675. *Synthesis of Fluoranthenes. Part IV.* 10- *and* 11-*Substituted Fluoranthenes.*

By S. Horwood Tucker and (Miss) Margaret Whalley.

Syntheses of ethyl fluoranthene-11-carboxylate * and of 11-methyl- and 10-methylfluoranthene from the naphthalene skeleton are described. The conversion of ethyl fluoranthene-11-carboxylate into 11-methylfluoranthene has been achieved.

Von Braun and Manz (*Annalen*, 1932, **496**, 170), by the action of oxalyl chloride and aluminium chloride on fluoranthene, obtained principally fluoranthene-11-carboxylic acid * with some dicarboxylic acid and a trace of fluoranthene-4-carboxylic acid. The formation of the first acid as the main product was confirmed by Campbell and Easton (this vol., p. 340),

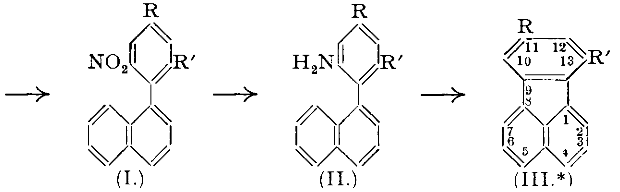
---

* The numbering of fluoranthene follows that of naphthalene in this series of papers.

who were unable to isolate any of the 4-substituted compound. The orientation of the substituent group in the main product, fluoranthene-11-carboxylic acid, is corroborated by our results.

The original method of synthesising fluoranthene derivatives, *i.e.*, starting from naphthalene and its derivatives (Forrest and Tucker, *J.*, **1948**, **1137**; Tucker and Whalley, this vol., p. 632), gave unambiguous syntheses. Those herein recorded start from naphthalene derivatives and may be represented:

o-Bromonitrobenzene derivative
+
1-Iodonaphthalene + Cu



(I.) (II.) (III.*)

Ethyl 4-bromo-3-nitrobenzoate and 1-iodonaphthalene were condensed in the presence of copper bronze to give 1-(2-*nitro*-4-*carbethoxyphenyl*)*naphthalene* (I; R = CO_2Et, R′ = H) which on reduction with hydrogen in the presence of Raney nickel yielded 1-(2-*amino*-4-*carbethoxyphenyl*)*naphthalene* (II; R = CO_2Et, R′ = H). Diazotisation of the amine and warming the diazonium solution with copper bronze effected cyclisation to *ethyl fluoranthene*-11-*carboxylate* (III; R = CO_2Et, R′ = H). Hydrolysis of this ester with alcoholic sodium hydroxide gave fluoranthene-11-carboxylic acid (von Braun and Manz, *loc. cit.*).

Ethyl fluoranthene-11-carboxylate was transformed by the method of McFadyen and Stevens (*J.*, **1936**, 384) through the acid hydrazide and benzenesulphonhydrazide into fluoranthene-11-aldehyde, whose 2 : 4-*dinitrophenylhydrazone* was prepared. Reduction of the aldehyde by the Huang-Minlon modification of the Kishner–Wolff reaction (*J. Amer. Chem. Soc.*, 1946, **68**, 2487) gave 11-*methylfluoranthene* (III; R = Me, R′ = H) whose *complexes* with picric acid, *s*-trinitrobenzene, and 2 : 4 : 7-trinitrofluorenone were prepared.

In order to obtain independent evidence of the structure of this 11-methylfluoranthene its direct synthesis was undertaken: 1-iodonaphthalene and 4-bromo-3-nitrotoluene were condensed in the presence of copper at 150° (higher temperatures led to some formation of 2 : 2′-dinitro-4 : 4′-dimethyldiphenyl) to form an oil which was mainly 1-(2-nitro-4-methylphenyl)naphthalene (I; R = Me, R′ = H). Reduction of the oil with hydrogen–Raney nickel gave 1-(2-*amino*-4-*methylphenyl*)*naphthalene* (II; R = Me, R′ = H) which on cyclisation, as before, yielded 11-methylfluoranthene, identical with that obtained by reduction of ethyl fluoranthene-11-carboxylate.

Oxidation of 11-methylfluoranthene with the theoretical quantity of sodium dichromate in acetic acid gave, instead of the desired fluoranthene-11-carboxylic acid, a compound which appears to be 6(or 7)-*methylfluorenone*-1-*carboxylic acid*.

10-Methylfluoranthene (III; R = H, R′ = Me) was synthesised by the method adopted for the 11-isomer, *viz.*, by reaction of 1-iodonaphthalene with 2-bromo-3-nitrotoluene to give 1-(2-*nitrophenyl*-6-*methylphenyl*)*naphthalene* (I; R = H, R′ = Me) (cf. Bell, *J.*, 1934, 835, who found that 1-iodonaphthalene could not be condensed with 2-iodo-3-nitrotoluene). The compound (I; R = H, R′ = Me) was reduced to 1-(2-*amino*-6-*methylphenyl*)*naphthalene* (II; R = H, R′ = Me), which, on cyclisation, gave 10-*methylfluoranthene* (III; R = H, R′ = Me).

EXPERIMENTAL.

Synthesis of Ethyl Fluoranthene-11-*carboxylate* (III; R = CO_2Et, R′ = H).—1-(2-*Nitro*-4-*carbethoxyphenyl*)*naphthalene*. 1-Iodonaphthalene (3 g.), ethyl 4-bromo-3-nitrobenzoate (3·2 g.), and copper bronze (2·5 g.) were heated at 210° for 1·25 hours with frequent stirring. After cooling, the mixture was extracted with boiling ethanol (4 × 15 ml.). Evaporation of the filtrate gave a sticky dark brown solid which after chromatography (alumina–benzene) and crystallisation from ethyl acetate gave golden-yellow, stout prisms of 1-(2-*nitro*-4-*carbethoxyphenyl*)*naphthalene* (I; R = CO_2Et, R′ = H), m. p. 117—119° (1·6 g., 42%) (Found: C, 70·7; H, 4·8; N, 4·6. $C_{19}H_{15}O_4N$ requires C, 71·0; H, 4·7; N, 4·4%).

1-(2-*Amino*-4-*carbethoxyphenyl*)*naphthalene* (II; R = CO_2Et, R′ = H). 1-(2-Nitro-4-carbethoxyphenyl)naphthalene (1·0 g.) was reduced catalytically (hydrogen–Raney nickel) with ethanol (100 ml.) as solvent. The Raney nickel was removed and extracted with boiling ether (4 × 20 ml.). The combined filtrates gave, on evaporation, 1-(2-*amino*-4-*carbethoxyphenyl*)*naphthalene* which crystallised from light petroleum (b. p. 60—80°) in colourless stellar clusters, m. p. 131—132° (0·75 g., 83%) Found: C, 78·45; H, 5·8; N, 4·9. $C_{19}H_{17}O_2N$ requires C, 78·3; H, 5·9; N, 4·8%).

Ethyl fluoranthene-11-*carboxylate* (III; R = CO_2Et, R′ = H). 1-(2-Amino-4-carbethoxyphenyl)-

naphthalene (2·89 g.) was diazotised (sodium nitrite and dilute sulphuric acid), excess of nitrite was removed by addition of a little urea, and the diazonium solution filtered and warmed for 1·5 hours with copper bronze (3·0 g.). Extraction of the copper with ethanol (6 × 15 ml.) gave an oil which, after chromatography (alumina–benzene) gave a pale yellow oil which crystallised from petroleum (b. p. 60—80°) in colourless plates of *ethyl fluoranthene*-11-*carboxylate*, m. p. 90—91° (0·41 g., 15%) (Found : C, 83·2; H, 5·15. $C_{19}H_{14}O_2$ requires C, 83·1; H, 5·1%). It formed a *complex* with 2 : 4 : 7-trinitrofluorenone—small yellow needles (glacial acetic acid), m. p. 167—169° (Found : C, 65·3; H, 3·3. $C_{19}H_{14}O_2,C_{13}H_5O_7N_3$ requires C, 65·2; H, 3·25%).

Hydrolysis of Ethyl Fluoranthene-11-*carboxylate*.—This ester (0·05 g.), sodium hydroxide (0·25 g.), water (4 ml.), and ethanol (0·5 ml.) were heated under reflux until all the solid dissolved (6 hours). The solution was acidified with dilute hydrochloric acid. Crystallisation of the precipitated acid gave colourless needles (glacial acetic acid) of fluoranthene-11-carboxylic acid, m. p. 278—280° (0·04 g., 95%).

Reduction of Ethyl Fluoranthene-11-*carboxylate*.—The ester (1·0 g.), ethanol (5 ml.), and hydrazine hydrate (90%; 4 ml.) were heated under reflux for 3 hours, a colourless solid, m. p. ~203—208°, slowly separating; it was practically insoluble in ethanol, benzene, or ether, and is probably the acid hydrazide (0·93 g., 98%). The crude hydrazide (0·93 g.) was dissolved in dry pyridine (7 ml.), and benzenesulphonyl chloride (0·65 g.) added. After 2·5 hours, the mixture was poured into dilute hydrochloric acid, and the precipitated solid separated, m. p. ~220° (0·86 g., 62%). This unpurified benzenesulphonhydrazide (0·86 g.) in ethylene glycol (8·6 ml.) was heated to 120°, and anhydrous sodium carbonate (1·2 g., 5 equivs.) added. The temperature was raised to 125° for 1 hour, then the reaction was stopped by addition of hot water. The solid (0·48 g.) which separated contained fluoranthene-11-aldehyde, which gave a 2 : 4-*dinitrophenylhydrazone*, small red crystals (glacial acetic acid), m. p. 296—298° (Found : N, 13·4. $C_{23}H_{14}O_4N_4$ requires N, 13·65%).

The solid (0·9 g.) containing fluoranthene-11-aldehyde, hydrazine hydrate (90%; 0·37 ml.), 2 : 2′-dihydroxydiethyl ether (6·2 ml.), and sodium hydroxide (0·38 g.) were heated under reflux for 1 hour. The condenser was then removed, the mixture boiled until the temperature reached 200°, and heating continued for 3 hours. The solution was acidified with dilute hydrochloric acid, the precipitated oil extracted with benzene, and the solvent removed. The residue was dissolved in ethanol, and picric acid (0·9 g.) added; the 11-*methylfluoranthene picrate* obtained—dark orange needles (ethanol)— has m. p. 150—153° (Found : C, 62·0; H, 3·3; N, 9·6. $C_{17}H_{12},C_6H_3O_7N_3$ requires C, 62·0; H, 3·4; N, 9·4%). On shaking of a benzene solution of this picrate with sodium hydrogen carbonate solution, followed by evaporation of the benzene, 11-*methylfluoranthene* (III; R = Me, R′ = H), m. p. 88—90°, was obtained in colourless needles from methanol (Found : C, 94·1; H, 5·6. $C_{17}H_{12}$ requires C, 94·4; H, 5·6%). It also formed a *s*-trinitrobenzene *complex*, yellow needles from ethanol, m. p. 171—174° (Found : C, 64·3; H, 3·45; N, 9·8. $C_{17}H_{12},C_6H_3O_6N_3$ requires C, 64·3; H, 3·5; N, 9·8%), and a 2 : 4 : 7-trinitrofluorenone *complex*, orange needles (glacial acetic acid), m. p. 196—198° (Found : C, 67·9; H, 3·3; N, 8·1. $C_{17}H_{12},C_{13}H_5O_7N_3$ requires C, 67·8; H, 3·2; N, 7·9%).

Synthesis of 11-*Methylfluoranthene* (III; R = Me, R′ = H).—*Condensation of* 1-*iodonaphthalene and* 4-*bromo*-3-*nitrotoluene*. 1-Iodonaphthalene (9·0 g.), 4-bromo-3-nitrotoluene (7·5 g.), and copper bronze (9·0 g.) were heated together on an oil-bath at 150° for 4 hours. Extraction of the resulting greenish mixture with ether and evaporation of the solvent yielded a heavy oil which on distillation gave (i) unchanged 4-bromo-3-nitrotoluene (0·7 g., 9%), (ii) an orange oil which on crystallisation from ethanol gave 2 : 2′-dinitro-4 : 4′-dimethyldiphenyl, m. p. 141° (2·1 g.), and (iii) a heavy red oil, b. p. 196—200°/0·7 mm. [from which more 2 : 2′-dinitro-4 : 4′-dimethyldiphenyl (0·5 g.) was obtained]. This on being chromatographed (alumina–benzene) yielded more 2 : 2′-dinitro-4 : 4′-dimethyldiphenyl and a yellow oil which resisted crystallisation (4·8 g.) and was assumed to be mainly 1-(2-nitro-4-methylphenyl)naphthalene.

1-(2-*Amino*-4-*methylphenyl*)*naphthalene* (II; R = Me, R′ = H). The above oil (4·8 g.) was reduced (hydrogen–Raney nickel). After filtration, evaporation, and crystallisation from ethanol, 1-(2-*amino*-4-*methylphenyl*)*naphthalene* was obtained as colourless prisms, m. p. 85—87° (2·6 g., 60%) (Found : C, 87·3; H, 6·3; N, 5·75. $C_{17}H_{15}N$ requires C, 87·5; H, 6·4; N, 6·0%). This amine formed a *picrate*, yellow needles (methanol), m. p. 110—112° (Found : C, 59·5; H, 4·4; N, 12·1. $C_{17}H_{15}N,C_6H_3O_7N_3$ requires C, 59·7; H, 3·9; N, 12·1%).

11-*Methylfluoranthene* (III; R = Me, R′ = H). 1-(2-Amino-4-methylphenyl)naphthalene (2·3 g.) was diazotised (sodium nitrite and dilute sulphuric acid), and the filtered diazonium solution warmed for 1 hour with copper bronze (3·5 g.). The copper was extracted with boiling alcohol (6 × 15 ml.), and picric acid added to the concentrated solution. Decomposition of the picrate, as before, yielded 11-methylfluoranthene, m. p. 88—90°, identical with that obtained by reduction of ethyl fluoranthene-11-carboxylate.

Oxidation of 11-*Methylfluoranthene*.—11-Methylfluoranthene (0·1 g.) was heated under reflux with sodium dichromate (0·18 g.), glacial acetic acid (4 ml.), and water (2 drops) for 40 minutes, the solution poured into dilute sulphuric acid, and the precipitated solid extracted with ether, which was then shaken with dilute aqueous ammonia. The ethereal layer gave unchanged 11-methylfluoranthene. Acidification of the aqueous layer yielded an acid, probably 6(or 7)-*methylfluorenone*-1-*carboxylic acid*, which crystallised from benzene in orange-brown needles softening at 156°, m. p. 166—168° (Found : C, 76·0; N, 4·3. $C_{15}H_{10}O_3$ requires C, 75·6; H, 4·2%).

Synthesis of 10-*Methylfluoranthene* (III; R = H, R′ = Me).—1-(2-*Nitro*-6-*methylphenyl*)*naphthalene* (I; R = H, R′ = Me) was prepared, by heating 1-iodonaphthalene with 2-bromo-3-nitrotoluene and copper bronze at 210°, as pale yellow prisms (methanol), m. p. 110—111° (Found : C, 77·3; H, 5·15; N, 5·4. $C_{17}H_{13}O_2N$ requires C, 77·6; H, 4·9; N, 5·3%).

1-(2-*Amino*-6-*methylphenyl*)*naphthalene* (II; R = H, R′ = Me). The foregoing nitro-compound (0·526 g.) in ethanol was reduced (hydrogen–Raney nickel). The evaporated filtrate deposited white needles of 1-(2-*amino*-6-*methylphenyl*)*naphthalene*, m. p. 114—116° (methanol) (0·31 g., 65%) (Found : C, 87·4; H, 6·4; N, 6·1. $C_{17}H_{15}N$ requires C, 87·5; H, 6·4; N, 6·0%).

10-*Methylfluoranthene* (III; R = H, R′ = Me). The above amine (0·7 g.) was diazotised, and the diazonium solution warmed with copper bronze as before. Extraction of the copper with boiling ethanol (4 × 10 ml.) gave a fluorescent oil from which, after crystallisation from light petroleum (b. p. 30—60°) 10-*methylfluoranthene*, m. p. 105—108°, was obtained (Found: C, 94·5; H, 5·6. $C_{17}H_{12}$ requires C, 94·4; H, 5·6%). It formed: a *complex* with *s*-trinitrobenzene, fine yellow needles (benzene-ethanol), m. p. 215—218° (Found: C, 64·6; H, 3·6; N, 9·6. $C_{17}H_{12},C_6H_3O_6N_3$ requires C, 64·3; H, 3·5; N, 9·8%); a *complex* with 2 : 4 : 7-trinitrofluorenone, orange-red micro-crystals (glacial acetic acid), m. p. 197—199° (Found: C, 67·8; H, 3·2; N, 7·7. $C_{17}H_{12},C_{13}H_5O_7N_3$ requires C, 67·8; H, 3·2; N, 7·9%); and a picrate, m. p. 196—199°, which decomposed fairly rapidly.

We are indebted to the Department of Scientific and Industrial Research for a grant to one of us (M. W.); to Mr. J. M. L. Cameron and Miss R. H. Kennaway of this Department for micro-analyses; and to Mr. A. B. A. Lundholm who prepared 1-(2-nitro-4-carbethoxyphenyl)naphthalene and the derived amino-compound.

University of Glasgow. [*Received, September 20th,* 1949.]