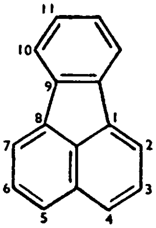
569. *Synthesis of Fluoranthenes. Part XIV.* Synthesis of 3-Methoxyfluoranthene.*

By A. E. JEMMETT, S. HORWOOD TUCKER, and (in part) I. WELLINGS.

3-Methoxyfluoranthene has been synthesised from Cleve's acid, 1-naphthylamine-6-sulphonic acid.

2-, 4-, 10-, and 11-METHOXYFLUORANTHENE have been synthesised [1] but the methods used were not applicable to the synthesis of the remaining isomer, 3-methoxyfluoranthene. This has now been prepared from Cleve's acid, 1-naphthylamine-6-sulphonic acid, by its conversion into 1-acetamido-6-naphthol,[2] thence into 1-iodo-6-methoxynaphthalene.[3] This was converted into 3-methoxyfluoranthene by the standard method of Forrest and Tucker,[4] *viz.*, 1-iodo-6-methoxynaphthalene ⟶ 6-methoxy-1-*o*-nitrophenylnaphthalene ⟶ amine ⟶ 3-methoxyfluoranthene.



Fierz-David and Blangey's method [5] for the separation of Cleve's acids, 1-naphthylamine-6- and -7-sulphonic acid, by means of the sodium salts failed in our hands: instead of the sodium salt of the 7-sulphonic acid being first precipitated, as claimed, we isolated a small amount of a salt whence the benzyl*iso*thiuronium salt of the 6-acid was obtained. A commercial mixture of the mixed sodium salts gave a similar result. Excellent separation was effected by means of the magnesium salts, that of the desired 6-sulphonic acid being almost insoluble in cold water. Improvements have been introduced into the other stages of the synthesis (see below).

An attempt to prepare 3-methoxyfluoranthene from 3-aminofluoranthene [6] was only partially successful. Fluoranthene-3-carboxylic acid has been synthesised, but could not be converted into 3-aminofluoranthene by a Curtius reaction. We failed also to improve on Campbell and Wang's [7] admittedly unsatisfactory synthesis of the above acid, even by use of 9-methylenefluorene.[8] We could not isolate 5-nitro-2-naphthoic acid by the methods of Harrison and Royle; [9] and, since the literature is not clear about the properties of the isomeric nitro-ester,[10] this line was not pursued.

The ultraviolet absorption spectrum of 3-methoxyfluoranthene in ethanol conforms to the theory put forward by Clar, Stubbs, and Tucker [11] regarding the inter-relation of the *p*-band and the position of the methoxyl group on the fluoranthene nucleus.

	p-Bands		β-Bands			
$\lambda_{\max.}$ (mμ)	364	326	288	280	272	236
log ε	2·88	2·82	3·36	3·31	3·38	3·70

The infrared spectra of the methoxyfluoranthenes have also been examined.[12]

EXPERIMENTAL

Separation of 1-*Naphthylamine*-6- *and* -7-*sulphonic Acid from a Mixture of Cleve's Acids*.—The commercial mixture of Cleve's acids (223 g.) was dissolved in water (2 l.) containing 32%

---

* Part XIII, *J.*, 1958, 1462.

[1] Hawkins and Tucker, *J.*, 1950, 3286; Stubbs and Tucker, *J.*, 1954, 227.

[2] Campbell, Laforge, and Campbell, *J. Org. Chem.*, 1949, **14**, 351.

[3] Butenandt and Schramm, *Ber.*, 1935, **68**, 2083; Wilds and Close, *J. Amer. Chem. Soc.*, 1947, **69**, 3079.

[4] Forrest and Tucker, *J.*, 1948, 1137.

[5] Fierz-David and Blangey, " Processes of Dye Chemistry," Interscience Publishers Ltd., London, 5th edn., p. 184.

[6] Kloetzel, King, and Menkes, *J. Amer. Chem. Soc.*, 1956, **78**, 1165.

[7] Campbell and Wang, *J.*, 1949, 1513.

[8] Burr, jun., *J. Amer. Chem. Soc.*, 1952, **74**, 1717.

[9] Harrison and Royle, *J.*, 1926, 84.

[10] Graff, *Ber.*, 1883, **16**, 2252; Ekstrand, *J. prakt. Chem.*, 1890, **42**, 273; Elsevier, Vol. **12**, *B*, p. 4167.

[11] Clar, Stubbs, and Tucker, *Nature*, 1950, **166**, 1075; Stubbs and Tucker, ref. 1.

[12] Jemmett, Ph.D. Thesis, Glasgow, 1956.

sodium hydroxide solution (95 ml.). The mixture was stirred with charcoal at 80—90° for 30 min., the insoluble material was removed and washed with boiling water (200 ml.), and the combined filtrates were diluted to 2·2 l. The solution, stirred at 80—90°, was treated with crystalline magnesium sulphate (367 g.) and allowed to cool slowly, the precipitated magnesium 1-naphthylamine-6-sulphonate was filtered off and dissolved in water (2·5 l.) at 80—90°, and 36% hydrochloric acid (140 ml.) slowly added. The precipitated pink powder was washed with water (500 ml.) and dried at 60°, to give 1-naphthylamine-6-sulphonic acid (104 g., 47%).

5-*Amino*-2-*naphthol*.—1-Naphthylamine-6-sulphonic acid (40 g.) was added to potassium hydroxide (70 g.) and water (10 ml.) at 250°. The temperature rose rapidly to 270—280°, and was there maintained for $\ngtr$ 7 min. (At 290° decomposition occurs with evolution of ammonia; below 270—280° reaction is incomplete: acid can be recovered.) The fused mass was dissolved in hot water (250 ml.), and the solution acidified, filtered from tar, neutralised with sodium hydroxide solution, and made alkaline with an excess of sodium carbonate, to give 5-amino-2-naphthol as a grey powder, m. p. 186° (25·2 g., 90%). 5-Acetamido-2-naphthol was prepared by suspending the aminonaphthol (16 g.) in boiling benzene (30 ml.) and adding an equivalent amount of acetic anhydride: it crystallised in blades (from methanol), m. p. 215° (100%) (cf. ref. 2).

2-*Methoxy*-5-o-*nitrophenylnaphthalene*.—1-Iodo-6-methoxynaphthalene[3] (2·8 g.) and *o*-bromonitrobenzene (2·2 g.) were heated to 180°, and copper powder (3·5 g.) was added with stirring. After 2 hr. at 180° the cooled mass was extracted with benzene, the solvent removed, and the red oil so obtained triturated with ethanol, and crystallised from light petroleum (b. p. 40—60°), then from methanol, as pale green leaflets, m. p. 107—108°, of 2-*methoxy*-5-o-*nitrophenylnaphthalene* (0·8 g., 30%) (Found: C, 72·9; H, 4·9; N, 5·0. $C_{17}H_{13}O_3N$ requires C, 73·1; H, 4·7; N, 5·0%).

5-o-*Aminophenyl*-2-*methoxynaphthalene*.—Reduction of the nitro-compound with hydrogen in presence of Raney nickel in ethanol gave (from ethanol) the *amine*, m. p. 114—115° (*ca.* 100%) (Found: C, 81·7; H, 5·9; N, 5·7. $C_{17}H_{15}ON$ requires C, 81·9; H, 6·1; N, 5·6%).

3-*Methoxyfluoranthene*.—The amine was dissolved in hot dilute sulphuric acid, and the solution cooled to effect precipitation of small crystals of sulphate which was then diazotised at room temperature. After 30 min. the scarlet solution was heated on the steam-bath with frequent shaking until colourless. The precipitate was filtered off and extracted with hot benzene, and the solution dried and chromatographed on alumina. The yellow eluate (strong blue fluorescence in ultraviolet light) gave 3-*methoxyfluoranthene* (50%) as cream crystals (from methanol containing a trace of water), m. p. 83—84° (Found: C, 87·7; H, 5·3. $C_{17}H_{12}O$ requires C, 87·9; H, 5·2%). It gave a *picrate*, orange-yellow needles (from ethanol), m. p. 178° (softening at 175°) (Found: C, 59·7; H, 3·0; N, 9·0. $C_{17}H_{12}O,C_6H_3O_7N_3$ requires C, 59·9; H, 3·3; N, 9·1%), and *complexes* with 1 : 3 : 5-trinitrobenzene, yellow needles (from ethanol–acetic acid), m. p. 178° (softening at 175°) (Found: C, 61·9; H, 3·2. $C_{17}H_{12}O,C_6H_3O_6N_3$ requires C, 62·0; H, 3·4%), and 2 : 4 : 7-trinitrofluorenone (from acetic acid), orange needles, m. p. 219—220° (Found: C, 65·8; H, 3·1. $C_{17}H_{12}O,C_{13}H_5O_7N_3$ requires C, 65·8; H, 3·1%).

Synthesis of Methyl Fluoranthene-3-*carboxylate* [with I. WELLINGS].—5-*Iodo*-2-*naphthoic acid*.[13] Silver sulphate (1 g., theor. 0·78 g.) was dissolved in sulphuric acid (40 ml.) and water (2 ml.) contained in a round-bottomed flask, and cooled to room temperature. 2-Naphthoic acid (0·86 g.) was added, then very finely powdered iodine (1·5 g., theor. 1·3 g.) portionwise whilst the whole was violently stirred by means of a tantalum wire stirrer (a vibro-mixer gave poorer results). After 2 hr., carbon tetrachloride (40 ml.) was added, and stirring continued for 1 hr. The mixture was poured into water (300 ml.), and the precipitated solid filtered through sintered glass. (Since the carbon tetrachloride layer was found to contain only a negligible amount of the desired acid, it was discarded.) The solid was extracted with 5% aqueous potassium hydroxide, and the solution filtered through charcoal, then acidified with dilute sulphuric acid. The precipitate (1·32 g.), after crystallisation from acetone and then from ethyl acetate, gave needles (1·02 g., 66%) of 5-iodo-2-naphthoic acid, m. p. 254° [lit.,[14] m. p. 264° (corr.)]. Preparations on a larger scale gave lower yields (*ca.* 35%). Addition of carbon tetrachloride at the commencement resulted in slightly lower yields: the carbon tetrachloride could not be recovered.

Methyl 5-*iodo*-2-*naphthoate*. This was prepared by refluxing pure 5-iodo-2-naphthoic acid

---

[13] Cf. Derbyshire and Waters, *J.*, 1950, 3694.

[14] Goldstein and Matthey, *Helv. Chim. Acta*, 1937, **20**, 1418.

(4·47 g.) with methanol (60 ml.) containing concentrated sulphuric acid (3 ml.) for 2 hr. The ester crystallised overnight. The filtrate was concentrated to two-thirds its bulk, then poured into ice-cold water. The washed products crystallised from ligroin (b. p. 60—80°) in cream needles (colourless from methanol) (4·2 g., 90%), m. p. 76—78° [lit., 78° (corr.)] (Found: C, 46·0; H, 3·0. Calc. for $C_{12}H_9O_2I$: C, 46·2; H, 2·9%).

When crude 5-iodo-2-naphthoic acid was esterified by hot methanol containing dry hydrogen chloride for 1 hr. and crystallised from much methanol, the first crops (recrystallised from ethanol–methyl cyanide) were of methyl 5 : 8(?)-di-iodo-2-naphthoate, m. p. 164—166° (see below). Later crops, from methanol, gave methyl 5-iodo-2-naphthoate. Chromatography failed to give a satisfactory separation.

5 : 8(?)-*Di-iodo-2-naphthoic acid*. When a greater excess of iodine (and of silver sulphate) was used than that just given, removal of the bulk of the monoiodo-acid by crystallisation from acetone and concentration of the filtrates gave the *di-iodo-acid*. Crystallisation from acetic acid, then from dioxan to which a trace of water was added, gave needles, m. p. 280° (Found: C, 31·3; H, 1·6; I, 59·6. $C_{11}H_6O_2I_2$ requires C, 31·15; H, 1·4; I, 59·9%). Esterification (Fischer–Speier) gave the *methyl ester* (from ethanol–methyl cyanide) as slightly pink needles, m. p. 164—166° (Found: C, 33·0; H, 2·1; I, 58·3. $C_{12}H_8O_2I_2$ requires C, 32·9; H, 1·8; I, 58·0%).

Methyl 5-o-*nitrophenyl-2-naphthoate*. Methyl 5-iodo-2-naphthoate (1·56 g.), *o*-bromonitrobenzene (1·02 g.), and copper bronze (2 g.) were heated at 180° for 1 hr. whilst stirred by a copper-wire stirrer. Extraction with acetone gave, ultimately, thick, hexagonal, pale yellow plates (from ethyl acetate), m. p. 170—171° (0·51 g., 33%) (Found: C, 70·2; H, 3·8; N, 4·7. $C_{18}H_{13}O_4N$ requires C, 70·35; H, 4·3; N, 4·6%). Results were not improved by use of activated copper.[15]

Methyl 5-o-*aminophenyl-2-naphthoate*. Raney nickel (1·4 g. of nickel in 7 ml. of ethanol) was saturated with hydrogen; ethyl acetate (previously treated with Raney nickel) was added, then finely powdered methyl 5-*o*-nitrophenyl-2-naphthoate (1·02 g.) was rinsed into the flask by ethyl acetate (20 ml.). Theoretical absorption took place in 30 min. The mixture was boiled and filtered, and the nickel residue thoroughly extracted with boiling ethyl acetate: the amine is nearly insoluble in ethanol. The concentrated filtrates, treated with ethanol, gave stout prisms of *methyl* 5-o-*aminophenyl-2-naphthoate*, m. p. 146—148° (total, 0·82 g., 90%) (Found: C, 78·2; H, 5·7; N, 5·3. $C_{18}H_{15}O_2N$ requires C, 78·0; H, 5·45; N, 5·05%). When heated in acetic anhydride to the b. p. it gave the *acetyl derivative*, prisms (from a concentrated solution in acetic acid), m. p. 180—181° (Found: C, 75·05; H, 5·2; N, 4·45. $C_{20}H_{17}O_3N$ requires C, 75·2; H, 5·4; N, 4·4%).

Methyl fluoranthene-3-carboxylate. The amino-ester (0·74 g.) was treated in acetic acid (10 ml.) with aqueous sulphuric acid (2 ml. of acid and 8 ml. of water) and then at room temperature with sodium nitrite (0·25 g.) in water (2 ml.). The deep yellow solution was diluted with water (20 ml.), and gave a positive reaction with starch–iodide. Sulphamic acid was added, and the solution warmed on the water-bath. Copper was added. After 10 min. on the boiling-water bath, the solid was collected and extracted with acetone, and the extracts were concentrated to give *methyl fluoranthene-3-carboxylate*, cream needles (from methanol), m. p. 122—123° (Found: C, 82·8; H, 4·4. $C_{18}H_{12}O_2$ requires C, 83·1; H, 4·65%). Further concentration gave a small amount of solid, which on crystallisation from acetic acid and then from ethyl-acetate gave pale greenish-yellow rosettes, m. p. 290° (decomp. from 270°), of fluoranthene-3-carboxylic acid[7] (Found: C, 82·8; H, 4·45. Calc. for $C_{17}H_{10}O_2$: C, 82·9; H, 4·1%). The acetic acid filtrates on slight concentration gave a sandy-coloured product which after crystallisation from benzene, then from acetic acid, gave crystals, m. p. 194—195°, of *methyl* 5-o-*hydroxyphenyl-2-naphthoate* (Found: C, 77·6; H, 5·0. $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·1%), soluble in 10—50% potassium hydroxide solution only after previous wetting with ethanol. Hydrolysis of methyl fluoranthene-3-carboxylate by boiling 50% potassium hydroxide solution with added ethanol, for 10 min. gave a product which separated reluctantly from ethyl acetate to give pale green crystals (efflorescence) of the above fluoranthene-3-carboxylic acid.

An attempt to prepare 3-aminofluoranthene by a Curtius reaction on fluoranthene-3-carboxylic acid gave in very small amount pale yellow needles, m. p. 115—123°; a mixture with genuine amine[6] (m. p. 128°) softened at 114° but did not melt even at 160°. Unchanged acid was recovered from benzene solutions. An attempt to prepare 3-methoxyfluoranthene from

---

[15] Kleiderer and Adams, *J. Amer. Chem. Soc.*, 1933, **55**, 4219.

3-aminofluoranthene [6] gave an unreliable result. In the course of the preparation of the amine by reduction of 4-nitrofluoranthene (first stage) by hydrogen in presence of Raney nickel in ethanol gave a small amount of orange-yellow NN′-*di-4-fluoranthenylhydrazine*, m. p. 303—304° [from benzene (red solution)] (Found: C, 88·8; H, 5·3; N, 6·3. $C_{32}H_{20}N_2$ requires C, 88·9; H, 4·7; N, 6·5%).

4-Acetamido-3-nitrofluoranthene (2·5 g.) was hydrolysed for 30 min. in a boiling mixture of 50% aqueous potassium hydroxide (2 ml.) and 2-methoxyethanol (25 ml.). The deep red solution, diluted with water, gave a brick-red product (2·02 g.) which after crystallisation from ethylene glycol, then from chlorobenzene, and finally from ethyl methyl ketone (during concentration), gave brick-red crystals, softening at 250°, melting at 253° [lit.,[6] 235° (misprint?)] (Found: C, 73·5; H, 4·0; N, 10·8. Calc. for $C_{16}H_{10}O_2N_2$: C, 73·3; H, 3·8; N, 10·7%).

3-Aminofluoranthene was converted in the usual way into the phenol. This was not isolated, but was treated with methyl sulphate in alkali. A very small amount of material was isolated, having m. p. 82° alone or mixed with 3-methoxyfluoranthene. A 2 : 4 : 7-trinitrofluorenone complex had m. p. 205—210°, but a mixture with genuine 3-methoxyfluoranthene complex (m. p. 219—220°) had m. p. 205—210° (quantities obtained were too small to allow further purification).

We thank the Department of Scientific and Industrial Research for a grant (to A. E. J.), and Imperial Chemical Industries Limited for supply of Cleve's acids and the account of the method of separation. Microanalyses were carried out under the supervision of Mr. J. M. L. Cameron by Miss S. U. Watt.

THE UNIVERSITY, GLASGOW.

[*Received, February* 6*th*, 1958.]