Nitration of 3-Methylfluoranthene

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3-Methylfluoranthene undergoes nitration at the 2-, 4-. and 8-positions in yields of ca. 20. 20. and 55%. respectively. A fourth isomer (probably the 10-nitro-isomer) was detected by gas chromatography. 3-Methyl-1-. 2-. 4-, 8--. 9-. and 10-nitrofluoranthenes have been synthesised. Dinitration of 3-methylfluoranthene gives the 4.8-dinitro-derivative. Loss of OH in the mass spectrometer seems to be characteristic of aromatic compounds containing methyl and nitro-groups on adjacent or peri-carbon atoms.

LITTLE is known about electrophilic substitution of the alkylfluoranthenes; a study of the nitration of the accessible 3-methylfluoranthene [1] was therefore undertaken. Treatment with concentrated nitric acid in acetic acid yielded a mixture from which three mono-nitro-products were isolated. The main product showed a u.v. spectrum similar to that of 8-nitrofluoranthene and was proved to be 3-methyl-8-nitrofluoranthene (I) by oxidation with chromic acid to 6-nitro-9-oxofluorene-1-carboxylic acid, identical with a sample obtained by oxidising 8-nitrofluoranthen-3-ol.[2] The methylnitro-fluoranthene was also synthesised from β-(2-methyl-fluoren-9-yl)propionic acid,[3] nitration of which yielded the 7-nitro-compound.[4] Ring closure then gave 1,10b-dihydro-4-methyl-9-nitrofluoranthen-3(2H)-one (II). Reduction of the ketone followed first by dehydration and then by dehydrogenation yielded 3-methyl-8-nitro-fluoranthene (I), identical with the nitration product.

The second product was 3-methyl-4-nitrofluoranthene (III; R = H) with a u.v. spectrum indicative of a nitro-group in the naphthalene portion of the molecule.[5] The identification of the compound was confirmed by synthesis from the oxime (IV; R = N·OH) of 1,10b-dihydro-4-methylfluoranthen-3(2H)-one (IV; R = O),[3] which when oxidised with trifluoroperoxyacetic acid and dehydrogenated gave 3-methyl-4-nitrofluoranthene.

The structure of the third isomer, 3-methyl-2-nitro-fluoranthene (V), was also proved by synthesis. 1,10b-Dihydro-3-methylfluoranthene was converted into the epoxide and rearranged by acid to 1,10b-dihydro-3-methylfluoranthen-2(3H)-one (VI), whose u.v. spectrum was similar to that of fluorene. The constitution of the compound was confirmed by the n.m.r. spectrum. A model of the compound shows that the reduced ring is a half-chair in which the C-1 methylene protons are non-equivalent with the adjacent C-10b proton. The pseudo-axial 10b-proton [τ 5·95 (2 × d)] couples with the pseudo-axial 1-proton [τ 8·1 (2 × d, J 15 Hz)] and with the pseudo-equatorial 1-proton [τ 6·95 (2 × d, J 7 Hz); C-1 J_{gem} 17 Hz]. The higher field position of the former methylene proton signal is probably the result partly of its pseudo-axial configuration and partly of its position above the plane of the aromatic ring system and the

consequent shielding by the aromatic ring current.[6] The other proton is deshielded by the neighbouring carbonyl group lying in the same plane. The methyl signal occurs as a doublet at τ 8·25 and the 3-proton signal as a quartet
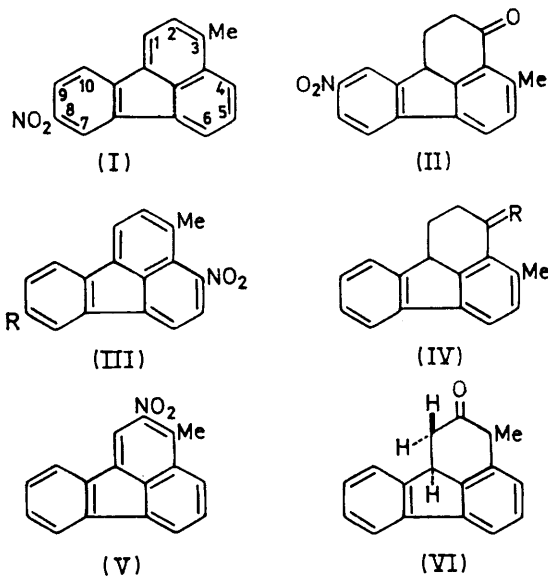
at τ 6·45. Oxidation of the oxime of the ketone [? oxime] with trifluoroperoxyacetic acid gave a nitro-product, dehydrogenation of which with o-chloranil yielded 3-methyl-2-nitrofluoranthene (V).

Gas chromatography of the products obtained by the nitration of 3-methylfluoranthene showed that the 8-nitro-compound was obtained in ca. 55% yield (cf. 20% for each of the other two isomers). The presence of a fourth isomer was indicated, but we failed to separate it completely from the 2-nitro-compound. This fourth isomer is probably 3-methyl-10-nitrofluoranthene (IX). This compound was prepared by applying the Beckmann transformation to the oxime of 1,10b-dihydrofluoranthen-3(2H)-one to give the lactam (VII), previously obtained by the interaction of the ketone with hydrazoic acid.[7] Hydrolysis gave β-(1-aminofluoren-9-yl)propionic acid, which with peroxymaleic acid yielded the nitro-compound (VIII; R = CO₂H). The acid chloride, on treatment with diethyl ethoxymagnesiomalonate gave

[1] N. Campbell and N. H. Wilson, Chem. and Ind., 1970, 1114.
[2] H. F. Andrew, N. Campbell, J. T. Craig, and K. J. Nichol, J. Chem. Soc., 1968, 1761.
[3] H. F. Andrew, N. Campbell, E. M. Swan, and N. H. Wilson, Proc. Roy. Soc. Edinburgh, in the press.
[4] Cf. N. Campbell, J. T. Craig, and K. J. Nichol, Proc. Roy. Soc. Edinburgh, 1960, 65, 223.
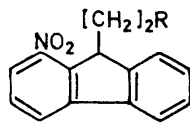
[5] H. F. Andrew, Thesis, Edinburgh, 1964, p. 37.
[6] E. A. Chandross and C. F. Sheley, jun., J. Amer. Chem. Soc., 1968, 90, 4347; D. A. Crombie and S. Shaw, J. Chem. Soc. (C), 1969, 2489.
[7] N. Campbell and D. A. Crombie, Proc. Roy. Soc. Edinburgh, 1962, 65A, 376.
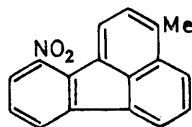
the methyl ketone (VIII; R = COMe), and this was reduced by sodium borohydride to the alcohol (VIII; R = CHMe·OH). Ring closure with sulphuric and
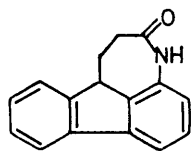
(VII)

(VIII)

(IX)

acetic acids yielded 1,2,3,10b-tetrahydro-3-methyl-10-nitrofluoranthene, dehydrogenation of which gave 3-methyl-10-nitrofluoranthene (IX).

TABLE 1

Nitration mixture	R_F
3-Methyl-8-nitrofluoranthene	1·00
3-Methyl-4-nitrofluoranthene	0·60
3-Methyl-2-nitrofluoranthene	0·70
3-Methyl-x-nitrofluoranthene	0·76
Synthetic compounds	
3-Methyl-9-nitrofluoranthene	0·99
3-Methyl-1-nitrofluoranthene	0·72
3-Methyl-10-nitrofluoranthene	0·76

Removal of the 4- and 8-nitro-isomers from the mixture of nitro-products obtained above left a mixture showing strong i.r. bands at 827, 780, and 755 cm⁻¹, belonging to 3-methyl-2-nitrofluoranthene, as well as bands at 840 and 772 cm⁻¹, which indicate the presence of 3-methyl-10-nitrofluoranthene. This was substantiated by g.l.c. of the crude nitration mixture and of synthetic nitro-isomers (see Table 1; R_F values are relative to 3-methyl-8-nitrofluoranthene). In the gas chromatogram of the nitration mixture three peaks were clearly observed, corresponding to the 2-, 4-, and 8-nitro-isomers, but the 2-nitro-isomer peak was accompanied by a fourth, incompletely resolved, whose R_F value corresponded to that of 3-methyl-10-nitrofluoranthene. This, together with peak enhancement observation, strongly supports the evidence that the fourth isomer is 3-methyl-10-nitrofluoranthene; the 7- (or 10-) position in fluoranthene is known to be susceptible to electrophilic attack.[8] Further it has been suggested that fluoranthene behaves in some respects as a biphenyl derivative,[9] and nitration of 3-methylfluoranthene at the 8- (55%) and 10-positions (5%) finds analogy in the nitration of 4-methylbiphenyl mainly in the 4′-position and to a lesser extent in the 2′-position.[10]

[8] K. C. C. Bancroft and G. R. Howe, *J. Chem. Soc. (C)*, 1970, 1541.
[9] N. Campbell and Nd 8-n Keir, *J. Chem. Soc.*, 1955, 1233.
[10] W. S. M. Grieve and ᴅ. H. Hey, *J. Chem. Soc.*, 1932, 1888.
[11] P. R. Wells, *Austral. J. Chem.*, 1964, 17, 967.

In the n.m.r. spectrum the methyl protons of 1-methylnaphthalene suffer a downfield shift when a nitro-group is inserted at the 2-position, but undergo an upfield shift when a nitro-group occupies the *peri*-position.[11] We have observed similar changes in 3-methylfluoranthene with shifts extrapolated to infinite dilution in deuteriochloroform (Varian HA-100 100 MHz instrument). While 3-methylfluoranthene resonates at 277 Hz downfield from tetramethylsilane, 3-methyl-2-nitrofluoranthene and 3-methyl-4-nitrofluoranthene show shifts of 290 and 259 Hz, respectively. The upfield shift thus seems to be a structural characteristic not only of *peri*-methylnitronaphthalene but also of its benzo-derivatives.

The mass spectra of the nitrofluoranthenes and nitromethylfluoranthenes present points of interest. In the mass spectrometer 1-nitronaphthalene loses first CO and then NO, the loss of CO not being generally encountered in monocyclic aromatic compounds.[12] 3-Nitrofluoranthene might be expected to behave similarly; it does not, however, giving (by loss of NO and NO₂) ions m/e 217 and 201, the former then yielding an ion m/e 189 by loss of CO. This contrasting behaviour may be explained in terms of the possibility that 1-nitronaphthalene loses CO *via* the formation of an indene derivative, whereas the analogous intermediate (X) would be too strained to exist.
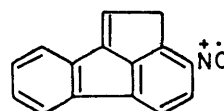
(X)

o-Nitrotoluene in the mass spectrometer loses first OH and then CO;[13] this suggested that such loss of OH might be diagnostic for aromatic compounds which contain methyl or methylene and nitro-groups attached to neighbouring or *peri*-carbon atoms. We have found this to be so; 1-nitrofluorene, 2-methyl-1-nitronaphthalene, 1-methyl-8-nitronaphthalene, and 3-methyl-2- and -4-nitrofluoranthenes which behave in this way in contrast to their isomers (see Table 2). These compounds also give peaks corresponding to loss of OH and CO. The other methylnitrofluoranthenes show no loss of OH and behave as expected, losing NO, NO₂, *etc.* (see Table 2).

The dinitration of 3-methylfluoranthene presented some difficulty, but eventually 3-methyl-4,8-dinitrofluoranthene (III; R = NO₂) was isolated; this compound was also obtained by the nitration of either 4- or the 8-nitro-isomer.

3-Methyl-1-nitrofluoranthene was prepared by the nitration of 1,2,3,10b-tetrahydro-3-methylfluoranthene, which yielded 2,3-dihydro-3-methyl-1-nitrofluoranthene.[14] This compound on oxidation yielded 9-oxofluorene-1-carboxylic acid and when dehydrogenated

[12] J. Harley-Mason, T. P. Toube, and D. H. Williams, *J. Chem. Soc. (B)*, 1966, 296.
[13] J. H. Beynon, R. A. Saunders, A. Topham, and A. E. Williams, *J. Chem. Soc.*, 1965, 6403.
[14] *Cf.* N. Campbell and J. F. K. Wilshire, *J. Chem. Soc.*, 1954, 867.

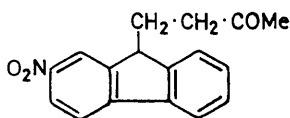gave 3-methyl-1-nitrofluoranthene (XI; $R^1 = H$, $R^2 = NO_2$).
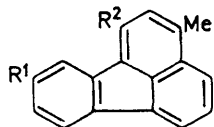
(XI)   (XII)

3-Methyl-9-nitrofluoranthene (XI; $R^1 = NO_2$, $R^2 =$ H) was synthesised from the ketone (XII), obtained by nitrating 2-fluoren-9-ylethyl methyl ketone. Ring closure of the corresponding alcohol (XII; CH·OH instead of CO) and subsequent dehydrogenation gave 3-methyl-9-nitrofluoranthene, since it differed from the other possible product, the 4-nitro-isomer.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus and chromatographic purification was effected on alumina (Spence type H). I.r. spectra were measured for Nujol

plates (from benzene), m.p. 180—181° (Found: C, 78·4; H, 4·3; N, 5·2%), $\lambda_{max.}$ 215, 236, 279, 290, and 364 nm (log ε 4·56, 4·49, 4·34, 4·41, and 3·94).

Later fractions gave a mixture, crystallisation of which from benzene–light petroleum yielded more of the 4-nitro-compound. The filtrate was chromatographed; the later fractions eluted with benzene gave 3-*methyl-2-nitrofluoranthene*, which formed crystals (after several crystallisations from acetic acid), m.p. 164—166° (Found: C, 78·4; H, 4·0; N, 5·55%), $\lambda_{max.}$ 210, 226, 249, 261, 289, 343, and 362 nm (log ε 4·46, 4·55, 4·45, 4·46, 4·43, 3·90, and 3·84).

3-*Methyl*-4,8-*dinitrofluoranthene*.— 3-Methylfluoranthene was added to warm concentrated nitric acid in portions. Much of the product separated as a plastic mass, but the supernatant liquor on cooling deposited 3-*methyl*-4,8-*dinitrofluoranthene* in poor yield, as yellow needles (from acetic acid), m.p. 278—280° (Found: C, 66·0; H, 3·0; N, 8·8. $C_{17}H_{10}N_2O_4$ requires C, 66·7; H, 3·2; N, 9·15%). Warming 3-methyl-4- or 3-methyl-8-nitrofluoranthene in concentrated nitric acid for 5 min and leaving overnight gave a yellow solid which crystallised from acetic acid to yield the same methyldinitrofluoranthene.

3-*Methyl*-8-*nitrofluoranthene*.— β-(2-Methylfluoren-9-yl)-

TABLE 2

Salient fragments (m/e values) from 3-methyl-x-nitrofluoranthenes

x	M^+	$M^+ - OH$	$M^+ - NO$	$M^+ - OH$ $-CO$	$M^+ - NO_2$	$M^+ - NO$ $-CO$	$M^+ - NO_2$ $-C_2H_2$
1	261 †				215	203	189
2	261	244		216 †	215		189
4	261	244 †		216	215		189
8	261 †		231		215	203	189
9	261 †		231		215	203	189
10	261 †		231		215	203	189

† Base peak.

suspensions unless otherwise indicated and u.v. spectra for solutions in methanol with a Unicam SP 800 instrument. N.m.r. spectra were recorded with a Perkin-Elmer R10 (60 MHz) instrument for solutions in deuteriochloroform and mass spectra with an A.E.I. MS902 instrument. G.l.c. was carried out on a 2% OV1 silicone oil–Chromosorb column (6 ft × ¼ in), with oven temperature 190° and carrier gas nitrogen at 20 lb in⁻².

Nitration of 3-*Methylfluoranthene*.—Concentrated nitric acid (20 ml) was added with stirring to 3-methylfluoranthene (2·0 g) in acetic acid (40 ml). After 1 h at 40° the solution was poured into water and the product was washed with water, dried, and chromatographed in benzene on alumina (80 g). A yellow band gave an oil which was dissolved in boiling benzene, and light petroleum was added until the solution became cloudy. The cooled solution yielded 3-*methyl*-8-*nitrofluoranthene* (0·93 g), m.p. 178—180° (Found: C, 78·2; H, 4·2; N, 5·4. $C_{17}H_{11}NO_2$ requires C, 78·15; H, 4·2; N, 5·4%), $\lambda_{max.}$ 213, 232, 250infl, 305, 328, and 380 nm (log ε 4·52, 4·59, 4·29, 4·30, 4·24, and 4·21). The compound (0·3 g) was boiled (4 h) with sodium dichromate (3·0 g) in acetic acid (10 ml) and poured into dilute sulphuric acid. 6-Nitro-9-oxofluorene-1-carboxylic acid [2] separated, and gave orange needles (from acetic acid), m.p. and mixed m.p. 275—276°.

The benzene–light petroleum filtrate was chromatographed with benzene–light petroleum (1 : 1 v/v) as eluant. An upper yellow band yielded more (0·23 g) of the foregoing methylnitrofluoranthene; elution of the lower band yielded first 3-*methyl*-4-*nitrofluoranthene* (10 mg), yellow

propionic acid,[3] when nitrated by the method of Campbell *et al.*,[4] gave β-(2-*methyl*-7-*nitrofluoren*-9-*yl*)*propionic acid* (62%), m.p. 206—207°, as plates (from acetic acid) (Found: C, 68·7; H, 4·9; N, 4·7. $C_{17}H_{15}NO_4$ requires C, 68·7; H, 5·1; N, 4·7%). The position of the nitro-group was assigned by analogy with that assumed in the nitration of fluoren-9-ylpropionic acid,[4] 9-alkylfluorenes,[15] and 2-methyl-fluorene.[16] The acid was heated (30 min) in polyphosphoric acid at 150° to yield 1,10b-*dihydro*-4-*methyl*-9-*nitrofluoranthen*-3(2H)-*one*, which was chromatographed in benzene to give needles (from benzene), m.p. 228—232° (Found: C, 72·8; H, 4·7; N, 4·9. $C_{17}H_{13}NO_3$ requires C, 73·1; H, 4·7; N, 5·0%). Reduction with sodium borohydride or by the Meerwein–Ponndorf method gave (respectively) 60 and 70% yields of the corresponding *carbinol*, as crystals (from aqueous ethanol), m.p. 206—212° (Found: C, 72·4; H, 5·3; N, 5·5. $C_{17}H_{15}NO_3$ requires C, 72·6; H, 5·4; N, 5·0%), which was dehydrated by shaking (24 h) with phosphorus pentoxide in benzene. Chromatography of the product in benzene gave a single yellow band which yielded 1,10b-*dihydro*-3-*methyl*-8-*nitrofluoranthene* (76%), lemon-yellow blades, m.p. 143—145° (Found: C, 77·9; H, 5·0; N, 5·3. $C_{17}H_{13}NO_2$ requires C, 77·6; H, 5·0; N, 5·3%). Heating (1 h) the dihydro-compound in benzene with chloranil gave 3-methyl-8-nitrofluoranthene, yellow needles (from acetic acid), m.p. 178—180°, identical (mixed m.p.) with the compound obtained by the nitration of the hydrocarbon.

[15] L. H. Klemm, E. Huber, and C. E. Klopenstein, *J. Org. Chem.*, 1964, **29**, 1960.

[16] E. Sawicki, *J. Amer. Chem. Soc.*, 1954, **76**, 2269.

3-Methyl-4-nitrofluoranthene.— 1,10b-Dihydro-4-methyl-fluoranthen-3(2H)-one (3·5 g) was heated (6 h) in pyridine (2·4 ml) and ethanol (60 ml) with hydroxylamine hydrochloride (2·4 g). Evaporation gave the *oxime* (95%), which was washed with water; m.p. 221—222·5° (Found: C, 82·2; H, 6·25; N, 5·3. $C_{17}H_{15}NO$ requires C, 81·9; H, 6·3; N, 5·6%). The oxime (3·2 g) was suspended in acetonitrile (27 ml) with urea (0·26 g) and disodium hydrogen phosphate (10 g). Trifluoroperoxyacetic acid [from 90% hydrogen peroxide (0·65 ml) and the acid anhydride (4·4 ml)] in acetonitrile (6·5 ml) was added to the boiling mixture during 2·5 h and after a further period of boiling (4 h) the mixture was poured into water. Extraction with methylene dichloride and evaporation of the extract left a residue which was triturated with methylene dichloride (10 ml). Unchanged oxime remained and the filtrate on evaporation gave a syrup (0·86 g) which was boiled (2 h) in benzene with *o*-chloranil (2·2 g). The cooled, filtered solution was chromatographed to give two yellow bands. The upper band gave 3-methyl-4-nitrofluoranthene (0·16 g), m.p. 178—181° (from acetic acid), identical (mixed m.p.; i.r. and u.v. spectra) with the compound already described.

3-Methyl-2-nitrofluoranthene.— 1,10b-Dihydro-3-methyl-fluoranthene (2 g), anhydrous sodium carbonate (4·5 g), and methylene chloride (20 ml) were boiled gently with stirring and trifluoroperoxyacetic acid [from 90% hydrogen peroxide (0·41 ml) and trifluoroacetic anhydride (2·54 g)] was added during 45 min. After further boiling (30 min) the mixture was poured into water and extracted with methylene dichloride. The extract was washed with water and evaporated to give the epoxide as a red oil. This was boiled overnight with ethanol (10 ml), water (7·5 ml), and concentrated sulphuric acid (1·5 ml). The solution was poured into water and extracted with ether. The extract was washed with water and on evaporation gave the crude ketone, which was chromatographed in benzene. Elution with the same solvent (100 ml fractions) yielded (in fractions 2—4) 1,10b-*dihydro-3-methylfluoranthen*-2(3H)-*one* (0·77 g), m.p. 114—116° (from methanol) (Found: C, 86·9; H, 6·0. $C_{17}H_{14}O$ requires C, 87·15; H, 6·0%), $\nu_{max.}$ 1705 cm^{-1}. The *oxime* gave needles (from benzene), m.p. 218—219° (decomp.), which slowly formed plates (Found: C, 82·2; H, 6·0; N, 5·9. $C_{17}H_{15}NO$ requires C, 81·9; H, 6·1; N, 5·6%), $\nu_{max.}$ 935s cm^{-1}. Oxidation with trifluoroperoxyacetic acid gave a nitro-product which was heated (1 h) with *o*-chloranil (4·5 g) in benzene (20 ml). The cooled solution was filtered and chromatographed. Development with benzene gave a small yellow band, followed by the main yellow band; the latter yielded 3-methyl-2-nitrofluoranthene (0·21 g) after crystallisation from acetic acid and then benzene–light petroleum; m.p. and mixed m.p. 163—166°, $\nu_{max.}$ (CS$_2$) 827s, 780s, and 755 cm^{-1}.

3-Methyl-1-nitrofluoranthene.— 1,2,3,10b-Tetrahydro-3-methylfluoranthene (2·3 g) was treated with nitric acid as described by Campbell and Wilshire [14] to give a red syrup (1·5 g), which was heated (1 h) with acetic acid (15 ml), acetic anhydride (5 ml), and concentrated sulphuric acid (3 drops). The solution was poured into water and the product, which showed no i.r. hydroxy-band, was dissolved in benzene–light petroleum and chromatographed. Development with the same mixture gave two yellow bands, the lower of which yielded 2,3-*dihydro-1-nitro-3-methyl-fluoranthene* (0·9 g), orange elongated prisms (from acetic acid), m.p. 104—106° (Found: C, 77·9; H, 4·9; N, 5·0. $C_{17}H_{13}NO_2$ requires C, 77·6; H, 4·95; N, 5·3%), which was

dehydrogenated by *o*-chloranil in boiling benzene to give 1-*nitro-3-methylfluoranthene*, yellow needles (from acetic acid), m.p. 179—181° (Found: C, 78·2; H, 4·3; N, 5·4), $\lambda_{max.}$ 215, 254, 283, 332, and 388 nm (log ε 4·54, 4·42, 4·35, 3·88, and 3·81). The compound was reduced by tin and hydrochloric acid to the amino-derivative, which with chromic anhydride and acetic acid yielded 9-oxofluorene-1-carboxylic acid, m.p. and mixed m.p. 190—193°.

3-Methyl-9-nitrofluoranthene.—2-Fluoren-9-ylethyl methyl ketone was nitrated [4] to give the nitro-ketone (20—40%), which was chromatographed in benzene. Some starting material was obtained and then the 2-*nitro-ketone*, pale green elongated plates (from benzene–light petroleum), m.p. 126·5—128° (decomp.) (Found: C, 72·6; H, 5·0; N, 5·5. $C_{17}H_{15}NO_3$ requires C, 72·6; H, 5·4; N, 5·0%). Oxidation with sodium dichromate and acetic acid yielded 2-nitrofluorenone, m.p. and mixed m.p. with an authentic sample 221—222°.

The nitro-ketone was also obtained by treating the acid chloride of β-(2-nitrofluoren-9-yl)propionic acid [from the acid (6·5 g)] with diethyl ethoxymagnesiomalonate and hydrolysing the product with water (120 ml), acetic acid (180 ml), and sulphuric acid (23 ml). The product was poured into water, basified, and extracted with ether. Evaporation gave the ketone, which was chromatographed; yield 2·2 g, m.p. and mixed m.p. 126°.

The ketone (0·5 g) in the minimum of ethanol was reduced by a saturated ethanolic solution (100 ml) of sodium borohydride at 30°. After 90 min dilute hydrochloric acid was added and the mixture was extracted with ether. Evaporation of the extract gave a yellow oil (0·41 g) which after being washed with aqueous sodium carbonate showed a broad OH band at 3500 cm^{-1}. This was cyclised by stirring on a water-bath with acetic acid (16 ml) and conc. sulphuric acid (8 ml) for 5 min. Pouring into water and extraction with ether followed by evaporation of the extract gave a yellow oil (0·26 g), which was heated (1 h) with *o*-chloranil in benzene. The solution was then chromatographed, giving a yellow band which on elution with benzene yielded 3-*methyl-9-nitrofluoranthene* (0·16 g), yellow prisms (from acetic acid), m.p. 166—169° (Found: C, 78·4; H, 4·25; N, 5·1%), $\lambda_{max.}$ 211, 235, 252infl, 313, 328, and 373 nm (log ε 4·51, 4·66, 4·26, 4·38, 4·33, and 4·14), u.v. spectrum similar to that of 3-methyl-8-nitrofluoranthene.

3-Methyl-10-nitrofluoranthene.—The oxime of 1,10b-di-hydrofluoranthen-3(2H)-one (6 g) was heated (15 min) with polyphosphoric acid (130 g) at 125°. The mixture was poured into water and extracted with chloroform. Evaporation of the extract gave a high yield of the crude lactam, as plates, m.p. and mixed m.p. [7] 233—235° (from acetic acid). The lactam was hydrolysed to the amino-acid. [7] Maleic anhydride (8·75 g) was added at 0° to methylene chloride (50 ml) and 90% hydrogen peroxide (2·5 ml) and after 10 min the mixture was heated to the b.p. The amino-acid (3·5 g) was then added; the mixture was boiled (1 h), cooled, and filtered. The residue was washed with methylene chloride and the combined methylene chloride solutions were washed with 5% hydrochloric acid (3 × 200 ml) and saturated sodium chloride (2 × 200 ml), and dried (MgSO$_4$). Evaporation gave β-(1-*nitrofluoren-9-yl)propionic acid*, orange prisms (from acetic acid) (2·73 g), m.p. 184—186° (Found: C, 67·6; H, 4·5; N, 5·2. $C_{16}H_{13}NO_4$ requires C, 67·8; H, 4·6; N, 4·95%). To obtain reproducible figures in carbon analysis a high combustion temperature and a catalyst were necessary.

The acid (1·5 g) was converted into the acid chloride with thionyl chloride, and excess of this reagent was removed by adding benzene and subsequent distillation. The oily acid chloride in ether with a little benzene was treated with diethyl ethoxymagnesiomalonate [from magnesium (0·2 g), ethanol (1 ml), and diethyl malonate (1·25 g) in dry ether]. The product was worked up to give an oil, which was boiled overnight with acetic acid (30 ml), water (20 ml), and concentrated sulphuric acid (3·8 ml). The mixture was poured into water and the product was taken up in benzene; the solution was chromatographed on deactivated alumina [water (6 g) added to alumina (100 g); *i.e.* grade 3 on the Brockmann scale]. Development with benzene gave a faint yellow band which yielded the *methyl ketone,* pale yellow plates (0·84 g) (from benzene–light petroleum), m.p. 112—113° (Found: C, 72·5; H, 5·1; N, 5·3. $C_{17}H_{15}NO_3$ requires C, 72·6; H, 5·4; N, 5·0%), $\nu_{max.}$ 1698 cm^{-1} (CO). The ketone was reduced with sodium borohydride as before to give the carbinol as a light oil (0·76 g), which showed no i.r. carbonyl peak and underwent ring closure with sulphuric acid. Work-up as before gave a yellow oil which yielded 1,2,3,10b-*tetrahydro-3-methyl*-10-*nitrofluoranthene,* elongated

plates or needles (0·68 g) after three crystallisations from ethanol, m.p. 104—106° (Found: C, 76·7; H, 5·5; N, 5·2. $C_{17}H_{15}NO_2$ requires C, 77·0; H, 5·7; N, 5·2%), with a u.v. spectrum similar to that of 1-nitrofluorene; τ 1·8—2·9 (6H, m, Ar), 5·8 (1H, 2 × d, 10b-H), 8·7 (3H, d, Me), and complex signals in the region 6·7—9·3 attributable to the remaining 5 protons. The tetrahydro-compound (3·5 g) was heated with *o*-chloranil in xylene (1·5 h) to give 3-*methyl*-10-*nitrofluoranthene,* yellow plates (after two crystallisations from acetic acid and one from benzene–light petroleum), m.p. 156—157° (Found: C, 78·4; H, 4·2; N, 5·65%), $\nu_{max.}$ (CS$_2$) 840s and 772s cm^{-1}, λ_{max} 212, 240, 314, 328, and 359 nm (log ε 4·59, 4·66, 4·22, 4·21, and 3·96).

1-*Nitrofluorene.*—1-Aminofluorene, prepared by the action of hydrazoic acid on 1-acetylfluorene and subsequent hydrolysis, was oxidised by peroxymaleic acid to 1-nitrofluorene, needles (from acetic acid), m.p. 105—106° (lit.,[17] 104—105°), $\lambda_{max.}$ 210, 260, and 333br nm (log ε 4·36, 4·43, and 3·51), u.v. spectrum similar to those of the 3- and 4-nitro-isomers.

[17] Y. Yost and H. R. Gutmann, *J. Chem. Soc.* (*C*), 1969, 343.