
October 1950, (535), pages 2784—2787.

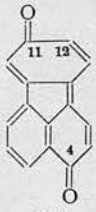
535. *The Orientation of Disubstituted Fluoranthene Derivatives.*

By Neil Campbell, W. W. Easton, (Miss) J. L. Rayment, and
(in part) J. F. K. Wilshire.

Bromination of fluoranthene gives 4 : 11-dibromofluoranthene, orientated by oxidation to 2 : 7-dibromofluorenone-1-carboxylic acid. By standard methods 4 : 11-dibromofluoranthene gives fluoranthene-4 : 11-dicarboxylic acid which differs from the acid obtained by the interaction of oxalyl chloride and fluoranthene in the presence of aluminium chloride.

The disubstitution products obtained from fluoranthene by bromination, etc., have not hitherto been rigidly orientated, though there is inconclusive evidence that such substances contain the substituents in the 4 : 11-positions (see Tobler *et al.*, *Helv. Chim. Acta*, 1941, **24**, 101E; Campbell *et al.*, *Nature*, 1950, **165**, 76). Von Braun's work shows clearly that one of the substituents must occupy the 4-position (von Braun and Manz, *Annalen*, 1931, **488**, 111) and suggests that the second fills the 11- or 12-position. A decision in favour of the former comes from Waters (*J.*, 1948, 727) who points out that in polycyclic aromatic hydrocarbons substitution occurs at the same positions as those which are converted into carbonyl groups when the hydrocarbons are oxidised to quinones. In the present instance, as noted by Tobler *et al.* (*loc. cit.*), a 4 : 11-quinone (I) can be formulated while a 4 : 12-quinone cannot. Disubstitution of fluoranthene may, therefore, be expected to occur at positions 4 and 11. The correctness of this prediction has now been shown by the proof that dibromination of fluoranthene gives 4 : 11-dibromofluoranthene (II).

Chromic acid oxidation of dibromofluoranthene gave a dibromofluorenone-1-carboxylic acid, decarboxylation of which with quinoline and copper was accompanied by debromination to 2-bromofluorenone, thus strongly indicating that the original acid was 2 : 7-dibromofluorenone-1-carboxylic acid. That it is the bromine atom contiguous to the carboxyl group which is removed was shown by the stability of 2-bromo- and 2 : 7-dibromofluorenone to boiling quinoline and copper, and the decarboxylation under similar conditions of 2-bromofluorenone-1-carboxylic



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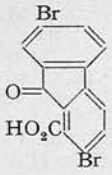

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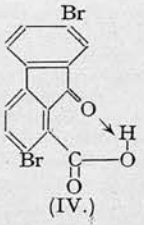


(IV.)

acid and 7-bromofluorenone-1-carboxylic acid to fluorenone and 2-bromofluorenone respectively. Conclusive evidence was finally obtained by decarboxylation of the dibromo-acid with mercuric oxide at 180° (cf. Dziewonski and Khal, *Chem. Abstr.*, 1935, **19**, 2941) to yield 2 : 7-dibromofluorenone. The acid is therefore 2 : 7-dibromofluorenone-1-carboxylic acid (III) and the original substance must in consequence be 4 : 11-dibromofluoranthene (II).

In some of the oxidation experiments a monobromo-acid was isolated and it is probably 6-bromofluorenone-1-carboxylic acid, ring A having been disrupted. The possibility that ring C had been oxidised giving 4-bromonaphthalic acid was excluded since our acid is yellow, easily esterified, and does not react with *o*-phenylenediamine, whereas 4-bromonaphthalic acid is white, is not esterified even by diazomethane, and readily forms two benziminazole derivatives with *o*-phenylenediamine.

Dehalogenation of aromatic compounds containing a carboxyl group adjacent to the halogen atom has frequently been observed, *o*-halogenobenzoic acids and 8-bromo-1-naphthoic acid, for example, yielding the halogen-free acids when boiled with toluene and copper bronze (Rule *et al.*, *J.*, 1934, 168; Pursell, Thesis, Edinburgh). Rather unexpectedly, similar treatment failed to debrominate 2 : 7-dibromofluorenone-1-carboxylic acid. Rule (*loc. cit.*) showed that such dehalogenations are effected by reduction, the requisite hydrogen coming from the carboxyl

group. Presumably in our acid there is some form of interaction between the carboxyl and carbonyl groups as shown in (IV). This formula is very similar to the oxonium formula for fluorenone-1-carboxylic acid advanced by Hantzsch (*Ber.*, 1916, **49**, 226), who, however, applied his formula only to the solid acid and regarded the acid in neutral solvents such as ethanol as having the norm " ketoid " form.

4 : 11-Dibromofluoranthene is a useful reference substance. For example, it is converted into 4 : 11-dicyanofluoranthene, hydrolysis of which gives fluoranthene-4 : 11-dicarboxylic acid which was at first regarded as identical with the acid obtained by Campbell and Easton (*J.*, 1949, 340) by the action of oxalyl chloride on fluoranthene in the presence of aluminium chloride. Recent investigations on larger quantities of material (Campbell and Wilshire, unpublished results) show, however, that the two acids are different. It would seem, therefore, that the Friedel–Crafts reaction, unlike bromination, does not give 4 : 11-disubstituted products.

Attempts to hydrolyse the above dicyano-compound by conversion into the imino-ethers (Hager *et al.*, *J. Amer. Chem. Soc.*, 1944, **66**, 1982) failed. The stability of the 4-cyano-group is not surprising since we found that α-naphthonitrile, in contrast to the β-compound, is not hydrolysed by this method, but the failure of the 11-cyano-group to react was unexpected.

The bromine atoms in 4 : 11-dibromofluoranthene are inert to magnesium, but are removed by nickel–aluminium alloy and alkali.

Experimental.

All chromatographic adsorptions were carried out on alumina (Brockmann). Analyses were done by Drs. Weiler and Strauss (Oxford). Compounds marked with an asterisk have been mentioned in patent literature but without analytical data.

Oxidation of 4 : 11-*Dibromofluoranthene.*—Dibromofluoranthene was prepared by the bromination of fluoranthene by the method of Tobler *et al.* (*loc. cit.*). Chromic anhydride (AnalaR; 10 g.) in water (20 ml.) and glacial acetic acid (24 ml.) was added slowly to dibromofluoranthene (6 g.) in glacial acetic acid (400 ml.) just below the boiling point and the mixture refluxed for 3 hours. Chromic anhydride (14 g.) in water (20 ml.) and glacial acetic acid (100 ml.) was added and the mixture boiled for 3 hours. The solution was reduced to 100 ml. and poured into water (*ca.* 200 ml.). The precipitate was extracted with barium carbonate or potassium carbonate solution, acidification of which then yielded 2 : 7-*dibromofluorenone*-1-*carboxylic acid* (2 g., 32%), which separated from benzene and methanol as yellow needles, subliming at 200°, m. p. 269—272° (Found : C, 44·9; H, 1·9; Br, 40·9. $C_{14}H_6O_3Br_2$ requires C, 44·0; H, 1·6; Br, 41·9%). The acid when boiled with methanol and sulphuric acid gave no ester, but with diazomethane yielded the *methyl* ester, which crystallised from methanol in yellow prisms, m. p. 197° (Found : C, 45·6; H, 2·2; Br, 40·6. $C_{15}H_8O_3Br_2$ requires C, 45·5; H, 2·0; Br, 40·4%).

In some experiments the crude acidic product was boiled with an aqueous suspension of barium carbonate, and the boiling mixture filtered. Acidification of the residual barium carbonate gave 2 : 7-dibromofluorenone-1-carboxylic acid, m. p. 266—267°, showing no m. p. depression when mixed with a sample prepared as above. The filtrate on acidification with dilute hydrochloric acid gave 6(?)-*bromofluorenone*-1-*carboxylic acid*, which after crystallisation from glacial acetic acid and sublimation separated as yellow needles, m. p. 253—255° (Found : Br, 26·3. $C_{14}H_7O_3Br$ requires Br, 26·4%). The *methyl* ester, made by use of methanol and sulphuric acid, crystallised from methanol in pale yellow needles, m. p. 126—127° (Found : C, 57·2; H, 3·3; Br, 25·8. $C_{15}H_9O_3Br$ requires C, 56·8; H, 2·9; Br, 25·2%).

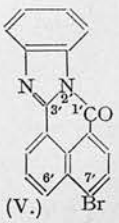
Decarboxylation of 2 : 7-*Dibromofluorenone*-1-*carboxylic Acid.*—The acid (0·5 g.) was heated at 180° with quinoline (15 ml.) and copper bronze for 30 minutes. The precipitate obtained by the addition of dilute hydrochloric acid was dissolved in benzene and chromatographed on a column $3\frac{1}{2}'' \times \frac{1}{2}''$. Development with benzene yielded a yellow zone which on extraction with ethanol gave 2-bromofluorenone, m. p. 141—142°, not depressed when mixed with an authentic sample.

The acid (0·5 g.), freshly precipitated mercuric oxide (0·32 g.), and water (5 ml.) were heated in a sealed tube at 185° for 30 hours, and the product refluxed with concentrated hydrochloric acid (15 ml.) for 3 hours. The residue was extracted first with ether, then benzene, and the combined extracts were washed with 5% aqueous potassium carbonate and dried (Na_2SO_4). Evaporation gave a solid which was dissolved in benzene and chromatographed on a column $4'' \times \frac{3}{16}''$. Development with benzene gave a yellow band which on elution and evaporation gave 2 : 7-dibromofluorenone, m. p. 201—202°, not depressed when mixed with an authentic sample prepared by the oxidation of 2 : 7-dibromofluorene with chromic anhydride (AnalaR) and acetic acid. The potassium carbonate solution on acidification yielded some of the original acid.

Oxidation of 4-*Bromofluoranthene.*—4-Bromofluoranthene (2·5 g.) was oxidised by chromic anhydride (AnalaR) as described above and the resulting 2-bromofluorenone-1-carboxylic acid when crystallised from glacial acetic acid was obtained as yellow needles, m. p. 252—254° (von Braun *et al.*, *Annalen*, 1932, **496**, 107, give 252°) (0·8 g., 30%) (Found : C, 55·1; H, 2·3; Br, 26·5. Calc. for $C_{14}H_7O_3Br$: C, 55·4; H, 2·3; Br, 26·4%). The acid could not be esterified by methanol and sulphuric acid, but with diazomethane yielded the *methyl* ester, yellow needles (from methanol), m. p. 140—142° (Found : C, 56·5; H, 3·1. $C_{15}H_9O_3Br$ requires C, 56·8; H, 2·8%). Decarboxylation with quinoline and copper at 180° gave a product which after chromatographic purification separated as a yellow oil, identified as fluorenone by

its 2 : 4-dinitrophenylhydrazone, m. p. 295—297°, not depressed on admixture with an authentic sample (Found : N, 15·2. Calc. for $C_{19}H_{12}O_4N_4$: N, 15·6%).

Preparation and Properties of 4-*Bromonaphthalic Acid.*—4-Bromoacenaphthene (4 g.) in glacial acetic acid (60 ml.) was heated with sodium dichromate (20 g.) for 1 hour on the water-bath and filtered. The filtrate with water (200 ml.) gave a precipitate which was dissolved in ether and extracted with 2·5% aqueous potassium carbonate, acidification of which then gave 4-bromonaphthalic acid. Crystallisation from benzene yielded needles, m. p. 218—219° (lit., 220°). Unsuccessful attempts were made to esterify the acid with methanol and sulphuric acid or with diazomethane. Equimolecular quantities of the acid and *o*-phenylenediamine were boiled for a few minutes in glacial acetic acid and gave on cooling a palpable mixture, subliming at *ca.* 165°, m. p. 228—266°, which was separated into its components by boiling benzene. The less soluble 7′(6′?)-*bromo*-1′-*keto*-2′-*azaperinaphthano*(2′ : 3′-1 : 2)*benziminazole* (V) was purified by repeated crystallisations from toluene which gave yellow needles, m. p. 270—272° after subliming at 228° (Found : N, 8·1. $C_{18}H_9N_2OBr$ requires N, 8·0%). The more soluble *isomer* crystallised from benzene in yellow needles, m. p. 219—221° (Found : N, 8·3; Br, 21·8. $C_{18}H_9N_2OBr$ requires N, 8·0; Br, 22·9%).



(V.)

7-*Bromofluorenone*-1-*carboxylic Acid.*—Fluorenone-1-carboxylic acid (2 g.) was added to bromine (25 ml.). The mixture at first gave a thick paste, but when kept overnight became liquid again and pouring it into water gave 7-*bromofluorenone*-1-*carboxylic acid* which was washed with ethanol, then crystallised first from glacial acetic acid and then from benzene in red elongated prisms, m. p. 226—228° (1·6 g., 60%) (Found : C, 55·3; H, 2·8; Br, 27·6. $C_{14}H_7O_3Br$ requires C, 55·4; H, 2·3; Br, 26·4%). The acid readily yielded the *ethyl* ester with ethanol and sulphuric acid; this formed yellow prisms, m. p. 102—103°, from ethanol or benzene–light petroleum (b. p. 40—60°) (Found : Br, 23·8. $C_{16}H_{11}O_3Br$ requires Br, 24·1%). The *methyl* ester, similarly obtained, separated from benzene in yellow prisms, m. p. 164° (Found : Br, 25·4. $C_{15}H_9O_3Br$ requires Br, 25·2%). Decarboxylation of the acid with quinoline and copper at 180° for 45 minutes gave 2-bromofluorenone, m. p. 136° either alone or when mixed with an authentic sample.

4 : 11-*Dicyanofluoranthene.*—4 : 11-Dibromofluoranthene (1 mol.) and cuprous cyanide (2·2 mols.) were thoroughly mixed and heated for 6 hours at 260° (cf. B.P. 533,962). The product was extracted successively with chloroform, xylene, and chlorobenzene, which yielded dibromofluoranthene, fluoranthene, and 4 : 11-*dicyanofluoranthene* * respectively. The last sublimed in yellow crystals at *ca.* 200° and had m. p. 321—323° (Found : N, 10·3. $C_{18}H_8N_2$ requires N, 11·1%). Oxidation of the dicyano-compound gave a *substance*, soluble in alkali, which contained only a trace of nitrogen (Found : C, 50·8; H, 3·2; N, 0·4%). Hydrolysis of the cyano-groups had, therefore, occurred and the analysis shows that the resulting acid cannot be the expected fluorenonetricarboxylic acid ($C_{16}H_8O_7$ requires C, 61·5; H, 2·65%). An attempt to esterify the acid by boiling it for 24 hours with methanol and sulphuric acid was unsuccessful.

4 : 11-Dicyanofluoranthene (0·1 g.) was boiled for 1 hour with glacial acetic acid (2 ml.), concentrated sulphuric acid (1 ml.), and water (1 ml.). The resulting 4 : 11-*fluoranthenedicarboxylic acid* * was only slightly soluble in the common organic solvents, but sublimed at *ca.* 280° to give yellow needles, m. p. >360° (Found : C, 75·2; H, 4·2. $C_{18}H_{10}O_4$ requires C, 74·5; H, 4·2%). The acid (0·35 g.) was boiled overnight with methanol (2 ml.) and concentrated sulphuric acid (8 drops), and the resulting flocculent precipitate dissolved in benzene, passed through a chromatographic column 4″ × ¼″, and developed with benzene. From the eluate *dimethyl fluoranthene*-4 : 11-*dicarboxylate* was obtained as a pale yellow flocculent mass (from methanol–glacial acetic acid), m. p. 168—169°, subliming at 145° (Found : C, 75·3; H, 4·8. $C_{20}H_{14}O_4$ requires C, 75·5; H, 4·4%). It gave a m. p. depression of 30° when mixed with the dimethyl ester of the diacid obtained from fluoranthene and oxalyl chloride (Campbell and Easton, *loc. cit.*).

Debromination of 4 : 11-*Dibromofluoranthene.*—Raney nickel–aluminium alloy (3·5 g.) was added to a boiling solution of 4 : 11-dibromofluoranthene (0·3 g.) in ethanol (10 ml.) and 10% ethanolic potassium hydroxide (75 ml.). The alloy was added in four portions during 10 minutes. The mixture was heated until all the alloy had reacted (1—1½ hours). The hot solution was filtered, and water was added to the filtrate which was then made acid to Congo-red paper by concentrated hydrochloric acid. The precipitate on crystallisation proved to be fluoranthene, m. p. and mixed m. p. 110° (0·1 g., 60%).

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THE UNIVERSITY, EDINBURGH.

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249. *The Oxidation of* 4 : 11-*Dibromofluoranthene.*

By Neil Campbell, W. H. Stafford, and J. F. K. Wilshire.

It was shown (Campbell, Easton, Rayment, and Wilshire, *J.*, 1950, 2784) that chromic acid oxidation of dibromofluoranthene yields 2 : 7-dibromofluorenone-1-carboxylic acid and a monobromo-acid provisionally regarded as 6-bromofluorenone-1-carboxylic acid (II). We have now

(I.) (II.)

confirmed this formulation by decarboxylation of the acid to 3-bromofluorenone, showing that the acid (II) is formed by oxidation of the ring A (I) and providing further evidence that the original compound is 4 : 11-dibromofluoranthene (cf. Holbro and Tagmann, *Helv. Chim. Acta*, 1950, **33**, 2178).

Experimental.—The mixture of acids obtained by oxidation of dibromofluoranthene was boiled with successive 500-ml. portions of calcium hydroxide solution and the hot solutions were filtered. The cold filtrates deposited the calcium salt of the dibromo-acid and the filtrate on acidification gave 6-bromofluorenone-1-carboxylic acid, which crystallised in yellow rosettes, m. p. 253—255°, from glacial acetic acid and gave a *methyl* ester, m. p. 126—127° (Found: Br, 25·8. $C_{15}H_9O_3Br$ requires Br, 25·2%). The acid on decarboxylation with quinoline and copper-bronze afforded 3-bromofluorenone, yellow leaflets (from light petroleum), m. p. 162—163°, undepressed on admixture with an authentic sample Found: Br, 31·2. Calc. for $C_{13}H_7OBr$: Br, 30·9%). This substance was prepared from *o*-(4-bromobenzoyl)benzamide by Miller and Bachman's method (*J. Amer. Chem. Soc.*, 1935, **57**, 2443), but we were unable to attain the high yields reported by them. By adding a benzene solution of the acid chloride to saturated methanolic ammonia we prepared the substituted benzamide, and after repeated crystallisation from xylene, xylene–acetone, and acetic acid obtained it as needles, m. p. 224° (Found: N, 4·4; Br, 24·1. Calc. for $C_{13}H_{10}O_2NBr$: N, 4·6; Br, 26·3%). The substance is clearly not quite pure (probably owing to adhering solvent), but nevertheless it melts nearly 40° higher than Miller and Bachman's product (m. p. 184·5—185°), which we think was a mixture of acid and amide. The amide was converted *via* 2-amino-4′-bromobenzophenone, m. p. 112°, into 3-bromofluorenone, which had the m. p. given by other workers (*e.g.*, Heilbron, Hey, and Wilkinson, *J.*, 1938, 113).

Thanks are expressed to the Carnegie Trust for the Universities of Scotland for the award of a scholarship to one of us (W. H. S.), and to the Anglo-Iranian Oil Co. Ltd. for a grant.

University of Edinburgh. [*Received, January 9th*, 1951.]

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322. *The Friedel–Crafts Reaction of Fluoranthene.*

By Neil Campbell, W. K. Leadill, and J. F. K. Wilshire.

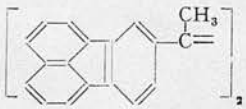
Fluoranthene and acetyl bromide in the presence of aluminium chloride give 4 : 12-diacetylfluoranthene which can be oxidised to fluoranthene-4 : 12-dicarboxylic acid identical with the acid obtained from fluoranthene and oxalyl chloride under Friedel–Crafts conditions (Campbell and Easton, *J.*, 1949, 340).

It has been proved that bromination of fluoranthene gives 4 : 11-dibromofluoranthene (Campbell *et al.*, *Nature*, 1950, **165**, 76; *J.*, 1950, 2784; Holbro and Tagmann, *Helv. Chim. Acta*, 1950, **33**, 2178; S. H. Tucker, personal communication). Nitration, sulphonation, etc., will most probably follow a similar course, but the mode of attack under Friedel–Crafts conditions is less predictable. Von Braun and Manz (*Annalen*, 1932, **496**, 170) showed that the Friedel–Crafts reaction yields 4- and 11-monosubstituted products, but the disubstituted products have never been orientated.

We have therefore investigated the action of acetyl bromide on fluoranthene in the presence of aluminium chloride and find that it yields a mixture of 4- and 11-acetylfluoranthene (I*a* and *b*) which can be separated chromatographically. Both substances on further treatment yield the same diacetylfluoranthene which accordingly must be the 4 : 11- or the 4 : 12-compound. A

(I.)

(I*a*; R = CO·CH$_3$, R′ = H.)
(I*b*; R = H, R′ = CO·CH$_3$.)
(I*c*; R = R′ = CO·CH$_3$.)
(I*d*; R = R′ = CO$_2$H.)
(I*e*; R = R′ = Br.)



(II.)

decision in favour of the second structure (I*c*) was obtained by oxidation to a fluoranthene-dicarboxylic acid which was different from fluoranthene-4 : 11-dicarboxylic acid prepared from 4 : 11-dibromofluoranthene *via* the dinitrile but identical with the acid obtained by the action of oxalyl chloride on fluoranthene in the presence of aluminium chloride (Campbell and Easton, *loc. cit.*). The Friedel–Crafts product therefore is 4 : 12-diacetylfluoranthene (I*c*), and the derived acid is fluoranthene-4 : 12-dicarboxylic acid (I*d*). This was confirmed by the conversion of the diacetylfluoranthene into the diacetamido-compound by the Schmidt reaction. Hydrolysis followed by diazotisation and the Sandmeyer reaction gave 4 : 12-dibromofluoranthene (I*e*) which was shown to be different from 4 : 11-dibromofluoranthene (Campbell *et al.*, *J.*, 1950, 2784).

It is difficult to say whether in the Friedel–Crafts reactions the 4 : 12-products predominate or not. The fact that considerable purification was required indicates that other isomers are present in quantity, but on the other hand 4-acetylfluoranthene gives a 67% yield of the diacetylfluoranthene.

The acetylfluoranthene prepared by Campbell and Easton (*loc. cit.*) has now been shown to be 11-acetylfluoranthene by conversion into fluoranthene-11-carboxylic acid (Tucker and Whalley, *J.*, 1949, 3213; Campbell and Easton, *loc. cit.*). The acetyl compound undergoes the Schmidt reaction to give 11-acetamidofluoranthene, m. p. 199—201°, previously prepared but not analysed by von Braun and Anton (*Annalen*, 1932, **496**, 191) whose product was not pure since its m. p. was 190°.

Clemmensen reduction of 11-acetylfluoranthene gives a product whose high m. p. suggests that it is not the ethyl derivative but the dimeric 2 : 3-di-(11-fluoranthyl)but-2-ene (II) (cf. Steinkopf and Wolfram, *ibid.*, 1923, **430**, 113. Bradlow and Vander Werf, *J. Amer. Chem. Soc.*, 1947, **69**, 1254).

Experimental.

All adsorptions were effected on alumina (Brockmann) and will be described in greater detail in a thesis (Edinburgh) to be submitted by one of us (W. K. L.). Unless otherwise stated, all fluorescence observations were made in ultra-violet light generated by a Hanovia lamp.

Acetylation of Fluoranthene.—Aluminium chloride (36 g., 0·272 mol.) was added to a stirred solution of fluoranthene (20 g., 0·1 mol.) and acetyl bromide (24·6 g., 0·204 mol.) in carbon disulphide (100 ml.) cooled to 0°. The mixture was stirred for 24 hours and then worked up as usual. The product was shaken with a large volume of ether, and the ether-insoluble portion (17·0 g.) was crystallised first from acetic acid and then from benzene to give a product, m. p. 108—125°. This was dissolved in benzene and chromatographed. Development with benzene–light petroleum gave a lower band (*A*) with a blue fluorescence, an intermediate pale yellow band (*B*), and a top dark yellow band (*C*). *A* gave fluoranthene; the lower part of *B* yielded 4-acetylfluoranthene, m. p. 127—129° (no depression when mixed with an authentic sample), and the upper part gave 11-acetylfluoranthene, m. p. 101—102° either alone or admixed with an authentic sample; and *C* gave diacetylfluoranthene, m. p. 137—139°. Further quantities of these products were obtained by evaporating the acetic acid, benzene, and ethereal filtrates, dissolving the residues in benzene, and separating the constituents chromatographically. Fluoranthene, 4-acetyl-, 11-acetyl-, and 4 : 12-diacetyl-fluoranthene were thus obtained in 17, 2·6, 6·2, and 12·2% yields respectively. By increasing the time of the Friedel–Crafts reaction to 72 hours the respective yields were 1, 4·5, 13, and 37%.

Reactions of 4-Acetylfluoranthene.—4-Acetylfluoranthene (0·38 g.) in trichloroacetic acid (2·32 g.) was treated at 60° with sodium azide (0·16 g.) and kept at this temperature for 6 hours. 4-Acetamidofluoranthene (0·2 g.) was isolated by the usual procedure in pale yellow needles, m. p. 244—245° (from acetic acid), with a greenish-yellow fluorescence in the solid state but not in solution (Found : N, 5·5. Calc. for $C_{18}H_{13}ON$: N, 5·4%). This substance (0·15 g.) was boiled with concentrated hydrochloric acid (5 ml.), water (2·5 ml.), and a little ethanol for 20 hours to give 4-aminofluoranthene hydrochloride, m. p. 285°, from which 4-aminofluoranthene was obtained as yellow crystals (from benzene–light petroleum), m. p. 113—115° (lit., 111—112°) (Found : N, 6·3. Calc. for $C_{16}H_{11}N$: N, 6·4%). 4-Acetylfluoranthene dissolves with a strong greenish-yellow fluorescence, and with acetyl bromide gives a 67% yield of 4 : 12-diacetylfluoranthene.

Reactions of 11-Acetylfluoranthene.—The acetyl compound with sodium azide and trichloroacetic acid yielded 11-*acetamidofluoranthene*, m. p. 199—201° after crystallisation from benzene (Found : N, 5·2. $C_{18}H_{13}ON$ requires N, 5·4%). 11-Acetylfluoranthene (0·80 g.) in methanol (50 ml.) was slowly added to sodium hypochlorite solution (prepared from 10 g. of sodium hydroxide) kept at 65°. The mixture was stirred at this temperature for 5 hours and the methanol was then removed by distillation. The yellow sodium salt of fluoranthene-11-carboxylic acid (0·41 g.) separated and the filtrate on acidification gave the free acid (0·07 g.). The acid from both sources crystallised from acetic acid in pale yellow needles (0·43 g.), m. p. 284—287° (Found : C, 82·9; H, 4·4. Calc. for $C_{17}H_{10}O_2$: C, 82·9; H, 4·1%). The acid in the solid state has a pale green fluorescence and in solution a blue fluorescence. The methyl ester crystallises in pale yellow needles (from methanol), m. p. 94—97° (Found : C, 82·8; H, 5·0. Calc. for $C_{18}H_{12}O_2$: C, 83·1; H, 4·7%). Both the acid and the ester show no m. p. depression when mixed with authentic samples.

The acetyl compound (2·05 g.) was acetylated as above by acetyl bromide in carbon disulphide in the presence of aluminium chloride. The product was chromatographed on a column 28″ × ¾″ and developed with benzene–light petroleum (3 : 1). The bottom, pale yellow zone yielded unchanged 11-acetylfluoranthene (0·49 g.), and the upper, dark yellow band on elution gave impure diacetylfluoranthene (1·29 g.), m. p. 124—134°, which was purified by further adsorption on a column 16″ × ½″. 4 : 12-Diacetylfluoranthene (0·61 g.), m. p. 138—142°, thus obtained, showed no m. p. depression when mixed with a sample of the compound prepared as above.

Clemmensen reduction of the acetyl compound (0·72 g.) gave a product which was chromatographed in benzene on a column 20″ × ½″. Development with benzene–light petroleum (b. p. 80—100°) gave several zones the lowest of which was pale yellow with a yellow fluorescence. This zone on elution yielded a syrup (0·59 g.) which was converted into the picrate (0·08 g.), orange crystals. The picrate in benzene was passed through a column 11″ × ½″ and development gave a pale yellow band which on elution afforded a product which is probably 2 : 3-*di*-(11-*fluoranthyl*)*but*-2-*ene*, crystallising from ethanol in pale yellow plates (0·2 g.) with a greenish-blue fluorescence, m. p. 272—275° (Found : C, 93·7; H, 5·5. $C_{36}H_{24}$ requires C, 94·7; H, 5·3%).

Reactions of 4 : 12-Diacetylfluoranthene.—Diacetylfluoranthene yields, by Brady's method, a *mono*-2 : 4-*dinitrophenylhydrazone*, which was purified by boiling it with ethanol and acetic acid and forms red crystals, m. p. >350°, which sublime in yellow needles (Found : N, 12·0. $C_{26}H_{18}O_5N_4$ requires N, 12·5%). It is probably the 11-compound (cf. Campbell and Easton, *loc. cit.*).

Attempts to reduce the diacetyl compound by the Wolff–Kishner method (Huang-Minlon modification) were unsuccessful, an impure compound containing nitrogen being the only product. Clemmensen reduction gave only unchanged material.

Diacetylfluoranthene (1·0 g.), potassium permanganate (8·7 g.), aqueous sodium carbonate (5 ml.), and water were boiled for 4 hours and yielded 0·60 g. of an acid, m. p. >350°, which was converted into the methyl ester by boiling methanol (20 ml.) and concentrated sulphuric acid (2 ml.) during 20 hours. The ester was purified by dissolving it in benzene and chromatographing the solution. Development with benzene gave a bottom, blue-fluorescing zone which was discarded, and an upper, pale yellow zone with a yellowish-green fluorescence. Elution of this band gave dimethyl fluoranthene-4 : 12-dicarboxylate, yellow elongated prisms (from methanol–acetic acid), m. p. 181·5—183°, not depressed when

admixed with the ester prepared by Campbell and Easton (*loc. cit.*) (Found : C, 75·0; H, 4·6. Calc. for $C_{20}H_{14}O_4$: C, 75·5; H, 4·4%).

Chlorine was passed into 100 ml. of an aqueous solution of sodium hydroxide (20 g.) until the solution was neutral to litmus. More sodium hydroxide (5 g.) and water (10 ml.) were added. Diacetylfluoranthene (1·00 g.) was suspended in this solution and was well stirred at 65—70° for 6 hours. The solution was kept overnight, treated with sulphur dioxide, and finally acidified by concentrated hydrochloric acid. Fluoranthene-4 : 12-dicarboxylic acid separated and more was obtained by extraction of the filtrate with ether to give a total yield of 94%.

4 : 12-*Dibromofluoranthene.*—Powdered sodium azide (0·27 g.) was added in two portions at an interval of ½ hour to 4 : 12-diacetylfluoranthene (0·38 g.) in trichloroacetic acid (4·2 g.) kept at 60°. After 8 hours at this temperature the mixture was poured on ice, and the precipitated 4 : 12-*diacetamidofluoranthene* (99%) was washed with water and then boiled with benzene; it had m. p. ~370° (Found : C, 76·0; H, 5·1; N, 8·9. $C_{20}H_{16}O_2N_2$ requires C, 75·9; H, 5·1; N, 8·9%). The compound (0·19 g.) was boiled with concentrated hydrochloric acid (10 ml.) for 2 hours and the solution on cooling deposited greenish-yellow needles of 4 : 12-*diaminofluoranthene dihydrochloride* (88%) (Found : N, 8·9; Cl, 22·8. $C_{16}H_{14}N_2Cl_2$ requires N, 9·2; Cl, 23·2%). Treatment with sodium hydroxide gave the yellow base which, however, was not obtained pure.

The dihydrobromide prepared from diacetylfluoranthene (2 g.) was suspended in 34% hydrobromic acid (20 ml.) and tetrazotised at 0° by 20% aqueous sodium nitrite. The solution was filtered and added slowly to a solution of freshly prepared cuprous bromide (1·1 g.) in 34% hydrobromic acid (3 ml.). The temperature of the mixture was increased during ½ hour to 60° and it was then boiled. The resulting black precipitate was boiled first with chlorobenzene and then with benzene and the combined extracts were passed down a column 12″ × ½″. Development with benzene gave a uniform yellow zone which on elution yielded 4 : 12-*dibromofluoranthene* (0·48 g.), m. p. 162—165° (after crystallisation from benzene) (mixed m. p. with 4 : 11-dibromofluoranthene, 144—152°) (Found : C, 53·4; H, 2·1; Br, 44·7. $C_{16}H_8Br_2$ requires C, 53·4; H, 2·2; Br, 44·4%).

Fluoranthene-4 : 11-*dicarboxylic Acid.*—4 : 11-Dicyanofluoranthene (0·2 g.) was boiled for 3 hours with potassium hydroxide (0·5 g.) in trimethylene glycol (5 ml.). The solution was poured into water, and the precipitate extracted with aqueous sodium carbonate. The extract with dilute sulphuric acid gave *fluoranthene*-4 : 11-*dicarboxylic acid* (87%) which sublimed in yellow needles, m. p. >350° (Found : C, 75·2; H, 3·3. $C_{18}H_{10}O_4$ requires C, 74·5; H, 3·6%). The acid was converted by thionyl chloride into the acid chloride and thence into the methyl ester (90 mg.) which was dissolved in benzene and passed through a column 9″ × ¾″. Development with benzene gave a main band, which was yellow and had a yellow fluorescence and on extraction with acetone gave the *dimethyl* ester, bright yellow needles (from methanol), m. p. 168—169°, with a bright yellow fluorescence (Found : C, 74·8; H, 4·3. $C_{20}H_{14}O_4$ requires C, 75·5; H, 4·4%). The ester sublimes in rhombic plates, whereas dimethyl fluoranthene-4 : 12-dicarboxylate sublimes in threads or needles. It gives a big m. p. depression when admixed with this ester.

Thanks are expressed to the Anglo-Iranian Oil Co. Ltd., for a grant, to Imperial Chemical Industries Limited for a grant to one of us (W. K. L.), and to Drs. S. H. Tucker and M. Whalley for a sample of ethyl fluoranthene-11-carboxylate.

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SECTION A ORIENTATIONS AND TRANSFORMATIONS OF DI- AND TRI-BROMOFLUORANTHENES

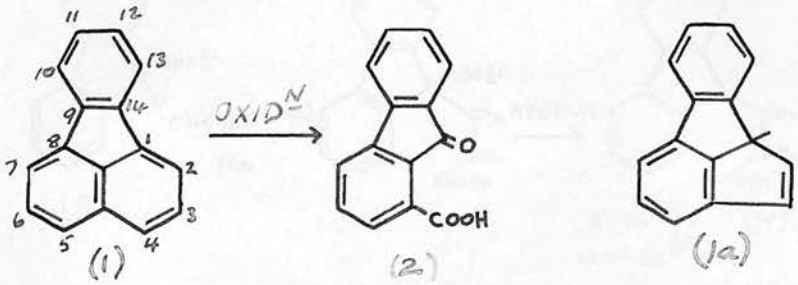
THE CHEMISTRY OF FLUORANTHENE

The polycyclic aromatic hydrocarbon fluoranthene has been known for a century although it is only within the last twenty-five years that its structure, the orientation of its substitution products and the synthesis of its derivatives have been extensively investigated. Fluoranthene, or "idryl" as it was known, was present in the material obtained by extracting the mercury ores of Idria with oil of turpentine (Dumas, Ann., 1833, 5, 16: Laurent, ANN. Chimie, 1837, 66, 137). Goldschmeidt showed that distillation of these mercury ores gave a mixture from which fluoranthene could be isolated (Ber., 1877, 10, 2022; 1878, 11, 1578; Monats., 1880, 1, 221).

Fluoranthene was first discovered in the high-boiling fraction of coal tar by Fittig and Gebhard (Ber., 1877, 10, 2141; Ann., 1878, 193, 142) and the pure hydrocarbon is obtained commercially to-day from this source by fractional distillation and repeated fractional recrystallisation.

STRUCTURE AND SYNTHESIS

Fluoranthene (1) (whose numbering is as shown), is oxidised to fluorenone-1-carboxylic acid (2) and the fact that fluoranthene possesses no reactive group indicates that C_9 of the fluorene skeleton is substituted. On this basis and from the incorrect empirical/

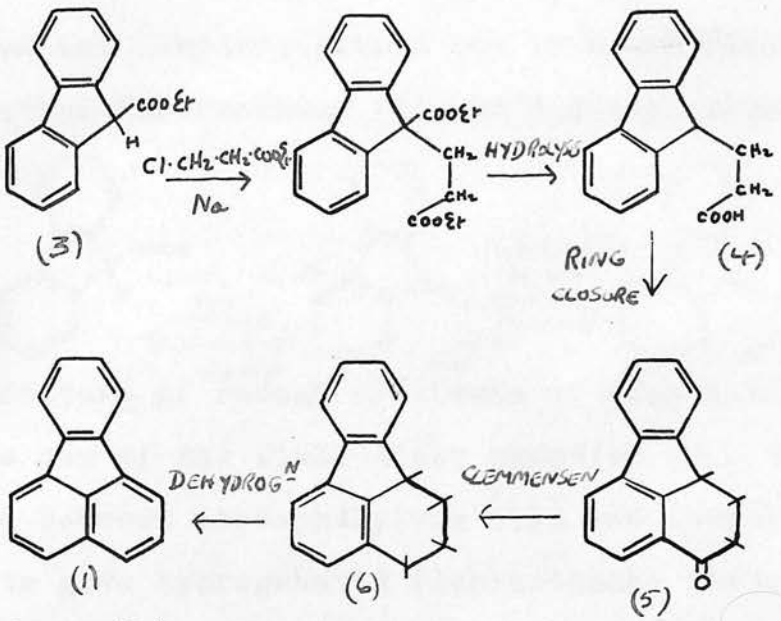


(1) (2) (1a)

empirical formula Fittig and Gebhard (loc. cit.) suggested the structure (1a).

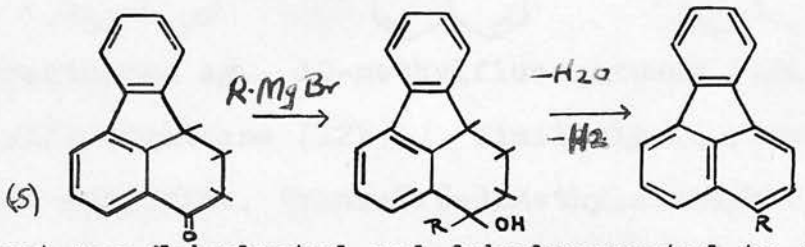
This formulation remained unchallenged until von Braun and Anton (Ber., 1929, 62, 145) pointed out that, according to the Sachse-Mohr concepts of bond strain in organic molecules, a compound of formula (1a) would be highly strained if, indeed, it existed at all. On the other hand formula (1) represents a stable structure and its formula, $C_{16}H_{10}$, requires analytical values for carbon and hydrogen which are almost the same as those required for $C_{15}H_{10}$ (1a).

Formula (1) was verified by synthesis (von Braun and Anton, loc. cit.). β-chloropropionic ester was condensed with 9-carbethoxyfluorene (3) and the condensation product hydrolysed to 9-fluorenepropionic acid (4) which was cyclised via its acid chloride to 4-keto-1:2:3:4-tetrahydrofluoranthene (5). Clemmensen reduction of this ketone led to 1:2:3:4-tetrahydrofluoranthene (6) which was then dehydrogenated to



fluoranthene (1).

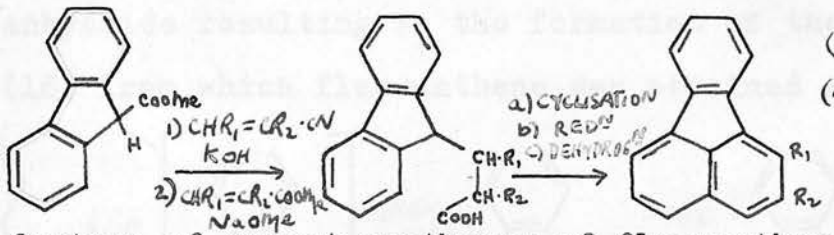
The ketone (5) was later used in the synthesis of 4-methyl- (7) and 4-phenyl-fluoranthene (8) (von Braun and Manz, Ber., 1937, 70, 1603). The carbinol obtained by the action of the appropriate Grignard



reagent was dehydrated and dehydrogenated to the required hydrocarbon.

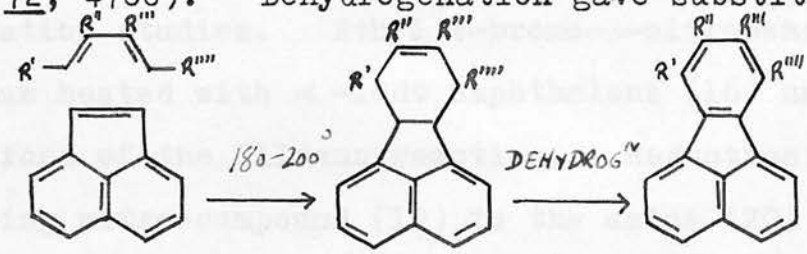
The attachment of a suitably substituted propionic acid chain to the 9- position of alkyl fluorene-9-carboxylates has been accomplished by Tucker and his co-workers (J.C.S., 1949, 2182; 1949, 2623: 1952, 803). Substituted acrylic esters or nitriles replace the remaining active hydrogen atom in the 4- position. These adducts were hydrolysed to substituted propionic acids and subsequent cyclisation, reduction/

reduction and dehydrogenation led to alkyl fluoranthenes eg. 2-methyl fluoranthene (9) and 3-methyl fluoranthene (10).



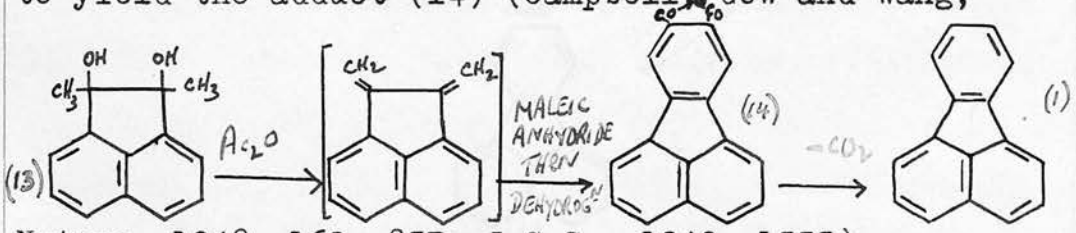
(9) $R_1 = CH_3$, $R_2 = H$
(10) $R_1 = H$, $R_2 = CH_3$

A feature of recent syntheses of fluoranthenes has been the use of the Diels-Alder reaction eg., the reaction between acenaphthylene (11) and substituted dienes to give hydrogenated fluoranthenes (Bergmann, Nature, 1948, 161, 889; Kloetzel and Mertel, J.A.C.S., 1950, 72, 4786). Dehydrogenation gave substituted



(12a) $R' = CH_3$, $R'' = R''' = R'''' = H$
(12b) $R'' = CH_3$, $R' = R''' = R'''' = H$

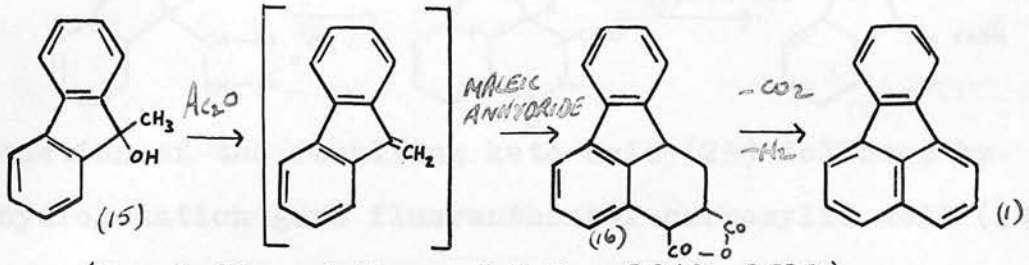
fluoranthenes eg., 10-methylfluoranthene (12a) and 11-methylfluoranthene (12b). Similarly in presence of acetic anhydride, trans-7:8-dimethylacenaphthene-7:8-diol (13) acts as a diene and adds on maleic anhydride to yield the adduct (14) (Campbell, Gow and Wang,



Nature, 1948, 162, 857; J.C.S., 1949, 1555). Dehydrogenation, followed by decarboxylation gave fluoranthene.

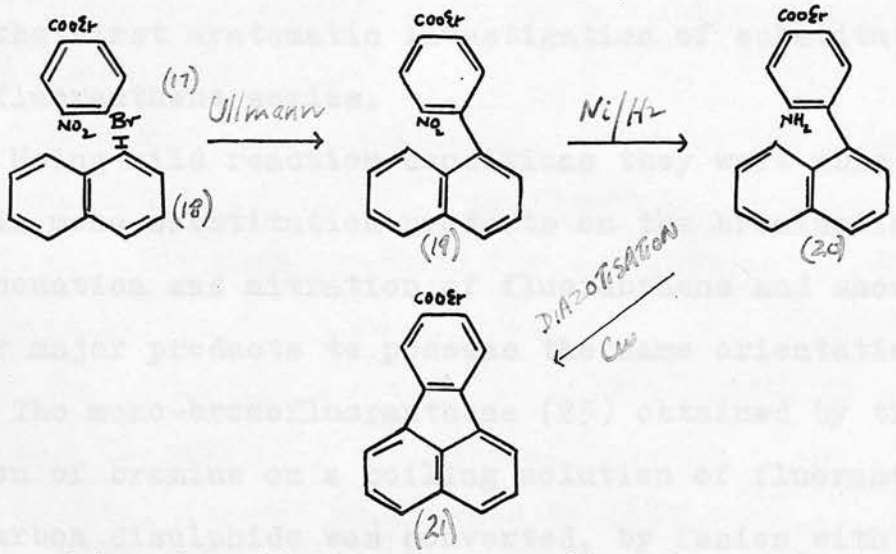
Yet/

Yet another example is the reaction of 9-methyl-9-fluorenol (15) with maleic anhydride in the presence of acetic anhydride resulting in the formation of the adduct (16) from which fluoranthene was obtained as



above (Campbell and Wang, J.C.S., 1949, 1513).

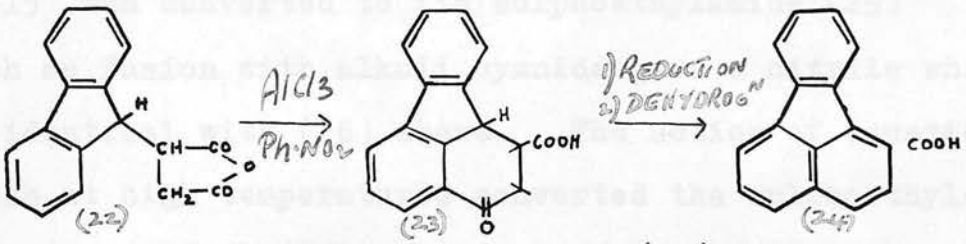
Forrest and Tucker (J.C.S., 1948, 1137) have evolved a synthesis on naphthalene which is useful in orientation studies. Ethyl 4-bromo-3-nitrobenzoate (17) was heated with α-iodo naphthalene (18) under the conditions of the Ullmann reaction. Reduction of the resulting nitro-compound (19) to the amine (20)



followed by diazotisation and cyclisation with copper powder led to ethyl fluoranthene-11-carboxylate (21).

A synthesis of fluoranthene derivatives has been reported involving the cyclisation of the anhydride (22) formed/

formed in the reaction between maleic anhydride and fluorene (Bergmann and Orchin, J.A.C.S., 1949, 71, 1917).



(22) (23) (24)

Reduction of the resulting keto-acid (23) followed by dehydrogenation gave fluoranthene-2-carboxylic acid (24).

SUBSTITUTION OF FLUORANTHENE

Although early workers had carried out some work on the nitration, sulphonation and bromination of fluoranthene (Goldschmeidt, Ber., 1877, 10, 2022; Monats., 1880, 1, 221; Fittig and Gebhard, loc. cit.), it was left to von Braun and Manz (Ann., 1931, 488, 111) to carry out the first systematic investigation of substitution in the fluoranthene series.

Using mild reaction conditions they were able to obtain mono-substitution products on the bromination, sulphonation and nitration of fluoranthene and showed their major products to possess the same orientation.

The mono-bromofluoranthene (25) obtained by the action of bromine on a boiling solution of fluoranthene in carbon disulphide was converted, by fusion with alkali cyanide, to the nitrile (26) which was hydrolysed to the carboxylic acid (27).

$C_{16}H_{10}$ (1) $\longrightarrow C_{16}H_9.Br$ (25) $\longrightarrow C_{16}H_9.CN$ (26) $\longrightarrow C_{16}H_9.COOH$ (27)

The/

The mono-sulphonic acid (28) obtained by the action of chlorosulphonic acid (1 mole.) in chloroform at -15° was converted to its sulphoethylamide (29) which on fusion with alkali cyanide gave a nitrile which was identical with (26) above. The action of caustic potash at high temperatures converted the sulphoethylamide to a phenol (30) which was converted to an amine (31) on treatment with ethanolic ammonia.

$$C_{16}H_{10}(1) \rightarrow C_{16}H_9.SO_3H\,(28) \rightarrow C_{16}H_9.SO_2.NH.C_2H_5\,(29) \rightarrow C_{16}H_9.CN\ (26)$$

$$\downarrow$$

$$C_{16}H_9.OH\ (30) \longrightarrow C_{16}H_9.NH_2\ (31)$$

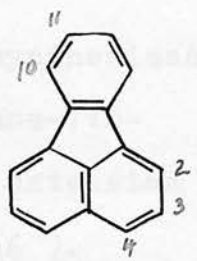
The nitration of fluoranthene in acetic acid gave a mono-nitro compound (32) which was reduced to an amine identical with the amine (31) above.

$$C_{16}H_{10}\ (1) \longrightarrow C_{16}H_9.NO_2\ (32) \longrightarrow C_{16}H_9.NH_2\ (31)$$

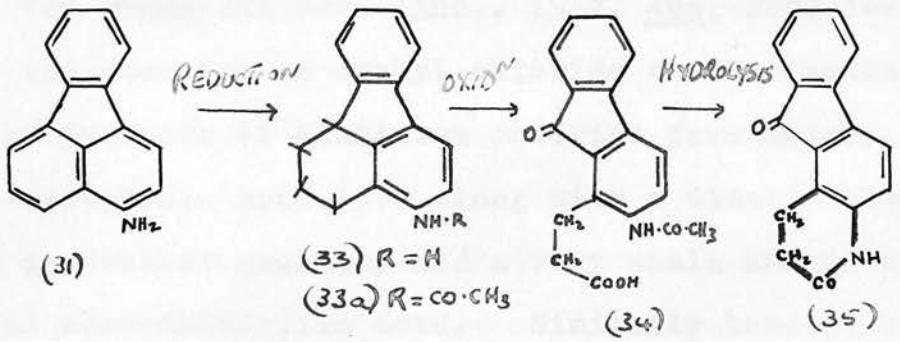
Hence these mono-substitution products have the same orientation.

There are five possible positions in fluoranthene for mono-substitution viz., positions 2-, 3-, 4-, 10- and 11-. The main evidence for 4- substitution was outlined by von Braun as follows:-

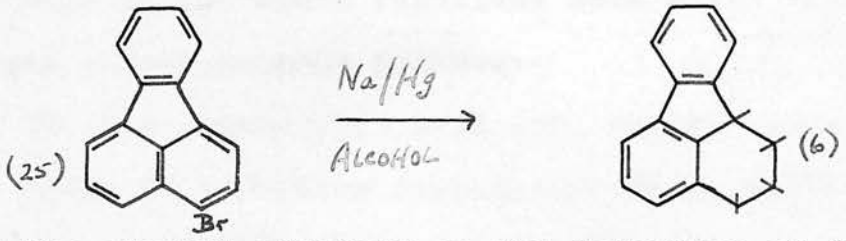
(a) The amine (31) was reduced to the tetrahydroamine (33) and the acetyl-derivative of the latter (33a) carefully oxidised to the acid (34) which was hydrolysed to an acid which lactamised spontaneously to the lactam (35). Such lactamisation is possible only if/



if the amine group occupied the 4- position.

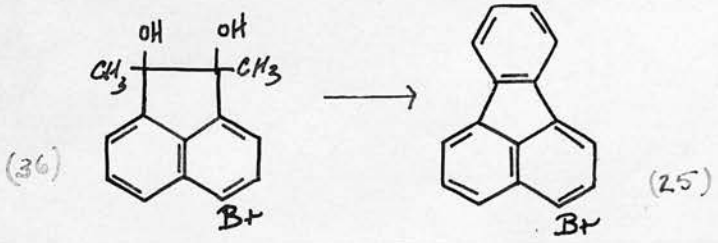


(b) Reduction of 4-bromofluoranthene (25) to 1:2:3:4-tetrahydrofluoranthene (6) indicated that substitution had taken place in the naphthalene portion of the fluoranthene nucleus.



(c) The alcohol obtained on the reduction of 4-keto-1:2:3:4-tetrahydrofluoranthene (5) was similar to that obtained on the hydrogenation of the phenol (30), each giving the same product with phenyl isocyanate. The alcohols themselves were dissimilar and were probably stereoisomers.

Later Campbell and Gow (loc. cit.) synthesised 4-bromofluoranthene (25) from 3-bromo-trans-7:8-dimethylacenaphthene-7:8-diol (36) in an extension of their Diels-Alder type synthesis (see p. 6).



FRIEDEL-CRAFTS ACYLATION OF FLUORANTHENE

Von Braun and Manz (Ann., 1932, 496, 188) found that the reaction of oxalyl chloride on fluoranthene in the presence of aluminium chloride gave mainly a mono-carboxylic acid (37) along with a dicarboxylic acid in smaller quantity and a very small amount of a second mono-carboxylic acid. Similarly benzoyl chloride gave a mono-benzoylfluoranthene (38) together with a small amount of a second monobenzoylfluoranthene. Phthalic anhydride gave two mono-o-carboxybenzoylfluoranthenes, one of these (39) in preponderance.

The mono-substituted products obtained in major quantities in the above reactions were shown to have the same orientations as follows:-

(a) The mono-carboxylic acid (37) was converted by means of a Curtius degradation to an amine (40).

$$C_{16}H_9.COOH\ (37) \longrightarrow C_{16}H_9.NH_2\ (40)$$

(b) Beckmann rearrangement of the oxime of the benzoyl chloride (38) followed by hydrolysis gave the same amine (40).

$$C_{16}H_9.CO.C_6H_5\ (38) \rightarrow C_{16}H_9.\underset{\underset{NOH}{\|}}{C}.C_6H_5 \rightarrow C_{16}H_9.NH_2\ (40)$$

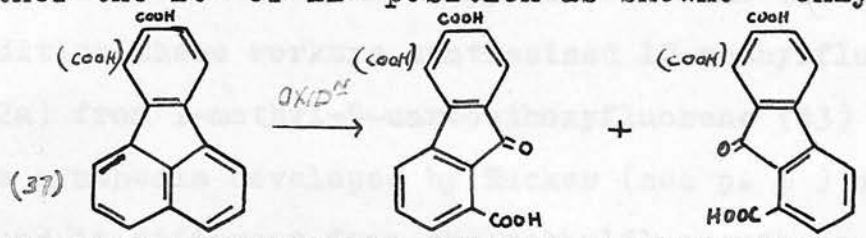
(c) A similar rearrangement of the oxime of the o-carboxybenzoylfluoranthene (39) gave the same amine (40).

All three amines were identical and different from 4-aminofluoranthene (31) orientated as described above.

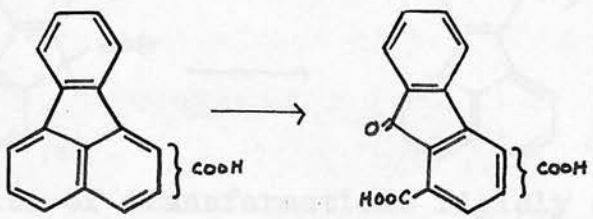
A/

A similar series of reactions converted the isomeric mono-substituted products obtained in small yield to 4-aminofluoranthene (31) proving them to be substituted in the 4- position.

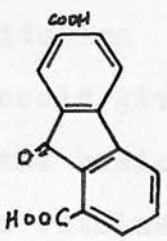
That the substituent did not occupy any position in the naphthalene portion of the nucleus was indicated by the formation of a mixture of fluorenone dicarboxylic acids when the mono-carboxylic acid (37) was oxidised. This was only possible if the substituent occupied either the 10- or 11- position as shown. Only one



fluorenone dicarboxylic acid is possible when an acid containing a substituent in the 2- or 3- position is oxidised.



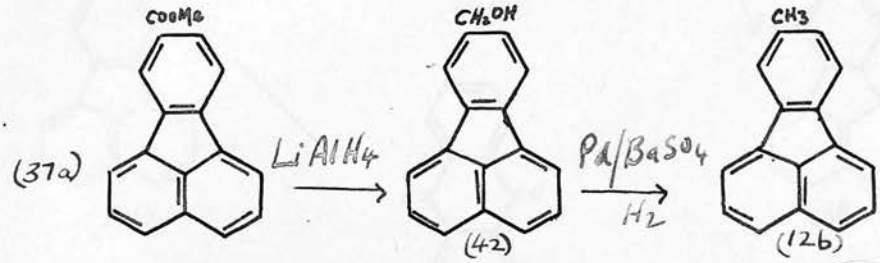
The mixture of acids was not separated but von Braun and Anton claimed to have isolated a dimethyl ester, on esterification of the acid mixture, which was very similar to the dimethyl ester of fluorenone-1:7-dicarboxylic acid (41) described earlier by Bamberger and Hooker (Ann., 1885, 229, 102).



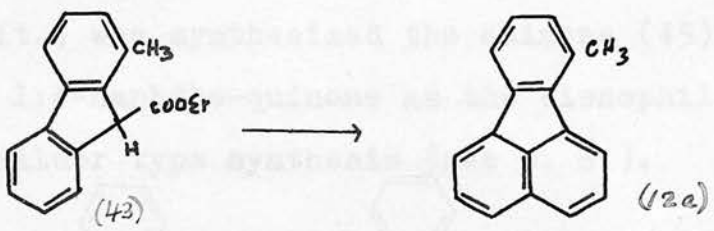
(41)

The/

The absolute orientation of this fluoranthene mono-carboxylic acid is shown by the following transformation of its methyl ester (37a) (Kloetzel and Mertel, loc. cit.). The reduction of this methyl ester with lithium aluminium hydride gave the alcohol (42) which



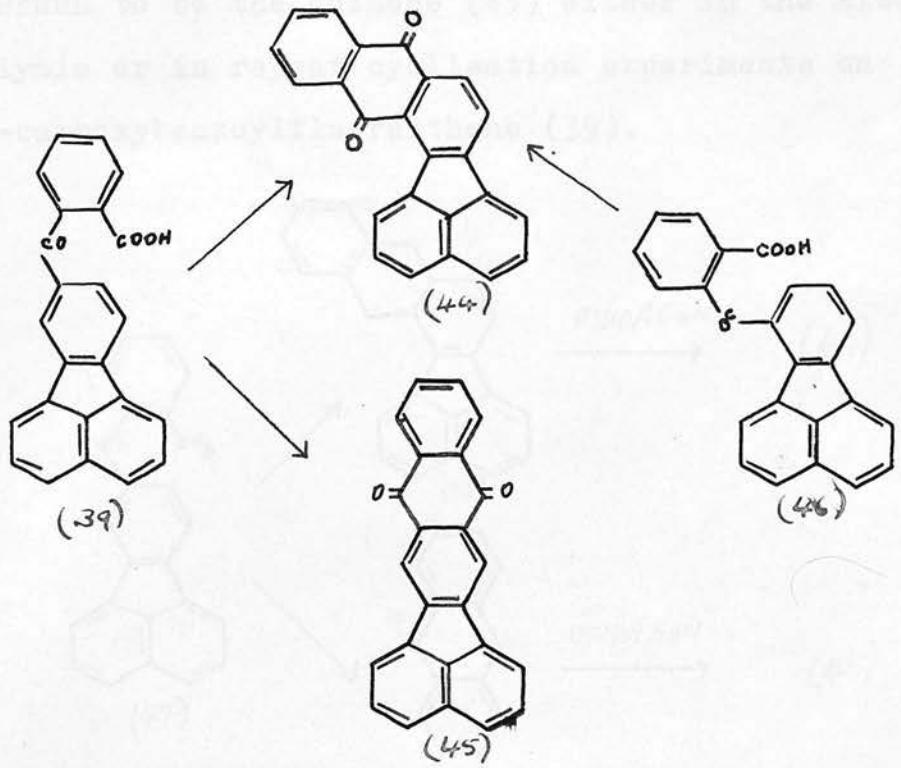
was hydrogenated to 11-methylfluoranthene (12b). In addition these workers synthesised 10-methylfluoranthene (12a) from 1-methyl-9-carboethoxyfluorene (43) using the synthesis developed by Tucker (see p. 5) and found it different from the methylfluoranthene (12b) obtained from the fluoranthene mono-carboxylic acid.



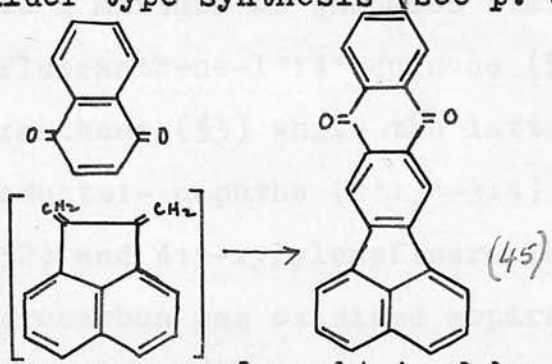
This series of transformations rigidly orientates the carboxylic acid group in the 11- position. A synthesis of ethyl fluoranthene-11-carboxylate is described on p. 7

Von Braun and Manz (loc. cit.) cyclised the o-carboxybenzoylfluoranthene (39) to a mixture of quinones (44) and (45) indicating 11- substitution since 10-o-carboxybenzoylfluoranthene (46) could give only one quinone (44) on cyclisation. On the basis of unsatisfactory evidence derived from results obtained

on/



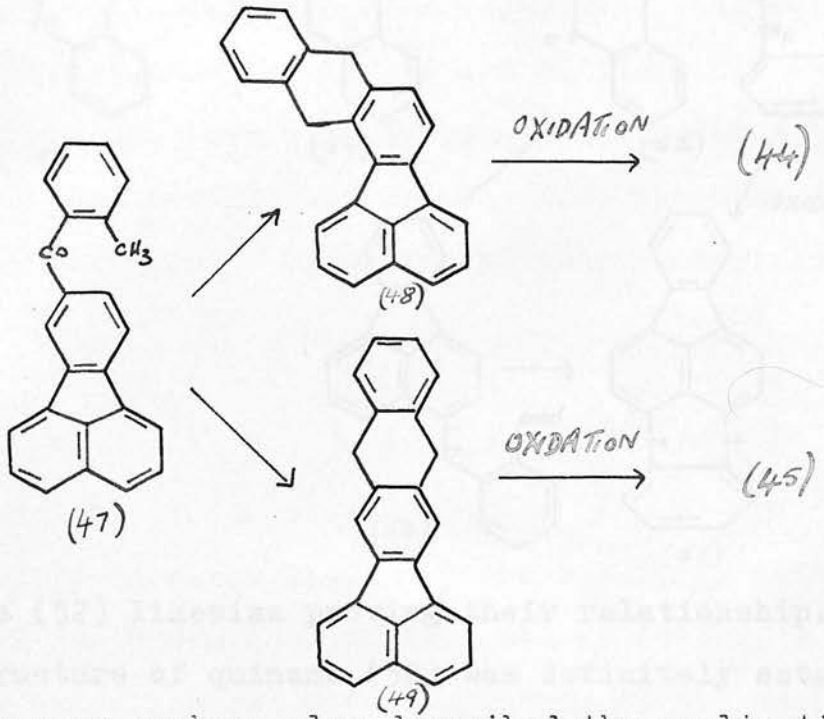
on oxidation of both quinones von Braun and Manz assigned definite structures to each of their quinones. These structures were later reversed by Campbell and Gow (loc. cit.) who synthesised the quinone (45) as shown using 1:4-naphtho-quinone as the dienophile in their Diels-Alder type synthesis (see p. 6).



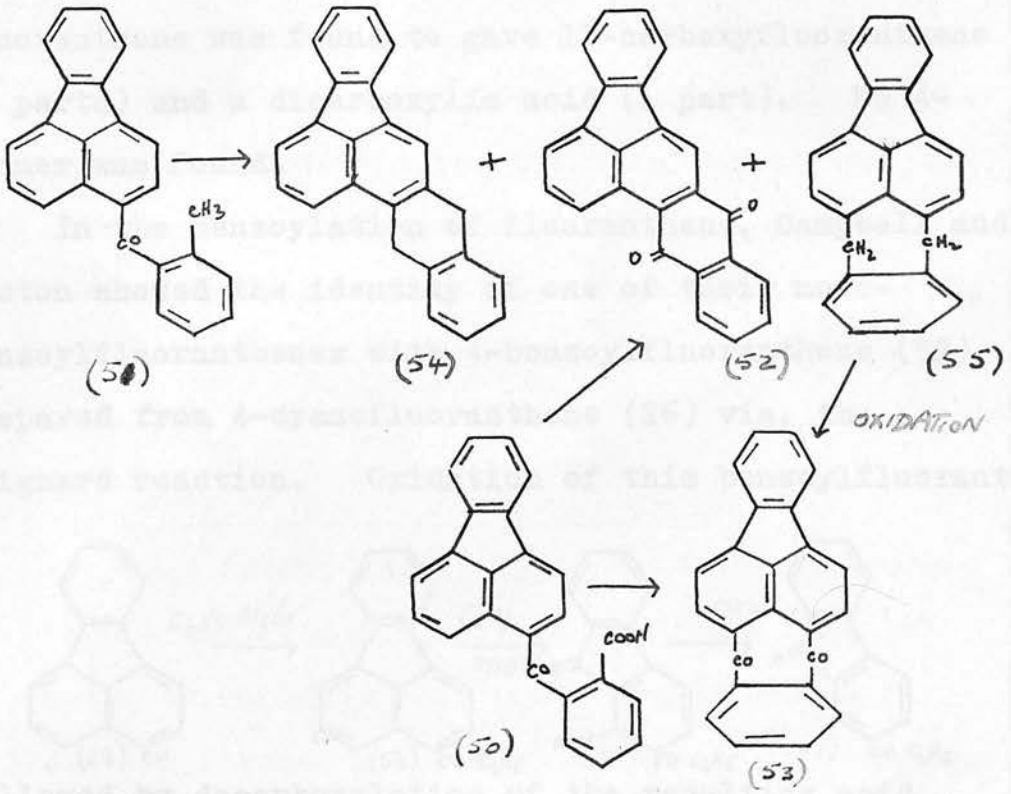
Both quinones were also obtained by oxidising the naphthofluoranthenes (48) and (49) obtained by the Elbs pyrolysis of 11-o-toluoylfluoranthene (47) (Campbell, Marks and Reid, J.C.S., 1950, 3466). These workers could not find the substance claimed by

von/

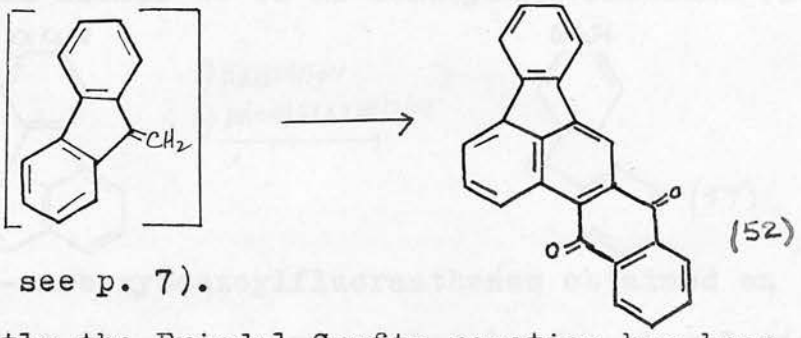
von Braun to be the quinone (45) either in the Elbs pyrolysis or in repeat cyclisation experiments on 11-o-carboxybenzoylfluoranthene (39).



The same workers also described the cyclisation of 4-o-carboxybenzoylfluoranthene (50) and the Elbs pyrolysis of 4-o-toluoylfluoranthene (51). The former experiment gave a mixture of quinones viz., naphtho (2':3':-3:4) fluoranthene-1':4'-quinone (52) and 4:5-phthaloylfluoranthene (53) while the latter experiment gave three products:- naphtho (2':3'-3:4) fluoranthene, its quinone (52) and 4:5-xylylenefluoranthene (55). The latter hydrocarbon was oxidised separately to the diketone (53) thereby proving their relationship while the hydrocarbon (54) was oxidised separately to the quinone/



quinone (52) likewise proving their relationship. The structure of quinone (52) was definitely established by its synthesis from 9-methylenefluorene with 1:4-naphthoquinone as the dienophile (Campbell and Wang,

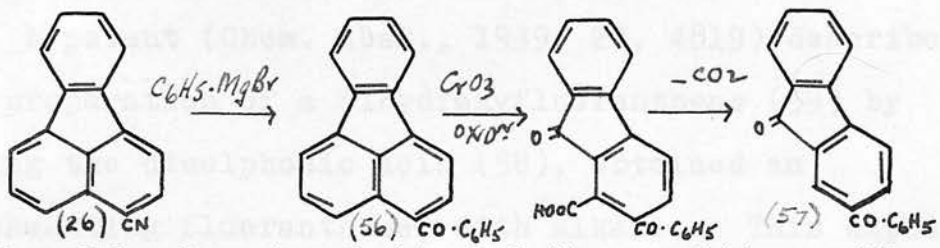


loc. cit., see p. 7).

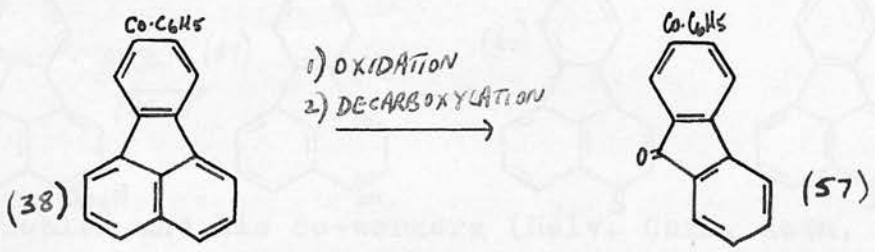
Recently the Friedel-Crafts reaction has been re-investigated by Campbell and Easton (J.C.S., 1949, 340) who showed that the 4- and 11-isomers obtained on phthaloylation and benzoylation are formed in equal quantities. However, the action of oxalyl chloride on fluoranthene/

fluoranthene was found to give 11-carboxyfluoranthene (2 parts) and a dicarboxylic acid (1 part). No 4-isomer was found.

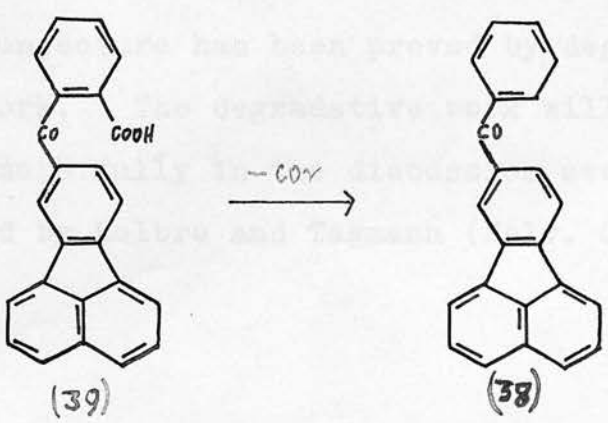
In the benzoylation of fluoranthene, Campbell and Easton showed the identity of one of their mono-benzoylfluoranthenes with 4-benzoylfluoranthene (56) prepared from 4-cyanofluoranthene (26) via. the Grignard reaction. Oxidation of this benzoylfluoranthene



followed by decarboxylation of the resulting acid afforded the known 2-benzoylfluorenone (57). A similar oxidation and decarboxylation of the other mono-benzoyl isomer also yielded 2-benzoyl fluorenone proving this isomer to be 11-benzoylfluoranthene (38).



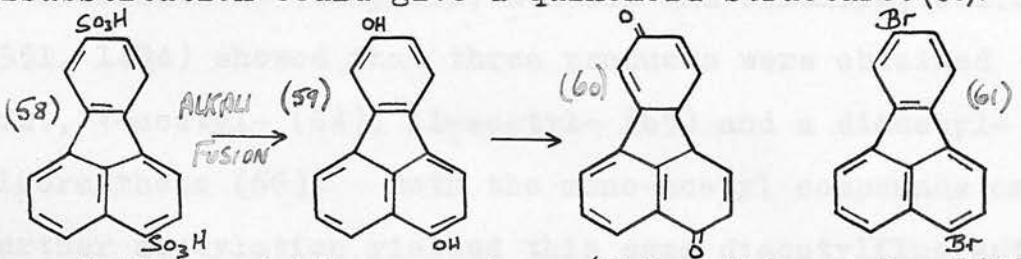
The o-carboxybenzoylfluoranthenes obtained on the phthaloylation were orientated by decarboxylation to the corresponding benzoylfluoranthenes eg.:-



Hence it has been shown that fluoranthene under goes mono-substitution in the 4- or 11- positions. It is interesting to note that von Braun and Manz (loc. cit.) were able to show the presence of 11-isomers in the mixtures obtained on the nitration, sulphonation and bromination of fluoranthene.

DISUBSTITUTION IN THE FLUORANTHENE SERIES

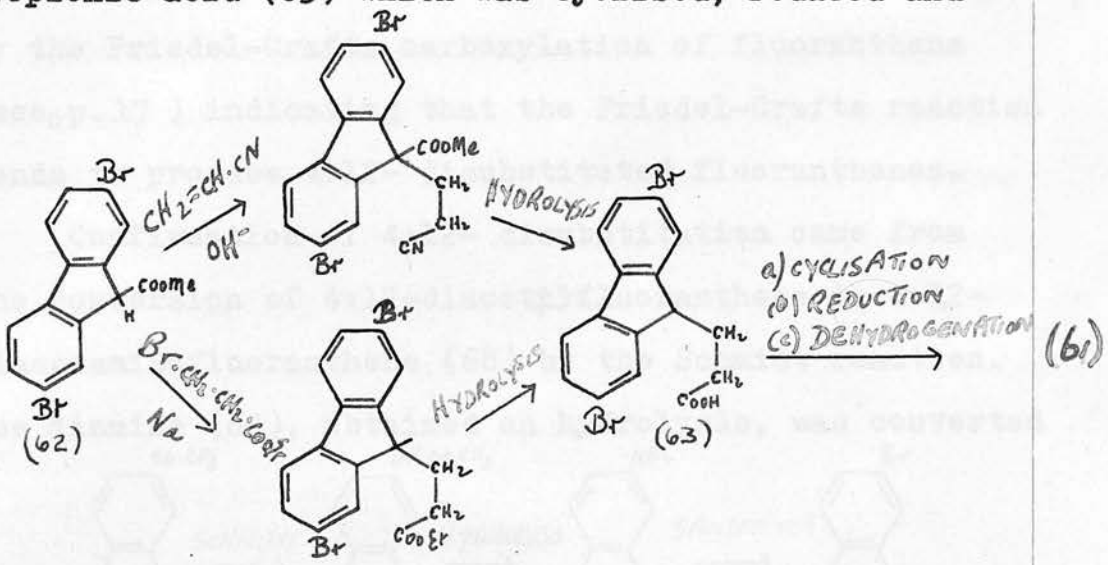
A patent (Chem. Abst., 1939, 27, 4819) described the preparation of a dihydroxyfluoranthene (59) by fusing the disulphonic acid (58), obtained on sulphonating fluoranthene, with alkali. This diphenol was oxidised to a green quinhydrone type of compound which seemed to indicate that diphenol was substituted in the 4:11-positions since only this type of disubstitution could give a quinonoid structure.(60).



Tobler and his co-workers (Helv. Chim. Acta, 1941, 24, 101E) therefore suggested that their dibromofluoranthene, obtained in the bromination of fluoranthene in nitrobenzene, had the 4:11-structure (61).

This conjecture has been proved by degradative and synthetic work. The degradative work will be considered more fully in the discussion section. Synthesis was achieved by Holbro and Tagmann (Helv. Chim. Acta, 1950/

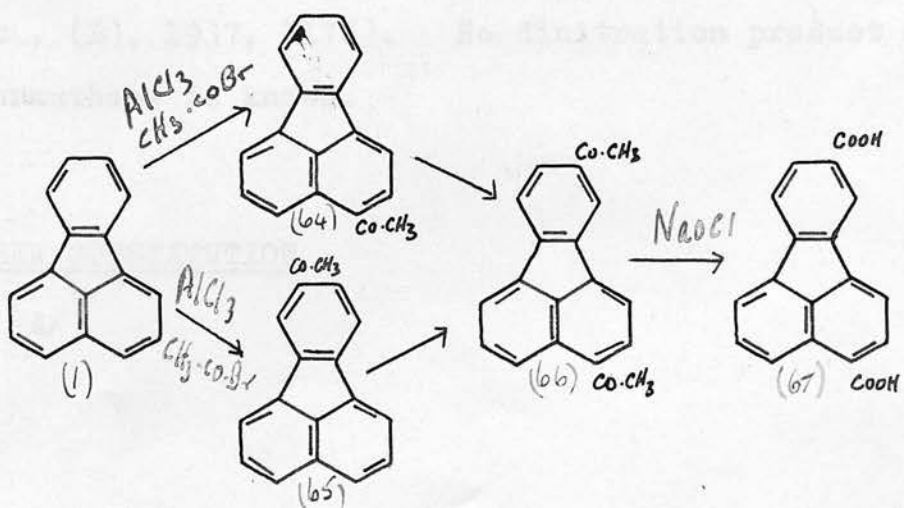
1950, 53, 2178) who treated 2:7-dibromofluorene-9-carboxylic ester (62) with (a) acrylonitrile or with (b) ethyl 2-bromopropionate. Hydrolysis of the products gave, in each case, β-2:7-dibromofluorene-9-propionic acid (63) which was cyclised, reduced and



(61)

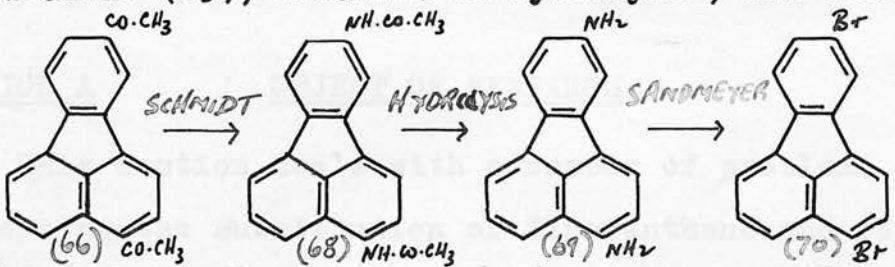
dehydrogenated to 4:11-dibromofluoranthene.

An investigation of the Friedel-Crafts acetylation of fluoranthene (Campbell, Leadill and Wilshire, J.C.S., 1951, 1404) showed that three products were obtained viz., 4-acetyl- (64), 11-acetyl- (65) and a diacetyl-fluoranthene (66). Both the mono-acetyl compounds on further acetylation yielded this same diacetylfluoranthene indicating the latter to be either 4:11-diacetyl- or 4:12-diacetylfluoranthene.



That it was actually the latter was shown by its oxidation to a dicarboxylic acid (67) which is different from the 4:11-diacid prepared by a different route (see discussion section). This dicarboxylic acid was also shown to be identical with that obtained by the Friedel-Crafts carboxylation of fluoranthene (see p. 17) indicating that the Friedel-Crafts reaction tends to produce 4:12- disubstituted fluoranthenes.

Confirmation of 4:12- disubstitution came from the conversion of 4:12-diacetylfluoranthene to 4:12-diacetamidofluoranthene (68) by the Schmidt reaction. The diamine (69), obtained on hydrolysis, was converted



to 4:12-dibromofluoranthene (70) which was different from 4:11-dibromofluoranthene (61).

A dicyano- compound and its related dicarboxylic acid have been described, both derived from 4:11-dibromofluoranthene (Swiss patent 208, 531). The action of sulphonic acid on 4- and 11-hydroxyfluoranthene has produced a 4- and a 11-hydroxysulphonic acid (Brit. Abst., (B), 1937, 1176). No dinitration product of fluoranthene is known.

HIGHER SUBSTITUTION

A/

A tetrabromofluoranthene (Tobler and co-workers, loc. cit.) and a trinitrofluoranthene (Fittig and Gebhard, Ann., 1878, 193, 147) have been described but are as yet unorientated. 4:11-Dibromofluoranthene (61) has been acetylated and the main product shown to be 4:11-dibromo-12-acetylfluoranthene (Campbell and Leadill, unpublished results). The conversion of this trisubstituted product to 4:11:12-tribromofluoranthene and the identity of the latter with the tribromofluoranthene reported by Tobler (loc. cit.) are reported in this thesis (see discussion section).

SECTION A OBJECT OF RESEARCH

This section deals with a number of problems concerning the substitution of fluoranthene and reports experiments proving the structure of the dibromo- and tribromofluoranthene prepared by Tobler and co-workers (Helv. Chim. Acta, 1941, 24, 100E).

In addition the reduction of the dibromofluoranthene and its conversion to a fluoranthene dicarboxylic acid are reported.

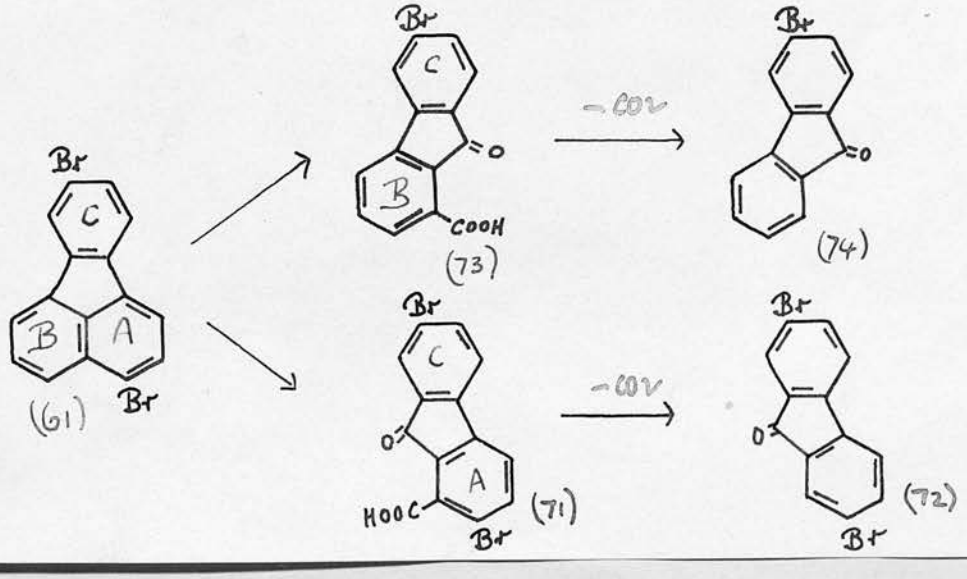
The exact nature of the problems involved is dealt with more fully in the discussion section.

SECTION A DISCUSSION OF RESULTS

OXIDATION OF DIBROMOFLUORANTHENE (pps.60ff).

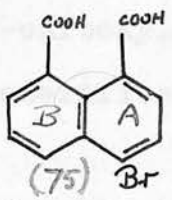
In/

In their investigation into the action of bromine on fluoranthene, Tobler, Holbro, Sutter and Kern (Helv. Chim. Acta, 1941, 24, 101E) isolated a dibromofluoranthene, M.P. 205°, which they regarded as 4:11-dibromofluoranthene (61) by analogy with the disulphonic acid obtained on the sulphonation of fluoranthene (see p. 18). This conjecture has since been proved to be correct by the unambiguous synthesis of 4:11-dibromofluoranthene by Holbro and Tagmann (see p. 19). Prior to this synthesis the oxidative degradation of 4:11-dibromofluoranthene was studied by Campbell, Easton and Rayment (Nature, 1950, 165, 176) who isolated two acids, a dibromofluorenone acid and a mono-bromo acid. This indicates that each of the bromine atoms occupies a different benzene nucleus in the fluoranthene molecule since if both bromine atoms were in the same nucleus a mono-bromo acid would not be obtained. The fact that the dibromotetrahydrofluoranthene, obtained on the bromination of 1:2:3:4-tetrahydrofluoranthene (Tobler et al., loc. cit.) can be dehydrogenated to 4:11-dibromofluoranthene indicates that the benzene nuclei involved are rings A and C.



The dibromofluorenone acid, isolated by Campbell and co-workers, proved to be 2:7-dibromofluorenone-1-carboxylic acid (71) since it was decarboxylated to the known 2:7-dibromofluorenone (72) by the method of Dziewonski and Khal (Chem. Abst., 1935, 19, 2941.

The mono-bromo acid was not orientated but was proved different from 4-bromonaphthalic acid (75) which would arise if ring C were disrupted. Hence it is likely that it was 6-bromofluorenone-1-carboxylic acid (73), formed from the disruption of ring A.



(75)

Accordingly, the work of Campbell and his co-workers (loc. cit.) was repeated, the mono-bromo acid again isolated and its structure proved.

The mixture of acids, obtained on the oxidation of 4:11-dibromofluoranthene with chromic anhydride in acetic acid, proved difficult to separate, success eventually being achieved by boiling with successive portions of saturated calcium hydroxide solution. The cold filtrates deposited the calcium salt of 2:7-dibromofluorenone-1-carboxylic acid while its filtrate on acidification gave a mono-bromo acid which proved to be 6-bromofluorenone-1-carboxylic acid (73) by its decarboxylation, with copper bronze in quinoline, to 3-bromofluorenone (74) which was identical with an authentic sample prepared by Dr. W.H. Stafford by another route (Campbell, Stafford and Wilshire, J.C.S., 1951, 1137).

The/

The isolation of 6-bromofluorenone-1-carboxylic acid fixes the bromine atom, which must be in ring C, in the 11- position and supports the degradative work of Campbell, Easton and Rayment (loc. cit.).

Attempted separations of the crude acid mixture, using the difference in solubilities of the sodium salts in water and the difference in solubility of the acids in benzene, failed. A partial separation was achieved using the fact that 2:7-dibromofluorenone-1-carboxylic acid is sterically hindered and therefore esterifies more slowly.

It is of interest that in their oxidation of 4:11-dibromofluoranthene, Holbro and Tagmann (loc. cit.) obtained a dibromo acid, M.P. 257-60°, and reported a good analysis for a dibromofluorenone acid. No monobromo acid was isolated.

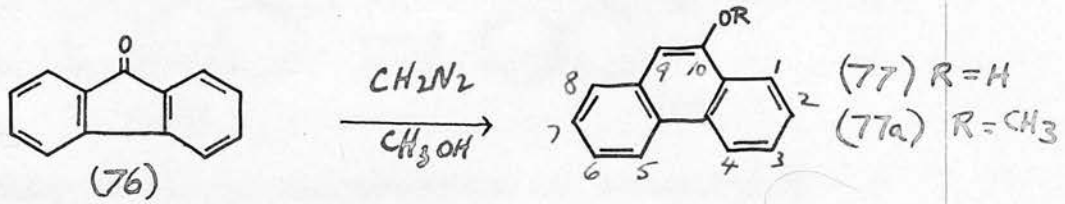
ACTION OF DIAZOMETHANE ON FLUORENONE ACIDS (pps. 66ff.)

In an effort to separate the above mixture of acids, the mixture in methanol and ether was treated with a solution of diazomethane in ether. The neutral product was separated, by means of chromatography, into a colourless solid which fluoresced blue in solution and a bright yellow solid which was identical with the methyl ester of 2:7-dibromofluorenone-1-carboxylic acid (71) prepared by Dr. Rayment (Ph.D. Thesis, Edinburgh).

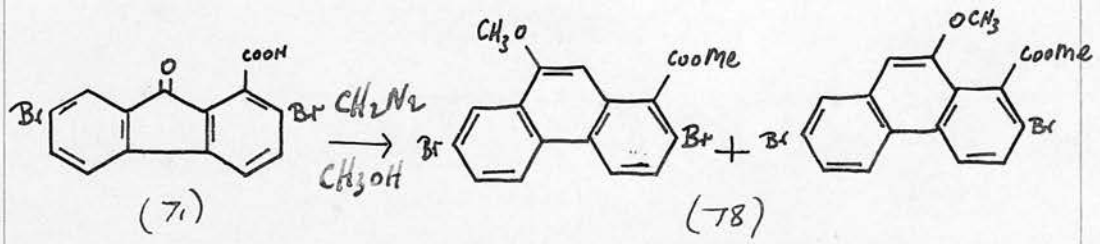
The colourless solid later proved to be a mixture of/

of an ester, colourless plates M.P. 143-5° and an ester, colourless elongated needles M.P. 159-161°.

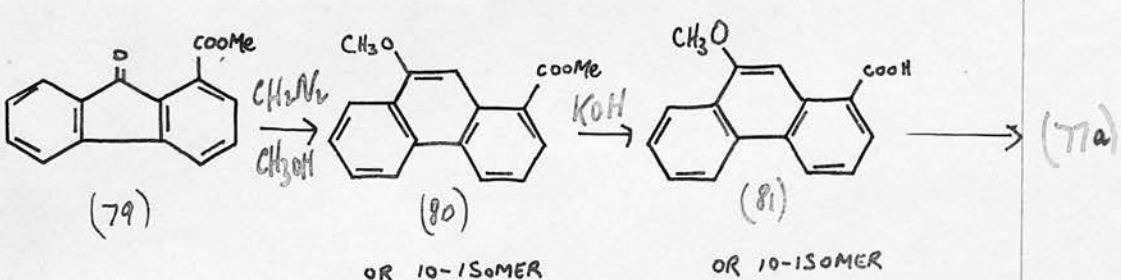
Schultz, Schultz and Cochran (J.A.C.S., 1940, 62, 2902) report the formation of 9-phenanthrol (77) and its methyl ether (77a), by the action of diazomethane on fluorenone (76) dissolved in methanol.



Therefore it is likely that the esters obtained above are the isomeric 9- and 10-methoxy-2:7-dibromo-1-carbomethoxyphenanthrenes (78).

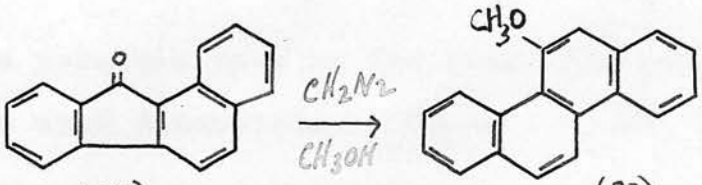


In support of these formulations, 1-carbomethoxy-fluorenone (79) gave a colourless solid, M.P. 110-122° in 25% yield when treated in methanol with diazomethane in ether. Recrystallisation of this solid from methanol gave a pure ester, M.P. 134-6°, which is probably 9-methoxy-1-carbomethoxyphenanthrene (80) or its 10- isomer. No other isomer was found but it may possibly be in the solid of M.P. 110-122°.



Hydrolysis of the pure ester gave its acid (81) which was then decarboxylated to 9-methoxyphenanthrene (77a).

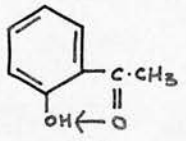
Cook and Schoental (J.C.S., 1945, 288) obtained 2-methoxychrysene (83) by the action of diazomethane in the presence of methanol, on 1:2-benzfluorenone (82).



(82) (83)

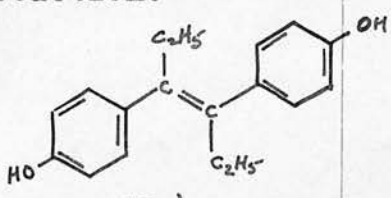
This action of diazomethane on substituted fluorenones is an example of its well-known property of ring enlargement and seems to be dependent on the presence of methanol, since excess diazomethane was used in the Arndt-Eistert reaction on β-1-fluorenone-propionic acid discussed later in this thesis (see p.127) and a high yield of the homologous fluorenone acid was obtained.

Schönberg and Mustafa found that o-hydroxyacetophenone (84) could not be methylated in ether and considered the failure to be due to the formation of a chelated ring system (J.C.S., 1946, 746). Methylation was achieved with methanol present.



(84)

They also found that the action of diazomethane in presence of n-propyl alcohol gave a n-propyl ether in the case of Stilboestrol (85), indicating the participation of the alcohol in the reaction.



(85)

Therefore, they assume that in alcoholic solution, diazomethane co-/

co-exists with a compound formed as in (A), which acts as a strong alkylating agent as in (B).

$$CH_2N_2 + R.OH \quad CH_3-N = N-OR \text{ (or } CH_2 = N.NH.OR) \quad (A)$$

$$CH_3-N = N-OR + Ar.OH \quad Ar.OR + CH_3-N = N-OH \quad (B)$$

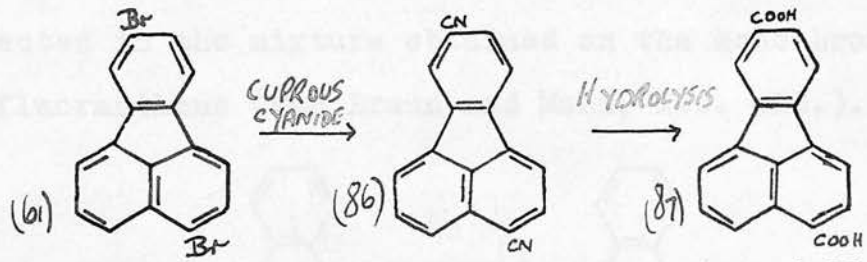
$$(\longrightarrow CH_3OH + N_2)$$

It is possible that in the ring enlargement of fluorenone with diazomethane, $CH_3-N = N-OCH_3$ is the agent. It would be interesting to study this ring enlargement of fluorenones in the presence of alcohols other than methanol.

THE PREPARATION OF FLUORANTHENE-4:11-DICARBOXYLIC ACID (pps.73ff)

Oxalyl chloride and fluoranthene gave a dicarboxylic acid which on esterification gives a dimethyl ester M.P. 181.5-183° (Campbell and Easton, loc. cit.). As it was suspected that this would be either the 4:11-diacid or the 4:12-diacid it was important to prepare the former acid for comparison.

This was done by the following route:-

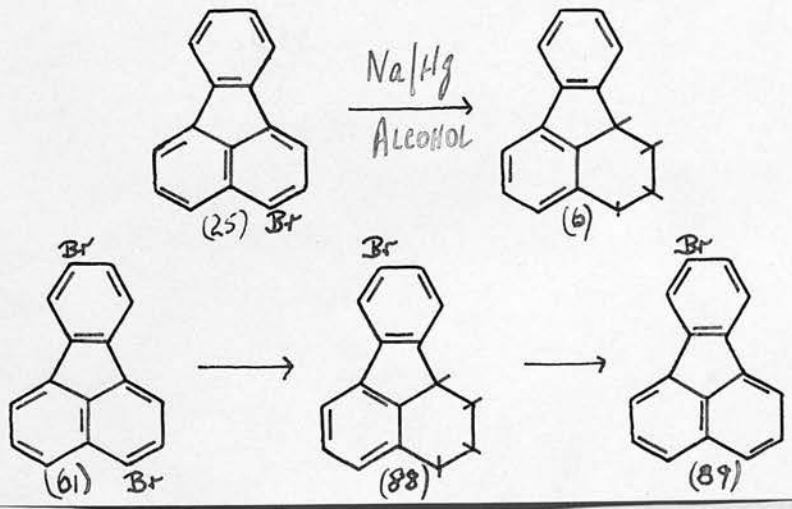


4:11 Dibromofluoranthene was converted into 4:11-dicyano-fluoranthene (86) either by fusion with cuprous cyanide or by heating with cuprous cyanide in pyridine, the yield/

yield in either case being 25%. Conversion of the dinitrile into the diacid (87) proceeded in good yield, either by alkaline hydrolysis in trimethylene glycol or by acid hydrolysis in acetic acid. Esterification of this diacid gave a dimethyl ester, M.P. 168-9°, which was different from the dimethyl ester obtained from the Friedel-Crafts reaction. The dissimilarity of these esters indicated different types of disubstitution, bromination of fluoranthene occurring in the 4:11-positions, while the Friedel-Crafts reaction causes 4:12-disubstitution as later proved by Campbell and co-workers (J.C.S., 1951, 1404).

THE REDUCTION OF 4:11-DIBROMOFLUORANTHENE (p.77)

Since 4-bromofluoranthene (25) is reduced with sodium amalgam in alcohol to 1:2:3:4-tetrahydrofluoranthene (6) it was hoped to reduce 4:11-dibromofluoranthene (61) to 11-bromo-1:2:3:4-tetrahydrofluoranthene (88) which could then be dehydrogenated to the unknown 11-bromofluoranthene (89) whose presence, however, has been detected in the mixture obtained on the mono-bromination of fluoranthene (von Braun and Manz, loc. cit.).

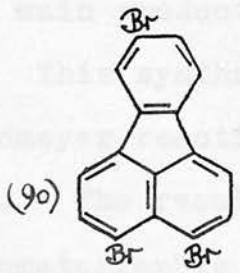


The only recognisable product was 1:2:3:4-tetrahydrofluoranthene indicating removal of both bromine groups. It is not known whether both bromine atoms are removed before reduction occurs or if ring A is reduced while it still contains the bromine group.

It would appear that one part of von Braun's evidence for 4- substitution is untenable since it is probable that a mono-bromofluoranthene substituted in ring C would be reduced to 1:2:3:4-tetrahydrofluoranthene.

THE ORIENTATION AND SYNTHESIS OF 4:11:12-TRIBROMOFLUORANTHENE (pps.78 ff).

All known fluoranthene derivatives have their substituents in the 4-(5-), 11-(12-), 4:11- or 4:12-positions and therefore it seemed likely that the tribromofluoranthene, M.P. 205°, obtained by Tobler (loc. cit.), was either 4:5:11-tribromofluoranthene (90) or 4:11:12-tribromofluoranthene (91).



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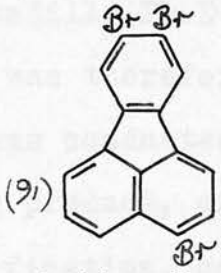
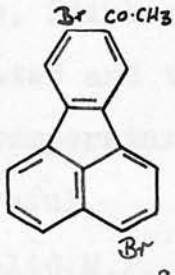


(91)

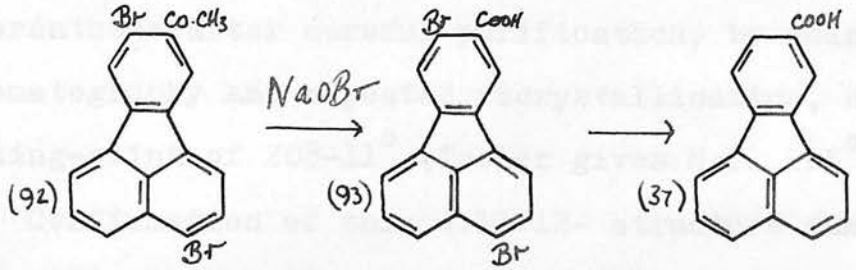


(92)

Support for the latter formulation comes from the preparation and orientation of 4:11-dibromo-12-acetylfluoranthene (92) obtained by the acetylation of 4:11-dibromofluoranthene (Campbell and Leadhill, unpublished results).

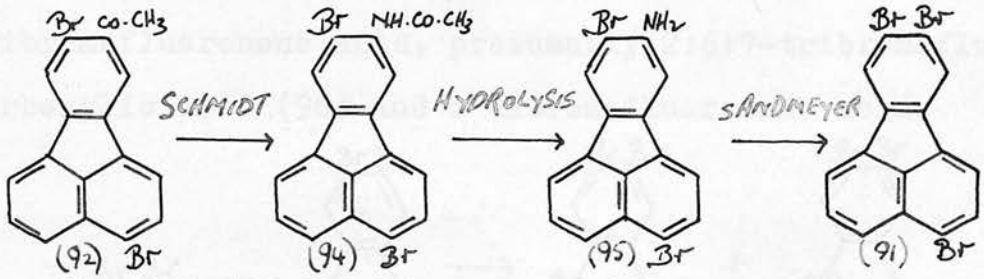
This/

This acetyl- compound was oxidised to the corresponding acid (93) which was debrominated to



fluoranthene-11-carboxylic acid (37).

These workers attempted a synthesis of 4:11:12-tribromofluoranthene from 4:11-dibromo-12-acetyl-fluoranthene by the following route:-



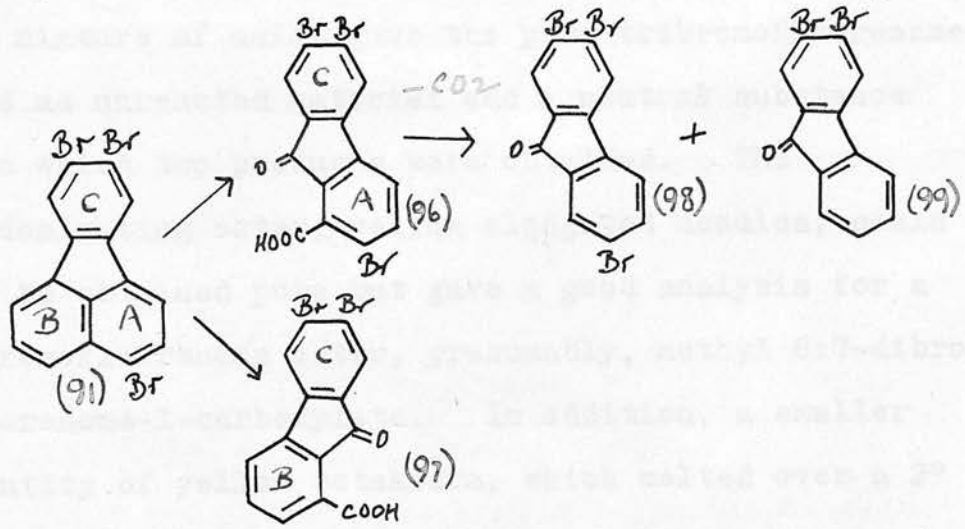
The Schmidt reaction gave 4:11-dibromo-12-acetamido-fluoranthene (94) which was hydrolysed to its amine (95) but the final stage, a Sandmeyer reaction at a temperature of 60°, gave a tetrabromofluoranthene as the main product (Leadill, Ph.D. Thesis, Edinburgh).

This synthesis was therefore repeated and the Sandmeyer reaction was conducted at a temperature of 35°. The resulting product, after careful chromatographic purification, gave a solid, M.P. 208-210.5°, analysis of which showed it to be a tribromo-fluoranthene.

This tribromofluoranthene was found to be identical (M.P. and mixed M.P.) with the tribromofluoranthene obtained/

obtained on the bromination of 4:11-dibromofluoranthene (Tobler et al., loc. cit.). This latter tribromofluoranthene after careful purification, by means of chromatography and repeated recrystallisation, had a melting-point of 208-11° (Tobler gives M.P. 205°).

Confirmation of this 4:11:12- structure came from the oxidative degradation with sodium dichromate in acetic acid. Oxidation for 20 hours at the boiling-point yielded a mixture of acids from which two yellow acids were isolated. Analysis showed these to be a tribromofluorenone acid, presumably 2:6:7-tribromofluorenone-1-carboxylic acid (96) and a dibromofluorenone acid,



presumably 6:7-dibromofluorenone-1-carboxylic acid (97).

The isolation of the tribromo-acid excludes the possibility of structure (90) although this acid's structure could not be rigorously proved because decarboxylation yielded a mixture which probably consists of 2:3:7-tribromofluorenone (98) and 2:3-dibromofluorenone (99). The latter ketone would be formed/

formed by simultaneous debromination and decarboxylation, a phenomenon which has been observed in the decarboxylation of 2:7-dibromofluorenone-1-carboxylic acid (Campbell, Easton and Rayment, Nature, 1950, 165, 76).

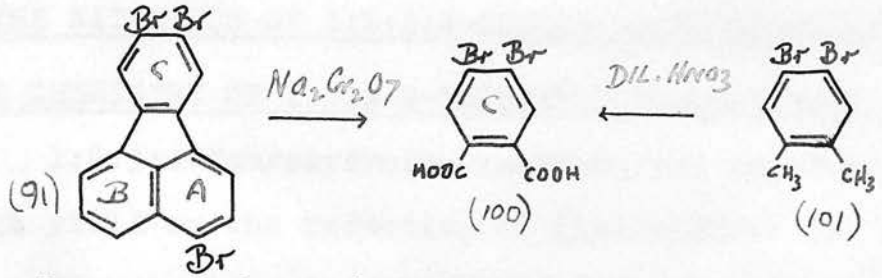
In one experiment, the mixture of acids was esterified for a short period and the resulting ester-mixture hydrolysed for a short period. The resulting acid was decarboxylated to a yellow crystalline solid which analysis showed to be a dibromofluorenone, probably 2:3-dibromofluorenone.

Another experiment involving the esterification of the mixture of acids gave the pure tribromofluorenone acid as unreacted material and a neutral substance from which two products were obtained. The predominating ester, yellow elongated needles, could not be obtained pure but gave a good analysis for a dibromofluorenone ester, presumably, methyl 6:7-dibromo-fluorenone-1-carboxylate. In addition, a smaller quantity of yellow octahedra, which melted over a 2° range, was obtained whose bromine analysis was some-what higher than that calculated for a dibromofluorenone ester. It is possible that these substances are different forms of methyl 6:7-dibromofluorenone-1-carboxylate.

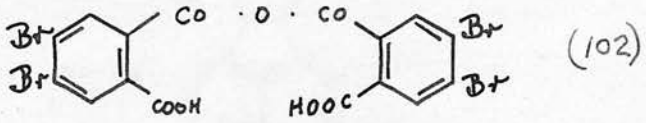
The final proof of structure was provided by oxidation of tribromofluoranthene to 4:5-dibromophthalic acid (100). In this case only ring C of the original

molecule/

molecule is unattacked.



For comparison, 4:5-dibromophthalic acid was prepared by the oxidation of 4:5-dibromo-o-xylene (101) with dilute nitric acid in a sealed tube at 170° for 7 hours. A longer period of oxidation gave a high-melting acid whose analysis corresponded closely with that of 4:5-dibromophthalic acid. This acid also appears to be formed on heating 4:5-dibromophthalic acid above its melting-point. Since it forms dimethyl 4:5-dibromophthalate on esterification with methanol and conc. sulphuric acid this acid may be a condensation product such as (102) although the analysis obtained



(102)

does not verify this conjecture.

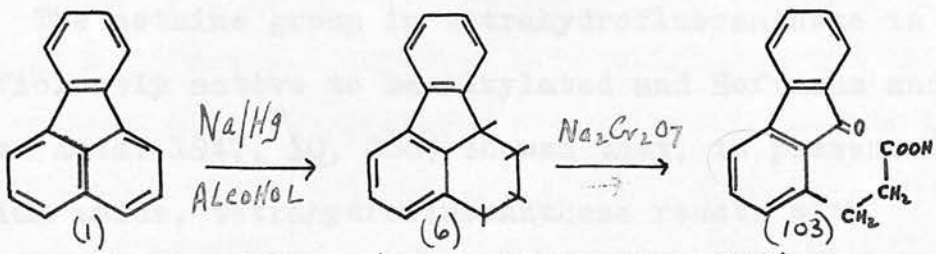
Since the melting-point of 4:5-dibromophthalic acid depends on the rate of heating, its dimethyl ester was prepared and was identical with the methyl ester of the acid obtained from the oxidation of tribromo-fluoranthene.

SECTION B

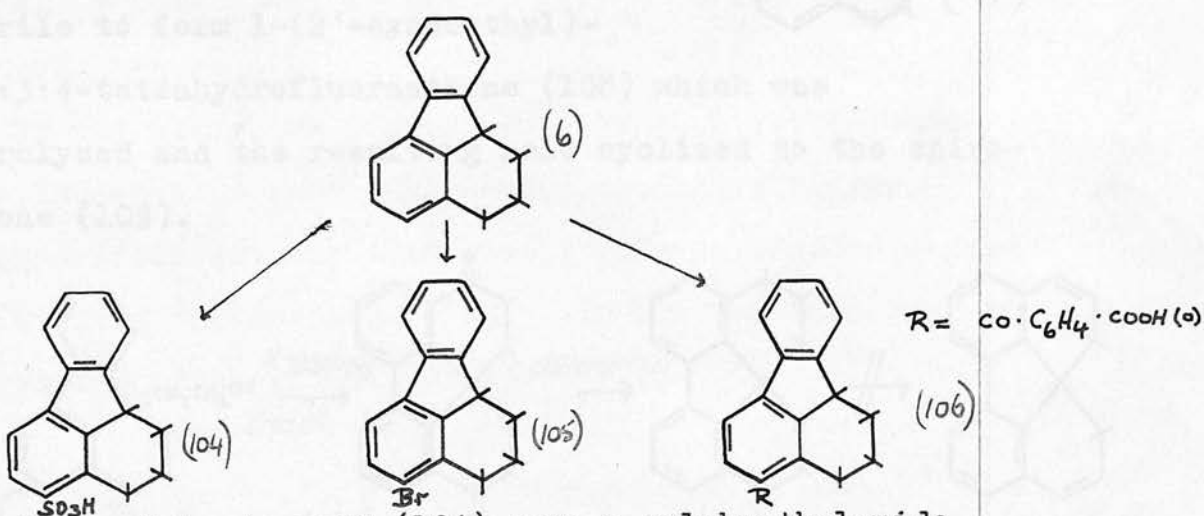
THE NITRATION OF 1:2:3:4-TETRAHYDROFLUORANTHENE

THE CHEMISTRY OF 1:2:3:4-TETRAHYDROFLUORANTHENE

1:2:3:4-Tetrahydrofluoranthene (6) is obtained in high yield on the reduction of fluoranthene (1) with 5% sodium amalgam in alcohol. Its structure is shown by its oxidation to β-1-fluorenonepropionic acid (103).



Von Braun and Manz (Ann., 1932, 496, 170) found that 1:2:3:4-tetrahydrofluoranthene is substituted in the 5- position on sulphonation, on bromination and on phthaloylation.

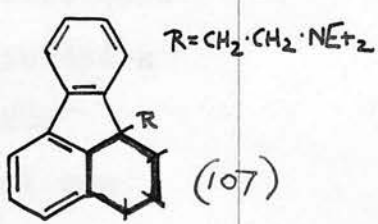


The sulphonic acid (104) gave a sulphoethylamide which was dehydrogenated with sulphur at 180-200° to fluoranthene-4-sulphoethylamide (29). The mono-bromo compound (105) was dehydrogenated with chloranil in xylene/

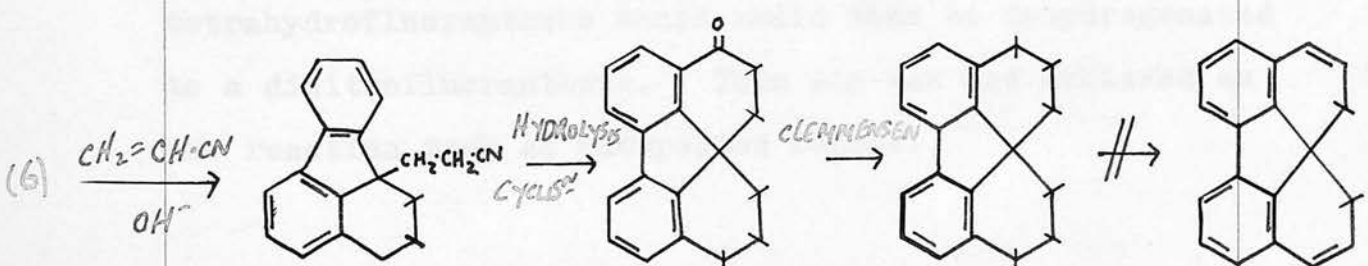
xylene (Tobler et al., loc. cit.) to 4-bromofluoranthene (25). The phthaloyl- compound (106) was converted to a tetrahydroamine by Beckmann arrangement of the oxime. This amine was identical with that (33) obtained on the reduction of 4-aminofluoranthene (31).

Tucker (unpublished results) has shown that iodination occurs in the 5- position.

The methine group in tetrahydrofluoranthene is sufficiently active to be alkylated and Hoffmann and Tagmann (Helv. Chim. Acta. 1947, 30, 288) showed that, in presence of sodium amide, tetrahydrofluoranthene reacts with tertiary aminoalkyl chlorides eg. diethylamino ethyl chloride to give compounds of the type (107). An an analogous fashion, tetrahydrofluoranthene reacted with acrylonitrile to form 1-(2'-cyanoethyl)-1:2:3:4-tetrahydrofluoranthene (108) which was hydrolysed and the resulting acid cyclised to the spiro-ketone (109).



(107)



(108) (109) (110) (111)

Clemmensen reduction of this ketone gave the parent hydrocarbon (110) which could not be dehydrogenated to/

to the spiro-cyclic system (111).(Hofmann and Tagmann, Helv. Chim. Acta, 1949, 32, 1470).

SECTION B OBJECT OF RESEARCH

To obtain further information about the substitution of fluoranthene it was decided to prepare a dinitrofluoranthene but early experiments proved unpromising although a very small quantity of dinitrofluoranthene was obtained when fluoranthene was nitrated according to the method of von Braun (Ann., 1931, 488, 111) and the product carefully chromatographed. The further nitration of 4-nitrofluoranthene (32) in acetic acid with a large excess of fuming nitric acid yielded a solid which melted over a wide range up to 280° indicating some reaction but no pure material was obtained.(see p. 97).

It was therefore decided to nitrate 1:2:3:4-tetrahydrofluoranthene in the hope of obtaining a dinitrotetrahydrofluoranthene which could then be dehydrogenated to a dinitrofluoranthene. This aim was not achieved as the reaction took an unexpected course.

SECTION B DISCUSSION OF RESULTS

NITRATION OF 1:2:3:4-TETRAHYDROFLUORANTHENE (pps.101ff)

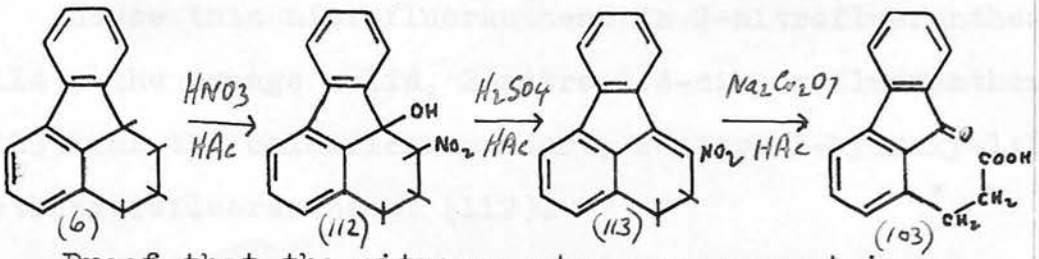
When 1:2:3:4-tetrahydrofluoranthene in acetic acid at 80° was treated with a 1½ molar quantity of fuming nitric/

nitric acid there were formed two products, a colourless solid, whose empirical formula was $C_{16}H_{13}NO_3$ and a deep orange solid, whose empirical formula was $C_{16}H_{11}NO_2$. As can be seen there is a difference of 1 molecule of water between the two formulae and it was soon found that the colourless solid could be transformed into the orange solid by boiling the former in acetic acid containing a trace of conc. sulphuric acid.

Hence it was likely that the colourless solid was an alcohol and the orange solid its dehydration product. Oxidation of the latter with chromic anhydride caused complete destruction of the molecule, but the milder action of sodium dichromate in acetic acid for three hours brought about the formation of an acid which proved to be β-1-fluorenonepropionic acid (103) as well as a neutral, orange compound of M.P. C. 150° which was later shown to be 2-nitrofluoranthene (114).

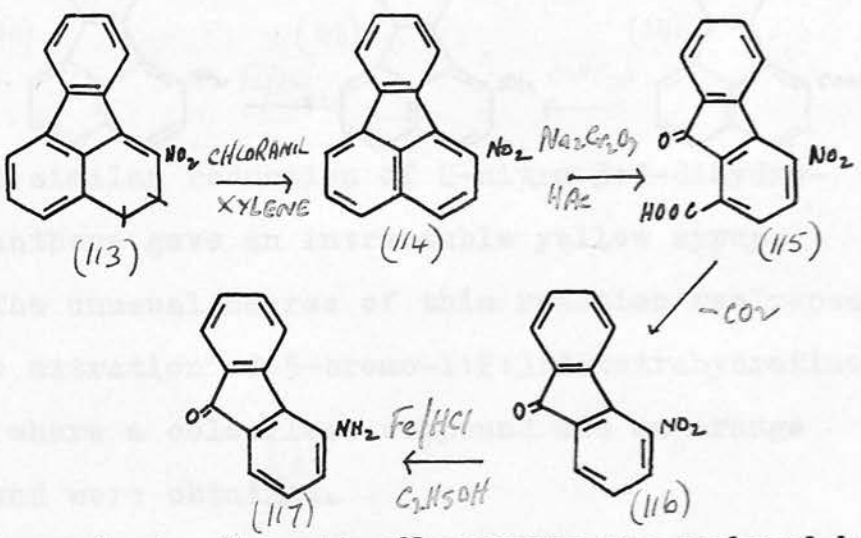
The complete removal of the nitrogen- containing portion on oxidation suggested that it was located in the reduced ring. In addition, since the orange compound is a dehydration product it probably contains a double bond which must be located as shown (formula 113) with the nitro-group in the 2- position to explain the presence of the propionic acid side chain in the acidic oxidation product. The colourless solid must therefore/

therefore have formula (112).



Proof that the nitrogen atom was present in a nitro-group was shown by the dehydrogenation of the orange solid with chloranil in xylene to a nitrofluoranthene identical with the neutral product obtained in its oxidation.

The structure of this nitrofluoranthene was shown by oxidation to a nitrofluorenone acid (115) (4-nitrofluorenone-1-carboxylic acid) and the decarboxylation of the latter to 4-nitrofluorenone (116) which was identical (M.P. and mixed M.P.) with an authentic sample provided by Professor J.W. Cook F.R.S.

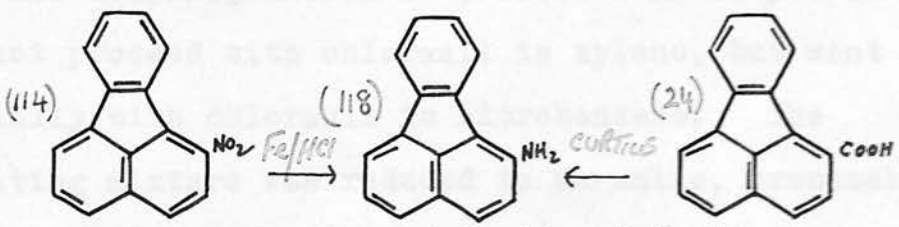


As a check, the nitrofluorenone was reduced by means of iron powder in ethanolic hydrochloric acid to an aminofluorenone whose melting-point and analysis corresponded/

corresponded to that of 4-aminofluorenone (117).

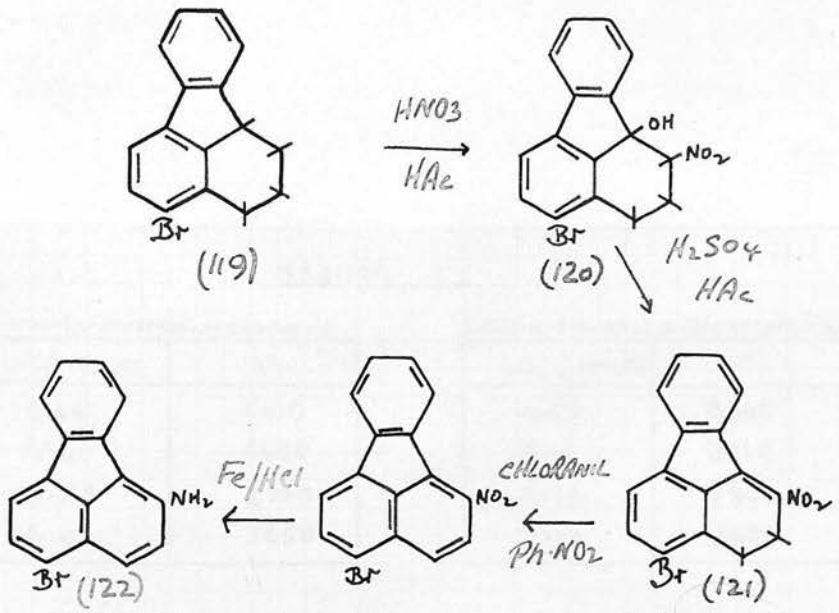
Hence this nitrofluoranthene is 2-nitrofluoranthene (114), the orange solid, 2-nitro-3:4-dihydrofluoranthene (113) and the colourless product, 2-nitro-1-hydroxy-1:2:3:4-tetrahydrofluoranthene. (112).

2-Nitrofluoranthene was reduced with iron powder in ethanolic hydrochloric acid to 2-aminofluoranthene (118) whose melting-point and that of its 2:4:7-trinitrofluorenone complex agreed with those given by Bergmann and Orchin (J.A.C.S., 1949, 71, 1917) who prepared the amine by a Curtius degradation of fluoranthene-2-carboxylic acid (24) (see p. 8). An attempt to prepare the latter acid from the amine via the corresponding nitrile failed at the Sandmeyer reaction stage, the product having a very low percentage of nitrogen.



A similar reduction of 2-nitro-3:4-dihydrofluoranthene gave an intractable yellow syrup.

The unusual course of this reaction was repeated in the nitration of 5-bromo-1:2:3:4-tetrahydrofluoranthene (119) where a colourless compound and an orange compound were obtained.



As above the colourless product, 5-bromo-2-nitro-1-hydroxy-1:2:3:4-tetrahydrofluoranthene (120) was transformed to the orange solid, 5-bromo-2-nitro-3:4-dihydrofluoranthene (121) with sulphuric acid in acetic acid.

The dehydrogenation of 5-bromo-2-nitro-3:4-dihydrofluoranthene did not proceed with chloranil in xylene, but went partially with chloranil in nitrobenzene. The resulting mixture was reduced to an amine, presumably 2-amino-5-bromofluoranthene (122), but unfortunately there was not enough for analysis.

Nitration of 1:2:3:4-tetrahydrofluoranthene with a mixture of sulphuric and nitric acids at low temperatures gave recovered starting material in moderate yield together with tarry oxidation products.

1a:1:2:3-Tetrahydroacenaphthene (123), a hydrocarbon related to tetrahydrofluoranthene, was recovered in moderate yield at 40°, but at 80° was almost completely destroyed/

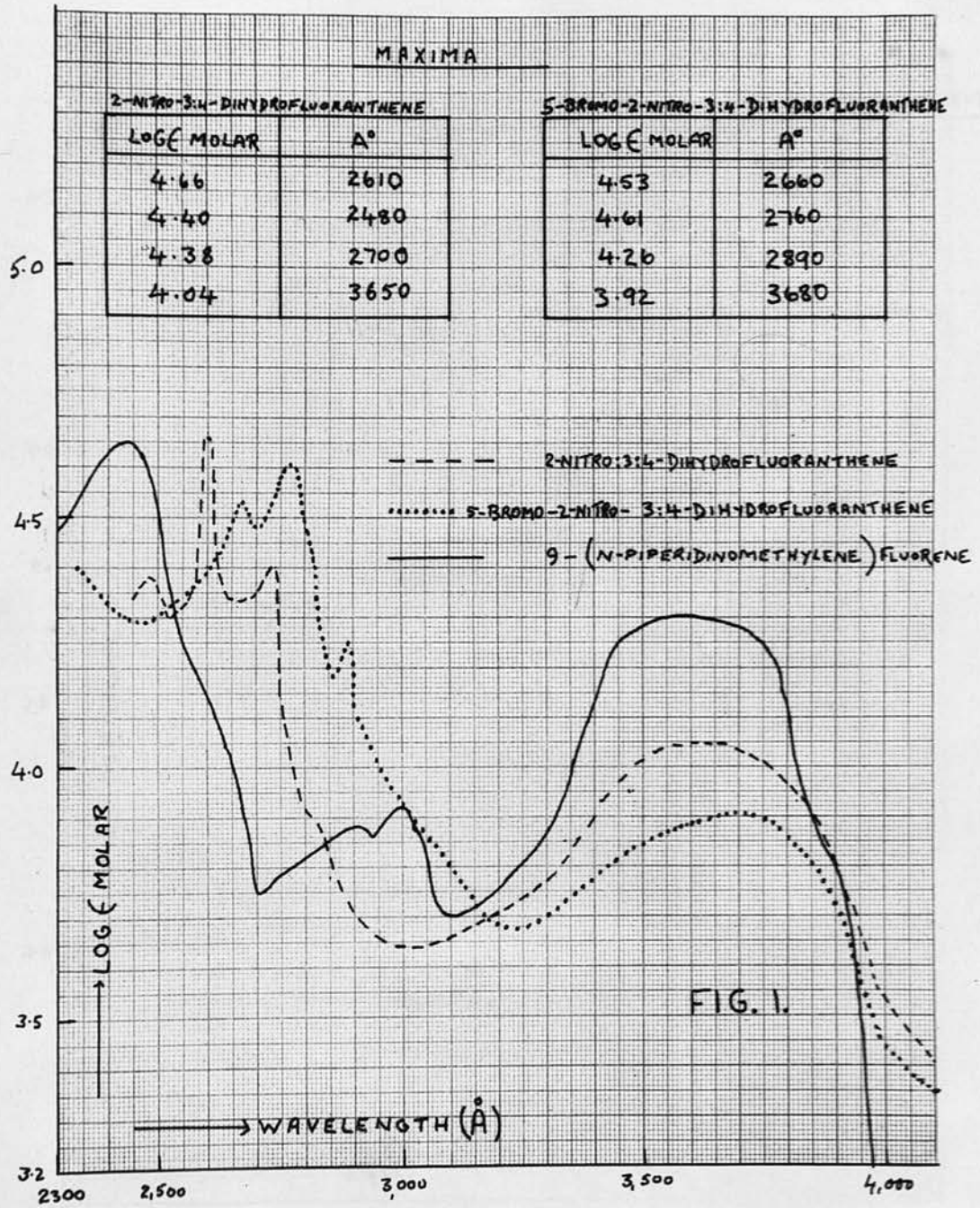
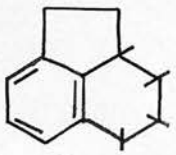

MAXIMA
2-NITRO-3:4-DIHYDROFLUORANTHENE
LOG ε MOLAR | A°
4·66 | 2610
4·40 | 2480
4·38 | 2700
4·04 | 3650
5-BROMO-2-NITRO-3:4-DIHYDROFLUORANTHENE
LOG ε MOLAR | A°
4·53 | 2660
4·61 | 2760
4·26 | 2890
3·92 | 3680
2-NITRO:3:4-DIHYDROFLUORANTHENE
5-BROMO-2-NITRO- 3:4-DIHYDROFLUORANTHENE
9-(N-PIPERIDINOMETHYLENE)FLUORENE
5·0
4·5
4·0
3·5
3·2
LOG ε MOLAR
WAVELENGTH (Å)
2300
2,500
3,000
3,500
4,000

FIG. 1.

destroyed, when nitration was attempted in acetic acid as above.



(123)

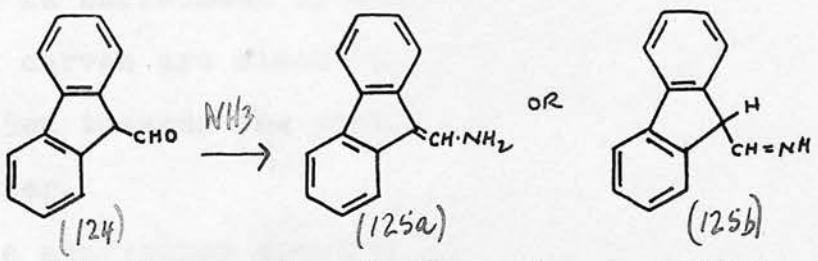
ABSORPTION SPECTRA OF THE HIGHLY-COLOURED NITRO-PRODUCTS (see opposite)

Additional evidence for the structure of these highly-coloured nitro- compounds comes from the similarity of their ultra-violet absorption curves with those of compounds containing an external double bond in the 9- position of fluorene.

Miller and Wagner (J. Org. Chem., 1951, 16, 279) found that when a double bond is thus situated, the resulting augmented conjugation leads to an absorption unlike that of fluorene.

It also appears that simple substituents in the 9- position of fluorene and the presence of an α,β double bond do not greatly alter the absorption of the fluorene system.

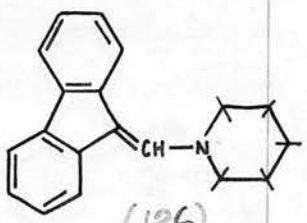
The action of ammonia on 9-formylfluorene (124) gives a yellow compound which can be either (125a) or



(124) (125a) (125b)

(125b). The former formulation, 9-aminomethylene-fluorene, is supported by the close similarity of the compound's/

compound's ultra-violet absorption curve with that of 9-(N-piperidinomethylene) fluorene (126).



(126)

The absorption curve of 2-nitro-3:4-dihydrofluoranthene (see Fig.I) has features which correspond quite well with those of 9-(N-piperidinomethylene)fluorene (Fig.I). They each possess similar and striking narrow band maxima which have identical values for log E molar but in the case of the nitro- compound, this band is shifted 20mu towards the visible portion of the spectrum. A second and broader band is found in both curves at 360mu.

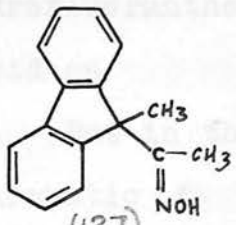
It is not to be expected that the curves will be identical since the presence of a nitro- group attached to a doubly-bound carbon atom will affect the absorption spectrum much more than does the saturated piperidine ring. The presence of the nitro- group is reflected in the shift of the marked maximum 20mu towards higher wavelength.

In both the absorption curves of the nitro-dihydro-fluoranthene and its bromo-analogue, the principal maximum is surrounded by subsidiary maxima and in fact the two curves are almost identical, but for a shift of about 15mu towards the visible spectrum in the case of the latter.

The absorption spectrum of 1:2:3:4-tetrahydro-fluoranthene (see Fig.II) was also determined and is quite different from that of its nitration product.

The/

The curve bears a strong resemblance to that of 9-(9-methylfluorenyl) methyl ketone oxime (127), (Miller and Wagner, loc. cit.), their maxima at 266mu and 303mu being practically identical. The curve of fluorene (128), which is included for comparison, is similar to both curves and has a maximum at 303mu. It therefore appears that the presence of the alicyclic ring causes no great alteration in the spectrum of the fluorene molecule.



(127)


(128)

MECHANISM OF THE REACTION

Nitration of aromatic hydrocarbons is usually carried out with a mixture of nitric and sulphuric acids and it is a well-established fact that such nitration involves the action of the nitronium ion (NO_2^+). Frequently it is found convenient to carry out nitrations in acetic acid without sulphuric acid, but in such cases the expected reactive positions are attacked eg. fluoranthene, which is attacked by sulphuric acid in the 4- position, is nitrated in acetic acid in the 4- position. Therefore, it is probable that in these nitrations the nitrating agent is again the nitronium ion (NO_2^+).

In 1:2:3:4-tetrahydrofluoranthene, the 5- position is/

is susceptible to attack by electrophilic agents as is shown by the formation of 5-bromotetrahydrofluoranthene and tetrahydrofluoranthene-5-sulphonic acid on bromination and sulphonation (see p. 33). But in the nitration reaction described above, the aromatic nucleus is left unattacked and substitution occurs in the reduced ring. It would appear, therefore, that the initial reaction at least, is not ionic and does not involve the nitronium ion (NO_2^+).

The other salient features of this reaction are:-

1). Nitration occurs only in acetic acid. A mixture of nitric and sulphuric acids at low temperatures either causes no reaction or destroys the molecule oxidatively.

2). Nitration occurs only if a reactive methine group is present. Under similar conditions 1a:1:2:3-tetrahydroacenaphthene is destroyed.

3). Reaction occurs at 85°, but at 50°, the only other temperature tried, no reaction took place.

4). The strength of the nitric acid was 88% (d=1.48).

The Russian chemist, Titov, claims that nitric acid of 50-70% strength and greater cannot be successfully freed from nitrogen oxides, hence in the present instance, the proportion at 85° will be quite high.

Titov contends that pure nitric acid(HNO_3) is ineffective in the nitration of cyclohexane and claims that the effective nitrating agent is the monomeric nitrogen/

nitrogen tetroxide (NO_2). In a non-polar or weakly polar medium the nitrating agent is NO_2, while an increase in the polarity of the medium favours the formation of nitrosyl nitrate ($NO.O.NO_2$) and the nitrosyl cation (NO^+) which then become the effective nitrating agents.

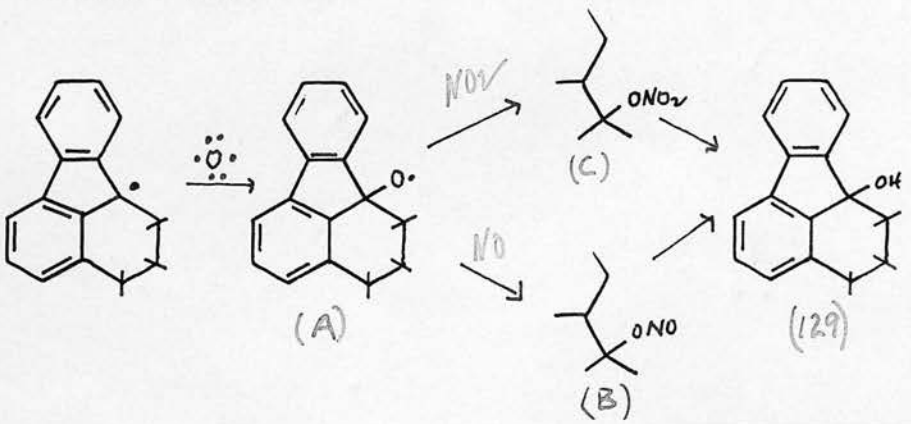
Titov believes that the fundamental difference between aromatic nitration and the nitration of saturated hydrocarbons is that the former involves complex ions or complexes of a crypto-ionic character, whereas the latter involves free radicals (Chem. Abst., 1947, 6526; 1948, 545; 1948, 7262; 1949, 4217; 1949, 6585; 1950, 1044).

Under the influence of the resonating benzene systems of the fluorene part of the molecule, the tertiary methine bond will be weakened and will be susceptible to attack by the electrophilic, monomeric nitrogen tetroxide with the formation of tetrahydrofluoranthyl radicals thus:-

$$RH + NO_2 \longrightarrow R^{\cdot} + HNO_2$$

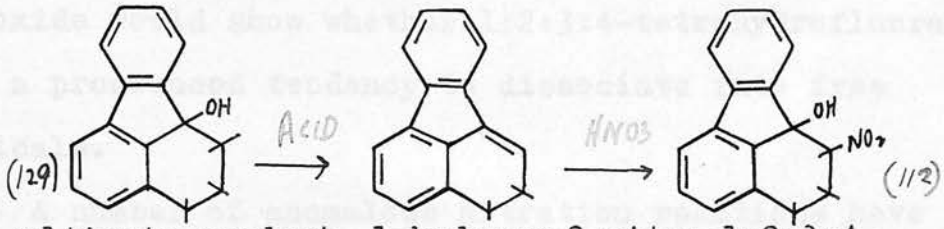
Assuming therefore the formation of tetrahydrofluoranthyl radicals, a possible mechanism is as follows:-

1) The radical is oxidised to the oxygen containing radical (A).



2) This oxygen-containing radical which has lone electron, is then attacked by the electrophilic nitric oxide and nitrogen-tetroxide to give the unstable, intermediate compounds (B) and (C) which are hydrolysed in the acid medium to 1-hydroxy-1:2:3:4-tetrahydrofluoranthene (129).

3) This hydroxytetrahydrofluoranthene may or may not be stable, but assuming instability, the dihydrofluoranthene, which results on dehydration, immediately adds on nitric acid to give the



(129) (112)

ultimate product, 1-hydroxy-2-nitro-1:2:3:4-tetrahydrofluoranthene, which itself is not very stable in acid media. The instability of 9-hydroxy-9-cyanoethylfluorene (130) has been noted, 9-cyanoethylidenefluorene (131) being formed. (Campbell and Wang, J.C.S., 1949, 1239).

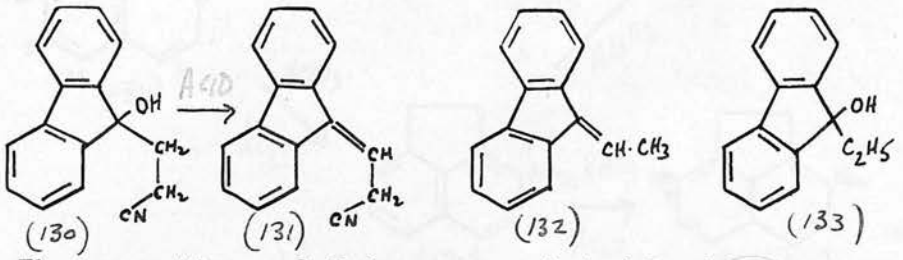
If the 1-hydroxytetrahydrofluoranthene is stable the nitration can be considered to proceed by a free radical mechanism as follows:-

(a) $$\text{--C(OH)--C(H)--} + NO_2 \longrightarrow \text{--C(OH)--C}\cdot + HNO_2$$

(b) $$\text{--C(OH)--C}\cdot + NO_2 \longrightarrow \text{--C(OH)(}NO_2\text{)--C--}$$

It/

It would be interesting to study the nitration in acetic acid of compounds with an external double bond in the 9- position eg. 9-ethylidenefluorene (132) and 9- substituted fluorenols eg. 9-hydroxy-9-ethylfluorene (133).



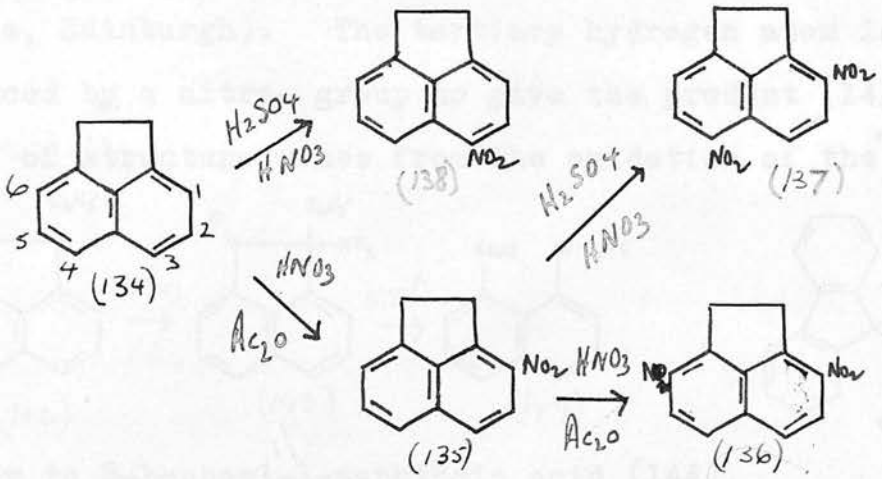
(130) (131) (132) (133)

The reaction of N-bromosuccinimide in presence of peroxide would show whether 1:2:3:4-tetrahydrofluoranthene has a pronounced tendency to dissociate into free radicals.

A number of anomalous nitration reactions have been reported which are of interest in the present discussion. These are the nitration of acenaphthene, N-benzoyltetrahydrocarbazole and 7-phenyl-acenaphthenone.

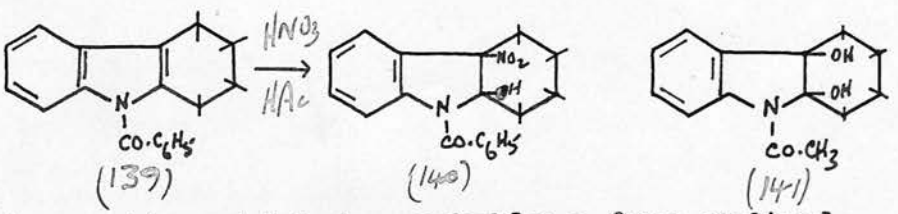
When acenaphthene (134) is nitrated with nitric acid in acetic anhydride at -5°, substitution occurs in the 1- position whereas substitution occurs in the normally reactive 3- position (138) when nitric and sulphuric acids are used. Further nitration of 1-nitroacenaphthene (135) with nitric acid in acetic anhydride gave 1:6-dinitroacenaphthene (136) whereas the action of nitric and sulphuric acids led to 1:4-dinitroacenaphthene (137) (Morgan and Harrison, Chem. and/

and Ind., 1930, 49, 413T). Apparently nitric acid in



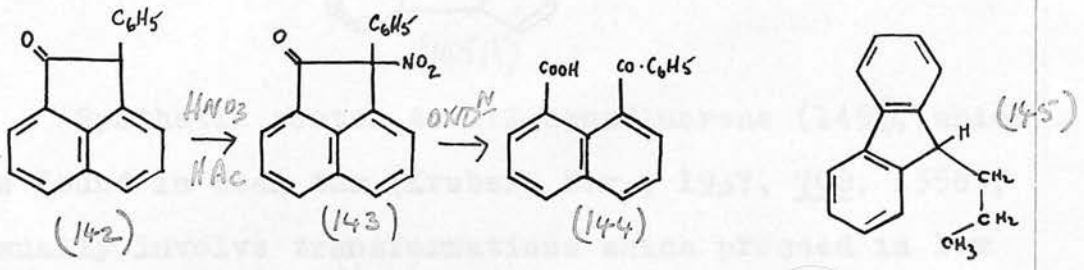
acetic anhydride involves a reaction where the nitrating agent is not NO_2^+ but is possibly acetyl nitrate. The 1- position was also attacked with benzoyl nitrate in light petroleum at -10°.

When N-benzoyltetrahydrocarbazole (139) is nitrated with nitric acid in acetic acid there is formed the product (140) by the addition of nitric acid to bare ethylenic linkage (Perkin and Plant, J.C.S., 1923, 676). A similar phenomenon was observed in the nitration in acetic acid of N-acetyltetrahydrocarbazole where the product, however, was (141), the nitro-group having been replaced by a hydroxyl group.



A reaction which is probably a free radical reaction/

reaction has been observed when 7-phenyl-acenaphthenone (142) is nitrated in acetic acid (K. Henderson, Ph.D. Thesis, Edinburgh). The tertiary hydrogen atom is replaced by a nitro- group to give the product (143). Proof of structure comes from the oxidation of the

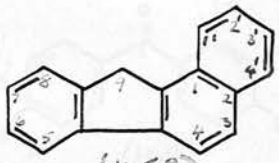


latter to 8-benzoyl-1-naphthoic acid (144).

In conclusion it must be admitted that the above mechanism is largely speculative and a rigid physico-chemical investigation will be necessary before the nature of this unusual reaction is understood. It would be of interest to study the nitration in acetic acid of 9-n-propylfluorene (145) which is very closely related to 1:2:3:4-tetrahydrofluoranthene.

SECTION C SYNTHESIS OF 1:2-BENZFLUORENE

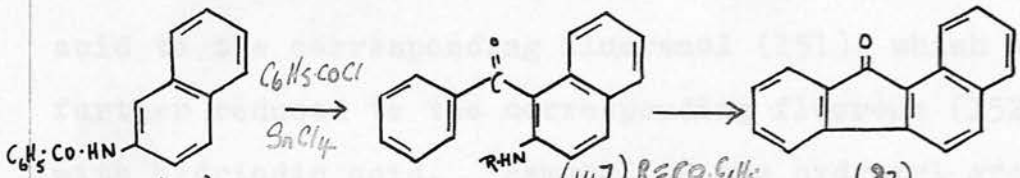
CHEMISTRY OF 1:2-BENZFLUORENE



(145A)

Synthetic routes to 1:2-benzfluorene (145A), which is found in coal tar (Kruber, Ber., 1937, 70B, 1556), usually involve transformations which proceed in low yield although the recent synthesis of Orchin and Reggel (J.A.C.S., 1951, 73, 436) affords the hydrocarbon in fair yield on the large scale.

The starting-point in their synthesis is the abundant β-naphthylamine whose N-benzoyl derivative (146) is treated with benzoyl chloride in presence of stannic chloride to give the ketone (147). Hydrolysis to the amine (148) followed by diazotisation and ring-closure afforded 1:2-benzfluorenone (82).

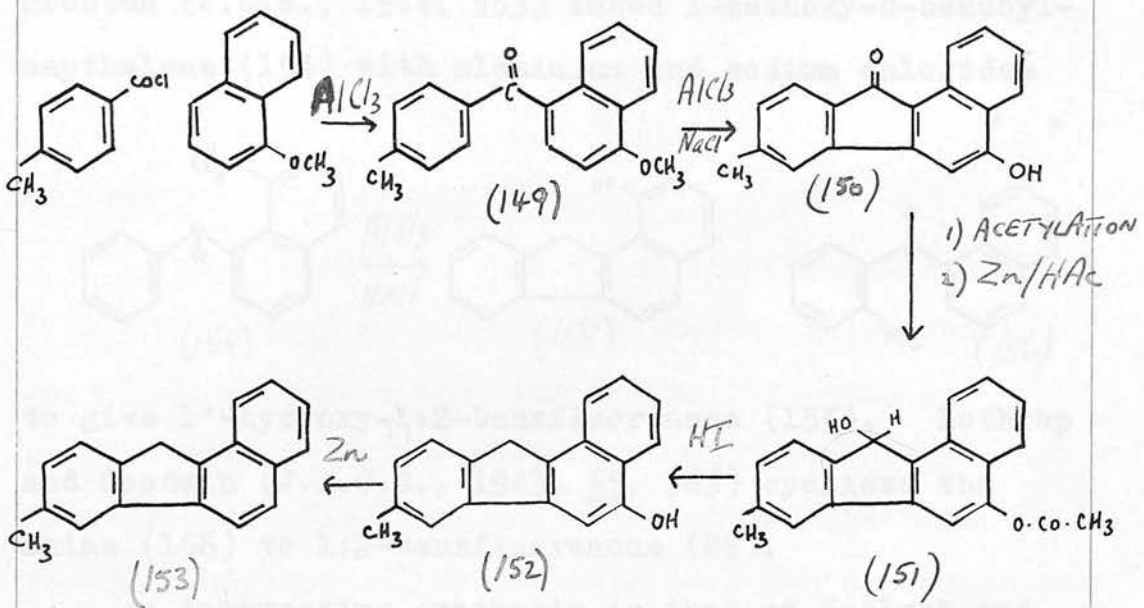


(146) (147) R=CO.C_6H_5 (148) R=H (82)

The overall yield of 1:2-benzfluorenone (82) from β-naphthylamine is 20%. Reduction of the ketone (82) gives 1:2-benzfluorene (145A).

Alkyl-1:2-benzfluorenes, e.g. 6-methyl-1:2-benzfluorene have been synthesised by Gross and Lankelma (J.A.C.S./

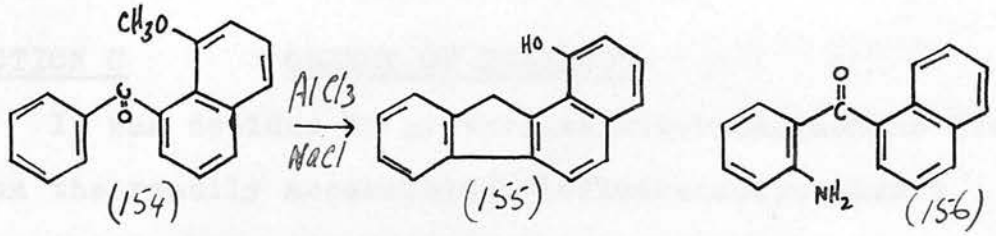
(J.A.C.S., 1951, 73, 3439). Their scheme is outlined below:-



A Friedel-Crafts reaction between *p*-toluoyl chloride and *α*-methoxynaphthalene furnished the ketone (149) in high yield. When fused with a mixture of sodium and aluminium chlorides, this ketone gave 6-methyl-3-hydroxy-1:2-benzfluorene (150) in low yield. This was acetylated and reduced with zinc dust in acetic acid to the corresponding fluorenol (151), which was further reduced to the corresponding fluorene (152) with hydriodic acid. Removal of the hydroxyl group was accomplished by a modified zinc dust treatment to give 6-methyl-1:2-benzfluorene (153) in low yield. Similarly, 7-methyl- and 8-methyl-1:2-benzfluorenes were obtained.

Other/

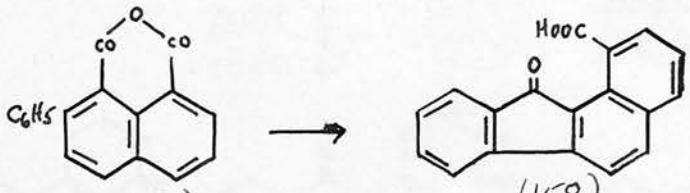
Other syntheses embodying principles similar to those outlined above have been reported. Cook and Preston (J.C.S., 1944, 553) fused 1-methoxy-8-benzoyl-napthalene (154) with aluminium and sodium chlorides



(154) (155) (156)

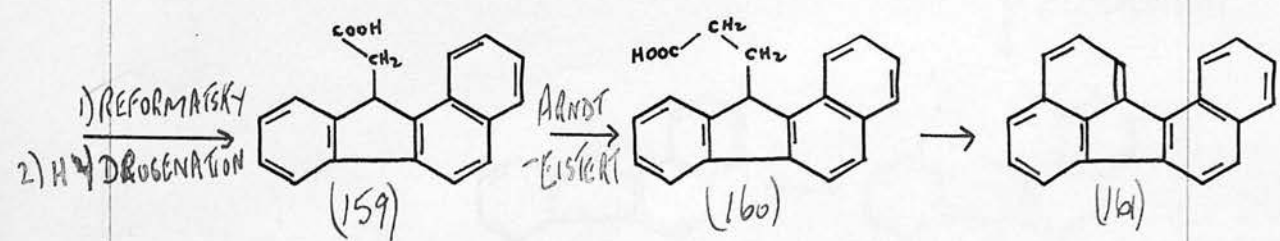
to give 1'-hydroxy-1:2-benzfluorenone (155). Lothrop and Goodwin (J.A.C.S., 1943, 65, 363) cyclised the amine (156) to 1:2-benzfluorenone (82).

An interesting synthesis is that of Koelsch and Rosenwald (J.A.C.S., 1937, 55, 2166) who cyclised 2-phenylnaphthalic anhydride (157) to the benzfluorenone acid (158) which was decarboxylated to 1:2-benzfluorenone (82).



(157) (158)

1:2-Benzfluorenone (82) has been used in the synthesis of 10:11-benzfluoranthene (Orchin and Reggel, J.A.C.S., 1951, 73, 436). A Reformatsky reaction on this ketone led to an acid which was hydrogenated to the acetic acid (159). This acid was converted to the substituted propionic acid (160) by means of an Arndt-

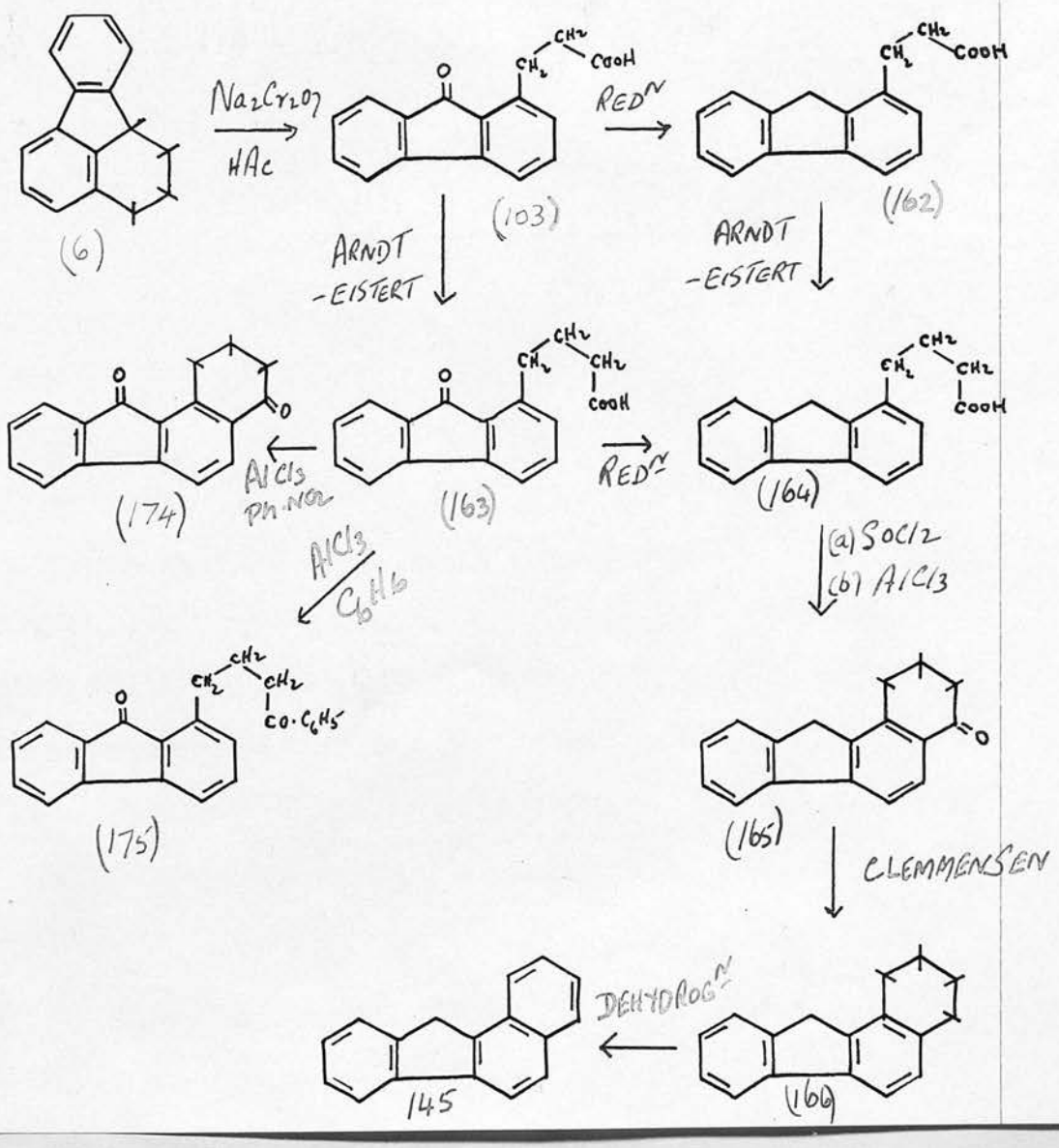


(159) (160) (161)

Eistert reaction. This acid was transformed into 10:11-benzfluoranthene (161) after the usual processes of cyclisation, reduction and dehydrogenation.

SECTION C OBJECT OF RESEARCH

It was decided to synthesise 1:2-benzfluorene (145) from the readily accessible β-1-fluorenonepropionic acid (103) which is obtained by the oxidation of 1:2:3:4-tetrahydrofluoranthene. The synthesis, which is outlined below, proved successful and shows the relationship between 1:2-benzfluorene and fluoranthene.

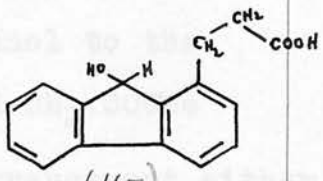


SECTION C DISCUSSION OF RESULTS (see pps. 122 ff).

The oxidation of 1:2:3:4-tetrahydrofluoranthene to β-1-fluorenonepropionic acid (103) was accomplished in 60% yield on the 20g. scale, when the conditions detailed by Kruber (Ber., 1931, 64, 84) were used.

The reduction of this acid was studied under a variety of conditions, the best method involving the two-stage process described by Bachmann and Sheehan (J.A.C.S., 1940, 62, 2687) for the reduction of fluorenone acids. The first stage is the preparation of the corresponding 9-fluorenol acid with zinc dust in caustic soda, while in the second stage this intermediate acid is reduced to the corresponding fluorene acid with a mixture of red phosphorus and iodine in acetic acid.

In the present investigation, the reduction of β-1-fluorenonepropionic acid (103) occurred in 83% yield. The product, β-9-fluorenol-1-propionic acid (167), was then reduced practically quantitatively to β-1-fluorenepropionic acid (162).

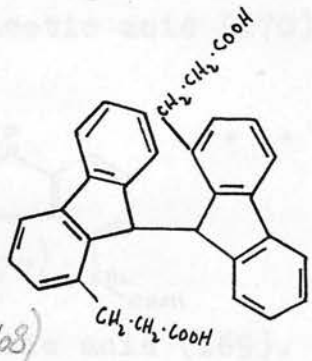


(167)

Clemmensen reduction with a solvent mixture of acetic acid, toluene and hydrochloric acid gave a mixture from which the requisite acid (162) was isolated only in 37% yield.

Wolff-Kischner reduction (cf. Orchin and Bergmann, J.A.C.S., 1949, 71, 1112) also gave the requisite acid (162)/

(162) which was unfortunately contaminated with a higher-melting acid, probably meso-bis-9:9'-(β-1-fluorenepropionic acid) (168), which could not be easily removed. Crystallisation from acetic acid, in which the dimeric acid is not very soluble, afforded the pure dimeric acid while the filtrate gave slightly impure β-1-fluorenepropionic acid in about 55% yield.



(168)

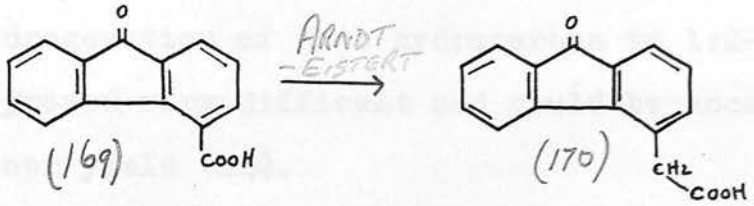
The next stage involved the lengthening of the propionic acid side chain so as to obtain γ-1-fluorene-butyric acid and this was accomplished in poor yield (39%) by means of the Arndt-Eistert reaction. The preparation of intermediate diazoketone seemed to occur smoothly and it is probable that the rearrangement stage was the cause of the poor yield. This was carried out with silver oxide in anhydrous methanol to the

$$R.COOH \longrightarrow R.COCl \longrightarrow R.CO.CHN_2 \longrightarrow R.CH_2.COOMe$$

homologous methyl ester but perhaps rearrangement either to the acid with silver oxide in water or to the amide with silver oxide in ammonia would proceed in better yield.

Fortunately β-1-fluorenonepropionic acid could be converted into its homologous acid, γ-1-fluorenone-butyric acid (163) in high yield (86%) after rearrangement of the crystalline diazoketone with silver/

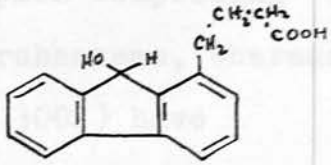
silver oxide in anhydrous methanol. This result is in agreement with the work of Bachmann and Sheehan (loc. cit.) who obtained 4-fluorenoneacetic acid (170)



(169) (170)

in high yield from 4-fluorenonecarboxylic acid (169). There is apparently no ring enlargement when diazomethane reacts with acid chlorides of fluorenone acids. (see p.23).

γ-1-Fluorenonebutyric acid was then reduced by the 2-stage synthesis described above and γ-1-fluorenonebutyric acid (164) could be obtained in 72% overall yield without purification of the intermediate γ-9-fluorenol-1-butyric acid (171). This latter acid was isolated in one experiment and characterised.



(171)

The cyclisation of γ-1-fluorenebutyric acid was accomplished in 76% yield by the cyclisation of its acid chloride in benzene by means of aluminium chloride in an inverse Friedel-Crafts reaction (cf. Johnson and Glenn, J.A.C.S., 1949, 71, 1092). The resultant ketone, 4'-keto-1':2':3':4'-tetrahydro-1:2-benzfluorene (165), which was also obtained with aluminium chloride in nitrobenzene, formed a 2:4-dinitrophenylhydrazone.

The Clemmensen reduction of 4'-keto-1':2':3':4'-tetrahydro-1:2benzfluorene to the tetrahydro-hydrocarbon proceeded/

proceeded in only 51% yield due to the formation of a high-melting impurity. This hydrocarbon, 1':2':3':4'-tetrahydro-1:2-benzfluorene (166) forms a complex with 2:4:7-trinitrofluorenone.

Dehydrogenation of this hydrocarbon to 1:2-benzfluorene proved very difficult and could be accomplished only in poor yield (12%).

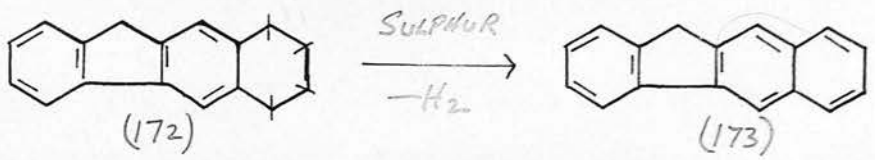
By boiling for 24 hours in α-methylnaphthalene in an atmosphere of nitrogen with 20% palladium-charcoal catalyst, a mixture was obtained which gave a s-nitrobenzene complex which was identical with an authentic sample of the s-nitrobenzene derivative of 1:2-benzfluorene (145°) (M.P. and mixed M.P.). It was found, however, that the percentage of nitrogen was in agreement with that required for a complex comprising 1 part hydrocarbon and 1 part s-trinitrobenzene, whereas Orchin and Reggel (J.A.C.S., 1950, 72, 3002) have prepared a complex of identical melting-point which analysis showed to consist of 1 part hydrocarbon and 2 parts s-trinitrobenzene.

Decomposition of the complex by passing its solution in benzene through a column of alumina gave colourless plates which, after recrystallisation, had M.P. 181-7° (Lit. M.P. 189-190°), indicating that partial decomposition of the hydrocarbon had occurred on the column (the complex had been recrystallised till it melted over a 2° range).

Dehydrogenation/

Dehydrogenation occurred to some extent with 20% palladium-charcoal catalyst in *p*-cymene and also with chloranil in xylene, the above s-trinitrobenzene complex being obtained in each case.

It is interesting to note that the dehydrogenation of tetrahydro-2:3-benzfluorene (172) with sulphur produced 2:3-benzfluorene (173) in low yield (12%) (Koelsch, J.A.C.S., 1933, 53, 3885) indicating that



(172) (173)

hydrogenated benzfluorenes are resistant to dehydrogenation.

γ-1-Fluorenonebutyric acid (163) was cyclised in 54% yield, on the basis of acid consumed, to the cyclic diketone, 4'-keto-1':2':3':4'-tetrahydro-1:2-benzfluorenone (174), with aluminium chloride in nitrobenzene. Half of the acid was recovered unchanged.

When, however, the Friedel-Crafts reaction was attempted in benzene under the condition of the inverse Friedel-Crafts reaction, the major product was γ-1-fluorenonylbutyrophenone (175). This product was isolated in 54% yield by means of chromatography and the material which was more highly adsorbed contained an impurity, probably the cyclic diketone (174). In this/

this case unreacted acid (25%) was also recovered. It therefore appears that this fluorenone acid is less highly reactive in the Friedel-Crafts reaction and, in particular, is more resistant to cyclisation than its fluorene analogue.

In conclusion, it may be said that, 1:2-benzfluorene has been synthesised but the synthesis is only of academic interest.

EXPERIMENTAL

Unless otherwise stated all melting-points in the following section are corrected and were determined by the use of a Kofler micro-M.P. apparatus (Kofler, Mikrochem, 1934, 15, 242). Fluorescence observations were made in ultra-violet light generated by a Hanovia lamp. Analyses were performed by Drs. Weiler and Strauss, Oxford. All yields are reported as the percentage of the theoretical yield.

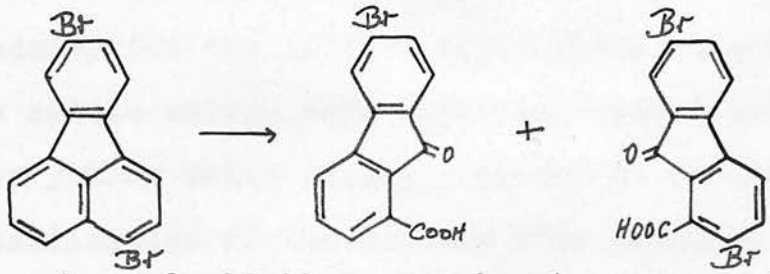
EXPERIMENTAL INDEX

SECTION A EXPERIMENTAL

PREPARATION OF 4:11-DIBROMOFLUORANTHENE

This compound was prepared in 57% yield according to the directions of Tobler and co-workers (Helv. Chim. Acta, 1941, 24, 105E), M.P. 197-200°. A portion purified by recrystallisation from chlorobenzene had M.P. 204-205.5° (Lit. M.P. 205°). In this preparation poly-brominated fluoranthene (1g.), M.P.>360°, was also obtained.

OXIDATION OF DIBROMOFLUORANTHENE



A number ofoxidation experiments were conducted all in the following manner except that in one case an extraction of the crude acid was carried out with saturated barium carbonate solution. This method, however, is inferior to that detailed below.

Chromic anhydride (A.R., 6.9g.) in water (90 ml.) and glacial acetic acid (60 ml.) was added dropwise to a suspension of dibromofluoranthene (5g.) in glacial acetic acid (375 ml.). During the addition the temperature of the mixture was maintained at just below the boiling-point. After boiling for 2 hours, a further solution of chromic anhydride (10.5g.) in glacial/

glacial acetic acid (600 ml.) was added and boiling continued for a further 3 hours. Half of the acetic acid was distilled off and the residual dark green solution poured into water (2 litres) whereupon a greenish-yellow solid was deposited.

The pale green solid was boiled with aqueous sodium carbonate solution, filtered hot and the golden-yellow alkaline extract acidified with conc. hydrochloric acid. The residue from the filtrate was further extracted with successive portions of dilute ammonia which proved a superior extracting agent. Each extract was acidified while still warm because of the tendency for the salt to crystallise on cooling. All the acidic solids were combined, washed and dried. The deep yellow solid (3.48g.) melted at 240-264°. Recrystallisation of the mixture from methanol did not alter the melting-point.

SEPARATION OF MIXTURE

The crude acid (2.5g.) was extracted 14 times with successive portions (250 ml.) of saturated calcium hydroxide solution and the extracts allowed to cool. A yellow crystalline salt crystallised, which was filtered, washed with a little water and dried. Acidification of the yellow-filtrate yielded a pale yellow acid (0.71g.) which crystallised from acetic acid in pale yellow rosettes (0.27g.), M.P. 253-5°.

Its/

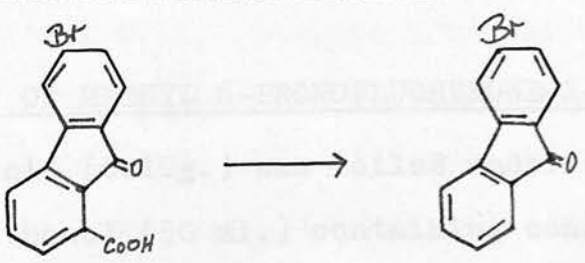
Its filtrate gave solid of M.P. 257-265°. This acid, M.P. 253-5°, gave a good analysis for a mono-bromo-fluorenone carboxylic acid (6-bromofluorenone-1-carboxylic acid) as shown below.

Analysis $C_{14}H_7O_3Br$ requires Br, 26.4%.
Found : Br, 26.3%.

The insoluble calcium salt was dissolved in boiling water and the hot solution acidified to give a yellow acid which was extracted with ether. Removal of the ether left an orange solid (1.04g.) which crystallised from acetic acid in deep yellow needles (0.64g.), M.P. 269-272°. When mixed with a sample of 2:7-dibromofluorenone-1-carboxylic acid, M.P. 266-7°, prepared by Dr. J. Rayment (Ph.D. Thesis, Edinburgh), the M.P. was 265-7°. This acid is thermochromatic, turning deep orange on heating and subliming to orange prisms.

The residue (0.13g.) from the main calcium hydroxide extraction melted over a wide range (210-280°) after recrystallisation from acetic acid.

DECARBOXYLATION OF MONO-BROMO ACID



When/

When the mono-bromo acid (125 mg.) was heated in quinoline (8 ml.) with a trace of copper bronze carbon dioxide was evolved at 190°. The temperature was allowed to rise to 205° and after 30 minutes evolution of carbon dioxide ceased. The cooled solution was poured into dilute hydrochloric acid and the acidic solution extracted with benzene. The benzene solution was washed once with water, once with aqueous sodium carbonate solution (no acid recovered) and again with water. The dried benzene solution (Na_2SO_4) was evaporated to small bulk and chromatographed on a column of alumina (6" x ½").

The pale yellow band was eluted with benzene and the pale yellow solid (95 mg.) obtained from the eluate recrystallised from glacial acetic acid to give pale yellow plates, M.P. 158-162°, undepressed when mixed with a sample of 3-bromofluorenone prepared by Dr. W.H. Stafford (J.C.S., 1951, 1137). A sample was recrystallised from light petroleum and melted at 162-3° (Lit. M.P. 165-6°).

Analysis $C_{13}H_7OBr$ requires Br, 30.9%.
Found : Br, 31.2%.

PREPARATION OF METHYL 6-BROMOFLUORENONE-1-CARBOXYLATE

Pure acid (0.10g.) was boiled under reflux overnight in methanol (50 ml.) containing conc. sulphuric acid/

acid (2.5 ml.). The cooled solution was poured into water and the pale yellow precipitate extracted with ether. The ether layer was shaken with aqueous sodium carbonate solution (no acid recovered), then with water and finally dried over anhydrous sodium sulphate. Removal of the solvent left a pale yellow solid which crystallised from methanol in pale yellow needles, M.P. 126-7°.

Analysis $C_{15}H_9O_3Br$ requires C, 56.8%; H, 2.9%; Br, 25.2%
Found : C, 57.2%; H, 3.4%; Br, 25.8%.

PARTIAL SEPARATION OF THE MIXTURE OF ACIDS

The crude acid (0.69g.) was boiled overnight in methanol (100 ml.) containing conc. sulphuric acid (5 ml.). The cooled solution was poured into water and extracted with ether. Unreacted acid (0.33g.) was removed by shaking the ether layer with aqueous sodium carbonate solution. Acidification of the alkaline extract gave a deep yellow acid which crystallised from acetic acid in orange needles, M.P. 262-4° with softening at 250°. This acid was identical (mixed M.P.) with 2:7-dibromofluorenone-1-carboxylic acid.

The neutral solid obtained from the ether layer was dissolved in benzene and the solution chromatographed on a column of alumina (6" x ½") and the pale yellow band eluted with benzene. Recrystallisation of the pale yellow ester, obtained from the eluate, from methanol/

methanol gave pale yellow needles, M.P. 110-116°. A second recrystallisation raised the M.P. to 115-8° (Compare with 126-7° for the pure ester).

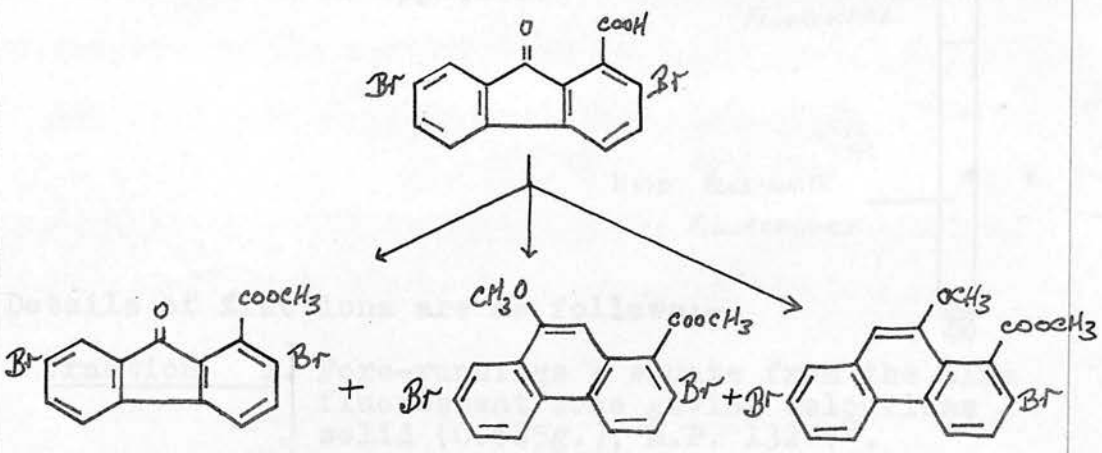
ATTEMPTED SEPARATION OF THE MIXTURE OF ACIDS

1. An attempted separation of the mixture using sodium carbonate solution in the fashion outlined for calcium hydroxide (see above) gave an acid of M.P. 266.5-272.5° from the soluble sodium salt portion and an acid of M.P. 251-266° from the insoluble sodium salt portion. Each of these acids was identical (mixed M.P.) with 2:7-dibromo-fluorenone-1-carboxylic acid).
2. When the mixture was boiled with benzene, the insoluble portion crystallised from methanol-acetic acid in orange needles, M.P. 274-7°, while the soluble portion on evaporation to low bulk yielded deep yellow solid, M.P. 274-7°. Each of these acids was identical (mixed M.P.) with 2:7-dibromo-fluorenone-1-carboxylic acid.

In both the above attempts no acid corresponding to the mono-bromo acid could be found.

ACTION/

ACTION OF DIAZOMETHANE ON THE MIXTURE OF ACIDS



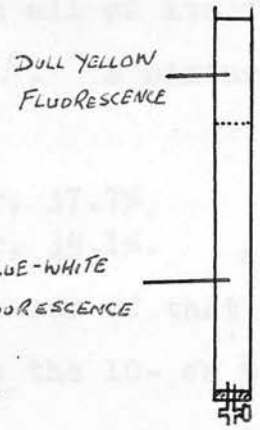
The mixture of acids (3.22g.) was dissolved in a mixture of methanol and ether and treated with a solution of diazomethane in ether (100 ml.) derived from nitrosomethylurea (10g.). No special precautions were taken to exclude moisture either from the solvents or during the reaction (For the preparation of diazomethane see p.127).

After standing overnight the solution exhibited a bluish fluorescence. Removal of the solvent left a yellow oily solid which was dissolved in benzene and the benzene layer shaken with aqueous sodium carbonate solution (no acid recovered).

The crude ester (2.52g.) obtained from the neutral benzene layer was dissolved in benzene (40 ml.) and the solution chromatographed on a column of alumina (12" x $\frac{3}{4}$"). Development with a 4:1 mixture of benzene and light petroleum gave five fractions (25 ml.). The

appearance/

appearance of the column in ultra-violet is shown as opposite.



Details of fractions are as follows:-

Fraction I. Fore-runnings + eluate from the blue fluorescent zone giving colourless solid (0.685g.), M.P. 132-7°.

Fraction II. Yellow eluate giving yellow solid (0.405g.), M.P. 70-160°.

Fraction III. Yellow eluate giving yellow solid (0.250g.), M.P. 158-188°.

Fraction IV. Yellow eluate giving yellow solid (0.260g.), M.P. 176-192°.

Fraction V. Pale yellow eluate giving low melting yellow solid (0.015g.).

Fraction I was purified by rechromatography on a column of alumina (4" x ½") rejecting eluate from the small yellow zone (see diagram). The benzene eluate was evaporated to small bulk and the resulting colourless solid melted at 134-7°. This solid was recrystallised from methanol and the colourless irregular plates had M.P. 143-5°. Analysis showed that this solid is probably 2:7-dibromo-9-methoxy-1-carbomethoxy-phenanthrene (or its 10-methoxy isomer).

Analysis $C_{17}H_{12}O_3Br_2$ requires Br, 37.7%
Found : Br, 39.1%.

At a later date a recrystallisation from methanol of/

of this solid combined with that from all of its filtrates gave colourless needles, M.P. 159-161°. A mixture of these two solids had M.P. 139-160°.

Analysis $C_{17}H_{12}O_3Br_2$ requires Br, 37.7%.
Found : Br, 39.1%.

This compound is probably the isomer of that of M.P. 143-5° with the methoxy-group in the 10- or 9-position.

Fraction IV was recrystallised from benzene-light petroleum to give bright yellow needles, M.P. 185-192° (uncorr.). A second recrystallisation raised the M.P. to 183-5° (corr.). The mother liquors gave yellow needles, M.P. 174-184°. The filtrate from this latter solid was combined with the solid of fraction III and the whole crystallised from benzene, M.P. 175-181.5°. This solid and that of M.P. 174-184° were combined and recrystallised from benzene to give bright yellow needles, M.P. 182-4°, identical with the solid of M.P. 183-5° (mixed M.P.). A mixed M.P. with 2:7-dibromo-1-carbomethoxyfluorenone (M.P. 180-2°) (see J. Rayment, Ph.D. Thesis, Edinburgh) was 179°. The total yield of pure ester was 0.118g.

Analysis $C_{15}H_8O_3Br_2$ requires C, 45.5%; H, 2.0%; Br, 40.4%.
Found : C, 45.4%; H, 2.2%; Br, 40.6%.

The pure ester, obtained after repeated recrystallisations from benzene-methanol, melted at 189-191° with sublimation.

During/

During the recrystallisations detailed above, stubby orange prisms as well as the bright yellow needlesseperated from the filtrates. These were separated manually and crystallised from benzene-methanol to give orange prisms which melted at 176°, then solidified and finally melted at 187-188°. Mixed M.P. with yellow needles, M.P. 187-188°. This solid is probably another form of 2:7-dibromo-1-carbomethoxy-fluorenone.

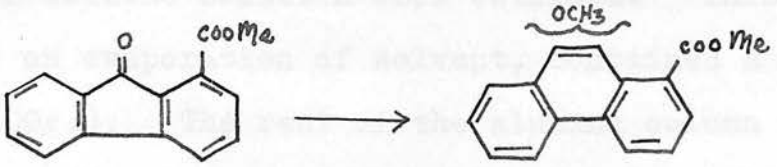
A second experiment conducted in a similar fashion on the acid mixture (4.231g.) followed by chromatographic separation afforded the colourless solid mixture (0.748g.), M.P. 123-158° and crude yellow fluorenone ester (1.494g.), M.P. 177-199° (uncorr.). Repeated recrystallisation of the latter from benzene-methanol gave bright yellow needles, M.P. 189-191° with sublimation.

PREPARATION OF METHYL FLUORENONE-1-CARBOXYLATE

Fluorenone-1-carboxylic acid (5g.) was boiled under reflux overnight in methanol (100 ml.) containing conc. sulphuric acid (5 ml.). The usual working-up (see p.63) gave unreacted acid (0.07g.) and the ester which was recrystallised from methanol. Yellow prisms (3.51g.), M.P. 86-88° (Lit. 86-9°).

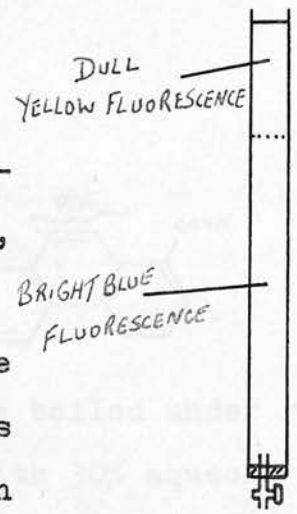
ACTION/

ACTION OF DIAZOMETHANE ON METHYL FLUORENONE-1-CARBOXYLATE



Pure ester (3g.) in a mixture of ether (100 ml.) and methanol (100 ml.) was treated with a solution of diazomethane in ether derived from nitrosomethylurea (10g.). No special precautions were taken to exclude moisture either from the solvents or during the reaction.

After standing overnight the solution exhibited a blue fluorescence. Removal of the solvents left a brown syrup which was chromatographed in benzene (20 ml.) on a column of alumina (16" x $\frac{3}{4}$"). The column when viewed in ultra-violet light appeared as opposite:-



The blue fluorescent band was eluted with benzene and the colourless solid (0.77g.), M.P. 110-122°, obtained from the eluate recrystallised from methanol. The resulting colourless rhombic prisms melted at 134-6°. Its filtrate on standing gave solid of M.P. 125-8°. The ester fluoresced vivid blue in ultra-violet light.

Analysis $C_{17}H_{14}O_3$ requires C, 76.7%; H, 5.3%
Found : C, 76.5%; H, 5.0%.

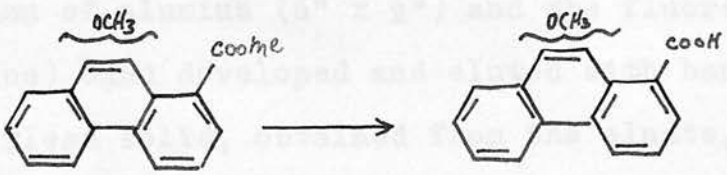
i.e. 9-(10)-methoxy-1-carbomethoxyphenanthrene.

Further/

Further elution was continued until a further 200 ml. of benzene solution were obtained. This solution, on evaporation of solvent, contained a yellow syrup (1.00g.). The rest of the alumina column was extracted with acetone and the resulting yellow syrup, obtained on the removal of the solvent, was dissolved in benzene and the solution chromatographed on a column of alumina (9" x $\frac{3}{4}$"). Development with a 2:1 mixture of benzene and light petroleum gave 6 fractions which all contained syrups (total weight 1.03g.).

The major product of this reaction was therefore a yellow syrup (2.03g.) which was not investigated further but probably contains unreacted fluorenone ester. The conversion to phenanthrene derivatives was 23%.

HYDROLYSIS OF COLOURLESS ESTER



Colourless ester (180 mg.) was boiled under reflux in methanol (20 ml.) for 4 hours with 30% aqueous potassium hydroxide solution (5 ml.). The solution was poured into acid and the resulting white solid extracted with benzene. Extraction of the benzene layer/

layer with aqueous sodium carbonate solution followed by acidification of the alkaline extract afforded a white acid (125 mg., 73%). Recrystallisation from acetic acid gave 9-(10-)-methoxyphenanthrene-1-carboxylic acid as colourless prisms, M.P. 256° (put in at 240°) with sublimation and sintering.

Analysis $C_{16}H_{12}O_3$ requires C, 76.2%; H, 4.7%.
Found : C, 76.1%; H, 4.9%.

DECARBOXYLATION OF ACID, M.P. 256°

When the acid (80 mg.) was heated in quinoline (5 ml.) with a trace of copper bronze bubbles of carbon dioxide dioxide were evolved at 195° and after heating at 220° for one hour evolution of carbon dioxide ceased. The reaction was worked up in the usual way (see p.63). No acid was recovered.

The neutral product in benzene was chromatographed on a column of alumina (6" x ½") and the fluorescent (vivid blue) band developed and eluted with benzene. The colourless solid, obtained from the eluate, crystallised from methanol in colourless elongated prisms, M.P. 90-93°. A further recrystallisation from light petroleum (B.P. 40-60°) raised the M.P. to 93-5° (Lit. M.P. 96-7°).

Analysis $C_{15}H_{12}O$ requires C, 86.5%; H, 5.9%.
Found : C, 86.2%; H, 5.8%.

All filtrates were combined, the solvent replaced

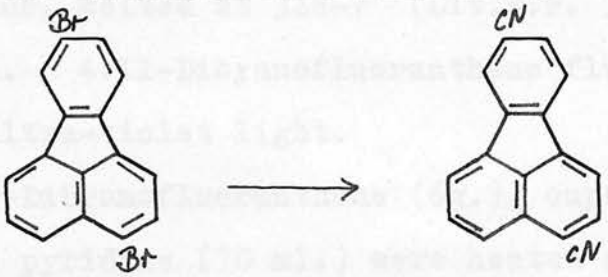
by/

by methanol and a saturated methanolic solution of picric acid added. The resultant orange-red picrate was filtered and washed with light petroleum. Orange prisms, M.P. 156-7° (Lit. M.P. 157-158.5°).

The analysis amd melting-point of the colourless solid indicate it to be 9-methoxyphenanthrene. The latter formulation is confirmed by the melting-point of the picrate.

SYNTHESIS OF 4:11-DICARBOXYFLUORANTHENE

PREPARATION OF 4:11-DICYANOFLUORANTHENE



This was achieved in two ways.

1). cf. German patent 533, 962.

4:11-Dibromofluoranthene (6g.) was stirred at 300° and cuprous cyanide (3.3g.) was added in small portions over a period of 20 minutes to the molten mass. Heating was continued at 320-330° for another 15 minutes. Bright yellow needles (4:11-dicyanofluoranthene) sublimed on the cooler parts of the reaction vessel and on cooling these were shaken free from the solidified residue.

The residual dark brittle mass was powdered, boiled with 20% nitric acid for one hour, filtered, washed/

washed and dried. The resultant ochre-coloured powder (3.21g.) was sublimed at 300° under reduced pressure (water pump). The sublimate was a bright yellow crystalline solid which was contaminated with unreacted 4:11-dibromofluoranthene. This contaminant was removed by boiling the solid with chloroform or acetic acid and filtering hot. The dicyanofluoranthene was practically insoluble. The total yield of elongated needles was 1.02g. (24%), M.P. 324-7°.

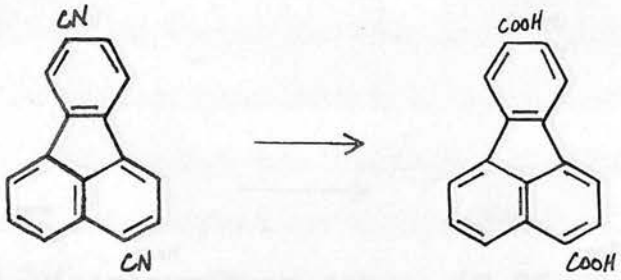
A pure sample, obtained by recrystallisation from chlorobenzene, melted at 326-7° (Lit.M.P. 321-3°) with sublimation. 4:11-Dicyanofluoranthene fluoresces yellow in ultra-violet light.

2). 4:11-Dibromofluoranthene (6g.), cuprous cyanide (3.3g.) and pyridine (70 ml.) were heated at 230° in a Carius tube for 6 hours. The reaction mixture was allowed to cool overnight and the dark crystalline solid filtered. Its filtrate was poured into dilute hydrochloric acid and the resulting brown precipitate filtered. Both solids were sublimed and purified as described above to give 4:11-dicyanofluoranthene (1g.).

In another experiment carried out as in (1) extraction of the solid residue with chlorobenzene gave poor yields of orange solids which melted over a wide range.

PREPARATION/

PREPARATION OF 4:11-DICARBOXYFLUORANTHENE



This was accomplished by two different methods.

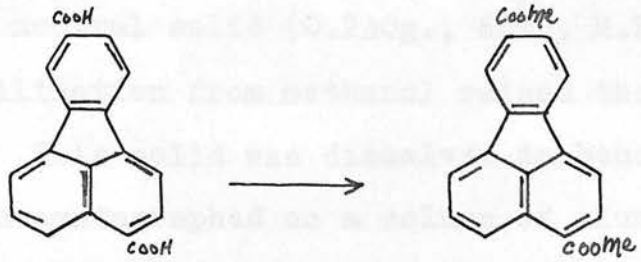
1). 4:11-Dicyanofluoranthene (0.4g.) was boiled under reflux in trimethylene glycol (10 ml.) with potassium hydroxide (0.5g.) for 3 hours. On cooling the solution was poured into dilute sulphuric acid and the resulting precipitate filtered, washed and dried. This precipitate (0.4g., 87%) was totally soluble in alkali.

2). 4:11-Dicyanofluoranthene (0.4g.) was boiled overnight in a mixture of acetic acid (8 ml.), conc. sulphuric acid (8 ml.) and water (8 ml.). Solid remained throughout but the crystallinity associated with 4:11-dicyanofluoranthene was no longer apparent. The yellow solid was filtered, washed with hot aqueous sodium carbonate solution and the filtrate acidified to give the yellow acid (0.37g., 81%).

4:11-Dicarboxyfluoranthene is a yellow solid, highly fluorescent in ultra-violet light, which could not be crystallised on account of its low solubility. It had M.P. 350° and sublimed to tiny yellow needles.

Analysis $C_{18}H_{10}O_4$ requires C, 74.5%; H, 3.5%.
Found : C, 75.2%; H, 4.2%.
C, 73.1%; H, 3.3%.

PREPARATION OF 4:11-DICARBOMETHOXYFLUORANTHENE



1). 4:11-Dicarboxyfluoranthene (0.25g.) was boiled for 2 hours with thionyl chloride (3 ml.), a further portion (3 ml.) of thionyl chloride added and boiling continued for a further 2 hours. Excess thionyl chloride was distilled off in vacuo at 100° (water bath).

The bright yellow acid chloride was boiled with methanol (100 ml.) for 5 hours. The solution was filtered from a small amount of residue and the filtrate evaporated to small bulk. The resulting crystalline yellow solid was filtered, washed with hot sodium carbonate and then withwater. The residual solid (90 mg., 33%), M.P. 145-154°, was dissolved in benzene (15 ml.) and the solution chromatographed on a column of alumina (9" x $\frac{3}{4}$"). The main, highly fluorescent, yellow band was extracted with acetone and this extract, on removal of solvent, yielded a bright yellow solid, M.P. 156-8°. Recrystallisation from methanol-acetic acid furnished 4:11-dicarbomethoxyfluoranthene as yellow needles, M.P. 168-9° with sublimation to rhombic plates, with bright yellow fluorescence.

2). 4:11-Dicarboxyfluoranthene (0.308g.) was boiled overnight in methanol (100 ml.) containing conc. sulphuric/

sulphuric acid (5 ml.). The usual procedure (see p. 63) afforded a neutral solid (0.230g., 68%), M.P. 161-4°. One crystallisation from methanol raised the M.P. to 168-171°. This solid was dissolved in benzene and the solution chromatographed on a column of alumina (6" x ½"). The highly fluorescent yellow band was developed with benzene and the solid, obtained from the eluate, crystallised from methanol-acetic acid to give yellow needles, M.P. 166-8°. A final crystallisation from benzene-light petroleum raised the M.P. to 167-9°. This ester was identical (mixed M.P.) with that obtained in the previous experiment.

A mixture of this dimethyl ester with that (M.P. 181.5-183°) obtained in Friedel-Crafts reactions (Campbell and Easton, J.C.S., 1949, 340; Campbell, Leadill and Wilshire, J.C.S., 1951, 1405) melted at 145°.

Analysis $C_{20}H_{14}O_4$ requires C, 75.5%; H, 4.4%.
Found : C, 74.8%; H, 4.3%.

REDUCTION OF 4:11-DIBROMOFLUORANTHENE

4:11-Dibromofluoranthene (5.5g.) was boiled overnight with sodium amalgam (77g.) in alcohol (165 ml.). The resulting orange-yellow solution was filtered from unreacted starting material, poured into water and neutralised with hydrochloric acid. On standing a white sticky solid was deposited which was filtered, washed/

washed and dried. This solid was low-melting and contained inorganic material. It was treated successively with methanol, acetic acid and chlorobenzene to give three separate fractions which, on evaporation to dryness, gave the following results:-

Fraction I (Methanol).	Oil containing colourless crystals.
Fraction II (Acetic Acid).	Colourless crystals, M.P. 65-70°.
Fraction III (Chlorobenzene).	Small amount of featherly greenish-yellow crystals which sublimed at 260°. This compound is probably a higher-brominated fluoranthene.

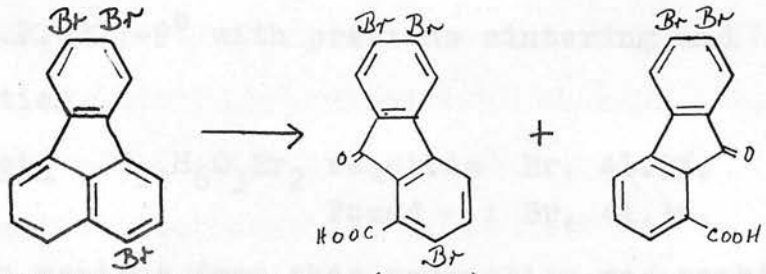
When the crystals of M.P. 65-70° from Fraction II were mixed with 1:2:3:4-tetrahydrofluoranthene (76-77°) the M.P. was 70-74°. The oil from Fraction I was dissolved in a mixture of methanol and ether. Over a week-end colourless crystals, M.P. 69-72°, were obtained. Mixed M.P. with 1:2:3:4-tetrahydrofluoranthene was 68-72°. Total yield of 1:2:3:4-tetrahydrofluoranthene was 0.80g. (25%).

OXIDATION AND SYNTHESIS OF 4;11:12-TRIBROMOFLUORANTHENE

The tribromofluoranthene used in this investigation was prepared by Dr. W.K. Leadill (Thesis, Edinburgh) and had M.P. 205-7°.

OXIDATION/

OXIDATION OF TRIBROMOFLUORANTHENE I



Tribromofluoranthene (10g.) was suspended in glacial acetic acid (700 ml.) and the suspension boiled for 20 hours with sodium dichromate (100g.). The resultant dark green solution was filtered hot to remove starting material and poured into water (1 litre). A pale green solid was slowly deposited while a sticky solid remained in the flask.

This sticky solid was boiled with sodium carbonate solution (500 ml.), filtered hot and the golden-yellow alkaline filtrate acidified with conc. hydrochloric acid. The orange acid (100 mg.) melted over the range 249-300°. An attempted recrystallisation from acetic acid did not alter the melting-point while a recrystallisation from alcohol gave a mixture of orange nodules and pale yellow leaflets, M.P. 260-300°.

The main solid, obtained on dilution of the reaction mixture was boiled with sodium carbonate solution (500 ml.) and filtered hot to avoid crystallisation of the sodium salt. Acidification of this alkaline extract gave a pale yellow solid (0.14g.) which melted over the range 220-260°. Recrystallisation from methanol-acetic acid gave a dibromofluorenone acid (0.03g.)/

(0.03g.), presumably 6:7-dibromofluorenone-1-carboxylic acid, M.P. 277-9° with previous sintering and sublimation.

Analysis $C_{14}H_6O_3Br_2$ requires Br, 41.9%.
Found : Br, 41.3%.

The residue from this extraction was combined with that from the carbonate extraction of the above-mentioned sticky solid and the combined solids extracted with two successive portions (500 ml. each) of saturated calcium hydroxide solution. Acidification of the cooled calcium hydroxide extracts gave a pale yellow acid (1.39g.) which was boiled with chlorobenzene and filtered. The residual solid was boiled with methanol and the solution allowed to cool. (0.090g.)

The chlorobenzene filtrate yielded yellow elongated prisms (0.090g.), M.P. 317-320° (dec.) while the ethanolic filtrate yielded an identical solid (0.215g.), M.P. 315-6°. Mixed M.P. of the two acids was 316-320°. Analysis showed this solid to be a tribromofluorenone acid, presumably 2:6:7-tribromofluorenone-1-carboxylic acid.

Analysis $C_{14}H_5O_3Br_3$ requires Br, 52.0%.
Found : Br, 51.8%.

All the filtrates were combined and evaporated to small bulk. The resulting yellow elongated prisms (0.72g.) melted over the range 244-288°. The filtrate from this product gave a small amount of yellow solid, M.P. 322-4° after recrystallisation from acetic acid, which was identical (mixed M.P.) with the above tribromo/

tribromo-acid.

An attempt to separate the acid mixture (0.72g.) into its components by esterification with methanol containing conc. sulphuric acid followed by chromatographic separation failed because of hydrolysis of the neutral product on the alumina column. No material was recovered even when the column was extracted with acetone.

DECARBOXYLATION OF TRIBROMO-ACID

Pure tribromofluorenone acid (0.210g.) was heated in quinoline (10 ml.) with a trace of copper bronze. At 180° carbon dioxide was evolved and after 90 minutes at 200° evolution had ceased. The reaction was worked up in the usual way (see p.63). No acid was recovered.

The neutral product in benzene (10 ml.) was chromatographed on a column of alumina. The pale yellow band was developed with a 2:1 mixture of benzene and light petroleum. The eluate yielded a deep yellow solid (85 mg.) which crystallised from alcohol-acetic acid in deep yellow prisms, M.P. 199-203° with some crystals melting at 206°. A recrystallisation from acetic acid raised the M.P. to 209-215° with a trace of solid melting at 218°. The filtrate gave yellow prisms, M.P. 192-200°.

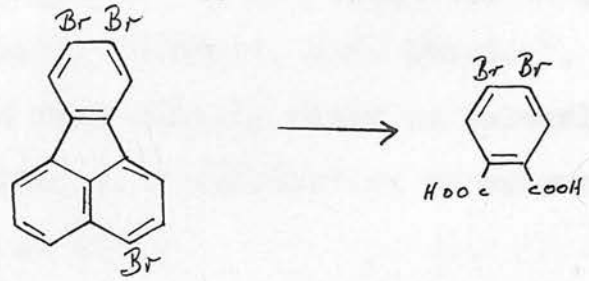
The solid of M.P. 209-15° was analysed and proved

to/

to be mixture of di- and tri-bromofluorenones.

Analysis For a dibromofluorenone, $C_{13}H_6OBr_2$ requires Br, 47.3%.
For a tribromofluorenone, $C_{13}H_5OBr_3$ requires Br, 57.5%.
Found : Br, 52.2%.

OXIDATION OF TRIBROMOFLUORANTHENE II



Tribromofluoranthene (10g.) in glacial acetic acid (1500 ml.) was boiled for 48 hours with sodium dichromate (150g.). The dark green solution was evaporated to half volume, poured into dilute sulphuric acid (1500 ml.) and the resulting green solid filtered, washed and dried. As this quantity of solid was small the acid filtrate was extracted with ether.

The green solid was extracted with two successive portions (500 ml. each) of saturated calcium hydroxide solution and finally with one portion (500 ml.) of sodium carbonate solution. The alkaline filtrates were acidified and the resultant yellow acid (0.56g.) had M.P. 240-300°.

An attempt to separate this mixture by means of the difference in solubilities of the calcium salts (cf. Campbell, Stafford and Wilshire, J.C.S., 1951, 1137) failed/

failed. The more soluble calcium salt gave an acid, which crystallised from alcohol-acetic acid in yellow needles, M.P. 259-275° with sublimation. The less soluble calcium salt gave a yellow acid, M.P. 240-300°.

The above ether extract of the main acid filtrate was shaken with sodium carbonate solution and the colourless alkaline extract acidified to give a colourless solid (0.28g.), M.P. 196-200°. This acid crystallised from boiling water in colourless plates, M.P. 207.5-208°.with sublimation to colourless prisms (anhydride) at 200°.

Analysis $C_8H_4O_4Br_2$ requires Br, 49.4%.
Found : Br, 49.5%.

A mixed M.P. with authentic 4:5-dibromophthalic acid (M.P. 211-2°) was 206-9°. As the M.P. of 4:5-dibromophthalic acid depends on the rate of heating the methyl ester of the acid was prepared in the usual way with methanol and conc. sulphuric acid (see p.63). The methyl ester crystallised from methanol in colourless needles, M.P. 78.5-79.5°.

Analysis $C_{10}H_8O_4Br_2$ requires Br, 45.4%.
Found : Br, 44.9%.

The mixed M.P. with authentic dimethyl 4:5-dibromophthalate (M.P. 78-79.5°) was 78-79.5°.

OXIDATION/

OXIDATION OF TRIBROMOFLUORANTHENE III

Tribromofluoranthene (5g.) was suspended in acetic acid (400 ml.) and boiled for 2 hours with a solution of chromic anhydride (A.R., 9g.) in water (50 ml.) and acetic acid (100 ml.). A further solution of chromic anhydride (9g.) in water (50 ml.) and acetic acid (100 ml.) was then added and boiling continued for a further 4 hours. The resultant dark green liquor was evaporated to small bulk (200 ml.) and poured into water (1 litre).

This solution was extracted with ether and the ether layer washed with water and extracted with dilute ammonia. The basic extract on acidification yielded a deep yellow solid (0.67g.), M.P. 260-75° with sintering from 235°.

This acid was boiled in methanol (100 ml.) and conc. sulphuric acid (5 ml.) for 24 hours and the reaction worked up in the usual way (p. 63) to give unreacted acid (0.335g.), M.P. 317-320°, identical with the tribromofluorenone acid described above (mixed M.P.) and a neutral oil.

The neutral oil was treated with light petroleum (B.P. 80-100°). A deposit, mostly of deep yellow rosettes mixed with smaller quantities of yellow elongated needles, separated over a week-end. The needles were separated partly manually and partly by swilling the mixture with benzene which showed a preference/

preference to dissolve them. The deep yellow rosettes were boiled with methanol and the solution allowed to cool. Deep yellow octahedra, M.P. 158-160°, were deposited.

Analysis $C_{15}H_8O_3Br_2$ requires Br, 40.4%.

Found : Br, 42.1%.

The supernatant liquor was decanted and immediately bright yellow prisms, M.P. 146-156°, crystallised. Recrystallisation from methanol did not alter the melting-point.

Analysis Found : Br, 39.6%.

Its filtrate deposited squat yellow prisms, M.P. 152-4°. There was not enough for analysis. The analysed esters may be different forms of methyl 6:7-dibromofluorenone-1-carboxylate.

The main oil from the light petroleum treatment was dissolved in methanol and on cooling yellow prisms, M.P. 144-153°, crystallised.

This experiment indicates only a partial separation of the mixture as a pure dibromofluorenone methyl ester was not isolated.

OXIDATION OF TRIBROMOFLUORANTHENE IV AND ISOLATION OF 2:3-DIBROMOFLUORENONE

Tribromofluoranthene (5g.) was suspended in acetic acid (600 ml.) and boiled with sodium dichromate (600g.) for/

for 16 hours. The dark green solution was evaporated to small bulk (50 ml.) and poured into water (1200 ml.). The dark green solid, which was deposited, was immediately extracted with ether and the ether layer then extracted with ammonia. Acidification of the basic extract gave a yellow solid (0.75g.).

This solid was partly esterified by boiling with methanol (100 ml.) and conc. sulphuric acid (5 ml.) for 6 hours. The usual method of separation afforded acid (9.43g.), M.P. 305-9°, identical with the tri-bromofluorenone acid described earlier, and an amorphous yellow methyl ester.

This ester was partially hydrolysed by boiling its methanolic solution with 20% potassium hydroxide (5 ml.) for 3 hours. This was again separated into acid (45 mg.), M.P. 252-262° with sublimation, and an oily unhydrolysed ester which was not investigated further.

The acid, M.P. 252-262°, was decarboxylated by heating in quinoline (10 ml.) with a trace of copper bronze at 200° for one hour. The usual working-up gave an orange neutral solid which crystallised from alcohol-acetic acid in yellow needles, M.P. 203-8°.

This solid and the material from its filtrate were dissolved in benzene (8 ml.) and the solution chromatographed on a column of alumina (12" x ½"). The pale yellow band was developed with benzene to give two yellow bands of which the upper band remained stationary/

stationary. The lower yellow band was eluted with benzene and the solid obtained from the elute crystallised from ethanol. The resulting pale yellow needles melted at 208-211° with sublimation.

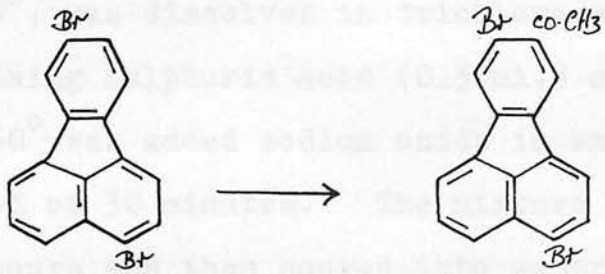
Analysis $C_{13}H_6OBr_2$ requires Br, 47.3%.

Found : Br, 44.9%.

It is likely that this solid, M.P. 208-211°, is 2:3-dibromofluorenone although its analysis indicated a rather low percentage of bromine.

SYNTHESIS OF 4:11:12-TRIBROMOFLUORANTHENE

ACETYLATION OF 4:11-DIBROMOFLUORANTHENE



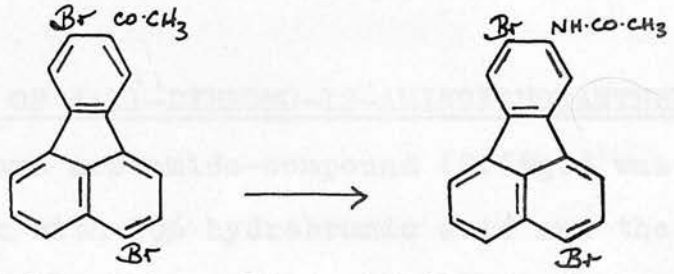
This was accomplished as described by Leadill (Ph.D. Thesis, Edinburgh) but in much lower yield (11%). This can only be explained by the fact that all reagents were specially purified and dried and therefore caused polyacetylation since the quantity of acetyl bromide used by Dr. Leadill was twice that required for mono-acetylation. As the quantity obtained was sufficient for the later stages of the synthesis the experiment/

experiment was not repeated. The product had M.P. 157-164° (Crude) (Lit. M.P. 164-5°).

An attempted acetylation in nitrobenzene failed and starting material was recovered.

PREPARATION OF 4:11-DIBROMO-12-ACETAMIDOFLUORANTHENE

cf. Dice and Smith, J. Org. Chem., 1949, 14, 179.



Crude 4:11-dibromo-12-acetylfluoranthene (1.30g.), M.P. 157-164°, was dissolved in trichloracetic acid (8g.) containing sulphuric acid (0.5 ml.) and to this mixture at 60° was added sodium azide in small portions over a period of 30 minutes. The mixture was kept at 60° for 20 hours and then poured into water. The ochre-coloured precipitate, M.P. c. 250°, was filtered, washed and dried. This solid was purified by boiling in methanol (100 ml.) for one hour and the suspension filtered. The residue was a greenish-yellow solid (1.07g., 79%), M.P. 282-9°.

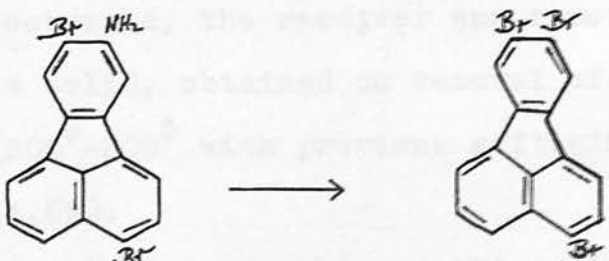
To obtain the acetamido-compound in a pure form for the next stage the previous solid was boiled with acetic acid (100 ml.) for one hour and the suspension filtered hot. The greenish-yellow needles (0.41g.) which/

which crystallised on cooling, melted at 285-8°(dec.). The residue from the hot filtration was dissolved in chloroform (20 ml.) and the solution added to the filtrate from the 0.41g. portion. On evaporation to small bulk, the resultant crystalline solid (0.34g.) melted at 286-9° (dec.). Dr. Leadill gives M.P. 284-8° (dec.).

PREPARATION OF 4:11-DIBROMO-12-AMINOFLUORANTHENE

The above acetamido-compound (0.69g.) was boiled under reflux with 50% hydrobromic acid and the resulting cream-coloured hydrobromide decomposed to its amine with conc. ammonia. The bright yellow amine (0.46g.) melted at 252-4°. (Leadill gives M.P. 256-8°).

PREPARATION OF 4:11:12-TRIBROMOFLUORANTHENE



4:11-Dibromo-12-aminofluoranthene (0.22g.) was boiled in acetic acid (20 ml.) for one hour, cooled to 15° and poured slowly into sodium nitrite solution (3.5 ml.), made by suspending sodium nitrite (0.5g.) in conc. sulphuric acid and proceeding according to the directions/

directions of Hodgson and Walker (J.C.S., 1933, 1620).

The resultant diazo complex was a suspension of a light yellow solid in a dark brown solution. This suspension was allowed to stand at 15° and then added to a solution of freshly prepared cuprous bromide (1.00g.) in constant-boiling hydrobromic acid (15 ml.) at 35°, acetic acid being used for washing. There was an immediate evolution of nitrogen bubbles. The solution was allowed to cool slowly over a period of 15 minutes and then poured into water. The resulting brownish-yellow precipitate (0.22g.) was filtered, washed and dried. It melted over the range 160-170° with darkening.

The product was dissolved in chlorobenzene and the solution chromatographed on a column of alumina (7" x 1"). Development with benzene gave a uniform yellow band but the eluate was initially pale yellow and eventually became bright yellow. When the change in colour occurred, the receiver was removed and the pale yellow solid, obtained on removal of the solvent, melted at 200°-206° with previous softening. Yield = 0.115g. (44.6%).

When this solid was recrystallised from benzene it formed pale yellow needles, M.P. 204-206.5°, which melted at 201-206° when mixed with an authentic sample of tribromofluoranthene (M.P. 205-7°) (Leadill, Ph.D. Thesis, Edinburgh). A second recrystallisation of

the/

the synthetic material raised its M.P. to 206-209°.

In order to be sure of the purity of the synthetic sample, the solid and its filtrates were combined in benzene (6 ml.) and chromatographed on a column of alumina (9" x ½"). Development was adjusted so that the three fractions removed formed 25%, 50% and 25% of the benzene eluate. The middle fraction afforded a pale yellow solid which crystallised from benzene in yellow needles, M.P. 204-8°. A second recrystallisation raised the M.P. to 208-210.5°. The last solid was analysed.

Analysis $C_{16}H_7Br_3$ requires Br, 54.6%.
Found : Br, 55.6%.

Mixed M.P. with a sample of tribromofluoranthene, obtained by the bromination of 4:11-dibromofluoranthene and purified as described below, was 208-211°.

PURIFICATION OF TRIBROMOFLUORANTHENE

The tribromofluoranthene used in this investigation was that prepared by the bromination of 4:11-dibromofluoranthene by Dr. W.K. Leadill (Thesis, Edinburgh) and had micro-M.P. 205-7°. Recrystallisation of this sample from benzene afforded pale yellow needles, M.P. 201-7°. A second recrystallisation from benzene gave solid of M.P. 201-5° while the solid from the filtrate of/

of the latter solid melted at 204-8°.

This last solid was chromatographed in benzene on a column of alumina (9" x ½") and the first and main fraction gave pale yellow needles, M.P. 207-210°. A recrystallisation of this material from benzene gave material of M.P. 206-9° while the filtrate from this solid deposited pale yellow needles, M.P. 208-211°. This purified material, M.P. 208-11°, was analysed.

Analysis $C_{16}H_7Br_3$ requires Br, 54.6%.

Found : Br, 52.1%.

It therefore appears that the solid, M.P. 205°, reported by Tobler et al. (loc. cit.) is not quite pure although they reported a bromine analysis : Br, 55.5%.

SYNTHESIS OF 4:5-DIBROMOPHTHALIC ACID

4:5-Dibromo-o-xylene was synthesised from o-4-xylidine following the procedure outlined by Mills and Nixon (J.C.S., 1930, 2524).

PREPARATION OF N-ACETYL-o-XYLIDINE

o-4-Xylidine (4.39g.) was placed in a test-tube and dissolved in acetic anhydride in the cold. Considerable evolution of heat was observed. The mixture was boiled for 30 seconds and then poured into water whereupon a grey solid was precipitated. This solid/

solid was stirred until the excess acetic anhydride had decomposed. The precipitate was then filtered, washed and dried. The dried solid was boiled in methanol with charcoal and the solution filtered hot. The pale yellow filtrate was concentrated and diluted with water. The resulting oil was dissolved in a little acetone. On standing, colourless needles (4.62g., 78%) were deposited, M.P. 95.5-97.5°. A portion crystallised from benzene-light petroleum had M.P. 97-8° (Lit. M.P. 99°).

PREPARATION OF 5-BROMO-4-ACETAMIDO-o-XYLENE

The bromination of the above acetyl-compound was carried out as described by Mills and Nixon (loc. cit.). Recrystallisation of the product from aqueous acetic acid afforded colourless elongated prisms, M.P. 164.5-165° (Lit. M.P. 164°). Yield = 74%.

PREPARATION OF 5-BROMO-4-AMINO-o-XYLENE

The above bromo-acetyl-derivative (4.30g.) was hydrolysed by boiling with 60% sulphuric acid (35 ml.) for 90 minutes. The resulting brown solution was poured into water and the solution basified with caustic soda. The white precipitate was steam-distilled from the alkaline solution. Yield = 3.11g. (88%). A portion crystallised from light petroleum in colourless plates, M.P. 84.5-85°. (Lit. M.P. 84-5°). The amine has/

has a characteristic smell.

PREPARATION OF 4:5-DIBROMO-o-XYLENE

5-Bromo-4-amino-o-xylene (1.445g.) was dissolved in 50% hydrobromic acid (15 ml.) and water (45 ml.) with slight warming. On cooling the hydrobromide crystallised in elongated colourless needles.

This suspension was cooled below 5° and excess 10% sodium nitrite was added. The resulting diazo complex, a bright yellow solid, was added in portions over a period of 10 minutes, to a solution of freshly prepared cuprons bromide (13.5g.) in 50% hydrobromic acid (40.5 ml.) and water (13.5 ml.) stirred at 90°.

After complete addition stirring was continued for a further 10 minutes and then the purple solution was diluted with water and the resultant white precipitate steam-distilled. The solid was extracted with a benzene-ether mixture, the organic layer being washed once with water, once with caustic soda solution and finally with three portions of water. After drying over anhydrous sodium sulphate, removal of solvent left a colourless solid (1.80g., 94%). A portion crystallised from methanol in elongated colourless needles, M.P. 87.5-88° (Lit. M.P. 87-8°).

PREPARATION OF 4:5-DIBROMOPHTHALIC ACID

4:5-Dibromo-o-xylene (1g.) was heated in a sealed tube at 170° with nitric acid (10 ml. d=1.15) for 7 hours. The reaction mixture, which contained colourless crystalline solid, was extracted with ether. The ether layer was extracted with aqueous sodium carbonate solution and the basic extract acidified to give a white solid (0.84g.), which melted mainly at 209° but which contained a small amount of a higher-melting product. The crude solid was boiled with aqueous acetic acid, allowed to cool somewhat and the higher-melting, less soluble impurity filtered. On standing the clear filtrate deposited glistening colourless irregular plates (0.455g.), M.P. 211-2°. A portion recrystallised for analysis from water had M.P. 219.5° with sublimation to rhombic prisms just before the melting-point (anhydride ?) (Lit. M.P. 209-10°). The melting-point of this acid is dependent on the rate of heating. Pure yield = 37%.

On heating to the melting-point and cooling several times it was found that solid was formed which no longer melted and is probably the high-melting acid described below.

A portion of the acid, M.P. 219.5°, was analysed.

Analysis $C_8H_4O_4Br_2$ requires Br, 49.4%.
Found : Br, 50.3%.

A portion (100 mg.) was esterified in the usual manner with methanol and conc. sulphuric acid. The ester/

ester (85 mg.) crystallised from light petroleum (B.P. 40-60°), M.P. 78-79.5° (Lit. M.P. 82-3°). This ester is identical (mixed M.P.) with that described below.

ISOLATION OF HIGH-MELTING ACID

An oxidation of 4:5-dibromo-o-xylene (1g.) for 15 hours followed by the procedure described in the previous oxidation afforded a colourless acid (0.685g.), M.P. 350°. The acid crystallised from boiling water in colourless plates, M.P. > 350°.

Analysis Found :C, 29.4%; H, 1.3%; Br, 49.3%.
$C_8H_4O_4Br_2$ requires C, 29.7%; H, 1.3%; Br, 49.4%.

A portion (0.25g.) of this acid was esterified overnight in methanolic conc. sulphuric acid and the usual procedure gave the ester (0.195g.) which crystallised from light petroleum (B.P. 40-60°) in colourless elongated needles, M.P. 77.5-78.5°.

Analysis $C_{10}H_8O_4Br_2$ requires C, 34.1%; H, 2.3%; Br, 45.4%.
Found :C, 34.9%; H, 2.1%; Br, 44.7%.

This ester was identical (mixed M.P.) with that obtained in the above oxidation and with that obtained by the oxidation of 4:11:12-tribromofluoranthene.

A sample of this ester (95 mg.) was hydrolysed by boiling its methanolic solution (5 ml.) with 10% sodium hydroxide solution (5 ml.). The resultant acid 25 mg.) melted at 218-9° with sublimation and was identical with 4:5-dibromophthalic acid (mixed M.P.).

SECTION B EXPERIMENTAL

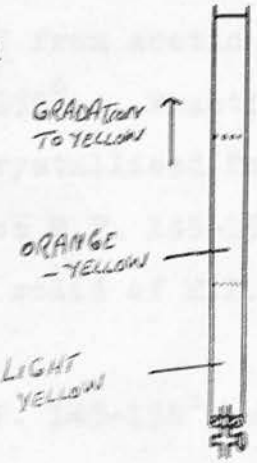
NITRATION OF FLUORANTHENE

Von Braun and Manz (Ann., 1931, 488, 111).

Fluoranthene (20g.) was dissolved in glacial acetic acid (200 ml.) heated to 95° on a water-bath and a solution of conc. nitric acid (16.3g., d=1.42) in glacial acetic acid (200 mls.) added dropwise over a period of one hour.

The greater part of the acetic acid was evaporated from the dark brown solution in vacuo and the residual liquor extracted with chloroform. The chloroform layer was washed free of acid with dilute caustic soda, then with water and finally dried over anhydrous sodium sulphate. Removal of the solvent left an orange solid (19g.).

A portion of this solid (1g.) was dissolved in benzene (20 ml.), the solution chromatographed on a column of alumina (30g.) and the column developed with benzene. The column in daylight appeared as opposite:-



The light yellow band was eluted and constitutes Fraction I. Three more fractions, each of 40 ml. (II, III and IV), were eluted. Fraction V represents the final benzene elution (100ml.).

Details of the fractions are as follows:-

Fraction/

Fraction I.	Yellow-orange solid	0.069g	M.P.74-144°
Fraction II.	Orange solid	0.788g	M.P.120-158°
Fraction III.	Orange solid	0.014g	M.P.130-242°
Fraction IV.	Yellow solid	0.024g	M.P.300-309° (sublimes)
Fraction V.	Yellow solid which fluoresces orange in ultra-violet light.	0.046g	M.P. 293dec.

Recrystallisation of Fraction II solid from benzene gave a deep yellow solid of M.P. 149-157° with softening from 128°. This crude solid in benzene was chromatographed on a column of alumina (20" x ½") and the column developed with a 3:1 mixture of benzene and light petroleum. As above, no real banding was observed. Fractions of 50ml. were removed.

Details of the fractions are as follows:-

Fraction B I.	Dull yellow solid	0.071g	M.P. 60-150°
Fraction B II.	Orange solid	0.229g	M.P.136-152°
Fraction BIII.	Orange solid	0.215g	M.P.118-145°
Fraction B IV.	Bright yellow solid	0.039g	M.P.119-140°
Fraction B V.	Orange-red solid	negligible wt.	M.P. 70-150°

Recrystallisation pf Fraction BII from acetic acid yielded deep yellow needles M.P. 155-159°. Fractions BIII and BIV were amalgamated and recrystallised from acetic acid to give deep yellow needles M.P. 145-158°. The combined filtrates yielded yellow solid of M.P.132-150°.

The solids of M.P. 155-9° and M.P. 145-158° were amalgamated/

amalgamated and recrystallised from glacial acetic acid to give deep yellow needles M.P. 162-164.5° (0.14g.) while its filtrate gave yellow solid M.P. 134-157.5°. All remaining filtrates were combined and gave solid of M.P.. 40-140° on standing.

Von Braun and Manz give M.P. 159-160° for 4-nitrofluoranthene.

The high-melting solid M.P. C.300° with sublimation was analysed.

Analysis Found : C, 64.3%; H, 3.3%; N, 8.4%.
$C_{16}H_8O_4N_2$ requires: C, 65.8%; H, 2.8%; N, 9.6%.

This suggests that this solid is a dinitrofluoranthene.

A repeat of this experiment on a 10g. scale, followed by direct recrystallisation of the crude solid without chromatographic purification, afforded 4-nitrofluoranthene (2g., 16.4%) M.P. 158.5-163° (uncorr.).

This experiment shows that with the nitration conditions specified above the main product is 4-nitrofluoranthene together with a very small amount of a high-melting solid which gave a good analysis for a dinitrofluoranthene.

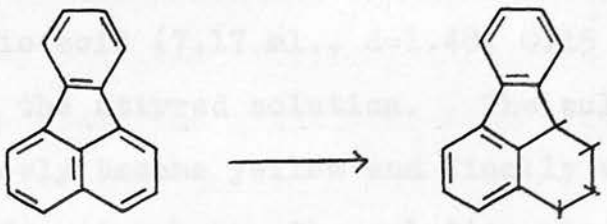
ATTEMPTED NITRATION OF 4-NITROFLUORANTHENE

1. 4-Nitrofluoranthene (1.64g.) in glacial acetic acid (60 ml.) was treated dropwise over a period of 20 minutes with fuming nitric acid (5 ml.), added at just below the boiling-point of the solution. The mixture was/

was kept as just below its boiling-point for a further hour and worked up as above. Removal of the chloroform followed by recrystallisation of the residue from benzene gave a yellowish-brown solid, M.P. 120-270° (1.45g.). Recrystallisation from benzene-acetic acid and then from benzene-chlorobenzene gave a yellow solid, M.P. 180-280°.

2. An experiment conducted as above omitting the further hour's heating, yielded only starting material, (M.P. and mixed M.P. 157-160°).

PREPARATION OF 1:2:3:4-TETRAHYDROFLUORANTHENE
Easton, Ph.D. Thesis, Edinburgh.



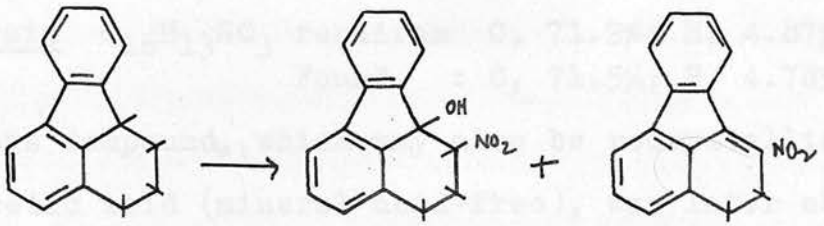
Fluoranthene (50g.) was dissolved in alcohol (1600 ml.) and 5% sodium amalgam (700g.) (cf. Fieser, Experiments in Organic Chemistry, p.330) added in portions over ¾ hour and the mixture refluxed overnight. The cold solution was neutralised with hydrochloric acid and poured into water (7 litres). The white solid, which was deposited on standing, was filtered washed and dried. Recrystallisation from alcohol (charcoal) gave colourless needles (41.84g.), M.P. 75-77°. A further quantity (1.55g.), M.P. 73·5-75.5°, from the filtrate brought the total yield to 85%.

(Lit./

(Lit. M.P. 75).

With 2:4:7-trinitrofluorenone an unstable derivative is formed which crystallises from alcohol in orange prisms which, however, dissociate on heating.

NITRATION OF 1:2:3:4-TETRAHYDROFLUORANTHENE



1:2:3:4-Tetrahydrofluoranthene (20.6g., 0.10 mols) was dissolved in glacial acetic acid (200 ml.), the solution heated to 80° (extended bath temperature) and fuming nitric acid (7.17 ml., d=1.48, 0.15 mols) added dropwise to the stirred solution. The colour of the solution slowly became yellow and finally very deep yellow. After one hour, the solution was cooled and poured into an ice-water mixture causing the precipitation of a pale yellow solid. This solid was filtered and dissolved in ether. The filtrate was extracted with ether and the combined extracts washed with aqueous sodium carbonate solution, then with water and finally dried over anhydrous sodium sulphate.

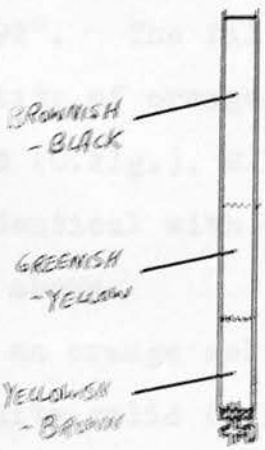
The orange-red ether solution was evaporated to small bulk under reduced pressure and benzene added to the resulting syrup. A white solid (6.06g.) crystallised and a further quantity (0.86g.) was obtained/

obtained by diluting the filtrate with light petroleum. The combined solids were washed with a 3:1 mixture of benzene and light petroleum. Recrystallisation of this solid from chlorobenzene gave large colourless octahedra, which sublimed on heating to similar octahedra, lost water and turned yellow near the melting-point and eventually melted at 192-3° with much frothing.

Analysis $C_{16}H_{13}NO_3$ requires C, 71.9%; H, 4.87%; N, 5.24%.
Found : C, 71.5%; H, 4.78%; N, 5.26%.

This compound, which may also be recrystallised from acetic acid (mineral acid-free), was later shown to be 2-nitro-1-hydroxy-1:2:3:4-tetrahydrofluoranthene.

The filtrate from this white solid was evaporated to small bulk but the resulting red syrup could not be crystallised. It was therefore dissolved in a 2:1 mixture of benzene and light petroleum, the solution chromatographed on a column of alumina (17" x 1") and the column developed with the same solvent mixture. The column took up zones (see diagram opposite) which were not distinct and no obvious banding could be observed. Fractions were therefore removed from the column arbitrarily as follows:-



Fraction I. Forerunnings + yellow solution (50ml.) giving orange-red syrup (4.95g.)

Fraction II. Yellow solution (100ml.) giving orange-red syrup (3.28g.)

Fraction/

Fraction III. Yellow solution (100ml.) giving yellow solid (0.65g.) + oil.

Fraction IV. Yellow solution (100ml.) giving yellow syrup (0.18g.)

Fraction V. Yellow solution (150ml.) giving yellow syrup (0.64g.)

The alumina was extracted with acetone to give a negligible amount of oil. Fraction I was triturated with methanol-ether to give an orange solid (2.70g.) while its filtrate deposited a low-melting white solid (0.07g.) which was probably tetrahydrofluoranthene. Fraction II was similarly triturated to give an orange solid (1.93g.) while its filtrate deposited a yellowish-red solid (0.11g.) which melted over a wide range up to 170°.

Both orange solids were amalgamated and re-crystallised from ethanol-ether to give orange elongated prisms (3.25g.), M.P. 90-92°. The filtrate, on standing, yielded a further quantity of orange solid (0.48g.) together with a white solid (0.21g.), M.P. 160-172° with frothing, which was identical with the colourless nitro-compound mentioned above.

Similarly Fraction III yielded an orange solid as above (0.65g.) together with a white solid (0.19g.) of indefinite M.P. up to 170°.

All filtrates were rechromatographed in benzene on a column of alumina (12" x 1") and the column developed as before to give three fractions:

Fraction/

Fraction B I. Semi-solid orange oil (1.65g.)
Fraction B II. Orange syrup (0.70g.)
Fraction BIII. Orange syrup (1.04g.)

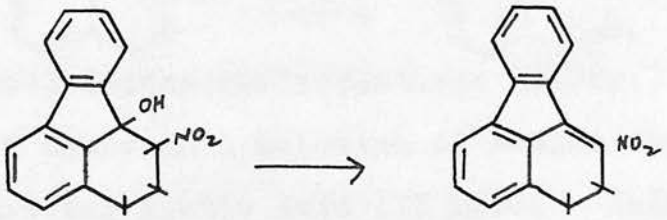
Only Fraction BI gave an orange solid (1.44g.) on the usual trituration procedure. All orange solids obtained were identical and later proved to be 2-nitro-3:4-dihydrofluoranthene. A portion recrystallised from ethanol for analysis had M.P. 92-94°. Elongated orange prisms.

Analysis $C_{16}H_{11}NO_2$ requires C, 76.7%; H, 4.4%; N, 5.6%.
Found :C, 76.3%; H, 4.4%; N, 6.1%.

From 20.6g. tetrahydrofluoranthene there was obtained 7.13g. white solid and 5.82g. orange solid representing a total yield of 50% on the basis of utilised tetrahydrofluoranthene.

An experiment carried out as above at 50° (external bath temperature) gave only 1:2:3:4-tetrahydrofluoranthene in good recovery.

DEHYDRATION OF 1-HYDROXY-2-NITRO-1:2:3:4-TETRAHYDRO-FLUORANTHENE

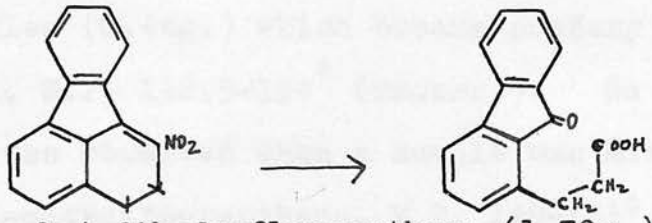


Pure 1-hydroxy-2-nitro-1:2:3:4-tetrahydrofluoranthene (4.8g.)/

(4.8g.) was dissolved in acetic acid (50 ml.) and conc. sulphuric (3 drops) added to the boiling solution. Immediately the acid reached the solution there was a colour change from almost colourless to orange. Boiling was continued for a further 10 minutes. The cooled solution was poured into ice-water whereupon a yellow solid was deposited. This was filtered, washed, dried and dissolved in methylated spirits. Charcoal was added and the solution was boiled and filtered hot. The cool solution deposited yellow crystals (1.65g.), M.P. 87.5-91°). Evaporation of the filtrate gave two further crops of yellow crystals (a) 0.60g., M.P. 88.5-91° and (b) 1.02g., M.P. 89-92°. Mixed M.P. with 2-nitro-3:4-dihydrofluoranthene showed no depression. Total yield = 3.27g. (73%).

The same dehydration can be accomplished with acetic anhydride as the solvent.

OXIDATION OF 2-NITRO-3:4-DIHYDROFLUORANTHENE



2-Nitro-3:4-dihydrofluoranthene (1.72g.) was boiled for 3 hours in a solution of sodium dichromate (10g.) in glacial acetic acid (75 ml.). Half of the acetic acid was distilled off and the residual liquid poured/

poured into dilute sulphuric acid. This acidic solution was extracted with benzene-ether and the yellow organic layer washed with water. Extraction of this organic layer with aqueous sodium carbonate solution afforded a pale yellow alkaline extract which on acidification gave a pale yellow acid. Extraction with ether followed by removal of the solvent left a greenish-yellow crystalline solid (0.27g.) which crystallised from a 2:1 mixture of benzene and light petroleum in yellow, irregular plates, M.P. 133.5-136°.

Analysis $C_{16}H_{12}O_3$ requires C, 76.2%; H, 4.8%.
Found : C, 75.5%; H, 4.7%.

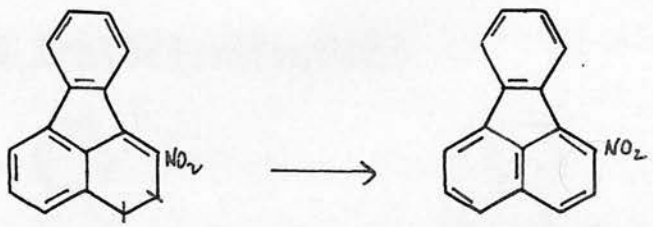
This acid proved to be β-1-fluorenonepropionic acid since a mixed M.P. with an authentic sample, M.P. 134.5-136°, obtained by the oxidation of tetrahydrofluoranthene (see p.122), was 134-8°.

The non-acidic material left in the original benzene-ether extract proved, on removal of the solvent, to be an orange solid (0.58g.). Recrystallisation from a 2:1 mixture of light petroleum and benzene gave long, orange needles (0.44g.) which became powdery on standing in solution, M.P. 148.5-154° (uncorr.). No M.P. depression was observed when a sample was mixed with a sample of 2-nitrofluoranthene, M.P. 149-151° (see next section).

Several oxidations were attempted with chromic anhydride in acetic acid but the compound was apparently destroyed. On one occasion a few crystals of 2-nitro-fluoranthene/

fluoranthene were obtained and on another, a trace of 4-nitrofluorenone-1-carboxylic acid (see p.108) was isolated.

CHLORANIL DEHYDROGENATION OF 2-NITRO-3:4-DIHYDRO-FLUORANTHENE.



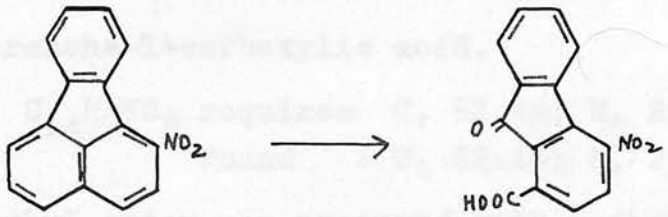
2-Nitro-3:4-dihydrofluoranthene (8.0g.) was boiled in sulphur-free xylene (120 ml.) with chloranil (16.0g.) for 23 hours. The solution was decanted from black solid and diluted with benzene. This solution was washed three times with 200 ml. portions of 5% caustic soda, once with 100 ml. 2N caustic soda and finally with water. The solution was dried over anhydrous sodium sulphate, the deep red solution evaporated to small bulk and light petroleum (B.P. 80-100°) added. This solution was boiled with charcoal and filtered hot. On cooling a deep yellow solid (3.92g.), M.P. 112-144°, crystallised while the filtrate gave a further quantity of yellow solid (1.33g.), M.P. 134-149°. The combined solids crystallised from glacial acetic acid in deep, yellow elongated prisms (4.40g.) which, on standing or on filtration became powdery, M.P. 148-150°. The filtrate gave a further quantity (0.35g.) M.P./

M.P. 145.5-149.5°. Yield 59%. This solid later proved to be 2-nitrofluoranthene.

A sample recrystallised from glacial acetic acid for analysis had M.P. 151-3° with sublimation.

Analysis $C_{16}H_9NO_2$ requires C, 77.7%; H, 3.6%; N, 5.7%.
Found : C, 77.9%; H, 3.5%; N, 5.7%.

OXIDATION OF 2-NITROFLUORANTHENE



2-Nitrofluoranthene (2.0g.) was dissolved in glacial acetic acid (150 ml.) and boiled for 20 hours with sodium dichromate (40.0g.). The resulting solution was evaporated to half volume, cooled, and poured into dilute sulphuric acid. The resulting yellow precipitate was extracted with chloroform. The chloroform layer was extracted with 5% aqueous potassium carbonate, but the formation of the insoluble potassium salt proved troublesome. Aqueous sodium carbonate was little better.

The salts were filtered off and the alkaline layer acidified to give a yellow solid. Hydrolysis of the mixture of sodium and potassium salts was achieved by boiling under reflux with a mixture of hydrochloric and acetic acids. Dilution of this hydrolysing/

hydrolysing mixture yielded the acid. This was combined with the acid from the alkaline layer, dissolved in chloroform, and the solution filtered. After drying over anhydrous sodium sulphate, removal of the chloroform left a yellow solid which crystallised from glacial acetic acid in light yellow elongated prisms (0.96g., 44%), M.P. 209-15° (uncorr.).

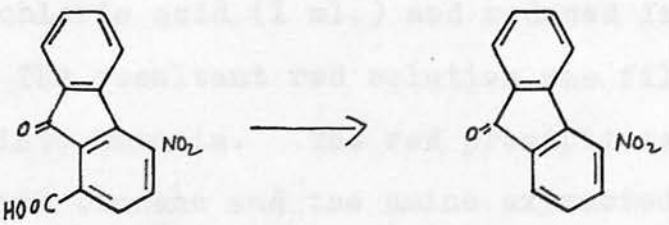
A portion recrystallised for analysis from glacial acetic acid had M.P. 213-4°. This solid proved to be 4-nitrofluorenone-1-carboxylic acid.

Analysis $C_{14}H_7NO_5$ requires C, 62.4%; H, 2.6%; N, 5.2%.
Found : C, 62.4%; H, 2.3%; N, 5.1%.

The methyl ester was prepared with methanol and conc. sulphuric acid in the usual way (see p.63) and the neutral product recrystallised from methanol. The pale yellow hexagonal prisms had M.P. 163.5-165°.

Analysis $C_{15}H_9NO_5$ requires C, 63.6%; H, 3.2%; N, 5.0%.
Found : C, 63.3%; H, 2.8%; N, 4.9%.

DECARBOXYLATION OF 4-NITROFLUORENONE-1-CARBOXYLIC ACID

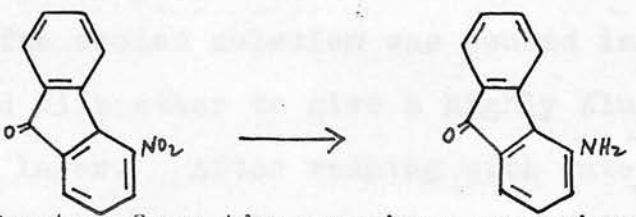


4-Nitrofluorenone-1-carboxylic acid (0.25g.) was heated with a trace of copper bronze in quinoline (10 ml.) in an oil bath. At 180° evolution of carbon dioxide began and/

and after one hour had ceased. The reaction was worked up as before (see p. 63) and the neutral product in benzene chromatographed on a column of alumina (6" x ½"). A pale yellow band was eluted with benzene and the benzene replaced by light petroleum. The pale yellow crystalline precipitate (65 mg.) melted at 165-173°. Recrystallisation from ethanol gave pale yellow needles (25 mg.), M.P. 173.5-175° with marked sublimation. A mixed melting-point with an authentic sample of 4-nitrofluorenone, M.P. 174-5°, was 174-5°.

Analysis $C_{13}H_7NO_3$ requires C, 69.3%; H, 3.1%; N, 6.2%.
Found : C, 69.0%; H, 2.8%; N, 6.1%.

REDUCTION OF 4-NITROFLUORENONE

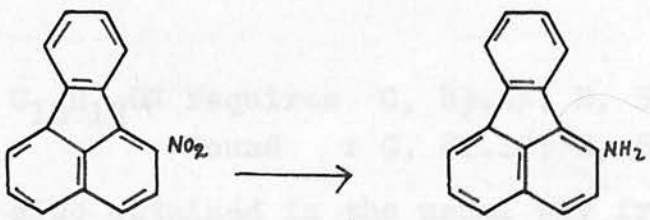


All filtrates from the previous experiment were combined and the solvent replaced by ethanol (10 ml.). The pale yellow solution was refluxed for 2 hours with conc. hydrochloric acid (1 ml.) and reduced iron powder (0.15g.). The resultant red solution was filtered hot and poured into ammonia. The red precipitate was extracted with benzene and the amine extracted from the benzene layer with dilute hydrochloric acid. The acid extract with ammonia gave a red precipitate which was extracted with benzene. The product from the benzene/

benzene layer crystallised from 50% aqueous ethanol in red glistening plates, M.P. 137-9° (Lit. M.P. 138°). This product was 4-aminofluorenone.

Analysis $C_{13}H_9ON$ requires C, 80.0%; H, 4.7%; N, 7.2%.
Found : C, 78.9%; H, 4.7%; N, 6.5%.

PREPARATION OF 2-AMINOFLUORANTHENE



2-Nitrofluoranthene (1.60g.), dissolved in ethanol (150 ml.), was boiled under reflux for 2 hours with reduced iron powder (2.0g.) and conc. hydrochloric acid (10 ml.). The cooled solution was poured into water and extracted with ether to give a highly fluorescent (blue) ether layer. After washing with water and drying over anhydrous sodium sulphate removal of solvent left a yellow solid which fluoresced strongly in ultra-violet light. Recrystallisation from 70% aqueous ethanol gave 2-aminofluoranthene as greenish-yellow needles (1.095g., 78%), M.P. 130-4°. Another experiment without crystallisation gave an 86.9% yield of crude amine.

A portion, recrystallised from aqueous ethanol for analysis, melted at 134-6° (Lit. M.P. 133-4°).

Analysis/

Analysis $C_{16}H_{11}N$ requires C, 88.6%; H, 5.1%.
Found : C, 89.0%; H, 5.3%.

Its acetyl-compound was prepared quantitatively by dissolving the amine in ethanol and adding acetic anhydride to the boiling solution. The acetyl- compound crystallised from the boiling solution in almost colourless elongated prisms M.P. 251-4°. A crystallisation from glacial acetic acid raised the melting-point to 253.5-255°.

Analysis $C_{18}H_{13}ON$ requires C, 83.4%; H, 5.0%; N, 5.4% .
Found : C, 82.1%; H, 5.2%; N, 5.4% .

It was also obtained in the usual way from acetic anhydride and pyridine.

The benzoyl- compound, M.P. 237-8°, was prepared in pyridine with benzoyl chloride and separated from acetic acid in pale yellow needles.

Analysis $C_{23}H_{15}ON$ requires N, 4.4% .
Found : N, 5.3% .

The 2:4:7-trinitrofluorenone complex separated in dark brown needles from benzene-ethanol, M.P. 250-2° (Lit. M.P. 254-5° uncorr.).

REDUCTION OF 2:NITRO-3:4-DIHYDROFLUORANTHENE

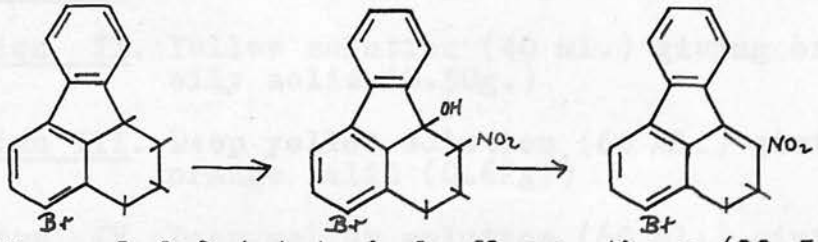
Pure 2:nitro-3:4-dihydrofluoranthene (0.43g.) was boiled for 90 minutes in ethanol (30 ml.) with reduced iron powder (0.60g.) and concentrated hydrochloric acid (5 ml.). The solution was filtered hot, cooled and/

and poured into water. Extraction of the aqueous solution with ether gave a highly fluorescent (green) ether layer which was washed with successive portions of dilute hydrochloric acid, aqueous sodium hydroxide solution and finally water. Removal of the ether left a yellow oil (0.25g.) which could not be crystallised.

PREPARATION OF 5-BROMO-1:2:3:4-TETRAHYDROFLUORANTHENE

This compound was prepared in 57% yield as specified by von Braun and Manz (Ann., 1932, 486, 170). M.P. 133-4° (Lit. M.P. 135°).

NITRATION OF 5-BROMO-1:2:3:4-TETRAHYDROFLUORANTHENE



5-Bromo-1:2:3:4-tetrahydrofluoranthene (11.5g.) was dissolved in glacial acetic acid (115 ml.) at an external bath temperature of 85° and fuming nitric acid (2.90 ml., d=1.48) added to the stirred solution. After one hour the solution was poured into water and worked up in the manner detailed for the nitration of 1:2:3:4-tetrahydrofluoranthene (see p. 101). On dilution of the benzene extract with light petroleum three crops of white solid, a total weight of 4.88g., were obtained.

A/

A portion of this solid was recrystallised for analysis from acetic acid and formed colourless hexagonal prisms, M.P. 163-4°. This solid, from its analysis and its easy dehydration, is 5-bromo-2-nitro-1-hydroxy-1:2:3:4-tetrahydrofluoranthene.

Analysis $C_{16}H_{12}O_3NBr$ requires C,55.5%; H,3.5%; N,4.1%; Br,23.1% .
Found : C,55.8%; H,3.5%; N,3.8%; Br,22.9% .

The red filtrate, remaining after removalof the white solid, was chromatographed on a column of alumina (12" x 1") and the column developed with benzene. There was no banding on the column, a uniform orange band being adsorbed. Fractions were therefore removed from the column arbitrarily. Details of these fractions are as follows:-

Fraction I. Fore-runnings giving white solid (0.42g.)

Fraction II. Yellow solution (40 ml.) giving orange oily solid (0.50g.)

Fraction III. Deep yellow solution (60 ml.) giving orange solid (0.62g.)

Fraction IV. Deep yellow solution (60 ml.) giving orange solid (0.39g.)

Fraction V. Deep yellow solution (100 ml.) giving orange solid (0.46g.)

Fraction VI. Deep yellow solution (400 ml.) giving orange solid (0.60g.)

} 2.07g.

Finally, elution of the alumina gave a red syrup (1.25g.) which was not investigated further.

All of the above fractions except Fraction II, was recrystallised with the following results:-

Fraction I./

Fraction I. From alcohol-acetic acid, M.P. 88-98° probably impure starting material.

Fraction III. From benzene-acetic acid, M.P. 161-175° raised to 180.5-183° after a further recrystallisation from benzene-ethylacetate (0.16g.).

Fraction IV. From benzene-acetic acid, M.P. 163-183°, raised to 173-8° after a further recrystallisation from benzene-light petroleum.(0.11g.).

Fraction V. Recrystallised benzene-light petroleum, M.P. 174-181° (0.17g.)

Fraction VI. Recrystallised benzene-light petroleum, M.P. 175-9° (0.48g.)

A portion of the solid, M.P. 180.5-183°, from fraction III was crystallised from benzene-ethyl acetate in orange needles, M.P. 181-3° with sublimation.

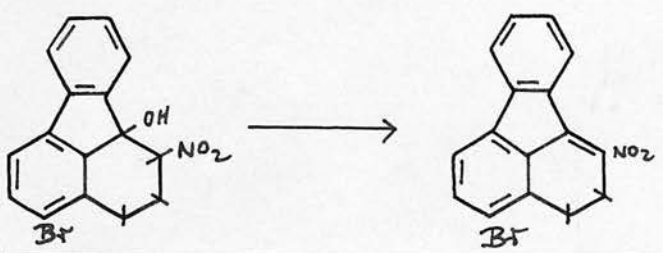
Analysis $C_{16}H_{10}O_2NBr$ requires Br, 24.4%; N, 4.3%.

Found : Br, 24.9%; N, 4.4%.

This solid was identical with that obtained on the dehydration of the colourless solid, M.P. 163-4°, and is 5-bromo-2-nitro-3:4-dihydrofluoranthene.

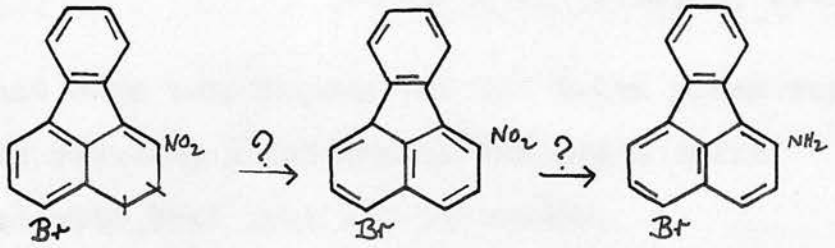
From 11.5g. starting material there was obtained 4.88g. white solid and 2.07g. crude orange solid representing a total yield of 48.5% based on the bromotetrahydrofluoranthene utilised.

DEHYDRATION OF 5-BROMO-2-NITRO-1-HYDROXY-1:2:3:4-TETRAHYDROFLUORANTHENE



Pure 5-bromo-2-nitro-1-hydroxy-1:2:3:4-tetrahydrofluoranthene (1.58g.), dissolved in acetic acid (25 ml.), was boiled and conc. sulphuric acid (2 drops) added to the boiling solution. After boiling for a further 15 minutes the dark orange solution was poured into an ice-water mixture. The resulting yellow precipitate was filtered, washed and dried. The crude solid (1.225g., 82%) crystallised from benzene-acetic acid in orange needles (1.05g.), M.P. 181-4° undepressed when mixed with a sample of the product (181-3°) obtained in the previous experiment.

PARTIAL DEHYDROGENATION OF 5-BROMO-2-NITRO-3:4-DIHYDROFLUORANTHENE



Pure dihydro-compound (0.15g.) was boiled in nitrobenzene (15 ml.) with chloranil (0.12g.: theoretical weight for the removal of 2 hydrogen atoms) for 48 hours. The nitrobenzene was removed by steam-distillation and the product dissolved in benzene. The benzene layer was washed once with 10% caustic soda/

soda, twice with dilute caustic soda, then with water and finally dried over anhydrous sodium sulphate. The benzene solution was evaporated to small bulk (10 ml.) and chromatographed on a column of alumina (6" x ½"). The bright yellow band was developed with benzene and the eluate contained 0.125g. orange crystalline solid which on recrystallisation from benzene-acetic acid formed orange needles which melted at 153-163°. A crystallisation from ethyl acetate and a final recrystallisation from acetic acid raised the melting-point to 165-8°. This product, whose colour was much lighter than that of the starting dihydro-compound, was apparently a mixture with the required 5-bromo-2-nitrofluoranthene in predominance.

Analysis $C_{16}H_8O_2NBr$ requires C, 58.9%; H, 2.5%; N, 4.3%; Br, 24.5%.

Found : C, 58.0%; H, 2.6%; N, 4.3%; Br, 24.3%.

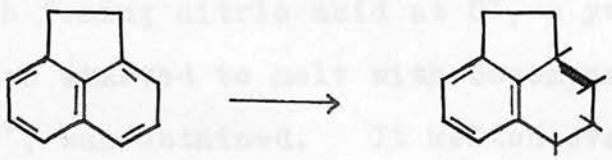
That some dehydrogenation had taken place was shown by reducing a portion of the above solid combined with that from its filtrates.

Reduction in ethanol (50 ml.) with reduced iron powder (0.20g.) and conc. hydrochloric acid for 90 minutes followed by the usual working-up (see p. 110) gave a pale yellow amine hydrochloride which was decomposed by shaking with benzene and caustic soda. The benzene layer, which fluoresced bluish-green in ultra-violet light, contained a solid which crystallised from/

from light petroleum in elongated greenish-yellow needles, M.P. 160-161.5°. There was not enough for analysis. (The amine is probably 2-amino-5-bromofluoranthene).

Chloranil dehydrogenation in sulphur-free xylene for 24 hours gave back starting material while the use of palladium-charcoal catalyst alone at 300°, or in α-methylnapthalene, furnished intractable oils.

PREPARATION OF 1a:1:2:3-TETRAHYDROACENAPTHALENE



This compound was prepared in 67% yield as described by Fleischer and Seifert (Ann., 1921, 422, 303). Tetrahydroacenapthalene is a pale yellow liquid which partially crystallised when kept in a refrigerator over a period of months.

ATTEMPTED NITRATION OF 1a:1:2:3-TETRAHYDROACENAPTHALENE

When nitration was attempted using the conditions specified in the nitration of tetrahydrofluoranthene (see p.101) extensive decomposition resulted. The tetrahydroacenapthalene was recovered in much reduced yield together with a black tar.

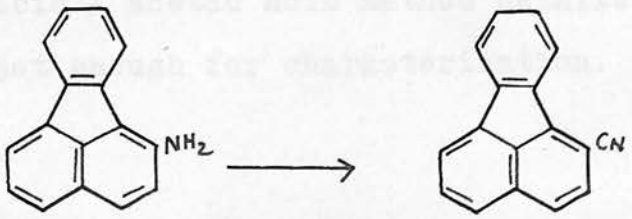
ATTEMPTED NITRATIONS OF 1:2:3:4-TETRAHYDROFLUORANTHENE

(a) Nitration at 0° with a mixture of sulphuric and nitric acids gave a low recovery of starting material together with much oxidised material in the form of tar.

(b) When tetrahydrofluoranthene in sulphuric acid at 0° was treated with powdered potassium nitrate, added in small portions, starting material was recovered in very low yield together with a small amount of a bright yellow solid which melted over the range 222-72°.

(c) With fuming nitric acid at 0°, a yellow solid which started to melt with decomposition at 120°, was obtained. It melted over a wide range.

ATTEMPTED PREPARATION OF 2-CYANOFLUORANTHENE



2-Aminofluoranthene (0.50g.) was stirred in conc. hydrochloric acid (15 ml.) at 5° and 30% sodium nitrite solution added until excess nitrous acid was present. A deep orange suspension, which gave a violet colour with alkaline β-naphthol, resulted. The suspension

was/

was poured into a well-stirred mixture of benzene and aqueous potassium cuprocyanide solution stirred below 5°. After addition stirring was continued for a further 30 minutes and the solution then heated to 65°. Separation of the highly fluorescent (blue) benzene layer was followed by chromatography of the dried benzene solution on alumina (8" x ½"). Elution with benzene gave a pale yellow solid (0.175g.) which crystallised from light petroleum in thin, elongated prisms which fluoresced yellow in ultra-violet light, M.P. 102-5° with softening at 91°. Mixed M.P. with fluoranthene was 70°.

Analysis $C_{17}H_9N$ requires N, 6.5%.

Found : N, 1.5%.

This was probably a mixture of the desired 2-cyanofluoranthene and fluoranthene. The presence of the cyano-compound was indicated by the isolation of a very small quantity of an acid on hydrolysis with the sulphuric acid / acetic acid method detailed on p.75. There was not enough for characterisation.

ABSORPTION SPECTRA

All spectra were determined with a Hilger Barfit Medium Spectrograph, the actual spectra being recorded by photographic methods.

The/

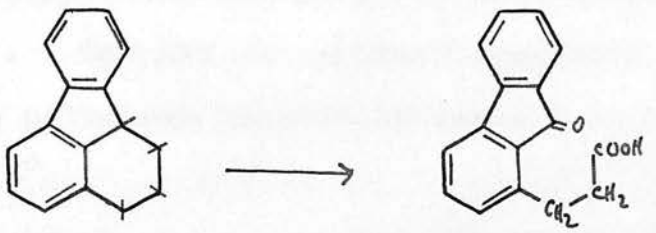
The solvent used was cyclohexane which was specially prepared by the makers for spectrographic measurements. No further purification was carried out.

The sample to be examined was weighed in a small beaker (10 ml.), covered with cyclohexane and warmed carefully on a hot plate to achieve solution. This solution was then carefully transferred to a 50 ml. graduated flask and made up to the mark. Before using, the solution was thoroughly shaken.

In all cases, dilution of the original standard solution was required and was achieved by transferring 5 ml. of the solution to a 10 ml. graduated flask and making the solution up to the mark.

SECTION C EXPERIMENTAL

PREPARATION OF β-1-FLUORENONEPROPIONIC ACID



1:2:3:4-Tetrahydrofluoranthene (20g.) (see p.100) was dissolved in acetic acid (120ml.) and the resulting solution stirred at 60°. Sodium dichromate (50g.) in acetic acid (280 ml.) was added dropwise to the stirred solution and the mixture stirred at 60° for 5 hours. The resultant, dark green solution was poured into water and the yellow precipitate allowed to settle. This precipitate and its solution were extracted with 3 separate portions (250 ml.) of ether. After washing with water acidic material was extracted from the ether layer with aqueous sodium carbonate, acidification of this extract yielding the crude propionic acid. This acid was extracted with a chloroform-ether mixture and after washing with water the chloroform-ether layer was dried over anhydrous sodium sulphate. Removal of solvent left a yellow solid which crystallised from 70 ml. 70% aqueous acetic acid (charcoal) in glistening yellow plates (12.83g.), M.P. 132-5°. A second crop, obtained from the filtrate, had M.P. 129-133°. The total yield of fairly pure acid (59.3%). The pure acid/

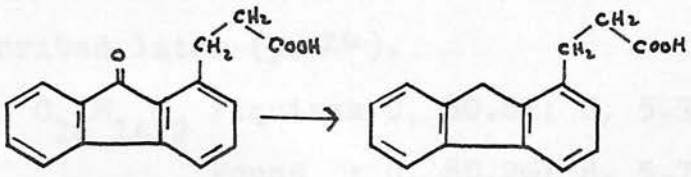
acid melted at 138-9° (Lit. M.P. 137-8°) after recrystallisation from aqueous acetic acid.

Its methyl ester was prepared in the usual way (see p.63). The neutral product separated from an ether-light petroleum mixture in massive yellow prisms M.P. 63-64.5°.

Analysis $C_{17}H_{14}O_3$ requires C, 76.7%; H, 5.4%.
Found : C, 76.9%; H, 5.3%.

REDUCTION EXPERIMENTS ON β-1-FLUORENONEPROPIONIC ACID

1. Clemmensen reduction



β -1-Fluorenonepropionic acid (5g.) was boiled under reflux for 24 hours with 5% amalgamated zinc (20g.) in a solvent mixture consisting of toluene (60 ml.), conc. hydrochloric acid (40 ml.), glacial acetic acid (15 ml.) and water (80 ml.). The yellow colour of the original toluene layer slowly disappeared and after 24 hours was practically colourless. A white solid had deposited at the interface between the toluene and acid layers. This solid was filtered, dissolved in toluene and its solution added to the main toluene layer. The acid layer was diluted with water and extracted with ether, the ether extract being added to the combined toluene/

toluene solutions. This toluene-ether solution was shaken with aqueous sodium carbonate solution and the alkaline extract yielded a white acid on acidification with hydrochloric acid. This acid crystallised from benzene-acetic acid in colourless plates (1.76g., 37.3%), M.P. 189-192.5°. Its filtrate gave a pale yellow solid which melted over a considerable range up to 190°.

A portion recrystallised from benzene-light petroleum had M.P. 196-8° and sublimed to colourless square plates on heating. This acid is identical with the acid, M.P. 198.5-199.5°, obtained by the 2-stage process described later (p.126).

Analysis $C_{16}H_{14}O_2$ requires C, 80.6%; H, 5.9%.
Found : C, 80.2%; H, 5.7%.

Its methyl ester was prepared in the usual way (see p.63). The neutral product formed large colourless plates from light petroleum (B.P. 40-60°), M.P. 77-8°.

Analysis $C_{17}H_{16}O_2$ requires C, 80.9%; H, 6.4%.
Found : C, 80.7%; H, 6.5%.

2. Wolff-Kischner reduction

cf. Orchin and Bergmann, J.A.C.S., 1949, 71, 1112.

β-1-Fluorenonepropionic acid (2.5g.) and sodium hydroxide (2g.) were dissolved in trimethylene glycol (25 ml.). Addition of 90% hydrazine hydrate (2 ml.) was followed by an immediate brisk effervescence. The resultant solution was boiled under reflux for 3 hours, the temperature of the boiling contents being 165°/

165°. The condenser was removed and the temperature of the boiling contents slowly raised to 205°. The condenser was then replaced and boiling continued for a further 2½ hours.

The cooled solution was poured into a mixture of ice and conc. hydrochloric acid and the resulting white precipitate filtered, washed and dried. Recrystallisation of this solid from acetic acid gave colourless plates, M.P. 281-3°. Reduction of the volume of the filtrate gave a further quantity (1.38g.) of white solid which melted mainly at 180° with a portion remaining solid until 269°. A further recrystallisation of this solid gave solid of M.P. 196-198.5° with some crystals melting at 245°. The sublimation to colourless square plates indicated the presence of the required fluorene acid. (Crude yield, 55%).

The acid, M.P. 281-3° was analysed.

Analysis $C_{32}H_{26}O_4$ requires C, 81.0%; H, 5.5%.
Found : C, 79.7%; H, 5.5%.

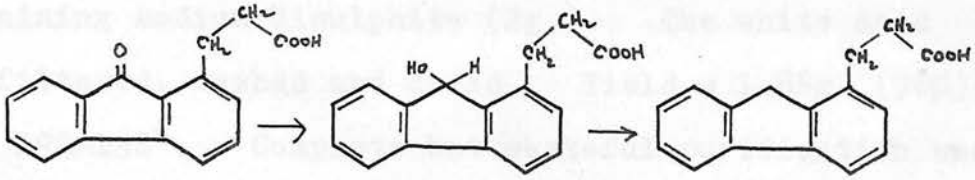
This acid is probably meso-bis-9:9'-(fluorene-1-β-propionic acid).

Its dimethyl ester was prepared in the usual manner (p. 63) and crystallised from methanol in colourless prisms, M.P. 109-110.5°, which fluoresced blue in ultra-violet light.

Analysis $C_{34}H_{30}O_4$ requires C, 81.3%; H, 6.0%.
Found : C, 80.7%; H, 6.0%.

3. Two-stage reduction

cf. Bachmann and Sheehan, J.A.C.S., 1940, 62, 2687.



(a). Preparation of β-1-fluorenolpropionic acid.

β-1-fluorenonepropionic acid (2.43g.) was dissolved in aqueous sodium hydroxide (3g. in 40 ml. water) and the solution boiled for 4 hours with zinc dust (3g.). The addition of toluene (0.5 ml.) prevented undue frothing. The toluene was boiled off and the solution filtered hot. The pale yellow filtrate, on careful acidification with conc. hydrochloric acid, yielded a white flocculent precipitate which was filtered, washed and dissolved in aqueous sodium carbonate solution, the alkaline solution being filtered and acidified. The resulting cream-coloured precipitate (2.26g.) melted at 164-8° (Crude yield 92%). One recrystallisation from aqueous methanol gave β-1-fluorenolpropionic acid as colourless prisms, M.P. 169-170°. (Pure yield, 83%).

Analysis $C_{16}H_{14}O_3$ requires C, 75.5%; H, 5.6%.
Found : C, 75.3%; H, 5.5%.

(b). Preparation of β-1-fluorenepropionic acid.

β-1-Fluorenolpropionic acid (2.03g.) was dissolved in a mixture of acetic acid (60 ml.) and water (6 ml.) and the solution boiled under reflux for 3 hours with red/

red phosphorus (2g.) and iodine (2g.). The solution was filtered hot and poured into water (500 ml.) containing sodium bisulphite (2g.). The white acid was filtered, washed and dried. Yield = 1.86g. (98%), M.P. 190-196°. Complete but wasteful purification was obtained by recrystallisation from benzene containing a few drops of acetic acid. Pure yield = 1.32g. (69%), M.P. 198.5-199.5° undepressed when mixed with the acid obtained from the Clemmensen reduction (mixed M.P.).

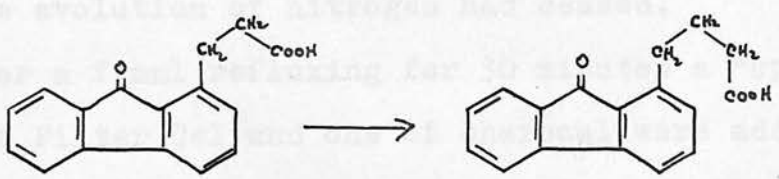
PREPARATION OF DRY DIAZOMETHANE

cf. Arndt, Organic Syntheses, Vol. 15, 3 (1935).

Powdered nitrosomethylurea was added in portions to a mixture of 40% aqueous potassium hydroxide solution and ether cooled to 5°. The diazomethane was distilled over into ether. The yellow ether solution was dried for 4 hours over caustic potash pellets and finally for 30 minutes over clean sodium wire just before use in the Arndt-Eistert reaction.

ARNDT-EISTERT REACTION ON β-1-FLUORENONEPROPIONIC ACID

cf. Bachmann and Sheehan, loc. cit.



β-1-Fluorenonepropionic acid (6g.) was suspended in anhydrous ether (100 ml.) containing dry pyridine (1 drop) and/

and thionyl chloride (2.54 ml.) was added to the suspension, with swirling, at room temperature. The solution, protected from moisture by a calcium chloride tube, was swirled periodically over a period of 3 hours.

Solvent was removed at the water-pump at room temperature and excess thionyl chloride removed by co-distillation with benzene at 40° in vacuo, 2 successive portions (25 ml.) being used.

The acid chloride, an orange oil, was dissolved in dry ether (50 ml.) and this solution added dropwise to a dry ether solution (250 ml.) of diazomethane (derived from 18g. nitrosomethylurea) stirred at -5° in an ice-salt bath. Overnight a yellow crystalline solid separated.

The ether was removed under reduced pressure and the crystalline diazoketone dissolved in dry methanol (150 ml.). This solution was added to a suspension of dry silver oxide (0.5g.) in anhydrous methanol (50 ml.) which had been boiled previously to obtain a silver mirror. Immediate evolution of nitrogen occurred. After 30 minutes, a further 2g. silver oxide was added in 0.5g. portions at intervals of 30 minutes. At the end of that time evolution of nitrogen had ceased.

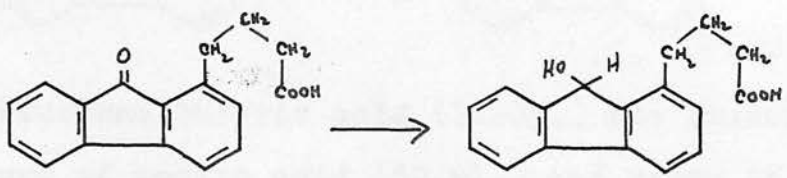
After a final refluxing for 30 minutes a "spatula-point" of Filter Cel and one of charcoal were added and the solution filtered hot. The resulting yellow solution was evaporated to 100 ml. and the ester hydrolysed/

hydrolysed by refluxing for 2 hours with 4% aq. sodium hydroxide solution (12 ml.). The resulting dark brown solution was boiled with charcoal, filtered hot and the methanol removed under reduced pressure at 40°. The residual dark brown oily emulsion was dissolved in water (charcoal) and the solution boiled, hot-filtered, cooled and acidified. A yellowish oil was deposited which solidified on scratching. After filtering, washing and drying the resultant yellow acid (5.40g., 85%) melted at 161-4°. One recrystallisation from dilute acetic acid raised the melting-point to 168-169.5°. (4.80g., 76%). γ-1-Fluorenonebutyric acid crystallises in yellow prisms.

Analysis $C_{17}H_{14}O_3$ requires C, 76.7%; H, 5.4%.
Found : C, 76.0%; H, 5.4%.

PREPARATION OF γ-1-FLUORENOLBUTYRIC ACID

cf. Bachmann and Sheehan, loc. cit.



γ-1-Fluorenonebutyric acid (2.05g.) was dissolved in water (30 ml.) containing sodium hydroxide (2.5g.) and the solution boiled under reflux for 4 hours with zinc dust (2g.) and toluene (1 ml.). The toluene was boiled off, the solution filtered hot and the pale yellow filtrate acidified to give a cream solid which was/

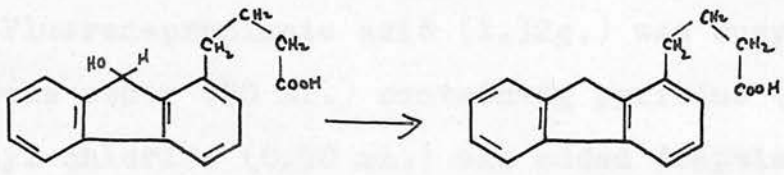
was filtered, washed and dissolved in aqueous sodium carbonate solution. The alkaline solution was boiled with charcoal, filtered hot, cooled and acidified. The acid (1.52g., 74%) melted at 131-7°. The acid was dissolved in acetone (charcoal) and filtered. Removal of the acetone followed by recrystallisation from benzene gave γ-1-fluorenolbutyric acid as colourless needles, M.P. 137-9°. Pure yield 63.9%.

A portion recrystallised from benzene for analysis melted at 139.5-141.5°.

Analysis $C_{17}H_{16}O_3$ requires C, 76.1%; H, 6.0%.
Found : C, 76.3%; H, 6.0%.

PREPARATION OF γ-1-FLUORENEBUTYRIC ACID

cf. Bachmann and Sheehan, loc. cit.



γ-1-Fluorenolbutyric acid (1.22g.) was dissolved in a mixture of acetic acid (60 ml.) and water (6 ml.) and the solution boiled under reflux for 2½ hours with red phosphorus (2g.) and iodine (2g.). The hot solution was filtered (Filter Cel) and poured into water (400 ml.) containing sodium bisulphite (3g.). The resultant crystalline solid (1.08g., 94%) was filtered washed and dried. M.P. 141-4°.

γ-1-Fluorenebutyric/

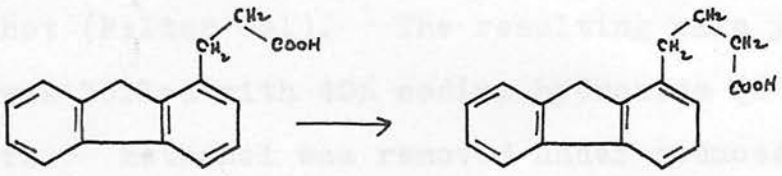
γ-1-Fluorenebutyric acid forms colourless glistening plates from aqueous acetic acid, M.P. 150.5-151°.

Analysis $C_{17}H_{16}O_2$ requires C, 80.9%; H, 6.4%.
Found : C, 80.3%; H, 6.3%.

This acid was also prepared directly from γ-1-fluorenonebutyric acid in 72% yield without purification of the intermediate fluorenol acid.

ARNDT-EISTERT REACTION ON β-1-FLUORENEPROPIONIC ACID

cf. Bachmann and Sheehan, loc.cit.



β-1-Fluorenepropionic acid (1.32g.) was suspended in anhydrous ether (50 ml.) containing pyridine (2 drops) and thionyl chloride (0.90 ml.) was added dropwise with swirling to the suspension at room temperature. After periodical swirling over a period of 90 minutes ether was removed at the water pump and excess thionyl chloride removed by co-distillation with 3 successive portions (15 ml. each) of benzene at 40°.

The colourless crystalline acid chloride was dissolved in anhydrous ether (50 ml.) and the solution added a stirred, dry solution of diazomethane (derived from/

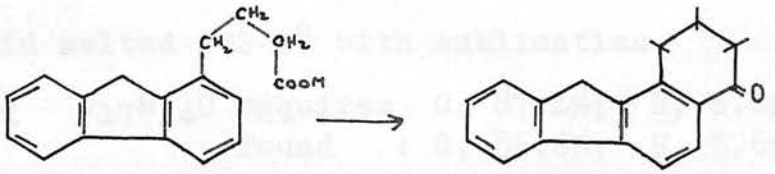
from 6g. nitrosomethylurea) in dry ether (250 ml.) cooled to -5°.

After standing overnight removal of ether left the pale yellow crystalline diazoketone which was dissolved in dry methanol (30 ml.) and the solution added to a suspension of dry silver oxide (0.25g.) in dry methanol (20 ml.) which had been boiled previously to obtain a silver mirror. A further quantity of silver oxide (0.75g.) was added in portions (0.25g.) at intervals of 30 minutes. After the addition of the final portion the solution was boiled under reflux for one hour.

The suspension was boiled with charcoal and filtered hot (Filter Cel). The resulting pale yellow solution was boiled with 40% sodium hydroxide (6 ml.) for 2 hours. Methanol was removed under reduced pressure and the resulting sodium salt dissolved in water. This alkaline solution was boiled with charcoal, filtered hot, cooled and acidified.

The white flocculent acid (0.939g., 67%), M.P. 140-145°, crystallised from aqueous acetic acid in colourless glistening plates (0.55g., 39%), M.P. 149-52°. The filtrate from this crystalline solid yielded a further quantity (0.165g.) of less pure material, M.P. 140-5°. Mixed M.P. of this acid with that obtained in the above 2- stage process was 150-151°.

PREPARATION OF 4-KETO-1':2':3':4'-TETRAHYDRO-1:2-BENZFLUORENE



γ-1-Fluorenebutyric acid (1.01g.) was suspended in dry ether (50 ml.) containing pyridine (1 drop) and thionyl chloride (0.70 ml.) was added dropwise to the solution at room temperature.

The acid chloride, a colourless oil, was isolated in the usual manner (see p.128) and dissolved in dry benzene (75 ml.). This solution was added dropwise to a stirred suspension of powdered aluminium chloride (1.35g.) in dry benzene (100 ml.) at room temperature. The solution assumed a blue fluorescence and slowly darkened. The solution was stirred at room temperature for one hour and then boiled under reflux for 4 hours during which time there was copious evolution of hydrogen chloride. After standing overnight the solution was poured into conc. hydrochloric acid containing ice. The benzene layer was separated, washed twice with aqueous sodium carbonate solution (no acid recovered on acidification) and finally with water. The dried solvent (Na_2SO_4) gave a tan solid which was dissolved in ethanol-acetone and this solution was boiled with charcoal and filtered. Evaporation of the solution/

solution to low bulk caused the crystallisation of colourless glistening plates (0.715g., 76%), M.P. 202-202.5°. A sample recrystallised for analysis from acetic acid melted 202-3° with sublimation.

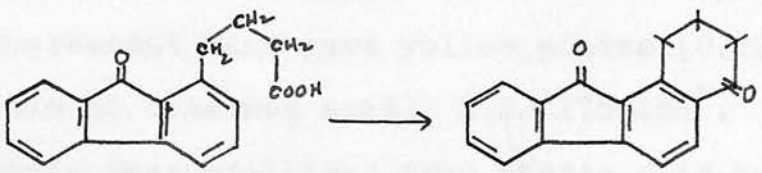
Analysis $C_{17}H_{14}O$ requires C, 87.1%; H, 6.0%.
Found : C, 86.6%; H, 5.8%.

The ketone gives a bright yellow colouration with conc. sulphuric acid. Its 2:4-dinitrophenylhydrazone was prepared as described in "Qualitative Organic Chemistry" (Campbell). It crystallised from tetralin-acetic acid in scarlet needles, M.P. 307° (dec.)

Analysis $C_{23}H_{18}N_4O_4$ requires N, 13.5%.
Found : N, 13.8%.

This ketone was also obtained when nitrobenzene was used for the ring-closure. From 110 mg. of starting acid 28 mg. of ketone, M.P. 203-4°, were obtained (Mixed M.P. with above ketone 202-3°). The ketone-fluoresces purple in ultra-violet light.

PREPARATION OF 4'-KETO-1':2':3':4'-TETRAHYDRO-1:2-BENZFLUORENONE



y-1-Fluorenonebutyric acid (1.00g.) was suspended in a mixture of anhydrous ether (25 ml.) and anhydrous benzene/

benzene (10 ml.) containing pyridine (2 drops). Thionyl chloride (0.53 ml.) was added to the suspension and the mixture allowed to stand at room temperature with occasional swirling for 6 hours. The acid chloride, a dark brown oil, was isolated as described previously.

This acid chloride in dry nitrobenzene (20 ml.) was treated with a solution of aluminium chloride (1.20g.) in dry nitrobenzene (20 ml.) at room temperature. This solution was kept in a refrigerator for 12 hours and then poured into a mixture of ice and conc. hydrochloric acid. After standing for one hour, the nitrobenzene was removed by steam-distillation and the oily, dark brown residue extracted with benzene. The benzene extract was shaken with two successive portions (50 ml.) of aqueous sodium carbonate solution, this alkaline extract, on acidification, yielding unreacted acid (0.55g.).

The neutral benzene layer was washed free of alkali and dried over anhydrous sodium sulphate. Removal of solvent left a dark brown crystalline solid which was chromatographed in benzene (15 ml.) on a column of alumina (10" x ½"). Elution of a greenish-yellow fluorescent band gave yellow plates (0.225g., 54% on basis of consumed acid), M.P. 176-186°.

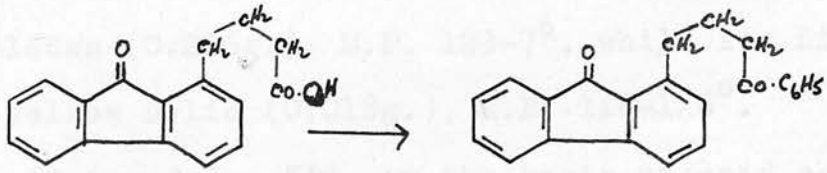
A sample recrystallised from acetic acid had M.P. 188-90°. The ketone fluoresces greenish-yellow in ultra-violet light and gives an orange colouration with/

with conc. sulphuric acid.

Analysis $C_{17}H_{12}O_2$ requires C, 82.2%; H, 4.9%.
Found : C, 81.4%; H, 5.2%.

This ketone was also obtained with methylene chloride and carbon disulphide as solvents.

PREPARATION OF γ-1-FLUORENONYLBUTYROPHENONE



cf. Johnson and Glenn, J.A.C.S., 1949, 71, 1092).

γ-1-Fluorenonebutyric acid (0.518g.) was suspended in dry ether (50 ml.) containing pyridine (2 drops) and thionyl chloride (0.5 ml.) added with swirling. The acid chloride was isolated as above.

The dark brown, oily acid chloride in dry benzene (50 ml.) was added dropwise to a stirred suspension of aluminium chloride (0.78g.) in dry benzene (100 ml.) at room temperature. After stirring for one hour the mixture was allowed to stand overnight and then boiled for 3 hours on the water-bath during which time there was copious evolution of hydrogen chloride.

The solution was then poured into ice and conc. hydrochloric acid. An hour later the benzene layer was separated, washed and extracted with aqueous sodium carbonate solution (acid recovered on acidification (0.134g.)).

The/

The neutral benzene layer was washed free of alkali and dried over anhydrous sodium sulphate, evaporated to small bulk (15 ml.) and chromatographed on a column of alumina (8" x ½"). The pale yellow band was developed with benzene and two fractions eluted arbitrarily from the column.

Fraction 1. Fore-runnings + benzene (50 ml.). The solid was recrystallised from methanol to give pale yellow blades (0.266g.), M.P. 123-7°, while its filtrate yielded yellow solid (0.018g.), M.P. 116-126°. Total yield (crude) = 54%, on the basis of acid consumed.

Fraction 2. Rest of column. The oily solid crystallised from light petroleum in yellow blades (0.088g.), M.P. 117-120° with some solid remaining till 185°. This was a mixture probably consisting mainly of the previous ketone together with some of the ring-closure ketone prepared in the previous experiment. The contaminant was not eliminated after several crystallisations from methanol-acetic acid. Careful chromatography would probably be more effective.

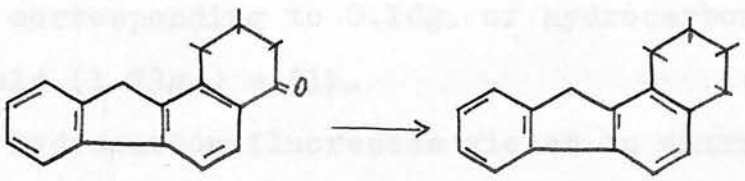
The solid of M.P. 123-7° formed pale yellow needles from methanol-acetic acid, M.P. 125.5-127° with slight previous softening. Analysis showed it to be γ-1-fluorenonylbutyrophenone.

Analysis $C_{23}H_{18}O_2$ requires C, 84.6%; H, 5.6%.
Found : C, 84.6%; H, 5.6%.

γ-1-Fluorenonylbutyrophenone fluoresces bright yellow/

yellow in ultra-violet light and gives a pink colouration with conc. sulphuric acid.

PREPARATION OF 1':2':3':4'-TETRAHYDRO-1:2-BENZFLUORENE



4'-Keto-1':2':3':4'-tetrahydro-1:2-benzfluorene (3.6g.) was dissolved in a mixture of toluene (50 ml.), acetic acid (80 ml.), conc. hydrochloric acid (50 ml.) and water (25 ml.) and the mixture boiled for 24 hours with 5% zinc amalgam (50g.). After one hour the solution showed a marked purple fluorescence. After 3 hours and after 7 hours, a mixture of acetic acid (20 ml.) and conc. hydrochloric acid (20 ml.) was added to the boiling solution.

The toluene layer was separated and the acetic acid layer diluted and extracted with ether. This extract was combined with the toluene layer and the combined layers washed with water and dried over anhydrous sodium sulphate. Removal of solvent left a pale yellow oil which soon solidified.

This solid was sublimed at 0.3mm. at 180° (external oil-bath temperature). A high-melting by-product remained in the flask. The colourless crystalline sublimate was dissolved in hot chloroform and the

chloroform replaced by ethanol. Evaporation of the solution to small bulk caused the crystallisation of colourless blades (1.63g.), M.P. 132-3°. Treatment of the filtrate with an ethanolic solution of 2:4:7-trinitrofluorenone gave the trinitrofluorenone complex (0.25g.) corresponding to 0.10g. of hydrocarbon. Total yield (1.73g.) = 51%.

The hydrocarbon fluoresces violet in ultra-violet light and is slightly volatile in steam and forms colourless blades from methanol, M.P. 133.5-134.5° with sublimation.

Analysis $C_{17}H_{16}$ requires C, 92.7%; H, 7.3%.
Found : C, 92.7%; H, 7.4%.

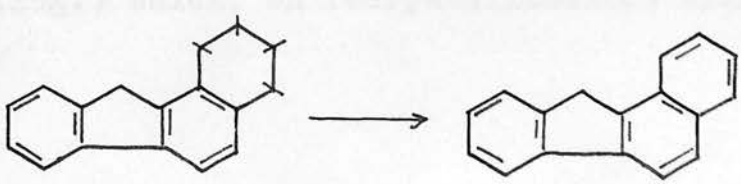
Its 2:4:7-trinitrofluorenone complex, prepared in methanol-acetic acid, forms orange elongated needles, M.P. 162-3°, and proved to be a complex of 1 part trinitrofluorenone with 1 part hydrocarbon.

Analysis $C_{30}H_{21}O_7N_3$ requires N, 7.8%.
Found : N, 7.7%.

The hydrocarbon forms an unstable complex with s-trinitrobenzene. Bright yellow needles, M.P. 109-119°.

Analysis $C_{23}H_{19}O_6N_3$ requires N, 9.7%.
Found : N,10.8%.

PREPARATION OF 1:2-BENZFLUORENE



Dehydrogenation of 1':2':3':4'-tetrahydro-1:2-benzfluorene proved unexpectedly difficult and was finally accomplished only in small yield.

1). Dehydrogenation with palladium-charcoal in α-methylnaphthalene.

Tetrahydro-1:2-benzfluorene (0.16g.) was dissolved in α-methylnaphthalene (15 ml.) and the solution boiled under reflux with 20% palladium-charcoal catalyst (50 mg.) for 5 hours in a nitrogen atmosphere. The cooled solution was filtered and the charcoal washed several times with benzene. The solvents were removed by steam-distillation and the residual solid extracted with benzene-ether. Removal of solvent followed by crystallisation of the residue from ethanol gave colourless plates, M.P. 158-165°.

This solid and that from its filtrate were redissolved in α-methylnaphthalene and boiled for a further 6 hours in an atmosphere of nitrogen with a further portion (100 mg.) of 20% palladium-charcoal catalyst and finally overnight with a final portion (50 mg.) of the catalyst, (a total of 24 hours).

After removal of α-methylnaphthalene by steam-distillation the residual brown solid was dissolved in light petroleum (B.P. 100-120°) and chromatographed on a column of alumina (6" x ½"). Elution of the single fluorescent (blue) band with benzene gave a colourless solid (0.15g.) which, on recrystallisation from methanol/

methanol, melted 164-175°.

The solid was redissolved in its filtrate and treated with a solution of s-trinitrobenzene in methanol. The resultant yellow needles (50 mg.) melted at 130-143°. Recrystallisation from ethanol raised the M.P. to 145-7° with sublimation (Lit. M.P. 144-5°). Pure yield (39 mg., 12%) based on a 1:1 complex of hydrocarbon and s-trinitrobenzene.

Mixed M.P. with the s-trinitrobenzene complex of 1:2-benzfluorene was 143-5°.

Analysis $C_{23}H_{15}N_3O_6$ requires N, 9.8%.
Found : N, 9.7%.

Orchin et al. (J.A.C.S., 1950, 72, 3002) report the formation of a complex, M.P. 144-5°, consisting of 2 molecules of s-trinitrobenzene and 1 molecule of hydrocarbon (N, 13.1%).

A sample was retained and the rest of the s-trinitrobenzene complex was dissolved in benzene and the solution chromatographed on a column of alumina (4" x ½"). The hydrocarbon crystallised from ethanol in glistening, colourless plates, M.P. 178-188.5°. A second recrystallisation from acetic acid raised the M.P. to 181-7° (Lit. M.P. 189-190°).

2). Dehydrogenation with palladium-charcoal in þ-cymene.
cf. Bergmann and Szmuszkovicz, J.A.C.S., 1951, 73, 5153.

Tetrahydro-1:2-benzfluorene (0.22g.) was boiled in

p-cymene (20 ml.) for 20 hours with 20% palladium-charcoal (0.11g.). The solution was cooled, filtered and the *p*-cymene removed by distillation under reduced pressure (1 mm.). The residual oily solid was dissolved in methanol and the solution treated with a methanolic solution of s-trinitrobenzene. The crude, yellow crystalline solid was recrystallised from methanol to give glistening yellow plates (55 mg., 12%), M.P. 142-4°. (Mixed M.P. again 143-5°).

Decomposition of the complex on alumina proceeded as above to give colourless glistening plates, which after 2 crystallisations from alcohol, had M.P. 181-184°.

3). Dehydrogenation with chloranil in xylene.

Tetrahydro-1:2-benzfluorene (220 mg.) was boiled under refluxed with chloranil (496 mg.) in sulphur-free xylene (20 ml.) for 17 hours. On cooling the solution was diluted with ether and extracted twice with 5% sodium hydroxide solution and then finally washed with water.

The dried solution (Na_2SO_4) was chromatographed, after removal of ether, on a column of alumina (9" x ½"). Development and elution of a pink band, which fluoresced purple in ultra-violet light, furnished a pink solution from which a pinkish solid (105 mg.) was obtained. This solid crystallised from glacial acetic acid in colourless plates, M.P. 147-160°, which were dissolved in ethanol and the solution treated with an ethanolic solution of s-trinitrobenzene. The resultant yellow blades/

blades (20 mg., 5%) had M.P. 142.5-144.5°. Mixed M.P. with 1:2-benzfluorene s-trinitrobenzene complex was 143-5°.

A number of other dehydrogenations were attempted and the results, in brief, were as follows:-

a). When heated in an nitrogen atmosphere at 300-320° with palladium-charcoal catalyst the tetrahydrobenzfluorene sublimed before dehydrogenation could occur.

b). With sulphur in quinoline (cf. Hewett, J.C.S., 1938, 1286) a very small quantity of colourless solid, which gave an amorphous brown powder with s-trinitrobenzene, was obtained.

c). With chloranil in boiling nitrobenzene overnight, no benzene-soluble material was isolated.

d). With chloranil in boiling toluene for 19 hours no s-trinitrobenzene complex could be isolated.

SUMMARY

1. The mixture of acids obtained on the oxidation of 4:11-dibromofluoranthene has been shown to consist of 2:7-dibromofluorenone-1-carboxylic acid and 6-bromofluorenone-1-carboxylic acid. The structure of the latter was proved by its decarboxylation to 3-bromofluorenone.
2. The action of diazomethane on fluorenone acids in presence of methanol has been investigated. The ring enlargement to substituted 9-phenanthrols, noted by previous workers, has been confirmed.
3. The reduction of 4:11-dibromofluoranthene to 1:2:3:4-tetrahydrofluoranthene has been accomplished.
4. The synthesis of 4:11-dicarboxyfluoranthene from 4:11-dibromofluoranthene was successfully accomplished. This di-acid was shown to be different from that obtained during Friedel-Crafts reaction on fluoranthene.
5. The tribromofluoranthene, obtained on the bromination of 4:11-dibromofluoranthene, has been shown, both by degradation and by synthesis, to be 4:11:12-tribromofluoranthene.
6. 4:5-Dibromophthalic acid was prepared by the oxidation of 4:5-dibromo-o-xylene and shown to be identical with one of the oxidation products of 4:11:12-tribromofluoranthene, thereby proving the structure of the latter.

7./

7. The nitration of 1:2:3:4-tetrahydrofluoranthene gave two products, which were shown to be 1-hydroxy-2-nitro-1:2:3:4-tetrahydrofluoranthene and its dehydration product, 2-nitro-3:4-dihydrofluoranthene.
8. The dehydrogenation of 2-nitro-3:4-dihydrofluoranthene to 2-nitrofluoranthene has made easily accessible fluoranthene compounds substituted in the 2-positions which are otherwise difficult to obtain.
9. The nitration of 5-bromo-1:2:3:4-tetrahydrofluoranthene also gave two products which are the bromo-analogues of those obtained in the nitration of 1:2:3:4-tetrahydrofluoranthene.
10. The synthesis of 1:2-benzfluorene has been accomplished, starting from β-1-fluorenonepropionic acid.

ACKNOWLEDGMENTS

The author wishes to express to Dr. Neil Campbell his sincere appreciation of the latter's valuable advice, encouragement and boundless enthusiasm without which this work could not have been accomplished.

Thanks are also due to Professor J.W. Cook, F.R.S., for a sample of 4-nitrofluorenone.

The award of a post-graduate studentship to the author by the University of Edinburgh authorities is gratefully acknowledged.

CORRECTIONS

p. 55. For y-fluorenone-butyric acid (lines 8 and 9) read y-1-fluorene-butyric acid.

p. 56. Fof s-nitrobenzene read s-trinitro-benzene.

p. 118. For Tetrahydroacenaphthalene read tetrahydroacenaphthene.

p. 119. For b-naphol read b-naphthol.

p. 127. In line 21 insert ''acid'' after b-1-fluorenonepropionic.