

79. *The Friedel-Crafts Reaction on Fluoranthene.*

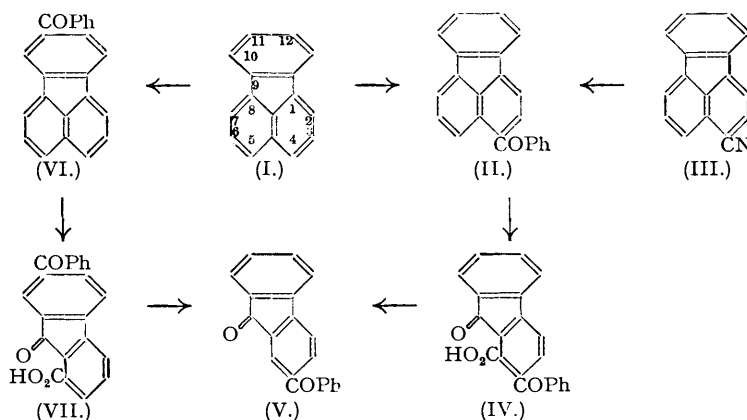
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The products of the Friedel-Crafts reaction on fluoranthene have been isolated by chromatographic separation. The results differ in some cases from those of previous workers. Benzoylation and phthaloylation give approximately equal quantities of the 4- and 11-isomers; acetylation, 4-, 11(?)-, and a diacetylfluoranthene; oxalyl chloride, fluoranthene-11-carboxylic acid and a dicarboxylic acid with the carboxyl groups probably in the 4 : 11- or 4 : 12-positions. The 11-acid is also formed by the Houben-Fischer method. 1 : 2 : 3 : 4-Tetrahydrofluoranthene and benzoyl chloride give 5-benzoyl-1 : 2 : 3 : 4-tetrahydrofluoranthene, while the benzoylation of naphthalene in nitrobenzene gives approximately equal quantities of 1- and 2-benzoylnaphthalenes.

VON BRAUN and MANZ (*Annalen*, 1932, **496**, 170), the only workers to investigate thoroughly the Friedel-Crafts reaction on fluoranthene, stated that the main products were 11-substituted derivatives. Since, however, separation of the isomers was difficult, too much reliance cannot be placed on these semi-quantitative results nor is the purity of the products always above

suspicion. It was, therefore, decided to repeat and expand von Braun's work, using the chromatographic technique to separate and purify the products. Our results confirm the necessity of these precautions.

The benzoylation of fluoranthene (I) with benzoyl chloride and aluminium chloride by either the Perrier method (*Bull. Soc. chim.*, 1904, **31**, 859) or the usual procedure gave a little unchanged fluoranthene and a mixture of 4- and 11-benzoylfluoranthenes, the quantitative separation of which was not effected. Nevertheless the results show that, contrary to the statement of von Braun and Manz (*loc. cit.*), 4-benzoylfluoranthene (II) is not a mere by-product, and indicate that it is formed in approximately equal quantities with the 11-isomer. The constitution of the 4-benzoylfluoranthene was established by showing it to be identical with a sample prepared from 4-cyanofluoranthene (III) (von Braun and Manz, *Annalen*, 1931, **488**, 111). On oxidation it yielded 1-carboxy-2-benzoylfluorenone (IV), m. p. 227—228°, which on decarboxylation gave 2-benzoylfluorenone (V).



The isomeric benzoylfluoranthene proved to be 11-benzoylfluoranthene (VI) since on oxidation it gave 7-benzoylfluorenone-1-carboxylic acid (VII), m. p. 206—209°, whose structure follows from the facts that while the acid is different from the above isomer it yields 2-benzoylfluorenone on decarboxylation. A feature of the 11-benzoyl compound is the ease with which it forms a dinitrophenylhydrazine in contrast to the 4-isomer. This is probably a steric effect, since it was found that 1-benzoylnaphthalene forms a dinitrophenylhydrazine by Allen's method (*J. Amer. Chem. Soc.*, 1930, **52**, 2955) only on boiling for some time, while the 2-benzoylnaphthalene reacts rapidly. Other benzoyl-hydrocarbons such as 2-benzoylfluorene also react rapidly with dinitrophenylhydrazine.

Buu-Hoï and Cagniant (*Rec. Trav. chim.*, 1943, **62**, 719) claim to have prepared pure 11-acetylfluoranthene, m. p. 68°, in good yield by the Friedel-Crafts reaction, but the difficulties obviously encountered hardly support their statement. They orientated the compound by submitting the oxime to the Beckmann transformation. The product, m. p. 190°, is stated to be identical with 11-acetamidofluoranthene (von Braun and Manz, *Annalen*, 1931, *loc. cit.*), but no mixed m. p. with an authentic sample is cited and it is noteworthy that this compound has not yet been analysed. Repetition of the work of Buu-Hoï and Cagniant has confirmed our suspicions that these workers obtained only a highly impure product. By following their instructions closely and submitting the crude product to chromatographic purification we found that it contains about 60% of fluoranthene; 4-acetylfluoranthene, m. p. 131—132°, identical with a sample prepared from 4-cyanofluoranthene; an isomer, possibly 11-acetylfluoranthene, m. p. 101—102°; and a diacetylfluoranthene, m. p. 140—142°. The oximes of the two acetylfluoranthenes had higher m. p.s than those quoted by Buu-Hoï and Cagniant.

In view of the above the 11'-fluoranthyl-2-cinchonic acid and 11'-fluoranthyl-2-quinoline prepared by these authors may well be the corresponding 4'-fluoranthyl compounds.

Von Braun and Manz (*Annalen*, 1932, *loc. cit.*) by the phthaloylation of fluoranthene obtained 4- and 11-benzoylfluoranthene-2'-carboxylic acids and we have confirmed the structures assigned by them by decarboxylation to the corresponding benzoylfluoranthenes. The same authors (*Annalen*, 1932, *loc. cit.*) by the action of oxalyl chloride and aluminium chloride on fluoranthene

obtained a mono- and a di-carboxylic acid in the ratio 2 : 1 together with a very small quantity of a second carboxylic acid, the main acid being shown to be fluoranthene-11-carboxylic acid and the other the 4-acid. Repetition of this work gave substantially the same results, but we were unable to isolate any 4-acid.

Fluoranthene-4-carboxylic acid was readily decarboxylated with copper in boiling quinoline, whereas the 11-acid was unaffected under these conditions. The fact that the dicarboxylic acid was decarboxylated to fluoranthene-11-carboxylic acid thus affords good evidence that it is the 4 : 11- or the 4 : 12-dicarboxylic acid.

Carboxylation of fluoranthene by the Houben method (Houben and Fischer, *Ber.*, 1931, **64**, 240, 2636) yielded a mixture from which we were able to isolate in the pure state only fluoranthene-11-carboxylic acid in 35% yield.

The 4-substituted fluoranthenes crystallise in deep yellow needles while the 11-isomers are colourless (or nearly so) plates with a blue fluorescence. The 4-isomers have higher m. p.s and are less strongly adsorbed on alumina.

The nature of the solvent greatly influences substitution of naphthalene by the Friedel-Crafts reaction, acetylation, for example, in carbon disulphide giving approximately 60% of 1-acetylnaphthalene (Chopin, *Bull. Soc. chim.*, 1924, **35**, 610; St. Pfau and Ofner, *Helv. Chim. Acta*, 1926, **9**, 669; Lock, *Monatsh.*, 1943, **74**, 77; cf. Buu-Hoi and Cagniant, *Bull. Soc. chim.*, 1945, **12**, 307) and in nitrobenzene 90% of the 2-isomer. We investigated the benzylation of naphthalene in nitrobenzene in the hope that 2-benzoylnaphthalene would be the main product and consequently that 3-benzoylfluoranthene might be obtained by the analogous method. So far as we could judge, however, the two benzylnaphthalenes resulted in almost equal quantities.

The main product from the reaction of benzoyl chloride and aluminium chloride with 1 : 2 : 3 : 4-tetrahydrofluoranthene was 5-benzoyl-1 : 2 : 3 : 4-tetrahydrofluoranthene with much smaller quantities of an isomer isolated as the dinitrophenylhydrazone and a *dibenzoyltetrahydrofluoranthene*. The result was contrary to expectations, since under similar conditions, tetrahydronaphthalene yields mainly 6-substituted products (Schwarin, *Ber.*, 1902, **35**, 2511; v. Braun, Kirschbaum, and Schuhemann, *Ber.*, 1920, **53**, 1155).

EXPERIMENTAL.

Unless otherwise stated the methods of preparation and the properties of the compounds used are those given in the literature. The identity of substances was established by mixed m. p.s with authentic samples, and the purity of products determined by the sharpness of their m. p.s determined on a Kofler micro-m. p. apparatus (*Mikrochem.*, 1934, **15**, 242). Chromatographic adsorptions (for fuller details see Easton, Thesis, Edinburgh, 1947) were carried out with alumina (Brockmann) as adsorbent, and analyses were done by Drs. Weiler and Strauss, Oxford. All fluorescence observations were made under a Hanovia ultra-violet lamp.

Benzylation of Fluoranthene.—(a) Aluminium chloride (17.5 g.) was slowly added with shaking to benzoyl chloride (17.5 g.), and the mixture heated gently and then cooled. Carbon disulphide (100 c.c.) was added, and the mixture heated on the water-bath, and then cooled slightly. Fluoranthene (25 g.) was added during $\frac{1}{2}$ hour, and the slurry heated on the water-bath for another 10 minutes, then cooled thoroughly, and filtered. The solid, after being stirred into water (400 c.c.) and concentrated hydrochloric acid (25 c.c.) and boiled for 15 minutes, yielded a dark brown oil which was extracted with ether (1000 c.c.). The extract, after being washed with sodium carbonate solution and dried (CaCl_2), yielded on distillation yellow crystals (25 g.), m. p. 78—105°.

The crude solid (5 g.) was dissolved in a 4 : 1 mixture of light petroleum (b. p. 80—100°) and benzene, and chromatographed on a column of alumina 28" \times 0.86", and developed with the same mixture. A blue fluorescent eluate was first obtained which yielded fluoranthene (0.4 g.), m. p. 109—110°. On the column was left a lower band with a dull yellow fluorescence and an upper band with a blue fluorescence. By continued elution 2.2 g. of 4-benzoylfluoranthene (see below) were obtained, which crystallised from ethanol in yellow, elongated prisms, m. p. 129—130° (Found: C, 90.22; H, 4.65. Calc. for $\text{C}_{23}\text{H}_{14}\text{O}$: C, 90.2; H, 4.6%). The blue fluorescent band was extracted with ethanol, and yielded 0.61 g. of 11-benzoylfluoranthene (see below), colourless hexagonal plates (ethanol) with blue fluorescence, m. p. 120—121° (mixed m. p. with 4-isomer 86—112°) (Found: C, 89.74; H, 4.6%). The lower half of the column on extraction with alcohol yielded 1.42 g. of a substance, which was chiefly the colourless isomer with a small quantity of the yellow compound. It appears that the two benzoylfluoranthenes are formed in approximately equal quantities.

(b) Benzoyl chloride (17.5 g.) was added dropwise to an ice-cold, stirred mixture of fluoranthene (25 g.) and aluminium chloride (17.5 g.) in carbon disulphide (150 c.c.), and the stirring continued for a further 8 hours at room temperature. The mixture was finally heated on the water-bath for 6 hours, the carbon disulphide removed by distillation, and the residue decomposed by ice. The resulting yellow solid was extracted with ether, washed first with sodium carbonate solution and then with water, and dried (CaCl_2). The ether was distilled off and left a dark yellow viscous mass (31 g.).

The product (5 g.) was separated chromatographically into fluoranthene (0.32 g.), 4-benzoylfluoranthene (1.55 g.), 11-benzoylfluoranthene (1.81 g.), and a mixture of the last two compounds (0.33 g.), thus showing again that the two isomers are formed in approximately equal quantities.

4-Benzoylfluoranthene.—The 2 : 4-dinitrophenylhydrazone was prepared by Brady's method but

required 9 hours' heating; it formed orange crystals (glacial acetic acid), m. p. 260—265° (decomp.) (Found: N, 11.7. $C_{20}H_{18}O_4N_4$ requires N, 11.53%). The *picrate* had m. p. 158—160° (Found: N, 8.00. $C_{20}H_{17}O_5N_3$ requires N, 8.42%). The *oxime*, prepared by refluxing 4-benzoylfluoranthene (0.5 g.) with hydroxylamine hydrochloride (2 g.) in pyridine (10 c.c.) for 3 hours, formed plates from isopropanol, m. p. 219—223° (v. Braun and Manz, *loc. cit.*, give m. p. ca. 170°) (Found: N, 3.95. $C_{23}H_{15}ON$ requires N, 4.36%). The *oxime* (0.25 g.) and phosphorus pentachloride (0.5 g.) in anhydrous ether (45 c.c.) were kept for 20 hours, and the solution treated in the usual way to give an *anilide*, m. p. 260—263° (Found: N, 4.51. $C_{23}H_{15}ON$ requires N, 4.36%). 4-Benzoylfluoranthene gave no m. p. depression when mixed with a sample prepared from 4-cyanofluoranthene. Attempts to prepare the latter by refluxing 4-bromofluoranthene in pyridine with cuprous cyanide for 16 hours gave only unchanged material. It was obtained by the method of von Braun and Manz (*Annalen*, 1931, *loc. cit.*) and purified by successive crystallisation from ethanol and light petroleum (b. p. 60—80°) and chromatographic adsorption on alumina on which it separated as a greenish-yellow fluorescing band. Final crystallisation from light petroleum (b. p. 80—100°) gave a yellow solid, m. p. 117—121° (lit. 112°), evidently not quite pure (Found: N, 5.58. Calc. for $C_{17}H_9N$: N, 6.17%). 4-Cyanofluoranthene (0.63 g.) was dissolved in anhydrous benzene (25 c.c.) and added to the Grignard reagent prepared from magnesium (0.10 g.), bromobenzene (0.45 c.c.), and anhydrous ether (1.85 c.c.), and refluxed for 10 hours. It was then decomposed by crushed ice (15 g.) and 10% sulphuric acid (25 c.c.), and steam-distilled. The residue was extracted with ether, and the extract washed first with dilute sulphuric acid, then with water, and dried ($CaCl_2$). Evaporation gave an oily solid which was crystallised from ethanol; m. p. 125—129° (m. p. depression with 4-cyanofluoranthene). It was chromatographed in benzene on a column 12" × 0.86" and the yellow band eluted. 4-Benzoylfluoranthene was thus obtained which crystallised from ethanol in yellow needles, m. p. 129—130°.

Chromic acid ("A.R.", 1.40 g.) in water (1 c.c.) and glacial acetic acid (1 c.c.) was slowly added to 4-benzoylfluoranthene (0.60 g.) in glacial acetic acid (10 c.c.). The mixture was kept overnight, then refluxed for 2 hours, poured into water (150 c.c.), and extracted with benzene, extraction of which with sodium hydroxide followed by acidification gave the yellow 2-benzoylfluorenone-1-carboxylic acid, m. p. 227—228° after purification *via* the barium salt and crystallisation from glacial acetic acid (Found: C, 74.64; H, 3.57. $C_{22}H_{12}O_4$ requires C, 76.83; H, 3.66%). The acid (0.01 g.) was heated with a trace of copper-bronze in quinoline for 10 minutes, and the mixture decomposed with hydrochloric acid. The mixture was extracted with benzene, which was then washed with water, dried (Na_2SO_4), and chromatographed on a column 4" × 0.4". Development with benzene gave a yellow band which was ultimately collected in the filtrate, and gave 2-benzoylfluorenone, bright yellow needles (from ethanol), m. p. 175—176°, no m. p. depression when mixed with a specimen prepared as follows. Sodium dichromate (0.185 g.) in glacial acetic acid (1 c.c.) and water (0.25 c.c.) was added to a gently boiling solution of 2-benzoylfluorenone (0.1 g.) in glacial acetic acid (2 c.c.), and refluxed for 2½ hours. Dilution with water (20 c.c.) and extraction with benzene gave 0.07 g. of crude product which was dissolved in benzene, chromatographed on a column 4" × 0.4", and developed with 3:1 benzene-light petroleum (b. p. 80—100°). A deep yellow eluate was obtained which yielded 2-benzoylfluorenone, m. p. 175—177°, after crystallisation from ethanol (Found: C, 84.3; H, 4.5. Calc. for $C_{20}H_{12}O_2$: C, 84.5; H, 4.2%).

11-Benzoylfluoranthene (0.90 g.) was oxidised by chromic acid ("A.R.", 2.1 g.) in water (1.5 c.c.) and glacial acetic acid (1.5 c.c.) in the same way as the 4-isomer, and gave 7-benzoylfluorenone-1-carboxylic acid, m. p. 206—209° (m. p. 184—195° when mixed with 2-benzoylfluorenone-1-carboxylic acid), obtained as a yellow solid (Found: C, 76.83; H, 3.81. $C_{21}H_{10}O_4$ requires C, 76.83; H, 3.66%), 0.05 g. of which was decarboxylated as above to give 2-benzoylfluorenone, m. p. 174—176°, no m. p. depression with an authentic sample.

Acetylation of Fluoranthene.—Fluoranthene was acetylated by acetyl chloride and aluminium chloride by the method of Buu-Hoi and Cagniant (*loc. cit.*), and a crude orange oily solid (18 g.) obtained. The product (1 g.) was converted into a picrate, which after crystallisation from methanol had m. p. 174—181° and when decomposed gave fluoranthene. Chromatographic separation was then attempted; the crude solid (1.5 g.) was dissolved in benzene, chromatographed on a column (24.5" × 0.86"), and developed with benzene. A blue fluorescing filtrate gave 0.88 g. of fluoranthene, leaving on the column a lower yellow band at the foot, an intermediate blue fluorescent band, and a dark band at the top. The yellow band gave 0.19 g. of 4-acetylfluoranthene (see below) which was crystallised from methanol; m. p. 128—129° (Found: C, 88.16; H, 4.75. $C_{18}H_{12}O$ requires C, 88.53; H, 4.92%). The blue fluorescent band gave 0.22 g. of pale yellow plates (methanol) of 11(?)-acetylfluoranthene, m. p. 101—102° (Found: C, 88.44; H, 5.21%). From the top of the column 0.15 g. of an uncrystallisable oil was obtained.

The remainder of the crude acetylation product (16 g.) and picric acid (10 g.) were dissolved in boiling ethanol. Decomposition of the resultant picrate gave fluoranthene (7 g.), and the alcoholic filtrate on the usual treatment gave a mixture of acetylfluoranthenes (3.8 g.) which when chromatographed gave fluoranthene (1.91 g.), 4-acetylfluoranthene, m. p. 125—129° (0.09 g.), a mixture of acetylfluoranthenes, m. p. 90—101° (1.08 g.), and a *diacetylfluoranthene*, yellow needles (from ethanol-acetic acid), m. p. 140—142° (Found: C, 83.6; H, 5.25. $C_{20}H_{14}O_2$ requires C, 83.9; H, 4.89%).

4-Acetylfluoranthene.—The 2:4-dinitrophenylhydrazone, formed easily by Allen's method as a red solid, was purified by being boiled with ethanol-acetic acid, m. p. 261—262° (Found: N, 14.3. $C_{24}H_{16}O_4N$ requires N, 13.2%). The *oxime*, prepared by refluxing the compound (0.06 g.) in pyridine (2.4 c.c.) with hydroxylamine hydrochloride (0.24 g.) for 7 hours, adding water, and crystallising the precipitate from ethanol, had m. p. 196—198° (Found: N, 4.67. $C_{18}H_{13}ON$ requires N, 5.41%). 4-Acetylfluoranthene was shown to be identical with a specimen prepared as follows. 4-Cyanofluoranthene (0.15 g.) in benzene (25 c.c.) was added to the Grignard reagent prepared from magnesium (0.10 g.) and methyl iodide (0.60 g.) in ether, and the mixture boiled under reflux for 40 hours. The product, obtained by the usual procedure, was dissolved in benzene and chromatographed on a column 5.5" × 0.53" and developed with benzene containing 1% of ethanol. A yellow band separated, and finally was filtered and evaporated. The dirty yellow residue was triturated with methanol and dissolved in the minimum amount of ethanol. The cold solution was filtered, and the filtrate on reduction to ½ of its volume gave a pale yellow solid,

m. p. 122—128°, which was dissolved in benzene and chromatographed on a column 8'' × 0.53''. Development with benzene gave a yellow band which was eluted and gave 4-acetylfluoranthene, m. p. 131—132°, yellow needles (from ethanol), showing no m. p. depression when mixed with the higher melting isomer from the Friedel-Crafts reaction.

11(?)*-Acetylfluoranthene*.—The 2 : 4-dinitrophenylhydrazone, obtained easily by Allen's method, was triturated with boiling ethanol-acetic acid; it sublimed in orange needles, m. p. 299—301° (Found : N, 12.8%). The oxime, prepared as above, was crystallised from glacial acetic acid containing a little ethanol, and then had m. p. 173—178° (with sublimation) (Found : N, 5.56%).

Phthaloylation of Fluoranthene.—Fluoranthene (20 g.) was treated with phthalic acid as described by von Braun and Manz (*Annalen*, 1932, *loc. cit.*), and 14 g. of crude product obtained. It was too strongly adsorbed on alumina to be purified by chromatographic adsorption. The crude solid was dissolved in chloroform which on standing deposited a solid *A* (5 g.), m. p. 203—214°, and the mother liquor on evaporation gave a resinous solid *B* (7 g.), m. p. 158—185°. Fraction *A* (4.5 g.) was esterified with methanol and sulphuric acid to give a mixture of methyl esters (2 g.), m. p. 100—145°, which was chromatographed in benzene on a column 24'' × 0.86'' and developed with 3 : 1 benzene-light petroleum (b. p. 80—100°). Two blue fluorescent bands separated by a deep yellow fluorescent band resulted, and were successively collected in the filtrate. The first blue band gave 0.09 g. of oily solid, and the yellow band gave 0.70 g. of methyl 4-benzoylfluoranthene-2'-carboxylate, yellow crystals, m. p. 103—105°, after crystallisation from light petroleum (b. p. 100—120°) (Found : C, 82.66; H, 4.64. C₂₅H₁₆O₃ requires C, 82.41; H, 4.39%). The upper band yielded 0.65 g. of methyl 11-benzoylfluoranthene-2'-carboxylate, yellow crystals with blue fluorescence, m. p. 172—174° after crystallisation from light petroleum (b. p. 100—120°) (Found : C, 81.79; H, 4.48%). Fraction *B* (5 g.) was chromatographed similarly on a column 24'' × 0.86'' and gave an uncrystallisable oil (0.34 g.), methyl 4-benzoylfluoranthene-2'-carboxylate, m. p. 101—103° (1.15 g.), and a mixture (1.72 g.), m. p. 120—160°, consisting mainly of the isomeric ester.

Methyl 4-benzoylfluoranthene-2'-carboxylate was hydrolysed with 10% sodium hydroxide and the resulting 4-benzoylfluoranthene-2'-carboxylic acid crystallised from glacial acetic acid; it formed bright yellow needle-prisms, m. p. 231—232° (lit. 230°) (Found : C, 81.66; H, 4.09. Calc. for C₂₄H₁₄O₃ : C, 82.28; H, 4.00%). The oxime had m. p. 221—225° (lit. 207—209°) (Found : N, 3.60. Calc. for C₂₄H₁₅O₂N : N, 3.83%). The acid (0.05 g.) was heated with a trace of copper in quinoline at 195° for 10 minutes, and the precipitate, obtained by the addition of dilute hydrochloric acid, dissolved in benzene and chromatographed on a column 3.75'' × 0.4''. Development with 3 : 1 benzene-light petroleum (b. p. 80—100°) gave a yellow band which on elution yielded 4-benzoylfluoranthene, yellow needles (ethanol), m. p. 129—130°; this gave no m. p. depression when mixed with authentic sample.

Methyl 11-benzoylfluoranthene-2'-carboxylate, m. p. 172—174°, was hydrolysed more slowly (4 hours) than the isomer, and gave 11-benzoylfluoranthene-2'-carboxylic acid, m. p. 227—228° (lit. 212°), depressed by the 4-isomer (Found : C, 82.39; H, 4.03. Calc. for C₂₄H₁₄O₃ : C, 82.28; H, 4.00%). Decarboxylation as above for 20 minutes at 175—180°, and adsorption of the product on a column 3.5'' × 0.40'', gave a blue fluorescent band which on elution with alcohol gave 11-benzoylfluoranthene, colourless plates, m. p. 117—119°, not depressed by an authentic sample. The oxime formed compact prisms (from benzene), m. p. 232—235° (lit. 224—225°).

Fluoranthene-carboxylic Acid by the Friedel-Crafts Reaction.—The crude product (17 g.) obtained by treating fluoranthene with oxalyl chloride according to the method of von Braun and Manz (*loc. cit.*) was refluxed with methanol (350 c.c.) and concentrated sulphuric acid (35 c.c.) for 5 hours, filtered from unchanged acids, and poured into water. The resulting oil was extracted with ether, the ether layer washed with sodium carbonate solution, and dried, and the ether removed by distillation, leaving a solid (5.13 g.), m. p. 75—90°. The solid was dissolved in benzene, chromatographed on a column 30'' × 0.86'', and developed with 3 : 1 benzene-light petroleum (b. p. 80—100°). Two bands containing the main products resulted : (a) a lower yellow band, (b) an upper band with a deep yellow fluorescence. Band (a) gave methyl fluoranthene-11-carboxylate (2.58 g.), m. p. 93—95° after crystallisation from ethanol (Found : C, 82.33; H, 4.90. C₁₈H₁₂O₂ requires C, 83.08; H, 4.61%), and (b) gave dimethyl fluoranthenedicarboxylate (1.33 g.), deep yellow crystals (ethanol), m. p. 183—185° (Found : C, 75.3; H, 4.60. C₂₀H₁₄O₄ requires C, 75.5; H, 4.40%).

Methyl fluoranthene-11-carboxylate was hydrolysed by being heated for 1 hour with 10% sodium hydroxide, and worked up in the usual way. Fluoranthene-11-carboxylic acid separated as colourless needles (glacial acetic acid), m. p. 278—280° subliming at 220° (Found : C, 82.6; H, 4.35. Calc. for C₁₇H₁₀O₂ : C, 82.9; H, 4.06%). It gave a m. p. depression when mixed with fluoranthene-4-carboxylic acid (see below), and was not decarboxylated when heated with quinoline and copper bronze for ½ hour at 235°.

4-Cyanofluoranthene (0.1 g.) was heated in a sealed tube with concentrated hydrochloric acid (10 c.c.) for 16 hours at 200°; the product gave fluoranthene-4-carboxylic acid, yellow crystals (glacial acetic acid), m. p. 281—288° (lit. 264—275°).

Dimethyl fluoranthenedicarboxylate was similarly hydrolysed (3 hours), and fluoranthenedicarboxylic acid obtained as yellow needles by sublimation, m. p. >350° (Found : C, 72.9; H, 4.18. C₁₈H₁₀O₄ requires C, 74.5; H, 3.45%). The analysis shows that the acid is not pure, and this was confirmed by decarboxylation in quinoline at 235° with copper bronze for ½ hour. A micro-sublimation gave first a little fluoranthene, and later almost colourless needles of fluoranthene-11-carboxylic acid, m. p. 276—279°, not depressed by a sample of the above mono-acid. Fluoranthene-11-carboxylic acid is not decarboxylated under the above conditions, but the 4-acid readily gives fluoranthene when heated in quinoline at 200—205° with copper for 20 minutes.

Fluoranthene-carboxylic Acids by the Houben Reaction.—Aluminium chloride (16 g.) was gradually added to fluoranthene (20 g.) and trichloromethyl cyanide (17.4 g.) in chlorobenzene (160 c.c.), and the mixture then saturated with hydrogen chloride. The temperature was raised to 100° during an hour, and kept there for 1 hour with frequent shaking. Decomposition of the product with excess of concentrated hydrochloric acid followed by steam-distillation gave a dark residue which was treated with

concentrated hydrochloric acid, collected, and washed free from acid. The crude solid was heated with sodium hydroxide solution and filtered, leaving a dark sludge which was thoroughly washed. Acidification of the filtrate and the washings with hydrochloric acid gave the crude mixture of acids which was washed, dried, and refluxed with methanol (400 c.c.) and concentrated sulphuric acid (40 c.c.) for 5 hours. The mixture was filtered, the filtrate poured into water, and the precipitate extracted with ether. Evaporation gave a pale yellow solid (5 g.) which was dissolved in benzene, chromatographed on a column $20.5'' \times 0.86''$, and developed with 3 : 1 benzene-light petroleum (b. p. $80-100^\circ$). A yellow band separated, and was eluted with ethanol, yielding methyl fluoranthene-11-carboxylate (3.78 g.), m. p. $96-97^\circ$, identical with a specimen prepared as above. It was hydrolysed to the acid by being heated with 10% sodium hydroxide. The dark sludge (above) was dried and refluxed with methanol (250 c.c.) and concentrated sulphuric acid (25 c.c.) for 5 hours. Working up as before gave 3.69 g. of methyl fluoranthene-11-carboxylate.

Benzoylation of Naphthalene in Nitrobenzene.—A clear solution was obtained by gently warming benzoyl chloride (11.5 c.c.), powdered aluminium chloride (14 g.), and nitrobenzene (80 c.c.). Naphthalene (12.8 g.) was added slowly, and the solution heated at 60° for 20 minutes. The mixture was poured into water and steam-distilled, leaving a dark oil which was extracted with ether. The ether solution was washed successively with water, sodium carbonate solution, and water, and dried (CaCl_2). The ether was distilled off and the residual dark red oil chromatographed on a column $21'' \times 0.86''$. Development with ether gave a red band which was finally collected in the filtrate, from which a solid (15 g.), melting over a wide range, was obtained. It was chromatographed in benzene on a column $24.5'' \times 1.18''$, and developed with 3 : 1 benzene-light petroleum (b. p. $40-60^\circ$); the product melted at $71-75^\circ$, and was shown to consist of 1- and 2-benzoylnaphthalenes in the ratio 2 : 1 by a further chromatographic separation. Further elution of the column with ethanol gave 2-benzoylnaphthalene (4.75 g.), m. p. $75-80^\circ$, colourless needles (from light petroleum, b. p. $60-80^\circ$). The yield ratio of 1- and 2-benzoylnaphthalene is thus approximately 46 : 54. 1-Benzoylnaphthalene was also prepared from 1-cyanonaphthalene (5.75 g.) in anhydrous ether (75 c.c.) and the Grignard reagent prepared from magnesium (1.0 g.), bromobenzene (4.45 c.c.), and ether (18.5 c.c.), by refluxing for $\frac{1}{2}$ hour. The mixture was decomposed with 10% sulphuric acid (25 c.c.) and ice (15 g.), steam-distilled, and the residue worked up to give 1-benzoylnaphthalene, m. p. $74-76^\circ$ after crystallisation from light petroleum (b. p. $60-80^\circ$). The 2 : 4-dinitrophenylhydrazones separated after 15 minutes when Brady's method was used. It was crystallised from ethanol-acetic acid, m. p. $248-249^\circ$ (Found: N, 13.8. $\text{C}_{23}\text{H}_{16}\text{O}_4\text{N}_4$ requires N, 13.6%). 2-Benzoylnaphthalene, prepared similarly, gave a 2 : 4-dinitrophenylhydrazone, m. p. $232-233^\circ$ (lit., $257-258^\circ$) (Found: N, 14.5%). 2-Benzoylfluorene dinitrophenylhydrazone, orange prisms (from glacial acetic acid), had m. p. 265° (Found: N, 12.2%. $\text{C}_{26}\text{H}_{18}\text{O}_4\text{N}_4$ requires N, 12.4%).

Benzoylation of 1 : 2 : 3 : 4-Tetrahydrofluoranthene.—Tetrahydrofluoranthene (11 g.) was added slowly to benzoyl chloride (8 g.) and aluminium chloride (8 g.) in carbon disulphide (60 c.c.), and the mixture decomposed and worked up to give a crude product (11 g.). By a series of long and tedious chromatographic separations four products were isolated. (a) Unchanged tetrahydrofluoranthene. (b) 5-Benzoyl-1 : 2 : 3 : 4-tetrahydrofluoranthene (60% yield), which formed pale yellow prisms (ethanol), m. p. $144-145^\circ$ (Found: C, 88.59; H, 5.75. $\text{C}_{23}\text{H}_{18}\text{O}$ requires C, 89.0; H, 5.81%). The compound (1 g.) was refluxed for 24 hours in sulphur-free xylene (20 c.c.) with chloranil (1.6 g.), an equal volume of ether added, and the tetrachloroquinol extracted with dilute sodium hydroxide. The xylene-ether layer was washed free from alkali and dried (CaCl_2); the solution on evaporation gave a yellow solid, m. p. $123-126^\circ$, which was chromatographed in benzene on a column $10.5'' \times 0.86''$ and developed with 3 : 1 benzene-light petroleum (b. p. $80-100^\circ$). The yellow filtrate yielded 4-benzoylfluoranthene (0.65 g.), m. p. $131-132^\circ$ after crystallisation from ethanol. 5-Benzoyltetrahydrofluoranthene does not form a picrate, and the 2 : 4-dinitrophenylhydrazone could not be prepared by Allen's method, but was obtained in an impure form by Brady's method after 12 hours' boiling under reflux; it was an orange solid (from ethanol-acetic acid), m. p. $216-217^\circ$ (Found: N, 10.0. $\text{C}_{29}\text{H}_{22}\text{O}_4\text{N}_4$ requires N, 11.43%). (c) An isomeric benzoyltetrahydrofluoranthene which was isolated as the orange 2 : 4-dinitrophenylhydrazone by Brady's method (Allen's method unsuccessful), m. p. $>350^\circ$ (Found: N, 11.40%). (d) A small quantity of an impure yellow dibenzoyltetrahydrofluoranthene, which had m. p. $173-178^\circ$ (Found: C, 87.06; H, 4.80. $\text{C}_{30}\text{H}_{18}\text{O}_2$ requires C, 87.80; H, 4.39%).