535. *The Orientation of Disubstituted Fluoranthene Derivatives.*

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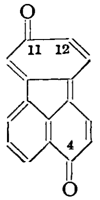
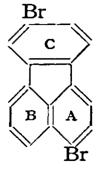
Bromination of fluoranthene gives 4 : 11-dibromofluoranthene, orientated by oxidation to 2 : 7-dibromofluorenone-1-carboxylic acid. By standard methods 4 : 11-dibromofluoranthene gives fluoranthene-4 : 11-dicarboxylic acid which differs from the acid obtained by the interaction of oxalyl chloride and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



(I.)



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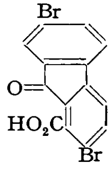

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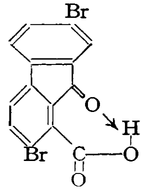


(IV.)

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%).

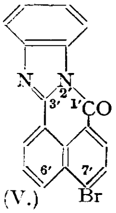
In some experiments the crude acidic product was boiled with an aqueous suspension of barium carbonate, and the boiling mixture filtered. Acidification of the residual barium carbonate gave 2 : 7-dibromofluorenone-1-carboxylic acid, m. p. 266—267°, showing no m. p. depression when mixed with a sample 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 3½″ × ½″. 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″ × $\frac{5}{16}$″. 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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