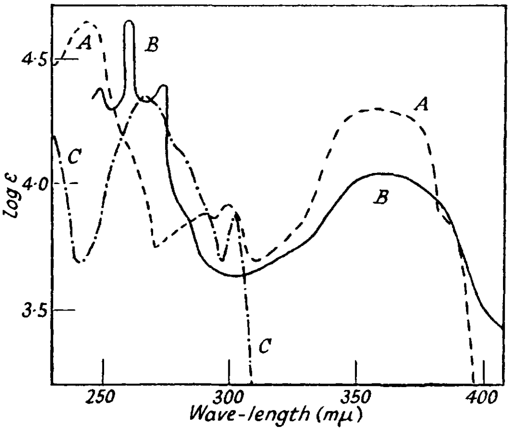
The Preparation of 2-Substituted Fluoranthenes.

By Neil Campbell and J. F. K. Wilshire.

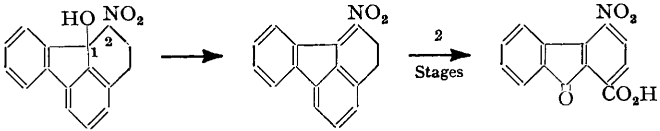
[Reprint Order No. 4702.]

A synthesis of 2-nitrofluoranthene from 1 : 2 : 3 : 4-tetrahydrofluoranthene is described, thereby providing a general method for the preparation of 2-substituted fluoranthenes.

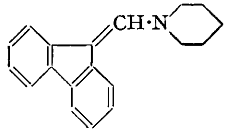
The few known 2-substituted fluoranthenes have been synthesised from fluorene (Bergmann and Orchin, *J. Amer. Chem. Soc.*, 1949, **71**, 1917; Campbell and Wang, *J.*, 1949, 1513; Forrest and Tucker, *J.*, 1948, 1137). We now record the first preparation of a 2-substituted fluoranthene from 1 : 2 : 3 : 4-tetrahydrofluoranthene, which is readily obtained by the reduction of fluoranthene. In an attempt to prepare a dinitrofluoranthene we nitrated tetrahydrofluoranthene with fuming nitric acid in acetic acid and obtained two products: a colourless solid (*A*), $C_{16}H_{13}O_3N$, and a deep orange solid (*B*), $C_{16}H_{11}O_2N$. *A* readily yielded *B* by loss of a molecule of water, thereby suggesting that *A* is a nitro-alcohol and *B* a nitro-hydrocarbon. Oxidation of *B* by sodium dichromate and acetic acid gave β-(9-oxofluoren-1-yl)propionic acid and a compound which was subsequently proved to be 2-nitrofluoranthene. This strongly suggested that *A* is 1 : 2 : 3 : 4-tetrahydro-1-hydroxy-2-nitrofluoranthene (I) and (*B*) 3 : 4-dihydro-2-nitrofluoranthene (II). Confirmation of this was



A, 9-*Piperidinomethylenefluorene.*
B, 3 : 4-*Dihydro-2-nitrofluoranthene.*
C, 1 : 2 : 3 : 4-*Tetrahydrofluoranthene.*



(I) (II) (III)



(IV)

afforded by dehydrogenation of *B* to 2-nitrofluoranthene (II; with a double bond in the 3 : 4-position) whose structure followed from its oxidation to 4-nitrofluorenone-1-carboxylic acid (III) which on decarboxylation yielded 4-nitrofluorenone identical with a sample kindly supplied by Professor J. W. Cook, F.R.S. The ultra-violet absorption spectrum of (II) should be similar to that of a fluorene derivative with a double bond at the 9-position. This was found to be so since the spectra of (II) and of 9-(piperidinomethylene)fluorene (IV) (Miller and Wagner, *J. Org. Chem.*, 1951, **16**, 279), though not identical, exhibited reasonable similarity (see Figure).

5-Bromo-1 : 2 : 3 : 4-tetrahydrofluoranthene reacted similarly with nitric acid, to give 5-bromo-1-hydroxy-1 : 2 : 3 : 4-tetrahydro-2-nitrofluoranthene and 5-bromo-3 : 4-dihydro-2-nitrofluoranthene, the latter on dehydrogenation yielding 5-bromo-2-nitrofluoranthene.

This preferential nitration in the alicyclic rather than in the aromatic nucleus is striking, especially since the 5-position in tetrahydrofluoranthene is susceptible to electophilic attack. Other examples of such nitrations are known and include that of 1: 4-dimethylnaphthalene to 4-methylnaphthyl-1-nitromethane (Robinson and Thompson, *J.*, 1932, 2015) and of 7-phenylacenaphthenone to the 7-nitro-compound (K. Henderson, Thesis, Edinburgh). Since these nitrations have all been effected in acetic acid it is tempting to ascribe the " abnormal " results to the formation of some nitrating agent such as acetyl nitrate. Against this, however, is the observation that side-chain nitration also occurs with other solvents such as nitromethane (see, *e.g.*, Robinson and Thompson, *loc. cit.*). A possible explanation, suggested by Titov (*Chem. Abs.*, 1948, **42**, 7262), is that under the conditions of our experiments (fuming nitric acid at 86°) the oxides of nitrogen which are formed may act an as anti-catalyst for nuclear nitration (see Hughes, Ingold, and Reed, *J.*, 1950, 2432) whilst promoting nitration and oxidation of the reduced ring.

As was expected the spectrum of 1 : 2 : 3 : 4-tetrahydrofluoranthene was found to resemble that of fluorene (see Figure).

EXPERIMENTAL

Chromatographic experiments were done with B.D.H. chromatographic alumina.

Nitration of 1 : 2 : 3 : 4-*Tetrahydrofluoranthene.*—Fuming nitric acid (*d* 1·48; 7·17 ml., 0·15 mole) was added dropwise to the tetrahydro-compound (20·6 g., 0·1 mole) in glacial acetic acid (200 ml.) maintained at 80°. After 1 hr. the solution was cooled and poured into iced water. The product was extracted with ether, washed with aqueous sodium carbonate, then with water, and dried (Na_2SO_4). Evaporation gave a syrup which when triturated with benzene yielded 1 : 2 : 3 : 4-*tetrahydro*-1-*hydroxy*-2-*nitrofluoranthene*, colourless octahedra (from chlorobenzene or acetic acid), m. p. 192—193° (decomp.) (Found : C, 71·5; H, 4·8; N, 5·3. $C_{16}H_{13}O_3N$ requires C, 71·9; H, 4·9; N, 5·2%). The filtrate on evaporation gave a red syrup which was dissolved in benzene–light petroleum and chromatographed (for details see J. F. K. Wilshire, Thesis, Edinburgh, 1952). More of the hydroxynitro-compound was thus obtained (total yield, 7·13 g.) together with, apparently, impure 3 : 4-dihydro-2-nitrofluoranthene (5·82 g.), elongated orange prisms (from ethanol), m. p. 92—94° (Found : C, 76·3; H, 4·4; N, 6·1. Calc. for $C_{16}H_{11}O_2N$: C, 77·1; H, 4·4; N, 5·6%). The nitro-compound was readily obtained from the hydroxynitro-compound by dehydration with acetic anhydride or acetic acid containing a few drops of sulphuric acid.

Structure of 3 : 4-*Dihydro*-2-*nitrofluoranthene.*—The nitro-compound (1·72 g.) was boiled for 3 hr. with sodium dichromate (10 g.) in glacial acetic acid (75 ml.). Half of the acetic acid was distilled off and the residual solution poured into dilute sulphuric acid. The acidic solution was shaken with benzene and ether, and the extract washed with water and then with sodium carbonate solution. Acidification of the sodium carbonate layer gave β-(9-oxofluoren-1-yl)-propionic acid (0·27 g.), yellow plates (from benzene–light petroleum), m. p. 134—136° undepressed when admixed with an authentic sample (Found : C, 75·5; H, 4·7. Calc. for $C_{16}H_{12}O_3$: C, 76·2; H, 4·8%). The non-acidic material left in the original benzene extract proved to be 2-nitrofluoranthene (0·58 g.) giving no m. p. depression when admixed with a sample prepared as below.

3 : 4-Dihydro-2-nitrofluoranthene (8·0 g.) was boiled in sulphur-free xylene (120 ml.) with chloranil (16 g.) for 23 hr. The solution was decanted and diluted with benzene, washed with 5% aqueous sodium hydroxide (3 × 200 ml.), once with 10% sodium hydroxide, and finally with water. The dried (Na_2SO_4) solution was evaporated to small volume, and light petroleum (b. p. 80—100°) was added. The solution was boiled with charcoal and filtered hot and on cooling deposited 2-*nitrofluoranthene* (4·75 g.), yellow elongated prisms, m. p. 151—153° (Found : C, 77·9; H, 3·5; N, 5·7. $C_{16}H_9O_2N$ requires C, 77·7; H, 3·6; N, 5·7%). 2-Nitrofluoranthene (2·0 g.) was boiled for 20 hr. with glacial acetic acid (150 ml.) and sodium dichromate (40 g.). The solution was evaporated to half-volume and poured into dilute sulphuric acid. The mixture was shaken with chloroform and the chloroform layer extracted with 5% aqueous potassium carbonate. The potassium salt which separated and the alkaline extract, on acidific-

ation, yielded 4-*nitrofluorenone*-1-*carboxylic acid* (0·96 g.), yellow elongated prisms, m. p. 213—214° (Found: C, 62·4; H, 2·3; N, 5·1. $C_{14}H_7O_5N$ requires C, 62·4; H, 2·6; N, 5·2%). It forms a *methyl* ester, hexagonal prisms (from methanol), m. p. 163·5—165° (Found: C, 63·3; H, 2·8; N, 4·9. $C_{15}H_9O_5N$ requires C, 63·6; H, 3·2; N, 5·0%). Decarboxylation of the acid (0·25 g.) with quinoline (10 ml.) and copper bronze at 180° for 1 hr. gave a neutral product which was chromatographed in benzene on a column 6″ × ½″. Development with light petroleum gave a pale yellow zone of 4-nitrofluorenone, yellow needles (from ethanol), m. p. 174—175°, undepressed when admixed with an authentic sample (Found: C, 69·0; H, 2·8; N, 6·1. Calc. for $C_{13}H_7O_3N$: C, 69·3; H, 3·1; N, 6·2%). Reduction with concentrated hydrochloric acid and reduced iron powder gave 4-aminofluorenone, red plates (from aqueous ethanol), m. p. 137—139° (lit., 138°) (Found: C, 78·9; H, 4·7. Calc. for $C_{13}H_9ON$: C, 80·0; H, 4·7%).

2-Nitrofluoranthene (1·6 g.) was boiled in ethanol (150 ml.) for 2 hr. with concentrated hydrochloric acid (10 ml.) and reduced iron powder (2 g.). The solution was poured into water and extracted with ether which on evaporation gave 2-aminofluoranthene, greenish-yellow needles (1·1 g.), m. p. 134—136° (lit., 133—134°) (Found: C, 89·0; H, 5·3. Calc. for $C_{16}H_{11}N$: C, 88·6; H, 5·1%). It forms an *acetyl* derivative, elongated prisms (from acetic acid), m. p. 254—255° (Found: C, 83·4; H, 5·2; N, 5·4. $C_{18}H_{13}ON$ requires C, 83·4; H, 5·0; N, 5·4%), and a *benzoyl* derivative, needles (from acetic acid), m. p. 237—238° (Found: N, 4·8. $C_{23}H_{15}ON$ requires N, 4·4%).

5-*Bromo*-2-*nitrofluoranthene*.—By a similar series of reactions 5-bromo-1 : 2 : 3 : 4-tetrahydrofluoranthene (11·5 g.) was converted into 5-*bromo*-1 : 2 : 3 : 4-*tetrahydro*-1-*hydroxy*-2-*nitrofluoranthene* (4·88 g.), hexagonal prisms (from acetic acid), m. p. 163—164° (Found: C, 55·8; H, 3·5; N, 3·8; Br, 22·9. $C_{16}H_{12}O_3NBr$ requires C, 55·5; H, 3·5; N, 4·1; Br, 23·1%) and 5-*bromo*-3 : 4-*dihydro*-2-*nitrofluoranthene* (2·07 g., crude), orange needles (from benzene–ethyl acetate), m. p. 181—183° (Found: N, 4·4; Br, 24·9. $C_{16}H_{10}O_2NBr$ requires N, 4·3; Br, 24·4%). The pure dihydro-compound (0·15 g.) was boiled in nitrobenzene (15 ml.) with chloranil (0·12 g.) for 48 hr. The nitrobenzene was removed by steam-distillation and the product dissolved in benzene which was then washed with 10% aqueous sodium hydroxide, twice with more dilute sodium hydroxide, then with water, and finally dried (Na_2SO_4). The benzene solution was reduced and passed down a column 6″ × ½″. Development with benzene gave a bright yellow band which yielded a crystalline solid (0·125 g.). Successive crystallisations from benzene–acetic acid, ethyl acetate, and acetic acid gave somewhat impure 5-*bromo*-2-*nitrofluoranthene*, orange needles, m. p. 165—168° (Found: C, 58·2; H, 2·6; N, 4·3; Br, 24·3. $C_{16}H_8O_2NBr$ requires C, 58·9; H, 2·5; N, 4·3; Br, 24·5%).

Spectroscopic Measurements.—The ultra-violet spectra of the following substances were measured by means of a Hilger Barfit Medium Spectrograph. The solvent was spectrographically pure *cyclo*hexane (B.D.H. Ltd.). Log ε is given in parentheses. 2-Nitro-3 : 4-dihydrofluoranthene: 248 (4·4), 261 (4·66), 270 (4·38), and 365 mμ (4·04). 5-Bromo-2-nitro-3 : 4-dihydrofluoranthene: 266 (4·53), 276 (4·61), 289 (4·26), and 368 mμ (3·92). The bathochromic influence of the bromine atom is thereby demonstrated. 1 : 2 : 3 : 4-Tetrahydrofluoranthene: 266 (4·33), 280 (4·13) (inflection), and 303 mμ (3·88). These bands correspond to the three main absorption bands of fluorene of nearly the same wave-lengths (Askew, *J.*, 1935, 512; Mayneord and Roe, *Proc. Roy. Soc.*, 1937, A, **158**, 640).

Thanks are expressed to the University of Edinburgh for the award of a post-graduate studentship to one of us (J. F. K. W.) and to the Anglo-Iranian Oil Company, Limited, for a grant.

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[*Received, October* 6*th*, 1953.]