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

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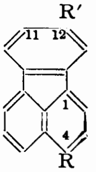
Fluoranthene and acetyl bromide in the presence of aluminium chloride give 4 : 12-diacetylfluoranthene which can be oxidised to fluoranthene-4 : 12-dicarboxylic acid identical with the acid obtained from fluoranthene and oxalyl chloride under Friedel–Crafts conditions (Campbell and Easton, *J.*, 1949,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

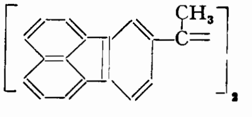
It has been proved that bromination of fluoranthene gives 4 : 11-dibromofluoranthene (Campbell *et al.*, *Nature*, 1950, **165**, 76; *J.*, 1950, 2784; Holbro and Tagmann, *Helv. Chim. Acta*, 1950, **33**, 2178; S. H. Tucker, personal communication). Nitration, sulphonation, etc., will most probably 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 decision in favour of the second structure (I*c*) was obtained by oxidation to a fluoranthenedicarboxylic 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).



(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.)

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′-fluoranthylbut-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′-*fluoranthylbut*-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.

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