The Nitration of 3-Methoxyfluoranthene

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The nitration of 3-methoxyfluoranthene yields 3-methoxy-2- and -8-nitrofluoranthene, each of which on further nitration gives 3-methoxy-2,8-dinitrofluoranthene. 3-Methoxy-8- and -9-nitrofluoranthene and 3-methoxy-2,9-dinitrofluoranthene have been synthesised. 3-Toluene-*p*-sulphonyloxy- and 3-acetoxy-fluoranthene undergo nitration in the 8-position. New methods are given for the preparation of 2-methoxy-7-nitrofluorene and 3-nitrofluorene.

SUBSTITUENTS in the 3-position of fluoranthene often direct a second substituent into the 8- or 9-positions,[1,2] but nitration and bromination of 3-acetamidofluoranthene occur at position 2.[3,4] We now find that 3-methoxyfluoranthene (I; $R^1 = Me$; $R^2 = R^3 = H$) with nitric acid in acetic acid yields a mixture of 3-methoxy-2- and -8-nitrofluoranthene from which the 2-nitro-isomer (II; $R^1 = Me$, $R^2 = R^3 = H$) was isolated. This compound was orientated by establishing its identity with the product obtained by the alkaline hydrolysis of 3-amino-2-nitrofluoranthene [3] followed by methylation. Further nitration of the mixture of 3-methoxy-mononitrofluoranthenes or of the 2-nitro-isomer yielded 3-methoxy-2,8-dinitrofluoranthene (II; $R^1 = Me$, $R^2 = NO_2$, $R^3 = H$), whose structure is proved below. The results are reminiscent of the nitration of 4-methoxybiphenyl, which gives 4-methoxy-3-nitro- (80%) and 4-methoxy-4′-nitro-biphenyl (15%), further nitration yielding 4-methoxy-3,4′-dinitrobiphenyl,[5] thus emphasising the similarity of biphenyl and fluoranthene substitution.[1] Since, however, 4-toluene-*p*-sulphonyloxybiphenyl nitrates mainly in the 4′-position,[5] it seemed probable that compound (I; $R^1 = SO_2{\cdot}C_6H_4{\cdot}Me$-*p*, $R^2 = R^3 = H$) would yield the 8-nitro-product at the expense of the 2-isomer, and this proved to be so. The product (I; $R^1 = SO_2{\cdot}C_6H_4{\cdot}Me$-*p*, $R^2 = NO_2$, $R^3 = H$) was hydrolysed to the phenol (I; $R^1 = R^2 = NO_2$, $R^3 = H$) which was oxidised to 6-nitro-9-oxofluorene-1-carboxylic acid (III). Decarboxylation of the acid yielded 3-nitrofluorenone, and since its m.p. differs greatly from that of 3-nitro-9-oxofluorene-1-carboxylic acid,[3] the structure of the acid is rigidly established. The phenol must therefore be 3-hydroxy-8-nitrofluoranthene (I; $R^1 = R^3 = H$, $R^2 = NO_2$). The methyl ether (I; $R^1 = Me$, $R^2 = NO_2$, $R^3 = H$) on nitration gave a dinitro-product identical with that described

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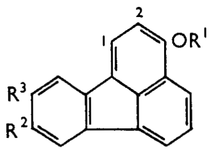
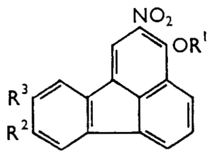
[1] N. Campbell and N. H. Keir, *J. Chem. Soc.*, 1955, 1233.
[2] T. Holbro and E. Tagmann, *Helv. Chim. Acta*, 1950, **33**, 2178.
[3] M. C. Kloetzel, W. King, and J. H. Menkes, *J. Amer. Chem. Soc.*, 1956, **78**, 1165.
[4] E. H. Charlesworth and B. J. Blackburn, *Canad. J. Chem.*, 1964, **42**, 353.
[5] F. Bell and J. Kenyon, *J. Chem. Soc.*, 1926, 3044.

above, which must be therefore 3-methoxy-2,8-dinitrofluoranthene (II; $R^1 = Me$, $R^2 = NO_2$, $R^3 = H$).

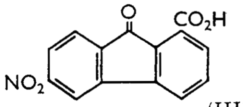
3-Acetoxyfluoranthene (I; $R^1 = COMe$, $R^2 = R^3 = H$) with nitric acid underwent considerable hydrolysis, but a product was obtained which was shown to be 3-hydroxy-8-nitrofluoranthene by conversion into 3-methoxy-8-nitrofluoranthene (I; $R^1 = Me$, $R^2 = NO_2$, $R^3 = H$). This is analogous to the nitration of 4-acetoxybiphenyl which gives initially the 4′-nitro-compound accompanied by much hydrolysis.[6]



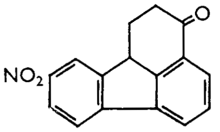
(I)



(II)



(III)



(IV)

In the nitration experiments described above the mononitro-compounds isolated are probably, but not certainly, the main products.

1,2,3,10b-Tetrahydro-9-nitro-3-oxofluoranthene (IV),[7] when heated with nitrobenzene and iodine, yielded 3-hydroxy-9-nitrofluoranthene (I; $R^1 = R^2 = H$, $R^3 = NO_2$) whose methyl ether differed from the 8-nitro-isomer described above. Further nitration gave a product almost certainly 3-methoxy-2,9-dinitrofluoranthene (II; $R^1 = Me$, $R^2 = H$, $R^3 = NO_2$) and differing from the above methoxydinitrofluoranthene.

Some promising methods for synthesising 3-methoxy-8-nitrofluoranthene unexpectedly failed. For instance, 2-methoxy-7-nitrofluorene did not react either with dimethyl oxalate in the presence of base [8] or with maleic anhydride.[9] 3-Nitrofluorene, unlike 2-nitrofluorene,[7] failed to condense with dimethyl oxalate in the presence of alkali, the only products isolated being 3-nitrofluorenone and a high-melting substance, probably 3,3′-dinitro-9,9′-bifluorenylidene, possibly identical with the product obtained from the attempted condensation of 9-bromo-3-nitrofluorene with ethoxymagnesium malonic ester.[7]

2-Methoxy-7-nitrofluorene, prepared by diazotising 2-amino-7-nitrofluorene and methylating the resulting phenol,[10] or preferably by oxidising 2-acetyl-7-nitrofluorene with perbenzoic acid,[11] has the same m.p. as that reported for a sample prepared by the nitration of 2-methoxyfluorene.[12] The structure of this nitro-compound is thus confirmed.

3-Nitrofluorenone was prepared by the method of Arcus and Coombs,[13] but at the Sandmeyer stage we were unable to obtain the yields reported by these workers. We therefore prepared it by deaminating the accessible 2-amino-3-nitrofluorenone.[14] Attempts to reduce the nitrofluorenone directly to the nitrofluorene were unsuccessful, and the following reaction sequence was used. Reduction of the nitrofluorenone with sodium sulphide gave 3-aminofluorenone, the acetyl derivative of which yielded 3-aminofluorene by the Wolff–Kishner method. Oxidation with peracetic acid [15] gave a 20% yield of 3-nitrofluorene. Attempts to prepare this compound by deaminating 2-amino-3-nitrofluorene were unsuccessful.[16]

EXPERIMENTAL

M.p.s were determined on the Kofler block, and chromatographic purification was effected on alumina.

3-*Methoxy*-2-*nitrofluoranthene*.—3-Hydroxyfluoranthene [7] (1·25 g.), and dimethyl sulphate (5 ml.) in dry methanol (10 ml.), were added to sodium (1·15 g.) in dry methanol (10 ml.), and heated (30 min.). The cooled mixture was shaken with ether and 2N-sodium hydroxide. The organic layer on evaporation yielded a solid which was chromatographed in benzene. A yellow band with a bright blue fluorescence was eluted with benzene and gave 3-methoxyfluoranthene (1·03 g.), m.p. 157—158° (lit.,[17] 159—160°). Concentrated nitric acid (1 ml.) was added dropwise to a stirred solution of the methyl ether (0·1 g.) in acetic acid (10 ml.). After 20 hr. the solution was poured into water and extracted with ether. The extract was washed with sodium carbonate solution and water, dried, and evaporated. The residue of mononitro-products, in benzene, was chromatographed on a column 8 in. × ¾ in. and developed with benzene. Evaporation of the second 100 ml. of eluate gave 3-*methoxy*-2-*nitrofluoranthene* (6 mg.), yellow needles (from benzene–light petroleum), m.p. 120° undepressed on admixture with a sample prepared below (Found: C, 73·6; H, 4·2; N, 4·7. $C_{17}H_{11}NO_3$ requires C, 73·6; H, 4·0; N, 5·0%). The first 100 ml. of eluate gave a mixture of mononitro-products (50 mg.) which, when dissolved in concentrated nitric acid and kept (18 hr.), yielded 3-methoxy-2,8-dinitrofluoranthene, m.p. 276—278° (see below), likewise obtained from 3-methoxy-2-nitrofluoranthene.

3-Amino-2-nitrofluoranthene (0·3 g.) was heated (1 hr.) in ethanol (30 ml.) and 10% sodium hydroxide (25 ml.), filtered, and the volume reduced by evaporation. Addition of acid gave 3-*hydroxy*-2-*nitrofluoranthene*, yellow prisms (from xylene) (0·2 g.), m.p. 185—186° (Found: C, 72·8; H, 3·5; N, 5·5. $C_{16}H_9NO_3$ requires C, 73·0; H, 3·4; N, 5·3%). Methylation with diazomethane in ether or di-

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[6] S. E. Hazlet, D. A. Stauffer, L. C. Hensley, and H. O. Van Orden, *J. Amer. Chem. Soc.*, 1944, **66**, 1245.

[7] N. Campbell, J. T. Craig, and K. Nichol, *Proc. Roy. Soc. Edinburgh*, 1960, **65**, *A*, 223.

[8] J. T. Craig, Thesis, Edinburgh, 1955, p. 158.

[9] Cf. E. Bergmann and M. Orchin, *J. Amer. Chem. Soc.*, 1949, **71**, 1917.

[10] F. Bielschowsky, *Biochem. J.*, 1945, **39**, 287.

[11] Cf. S. L. Friess, *J. Amer. Chem. Soc.*, 1949, **71**, 14.

[12] N. Ishikawa and M. Okazaki, *J. Soc. Org. Synth. Chem. Japan*, 1958, **16**, 467 (*Chem. Abs.*, 1958, **52**, 18340).

[13] C. L. Arcus and M. M. Coombs, *J. Chem. Soc.*, 1954, 3977.

[14] N. Ishikawa, M. Okazaki, and M. Hayashi, *Yûki Gôsei Kagaku Kyôkaishi*, 1958, **16**, 34 (*Chem. Abs.*, 1958, **52**, 5439).

[15] W. D. Emmons, *J. Amer. Chem. Soc.*, 1957, **79**, 5528.

[16] Cf. N. Campbell and W. Stafford, *J. Chem. Soc.*, 1952, 299; K. J. Nichol, Thesis, Edinburgh, 1958, p. 34.

[17] A. S. Bailey, G. A. Dale, A. J. Shuttleworth, and D. P. Weizmann, *J. Chem. Soc.*, 1964, 5110.

methyl sulphate and sodium carbonate yielded 3-methoxy-2-nitrofluoranthene, m.p. 118°.

Nitration of 3-*Toluene*-p-*sulphonyloxyfluoranthene*.—Toluene-*p*-sulphonyl chloride (2·0 g.) in acetone (15 ml.) and 3-hydroxyfluoranthene (1·0 g.) in 2N-sodium hydroxide (10 ml.) were mixed and shaken (20 min.). The mixture was poured into water and the *toluene*-p-*sulphonyloxy-compound* washed with water and crystallised from benzene–light petroleum, yellow prisms (1·5 g.), m.p. 135—136° (Found: C, 73·7; H, 4·4; S, 8·5. $C_{23}H_{16}O_3S$ requires C, 74·2; H, 4·3; S, 8·6%).

Concentrated nitric acid (35 ml.) was added dropwise to the 3-toluene-*p*-sulphonyloxy-compound (7·0 g.) in acetic acid (75 ml.), and the solution was warmed to 70° for 1 min. The cooled solution was decanted from a little tarry matter and poured on ice. The product (6·2 g.) in benzene was chromatographed, and elution of a yellow band with benzene gave a yellow solid which, when crystallised from benzene–light petroleum, yielded 8-*nitro*-3-*toluene*-p-*sulphonyloxyfluoranthene* (2·3 g.), m.p. 180—183° raised by further crystallisation to 189—190° (Found: N, 3·3; S, 7·3. $C_{23}H_{15}NO_5S$ requires N, 3·4; S, 7·7%). From the combined filtrates an impure mononitro-compound, m.p. 226—230°, was isolated.

The nitro-compound, m.p. 187—190° (1·0 g.), was warmed with potassium hydroxide (1·0 g.) in ethanol (10 ml.), to give a deep-purple solution, and the cooled solution poured on concentrated hydrochloric acid and ice. The yellow precipitate of 3-hydroxy-8-nitrofluoranthene was crystallised from acetic acid and then from ethanol (0·6 g.), m.p. *ca.* 240°. The impure nitrophenol (1·0 g.) was boiled (30 min.) in sulphur-free xylene (10 ml.) with dimethyl sulphate (1 ml.) and anhydrous potassium carbonate (1 g.). The filtered solution was shaken with 10% sodium hydroxide, and the xylene layer was washed with water, dried, and the volume reduced to 2 ml. This was chromatographed, and a bright yellow band was eluted with benzene. Evaporation of the eluate gave 3-*methoxy*-8-*nitrofluoranthene* (0·25 g.), yellow needles (from benzene), m.p. 208—209° (Found: C, 73·7; H, 4·1; N, 7·0. $C_{17}H_{11}NO_3$ requires C, 73·6; H, 4·0; N, 5·1%).

Nitration of 3-*Acetoxyfluoranthene*.—Concentrated nitric acid (5 ml.) was added to 3-acetoxyfluoranthene (1 g.) in acetic acid (10 ml.) at 0°. The resulting solid was washed with water, dried, and chromatographed in benzene on alumina (40 g.). Elution with benzene gave a pale yellow band from which 3-*acetoxy*-8-*nitrofluoranthene* (0·11 g.) separated as light brown needles, m.p. 208—210° (Found: N, 4·5. $C_{18}H_{11}NO_4$ requires, 4·6%). The acetoxy-compound was converted into 3-methoxy-8-nitrofluoranthene by the method applied to the corresponding toluenesulphonyloxyfluoranthene.

3-*Methoxy*-2,8-*dinitrofluoranthene*.— 3-Methoxyfluoranthene (0·1 g.) in concentrated nitric acid (5 ml.) was kept (18 hr.) at room temperature and poured into water. 3-*Methoxy*-2,8-*dinitrofluoranthene* separated and crystallised from toluene–1-methylnaphthalene as pale yellow needles, m.p. 278—283° (decomp.) (Found: C, 63·4; H, 3·7; N, 8·7; $C_{17}H_{10}N_2O_5$ requires C, 63·5; H, 3·35; N, 8·7%). It is similarly obtained from 3-methoxy-8-nitrofluoranthene. When mixed with 3-methoxy-2,9-dinitrofluoranthene the m.p. fell to 235—250°.

6-*Nitro*-9-*oxofluorene*-1-*carboxylic Acid*.—3-Hydroxy-8-nitrofluoranthene (1·0 g.), potassium permanganate (2·0 g.), and water (50 ml.) was made alkaline with sodium hydroxide and boiled (1 hr.). Filtration followed by acidification with sulphurous acid yielded 6-*nitro*-9-*fluorene*-1-*carboxylic acid* (0·3 g.), needles (from acetic acid), m.p. 275—276° (sublimes at 250°) (Found: C, 62·1; H, 2·7; N, 5·6. $C_{14}H_7NO_5$ requires C, 62·5; H, 2·6; N, 5·2%). Decarboxylation with copper in 4-methylquinoline at 200—210° (15 min.) or by heating with copper acetate [18] gave 3-nitrofluorenone, purified by sublimation, m.p. and mixed m.p. 235—237°.

3-*Methoxy*-2,9-*dinitrofluoranthene*.— 1,2,3,10b-Tetrahydro-9-nitro-3-oxofluoranthene [7] (0·3 g.) was boiled (10 min.) in nitrobenzene (10 ml.) with iodine (one crystal). After removal of the nitrobenzene the residue was treated overnight with diazomethane (1 g.) in ether (200 ml.). The solvent was evaporated, the residue extracted with benzene (2 × 50 ml.), and the filtered extracts were chromatographed. Development with benzene gave a yellow fluorescent solution, which on evaporation yielded 3-*methoxy*-9-*nitrofluoranthene* (80 mg.), orange needles (from ethanol), m.p. 191—192° (Found: C, 73·3; H, 4·1; N, 4·7. $C_{17}H_{11}NO_3$ requires C, 73·6; H, 4·0; N, 5·1%). The nitro-compound (30 mg.) was kept overnight in concentrated nitric acid (1 ml.) and poured into water. 3-*Methoxy*-2,9-*dinitrofluoranthene* separated and crystallised from xylene as yellow needles, m.p. 272—284° (Found: C, 63·7; H, 3·2; N, 8·8. $C_{17}H_{10}N_2O_5$ requires C, 63·5; H, 3·35; N, 8·7%).

2-*Methoxy*-7-*nitrofluorene*.—(*a*) 2-Acetyl-7-nitrofluorene [19] was purified by extraction of the crude material with ether and crystallisation of the residue from acetic acid (yield 45%), m.p. 228° (lit.,[19] 228°). The fluorene (5 g.) in tetrachlorethane (100 ml.) was added to 100 ml. of 5% perbenzoic acid in chloroform and kept in the dark for 10 days. Evaporation of the solvent left the crude ester which was hydrolysed by boiling (2 hr.) with ethanol (100 ml.) and concentrated hydrochloric acid (100 ml.). The filtered solution on cooling gave crude 2-hydroxy-7-nitrofluorene, which was boiled in sulphur-free xylene (200 ml.) with dimethyl sulphate (35 ml.) and potassium carbonate (50 g.) for 1 hr. The volume was reduced to 50 ml., and addition of light petroleum precipitated 2-methoxy-7-nitrofluorene. This was chromatographed in benzene, and elution with benzene gave a bright yellow band which yielded 2-methoxy-7-nitrofluorene, yellow needles (from benzene) (1·2 g.), m.p. 214—215° undepressed on admixture with an authentic sample (see below). 2-Methoxyfluorene was similarly obtained (49%) from 2-acetylfluorene.

(*b*) 2-Amino-7-nitrofluorene (1 g.), obtained (45%) tediously by reducing 2,7-dinitrofluorene in boiling ethanol with ammonium sulphide,[20] was diazotised in concentrated sulphuric acid (45 ml.) by the dropwise addition of sodium nitrite (0·35 g.) in water (25 ml.), and stirring was continued for 45 min. The suspension was added (25 min.) to a boiling solution of concentrated sulphuric acid (10 ml.) and water (500 ml.). 2-*Hydroxy*-7-*nitrofluorene* (20—50% yield) separated and was purified by conversion into the *acetate*, plates, m.p. 193—195° (Found: C, 66·4; H, 4·0; N, 5·3. $C_{15}H_{11}NO_4$ requires C, 66·9; H, 4·1; N, 5·2%), followed by hydrolysis (EtOH–HCl), and was obtained from aqueous

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[18] C. F. Koelsch and A. F. Steinhauer, *J. Org. Chem.*, 1953, **18**, 1516.

[19] H. F. Oehlschlaeger and I. R. MacGregor, *J. Amer. Chem. Soc.*, 1949, **71**, 3224.

[20] F. E. Cislak and C. S. Hamilton, *J. Amer. Chem. Soc.*, 1931, **53**, 748.

ethanol as yellow needles, m.p. 241—251° (lit.,[10] 250°) (Found: C, 68·3; H, 4·0; N, 5·9. Calc. for $C_{13}H_9NO_3$: C, 68·7; H, 4·0; N, 6·2%). The phenol (0·34 g.) in methanol (30 ml.) was added to diazomethane in dry ether (45 ml.). After 20 hr. the solution was treated with concentrated hydrochloric acid (5 drops) and the volume reduced to 5 ml. The resulting solid, in chloroform, was chromatographed on a column 4 in. × $\frac{3}{4}$ in. and development with chloroform gave a pale yellow band which was readily eluted. Evaporation of the eluate gave 2-methoxy-7-nitrofluorene, yellow needles (first from acetic acid and then from benzene–light petroleum), m.p. 217—218° (lit.,[12] 218—219°) (Found: C, 69·8; H, 4·6; N, 6·3. Calc. for $C_{14}H_{11}NO_3$: C, 69·7; H, 4·6; N, 5·8%).

3-*Nitrofluorene*.—3-Acetamidofluorenone (0·5 g.), potassium hydroxide (0·25 g.), and hydrazine hydrate (0·6 ml.) were boiled (30 min.) in diethylene glycol, and the condenser removed until the temperature reached 205°. The condenser was replaced and the boiling continued (45 min.). Addition of water gave 3-aminofluorene (0·35 g.), needles (from ethanol), m.p. 152—153° (lit.,[21] 152—153°). 40% Peracetic acid solution (18 ml.) was added to 3-aminofluorene (0·90 g.) in acetic acid (minimum quantity). After the initial reaction had subsided, acetic acid (5 ml.) was added, and the solution boiled for 5 min. and filtered. Addition of water yielded a solid which was extracted with ether and the extract washed with hydrochloric acid and water. Evaporation of the ether gave a red tar which was heated with light petroleum (b.p. 40—60°). The cooled solution deposited 3-nitrofluorene, needles (0·28 g.), m.p. 100—102° (from methanol). 2-Aminofluorene was similarly converted into 2-nitrofluorene (60%).

Attempted Synthesis of 3-*Nitrofluorene*-9-*carboxylic Acid*.—3-Nitrofluorene (0·05 g.) and dimethyl oxalate (0·06 g.) were added to a solution of potassium (0·02 g.) in methanol (0·6 ml.) and boiled for a few min. The methanol was distilled off and the remaining red solid was dissolved in boiling nitrobenzene. A brownish red powder separated, m.p. >340°, probably 3,3′-dinitro-9,9′-bifluorenylidene [Found: N, 6·2%; *m*, 425 (Rast). Calc. for $C_{26}H_{14}N_2O_4$: N, 6·7%; *m*, 418].

We thank the S.R.C. for studentships to H. F. A., J. T. C., and K. J. N.

[8/183 *Received, February* 8*th*, 1968]

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[21] E. K. Weisburger, *J. Amer. Chem. Soc.*, 1955, **77**, 1914.