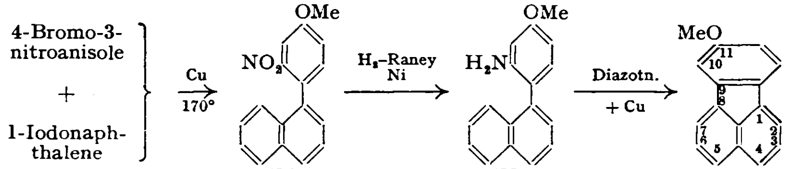
639. *Synthesis of Fluoranthenes. Part V. 11-Methoxyfluoranthene.*

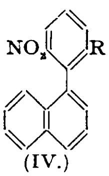
By John Hawkins and S. Horwood Tucker.

1-Iodonaphthalene has been condensed by the crossed Ullmann reaction with 4-bromo-3-nitroanisole, 2-bromo-3-nitroanisole, methyl 2-bromo-3-nitrobenzoate, and 1-chloro-2 : 6-dinitrobenzene to give 1-(*o*-nitrophenyl)naphthalene derivatives. The product from 4-bromo-3-nitroanisole and 1-iodonaphthalene has been converted into 11-methoxyfluoranthene. 1-Chloro-2 : 6-dinitrobenzene gave a workable yield of 1-(2 : 6-dinitrophenyl)-naphthalene; but the other nitro-compounds gave low yields.

Action of reagents on fluoranthene gives rise to mono-, almost invariably mixed with disubstituted, derivatives. The separation of these is usually difficult (see, *e.g.*, von Braun and Manz, *Annalen*, 1931, **488**, 111; N. Campbell and Easton, *J.*, 1949, 340). Hence any synthetic method which provides unequivocal evidence of the position of one or more substituents is of great value. An original method has been found in the crossed Ullmann condensation (Fanta, *Chem. Reviews*, 1946, **38**, 139) of 1-iodonaphthalene or its derivatives with *o*-bromonitrobenzene or its derivatives (Forrest and Tucker, *J.*, 1948, 1137; Tucker and Whalley, *J.*, 1949, 632, 3213). The importance of methoxyl derivatives in Nature has turned our attention to the hitherto unknown methoxyl derivatives of fluoranthene. We have now synthesised 11-methoxyfluoranthene (III) as shown :



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



(IV.)

Condensation was effected in four hours at 170° to give (I) (50%) ; the product was reduced in nearly quantitative yield to the amine (II); and this, on diazotisation and addition of copper bronze, gave 11-methoxyfluoranthene (III) (52%).

Preparation of 10-methoxyfluoranthene has proved difficult. 2-Bromo-3-nitroanisole has been successfully condensed with 1-iodonaphthalene to give 1-(2-methoxy-6-nitrophenyl)-naphthalene (IV; R = OMe), but the yield was so low (2%) that work along the lines used for the synthesis of (III) was discontinued. It is probable that the presence of two substituents *ortho* to the bromine atom is sterically hindering reaction. One can avoid this drawback by using 3-bromo-2-nitroanisole; and work is in hand with the object of condensing this compound with 1-iodonaphthalene.

Attempts to prepare 10-carbomethoxyfluoranthene by a method similar to that described for 11-carbomethoxyfluoranthene (Tucker and Whalley, *loc. cit.*) failed for another reason. Methyl 2-bromo-3-nitrobenzoate was heated with 1-iodonaphthalene in presence of copper, but in this case the bromine atom, instead of being sterically hindered, was, as expected, greatly activated by the *o*-nitro- and *o*-carbomethoxy-groups. Consequently, the main product was dimethyl 2 : 2′-dinitro-6 : 6′-diphenate. Chromatography removed, however, a deeper yellow crystalline material from the main product, and this proved to be the desired 1-(2-carbomethoxy-6-nitrophenyl)naphthalene (IV; R = CO_2Me). The corresponding methyl 2-chloro-3-nitrobenzoate failed to react.

The condensation of 1-chloro-2 : 6-dinitrobenzene with 1-iodonaphthalene gave 1-(2 : 6-dinitrophenyl)naphthalene (IV; R = NO_2), with which work is in progress.

EXPERIMENTAL.

4-Amino-3-nitroanisole was prepared by acetylating *p*-anisidine by means of acetic anhydride in aqueous emulsion, and nitrating the *p*-acetanisidide (cf. Reverdin, *Ber.*, 1896, **29**, 2595) as follows: *p*-Acetanisidide (37 g.) was treated with a mixture of concentrated nitric acid (15 ml.) and water (135 ml.) and gradually heated nearly to boiling; the mixture eventually boiled without further heating. If the temperature rises too high, much tarring occurs. On cooling, a brown oil with yellow crystals separated; the whole was crystallised from hot water to give yellow needles of 4-acetamido-3-nitroanisole, m. p. 116—117° (18 g., 38%). Hydrolysis with ethanolic potassium hydroxide gave 4-amino-3-nitroanisole, from which by a Sandmeyer reaction 4-bromo-3-nitroanisole was obtained (yellow needles, m. p. 32°). Application of Hodgson and Walker's method (*J.*, 1933, 1620) gave a tar at the last stage.

1-(4-*Methoxy*-2-*nitrophenyl*)*naphthalene* (I).—1-Iodonaphthalene (12·5 g.), 4-bromo-3-nitroanisole (11·6 g.), and copper bronze (12·5 g.) were heated together in an oil-bath for 4 hours at 170° with vigorous stirring. Extraction with ether, evaporation, and crystallisation of the residue from methanol gave yellow stellar crystals of 1-(4-*methoxy*-2-*nitrophenyl*)*naphthalene* (I), m. p. 103—104° (6·9 g., 50%) (Found: C, 73·3; H, 4·9; N, 5·2. $C_{17}H_{13}O_3N$ requires C, 73·1; H, 4·7; N, 5·0%).

1-(2-*Amino*-4-*methoxyphenyl*)*naphthalene* (II).—The above nitro-compound (2·78 g.) was reduced by hydrogen–Raney nickel (1 g.) in ethanol (20 ml., previously distilled from Raney nickel) in 45 minutes. The boiled mixture was filtered, and the ethanol solution concentrated. Re-extraction of the nickel with boiling ethanol (2 × 10 ml.) gave another considerable crop (total yield, 2·38 g., 95%) of plates of 1-(2-*amino*-4-*methoxyphenyl*)*naphthalene*, m. p. 110—113° (Found: C, 81·6; H, 6·1; N, 5·7. $C_{17}H_{15}ON$ requires C, 81·9; H, 6·1; N, 5·6%).

11-*Methoxyfluoranthene* (III).—The above amine (II) (2·32 g.) was diazotised by means of sodium nitrite and dilute hydrochloric acid, and the solution warmed with copper bronze (1 g.) on a boiling-water bath for 1 hour. The copper became covered with tar; it was washed with water and extracted with acetone (4 × 10 ml.). After evaporation, a brown oil was left which was dissolved in benzene, and the solution was chromatographed (alumina). The product, crystallised from light petroleum (b. p. 60—80°) and then from ethanol, gave 11-*methoxyfluoranthene* as pale green flakes, exhibiting a green fluorescence in daylight, softening at 120°, melting at 123—124° (1·3 g., 52%), (Found: C, 87·6; H, 5·4. $C_{17}H_{12}O$ requires C, 87·9; H, 5·2%). 1-(*p*-Methoxyphenyl)naphthalene has m. p. 116·5° (Howell and Robertson, *J.*, 1936, 587). 11-Methoxyfluoranthene gave a *picrate* as orange-red needles (from ethanol), m. p. 132—134° (Found: C, 59·7; H, 3·5. $C_{17}H_{12}O,C_6H_3O_7N_3$ requires C, 59·9; H, 3·3%). 2 : 4 : 7-Trinitrofluorenone gave a *complex* as bright scarlet needles (from ethyl acetate), m. p. 185—186° (Found: C, 65·6; H, 2·9. $C_{17}H_{12}O,C_{13}H_5O_7N_3$ requires C, 65·8; H, 3·1%).

1-(2-*Carbomethoxy*-6-*nitrophenyl*)*naphthalene* (IV; R = CO_2Me).—2-Bromo-3-nitrobenzoic acid (*Org. Synth.*, Coll. Vol. I, p. 124) was converted into its methyl ester by saturating its methanolic solution with hydrogen chloride and boiling the solution under reflux whilst hydrogen chloride was slowly passed through it during 2 hours. Methyl 2-bromo-3-nitrobenzoate (2·6 g.), 1-iodonaphthalene (2·5 g.), and copper bronze (2·5 g.) were heated in an oil-bath at 120° for 1·5 hours during which the liquid solidified to a greenish-brown solid. It was extracted with light petroleum (b. p. 60—80°), and the solid obtained on evaporation was chromatographed (benzene–alumina). The main fraction proved to be dimethyl 2 : 2′-dinitro-6 : 6′-diphenate; but a small band of the chromatogram on crystallisation (light petroleum, b. p. 60—80°) gave a few deep yellow crystals of 1-(2-*carbomethoxy*-6-*nitrophenyl*)*naphthalene* crystallising from benzene–light petroleum (b. p. 60—80°) in pale yellow, thick, hexagonal plates, m. p. 90—91° (Found: C, 71·2; H, 4·2. $C_{18}H_{13}O_4N$ requires C, 70·35; H, 4·3%).

1-(2 : 6-*Dinitrophenyl*)*naphthalene* (IV; R = NO_2).—1-Chloro-2 : 6-dinitrobenzene (preparation to be described shortly) (1·0 g.), iodonaphthalene (1·25 g.), and copper bronze (1·25 g.) were heated at 120°

in an oil-bath for 2 hours. After the usual extraction with ether, methanol gave yellow rods of 1-(2 : 6-*dinitrophenyl*)*naphthalene*, m. p. 157—159° (0·5 g., 34%) (Found : C, 65·25; H, 3·3; N, 9·3. $C_{16}H_{10}O_4N_2$ requires C, 65·3; H, 3·4; N, 9·5%). Under comparable conditions (160°/3 hours) 1-bromo-2 : 6-dinitrobenzene gave 2 : 2′ : 6 : 6′-tetranitrodiphenyl (50%).

1-(2-*Methoxy*-6-*nitrophenyl*)*naphthalene* (IV; R = OMe).—2-Bromo-3-nitrophenol (Schlieper, *Ber.*, 1892, **25**, 552) (5 g.) and potassium hydroxide (4 g.) were dissolved in methanol (100 ml.), and methyl iodide (11·7 g.) was added. The solution was boiled under reflux until decolourised. Distillation left a yellow mass, which was cleared of oil on porous plate. After being ground with water, it was crystallised from ligroin (b. p. 40—60°), forming needles, m. p. 103—104° (3·5 g., 66%), of 2-bromo-3-nitroanisole. The use of methyl sulphate in place of methyl iodide and in absence of methanol gave a low yield (19%) (cf. Pfaff, *Ber.*, 1883, **16**, 614).

2-Bromo-3-nitroanisole (2 g.), 1-iodonaphthalene (2·2 g.), and copper bronze (2·2 g.) were heated at 250° for 2 hours. The dark brown product was extracted with ether, the extract evaporated, and the residue chromatographed (benzene–alumina) to give *inter alia* a yellow band which fluoresced in ultra-violet light. It was eluted, and gave (from ethanol and then light petroleum, b. p. 60—80°) pale yellow crystalline balls (0·08 g., 2%) of 1-(2-*methoxy*-6-*nitrophenyl*)*naphthalene* (Found : C, 73·0; H, 4·6; N, 5·1. $C_{17}H_{13}O_3N$ requires C, 73·1; H, 4·7; N, 5·0%).

The preparation of 1-(2-methoxy-6-nitrophenyl)naphthalene was carried out by Mr. R. W. Chappell, B.Sc. We thank Mr. J. M. L. Cameron and Miss R. H. Kennaway for microanalyses.

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