900. 4 : 11 : 12-*Tribromofluoranthene.*

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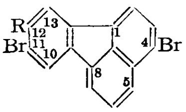
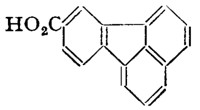
4 : 11-Dibromofluoranthene on Friedel–Crafts acetylation affords 12-acetyl-4 : 11-dibromofluoranthene, from which is obtained 4 : 11 : 12-tribromofluoranthene identical with the product obtained by the direct bromination of fluoranthene. The structure of the tribromofluoranthene is confirmed by oxidation to 4 : 5-dibromophthalic acid.

Since no trisubstituted fluoranthene has been orientated it was decided to determine the structure of the tribromofluoranthene, m. p. 204—205°, which is readily obtained by the direct bromination of the hydrocarbon (Tobler, Holbro, Sutter, and Kern, *Helv. Chim. Acta,* 1941, **24**, 100E). This has been accomplished by an unambiguous synthesis and by oxidative degradation.

4 : 11-Dibromofluoranthene (Campbell, Easton, and Rayment, *J.*, 1950, 2784; Holbro and Tagmann, *Helv. Chim. Acta,* 1950, **33**, 2178) with acetyl bromide and aluminium chloride yielded 12-acetyl-4 : 11-dibromofluoranthene (I; R = COMe). The constitution of this substance followed from its oxidation with sodium hypobromite to 4 : 11-dibromofluoranthene-12-carboxylic acid (I; R = CO_2H) which on debromination with nickel–aluminium alloy yielded the known fluoranthene-11-carboxylic acid (II). The acetyl compound with sodium azide and trichloroacetic acid readily formed 12-acetamido-4 : 11-dibromofluoranthene (I; R = NHAc). Diazotisation of the derived base by the Hodgson–Walker method (*J.*, 1933, 1620) followed by treatment with cuprous bromide gave a



(I)



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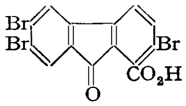
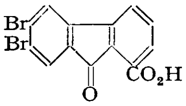


(III)



(IV)

mixture of tri- and tetra-bromofluoranthenes, whence was isolated a reasonably pure tetrabromofluoranthene, m. p. 223—228°, which is patently different from the tetrabromofluoranthene, m. p. 312°, obtained by the direct bromination of fluoranthene (Tobler *et al.*, *loc. cit.*). This unexpected result is probably due to the liberation of bromine from the hydrobromic acid by the sulphuric acid at the temperature (60°) of the experiment. Correspondingly, diazotisation at $<40°$, led to 4 : 11 : 12-tribromofluoranthene (I; R = Br), identical with that obtained by the direct bromination of fluoranthene.

From a series of chromic acid oxidations of tribromofluoranthene three products were isolated, each in small yield. The first was a tribromofluorenone-1-carboxylic acid (III), proving that the bromination had occurred in only two of the benzene nuclei. Another was 6 : 7-dibromofluorenone-1-carboxylic acid (IV) which is distinguished from the tribromo-acid by the ease with which it is esterified by methanol and sulphuric acid: the steric hindrance encountered in esterifying 2-bromofluorenone-1-carboxylic acids has already been noted (Campbell *et al.*, *loc. cit.*). In one experiment use was made of this to prepare the dibromo-acid in a somewhat impure form by esterifying a mixture of di- and tri-bromo-acids, removing unchanged tribromo-acid, and hydrolysing the ester back to the dibromo-acid. Decarboxylation of this acid gave 2 : 3-dibromofluorenone.

Finally, in one experiment, 4 : 5-dibromophthalic acid was obtained, identical with a sample prepared by the oxidation of 4 : 5-dibromo-*o*-xylene. This shows that the original tribromofluoranthene contains two of its bromine atoms in the 11 : 12-positions and hence must be the 4 : 11 : 12-tribromo-compound. Oxidation of any other tribromofluoranthene to 4 : 5-dibromophthalic acid could occur only by accompanying decarboxylation—an improbable event. The isolation of 4 : 5-dibromophthalic acid established the structures of acids (III) and (IV) (as shown).

EXPERIMENTAL

Chromatographic experiments were done with B.D.H. chromatographic alumina. Analyses were by Drs. Weiler and Strauss, Oxford.

Acetylation of 4 : 11-*Dibromofluoranthene.*—Dibromofluoranthene (10 g.), acetyl bromide (6·80 g.), and carbon disulphide (50 ml.) were stirred at 0° and aluminium chloride (11·0 g.) was added during ½ hour. The mixture was stirred at room temperature for 72 hours, then poured into ice-cold concentrated hydrochloric acid. Removal of the carbon disulphide in steam gave a crude product (10·9 g.), m. p. 130—145°, after washing with water and drying. This powder (5·04 g.) in benzene was passed down a column (26″ × ¾″), and development with benzene gave a colourless zone (A) at the foot, an intermediate yellow zone (B), and an orange zone at the top. Zone A gave unchanged dibromofluoranthene (0·08 g.), m. p. and mixed m. p. 195—200°. The bottom of zone B gave on elution with benzene 12-*acetyl*-4 : 11-*dibromofluoranthene* (0·36 g.), yellow prisms (from benzene), m. p. 164—165° (Found: C, 53·6; H, 2·5; Br, 39·6. $C_{18}H_{10}OBr_2$ requires C, 53·8; H, 2·5; Br, 39·8%). The middle of the zone was extracted with acetone and yielded 1·46 g. of the acetyl compound, m. p. 159—162°, after reduction to small volume. The mother-liquors gave a product (0·64 g.), m. p. 120—134°. Similar treatment of the top of the zone gave products (0·41 g.), m. p. 148—158°, and (0·77 g.) m. p. 122—142°. The remainder of the crude powder (5·89 g.) was similarly chromatographed, and all material of m. p. $<153°$ from the two experiments was dissolved in benzene and passed down a column 26″ × ¾″. Development with benzene gave the zones A and B as before. Extraction of A with benzene and reduction of the solution to a small volume gave what appeared to be a *tribromofluoranthene* (0·02 g.), m. p. $>360°$ (Found: Br, 56·0. $C_{16}H_7Br_3$ requires Br, 54·6%), and a little 4 : 11-dibromofluoranthene. Zone B gave 12-acetyl-4 : 11-dibromofluoranthene (1·38 g.), m. p. 154—163°, which crystallised from benzene in a purer form (0·92 g.), m. p. 162—164°. It forms by Brady's method a 2 : 4-*dinitrophenylhydrazone*, an orange, non-crystalline solid, after trituration with boiling ethanol or acetic acid, m. p. 275—279° (Found: N, 9·8. $C_{24}H_{14}O_4N_4Br_2$ requires N, 9·6%).

An attempt to acetylate 4 : 11-dibromofluoranthene as above, but with nitrobenzene as solvent, was unsuccessful.

12-Acetyl-4 : 11-dibromofluoranthene (0·80 g.) was added to a solution prepared by adding bromine (6·7 ml.) dropwise to 3N-sodium hydroxide (93 ml.) at 0° with occasional shaking. The mixture was stirred vigorously for 22 hours at 60° and filtered. The residue was washed with water and dried, and the yellow powder (0·67 g.) was boiled with benzene and then with concentrated hydrochloric acid (50 ml.). The product (0·35 g., 44%) crystallised from benzene in pale yellow needles, m. p. 306—308°, and proved to be 4 : 11-*dibromofluoranthene*-12-*carboxylic acid* (Found : C, 51·0; H, 2·1; Br, 39·1. $C_{17}H_8O_2Br_2$ requires C, 50·5; H, 2·0; Br, 39·6%). Oxidation for 44 hours gives a 77% yield. Boiling the acid (0·3 g.) with methanol (100 ml.) and concentrated sulphuric acid (3 ml.) for 18 hours gives the *methyl* ester (0·25 g.), yellow needles (from methanol), m. p. 190—191° (Found : C, 51·9; H, 2·4; Br, 38·7. $C_{18}H_{10}O_2Br_2$ requires C, 51·7; H, 2·4; Br, 38·2%). The acid (0·22 g.) was boiled with 10% ethanolic potassium hydroxide (100 ml.) and nickel–aluminium alloy (3·5 g.) was added in 4 portions over 10 minutes. The mixture was boiled for 2½ hours, then filtered, and the filtrate acidified with hydrochloric acid. Fluoranthene-11-carboxylic acid (0·05 g.) separated as needles (from acetic acid), m. p. 284—287°, undepressed when admixed with an authentic sample. The methyl ester, m. p. 93—94° (Found : C, 82·7; H, 5·3. Calc. for $C_{18}H_{12}O_2$: C, 83·1; H, 4·7%), also showed no depression when admixed with an authentic sample.

Attempts to remove the 11-bromine atom by heating the dibromo-acid with copper bronze (cf. Rule, Pursell, and Brown, *J.*, 1934, 168) yielded only unchanged acid.

Preparation of 4 : 11 : 12-*Tribromofluoranthene.*—Powdered sodium azide (0·24 g.) was added portionwise to 12-acetyl-4 : 11-dibromofluoranthene (1·00 g.) dissolved in trichloroacetic acid (7 g.) at 60°. The solution was kept at 60° for 8 hours and was then poured on ice. The precipitate was boiled with ethanol (130 ml.), and the residual 12-*acetamido*-4 : 11-*dibromofluoranthene* (0·33 g.) crystallised from glacial acetic acid in pale yellow needles, m. p. 284—288° (decomp.) (Found : C, 51·8; H, 2·7; N, 3·2; Br, 38·1. $C_{18}H_{11}ONBr_2$ requires C, 52·0; H, 2·7; N, 3·4; Br, 38·2%). The acetamido-compound (0·06 g.) was boiled with constant-boiling hydrobromic acid (10 ml.) for 3 hours. 12-*Amino*-4 : 11-*dibromofluoranthene hydrobromide* (0·07 g.) thus obtained was washed with hydrobromic acid and then ether, and dried; it had m. p. 245—260° (decomp.) (Found : Br, 51·2. $C_{16}H_{10}NBr_3$ requires Br, 52·6%). It gave with aqueous ammonia (*d* 0·880) the *amine*, golden yellow elongated prisms (from benzene or by sublimation), m. p. 256—258° (decomp.) (Found : N, 3·8; Br, 42·3. $C_{16}H_9NBr_2$ requires N, 3·7; Br, 42·6%).

The amine (0·90 g.) was boiled with glacial acetic acid (12 ml.), and the cooled suspension was added at <20° to 5 ml. of a sodium nitrite solution prepared by dissolving sodium nitrite (1 g.) in concentrated sulphuric acid (7 ml.). After an hour the suspension was slowly added to freshly prepared cuprous bromide (1·5 g.) in constant-boiling hydrobromic acid (20 ml.), at <20°. After ½ hour the temperature was raised to 60° and kept thereat for 10 minutes. The mixture was then heated to 95° and finally diluted with water (300 ml.) and boiled. The dry crude orange product (1·06 g.) was dissolved in chlorobenzene and chromatographed, to give a number of products (for details, see W. K. Leadill, Thesis, Edinburgh, 1951) which seemed to be mixtures of tri- and tetra-bromofluoranthenes, and a *tetrabromofluoranthene*, pale yellow needles (from benzene), m. p. 223—228° (Found : C, 36·7; H, 1·4; Br, 61·6. $C_{16}H_6Br_4$ requires C, 37·1; H, 1·2; Br, 61·7%).

The crude amine (0·22 g.) was boiled for 1 hour with acetic acid (20 ml.), cooled to 15°, and poured slowly into a solution of sodium nitrite (0·5 g.) in concentrated sulphuric acid (3·5 ml.). The mixture was kept for an hour and added to a solution of freshly prepared cuprous bromide (1 g.) in constant-boiling hydrobromic acid (15 ml.) at 35°, acetic acid being used for washing. The solution was allowed to cool to 30° and was then poured into water. The product was dried, dissolved in chlorobenzene, and chromatographed on alumina (7″ × 1″). Development with benzene gave a yellow band with no visible separation. The eluate was collected until it began to run bright yellow and on evaporation gave a product which crystallised from benzene in pale yellow needles, m. p. 206—209°. This was chromatographed on alumina (9″ × ½″) with benzene as solvent and developer. Three fractions of the filtrate were removed forming 25%, 50%, and 25% of the total filtrate. The middle fraction gave pale yellow needles (from benzene) of 4 : 11 : 12-tribromofluoranthene, m. p. 208—210·5°, which showed no m. p. depression with the tribromofluoranthene obtained by the bromination of fluoranthene (Found : Br, 55·6. $C_{16}H_7Br_3$ requires Br, 54·6%). We noted that the tribromofluoranthene, m. p. 205°, prepared by Tobler's method was not quite pure and even after purification by chromatography and recrystallisation had m. p. 208—211°.

Oxidations of Tribromofluoranthene.—Tribromofluoranthene (10 g.) was boiled for 48 hours with sodium dichromate (150 g.) in glacial acetic acid (1500 ml.), and the solution after evaporation to half volume was poured into dilute sulphuric acid (1500 ml.) and filtered. The filtrate was extracted with ether, and the acidic material extracted from the ether by means of

5% aqueous sodium carbonate. Acidification gave 4 : 5-dibromophthalic acid which crystallised from water in plates (0·28 g.), m. p. 200—201° (Found : Br, 49·5. Calc. for $C_8H_4O_4Br_2$: Br, 49·4%), subliming to prisms, m. p. 213°, probably of the anhydride. The methyl ester, needles (from methanol), had m. p. 78—79° (Found : Br, 44·9. Calc. for $C_{10}H_8O_4Br_2$: Br, 45·4%) alone or mixed with an authentic sample.

Tribromofluoranthene (10 g.) was boiled for 20 hours with sodium dichromate (100 g.) in glacial acetic acid (700 ml.). The solution was filtered hot, evaporated to 200 ml., and poured into water (1 l.). A pale green solid was slowly deposited, while a sticky solid adhered to the flask. The former was boiled with 5% sodium carbonate solution (500 ml.), and the hot filtrate acidified. Recrystallisation of the product from methanol–acetic acid gave 6 : 7-*dibromofluorenone*-1-*carboxylic acid* (30 mg.), yellow prisms, m. p. 277—279° (Found : Br, 41·3. $C_{14}H_6O_3Br_2$ requires Br, 41·9%). The filtrate slowly deposited an acid, m. p. 320°, identical with that described below. The residue from the hot filtration and from the sodium carbonate extraction of the sticky solid was extracted with saturated calcium hydroxide solution (2 × 500 ml.). Acidification gave a light yellow acid (1·39 g.) which was boiled with chlorobenzene. The insoluble portion was crystallised from ethanol and gave 2 : 6 : 7-*tribromofluorenone*-1-*carboxylic acid* (90 mg.), yellow, elongated prisms, m. p. 317—320° (decomp.). The cooled chlorobenzene solution gave the same acid (0·22 g.), m. p. and mixed m. p. 315—316° (Found : Br, 51·8. $C_{14}H_5O_3Br_3$ requires Br, 52·0%). One sample crystallised from glacial acetic acid had m. p. 322—324°.

Tribromofluoranthene (5 g.) suspended in glacial acetic acid (600 ml.) was boiled with sodium dichromate (600 g.) for 16 hours. Acetic acid (450 ml.) was distilled off and the residual solution poured into water (1·2 l.). The precipitate was extracted with ether from which an acidic substance (0·75 g.) was obtained by means of ammonia and subsequent acidification. The acid was boiled with methanol (100 ml.) and concentrated sulphuric acid (5 ml.) for 6 hours. Unchanged 2 : 6 : 7-tribromofluorenone-1-carboxylic acid (0·43 g.), m. p. 305—309°, was obtained, and the neutral product in methanol (50 ml.) was hydrolysed with boiling 20% aqueous potassium hydroxide (5 ml.) for 3 hours. The mixture was poured into acid, and the resulting precipitate extracted with ether from which the acidic portion (45 mg.) was removed with sodium carbonate solution. Acidification gave impure 6 : 7-dibromofluorenone-1-carboxylic acid, m. p. 252—262° (with sublimation), which was decarboxylated by heating it in quinoline (10 ml.) at 200° for 1 hour with a trace of copper bronze. Working up in the usual way gave 2 : 3-*dibromofluorenone*, m. p. 203—208°, which was dissolved in benzene and passed down a column (12″ × ½″). Development with benzene gave a pale yellow lower band which rapidly passed down the column. The filtrate was evaporated to small volume and the precipitate crystallised from boiling ethanol. A small quantity of 2 : 3-*dibromofluorenone* separated in pale yellow needles, m. p. 208—211° (sublimation) (Found : Br, 44·9. $C_{13}H_6OBr_2$ requires Br, 47·3%).

Oxidation of 4 : 5-*Dibromo*-o-*xylene*.—4 : 5-Dibromo-*o*-xylene (1 g.) was heated at 170° with nitric acid (*d* 1·15; 10 ml.) for 7 hours. The crude product was extracted with 5% sodium carbonate solution and on acidification gave a solid (0·84 g.) which was dissolved in boiling aqueous acetic acid. The solution was cooled somewhat and separated from some high-melting material, and when kept, deposited 4 : 5-dibromophthalic acid (0·46 g.), which after crystallisation from boiling water had m. p. 219·5° (depends on rate of heating) (Found : Br, 50·3. Calc. for $C_8H_4O_4Br_2$: Br, 49·3%). It formed a methyl ester which, crystallised from light petroleum (b. p. 40—60°), had m. p. 78—79° (Found : C, 34·9; H, 2·1; Br, 44·7. Calc. for $C_{10}H_8O_4Br_2$: C, 34·1; H, 2·3; Br, 45·4%).

Thanks are expressed to the Anglo-Iranian Oil Company Limited for a grant; to the University of Edinburgh for the award of a scholarship to one of us (J. F. K. W.); and to Imperial Chemical Industries Limited, Billingham Division, for a grant to one of us (W. K. L.).

UNIVERSITY OF EDINBURGH. [*Received, August* 28*th*, 1952.]