

610. *Synthesis of Fluoranthenes. Part X.* 10-Methylfluoranthene. Correction of its Melting Point.*

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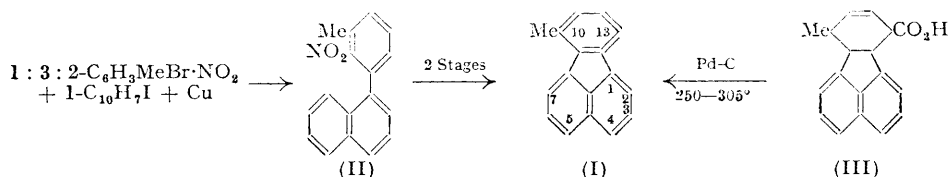
Two additional syntheses of 10-methylfluoranthene have shown that the original synthesis by Tucker and Whalley (*J.*, 1949, 3213) was sound, but that the material isolated was contaminated with a by-product. We are now in substantial agreement with Kloetzel and Mertel (*J. Amer. Chem. Soc.*, 1950, **72**, 4786).

THE original synthesis of 10-methylfluoranthene (Tucker and Whalley, *loc. cit.*) gave a low overall yield, and was tedious since the starting material, 2-bromo-3-nitrotoluene had to be synthesised from *o*-toluidine by a method which involved separation of the 3-, 4-, and 5-nitro-derivatives of *o*-toluidine (Gabriel and Thieme, *Ber.*, 1919, **52**, 1079; McGookin and Swift, *J. Soc. Chem. Ind.*, 1939, **58**, 152; cf. Govaert, *Bull. Soc. chim. Belg.*, 1929, **38**, 372). Separation of pure 2-amino-3-nitrotoluene was, however, accomplished in good yield, and this by the Sandmeyer reaction gave 2-bromo-3-nitrotoluene. Even if the 2-amino-3-nitrotoluene had been contaminated with the corresponding 4- and 5-nitro-isomers, the 2-bromo-4-nitrotoluene would not have reacted with 1-iodonaphthalene, and the corresponding 5-nitro-isomer if sufficiently active to combine with 1-iodonaphthalene could not have given a cyclisable product.

Repetition of our work gave indeed the product (m. p. 105—108°) alleged to be 10-methylfluoranthene; but we now discover that this product was contaminated with a small amount of 1-(2-methyl-6-hydroxyphenyl)naphthalene. After removal of this by chromatography we obtained genuine 10-methylfluoranthene, m. p. 132—133.5°. Kloetzel and Mertel (*loc. cit.*) reported m. p. 136—137°, but Professor Kloetzel (private communication) has revised this to m. p. 135—135.5°. A sample which he kindly supplied had, by our handling, alone or mixed with our sample, m. p. 132—133.5°.

The ultra-violet absorption spectra of the two samples of 10-methylfluoranthene (*A*) were practically identical: one graph is given and compared with that of fluoranthene (*B*).

To satisfy ourselves, we have confirmed the identity of 10-methylfluoranthene by two syntheses: (i) *o*-Nitrotoluene was mercurated, then treated with bromine to give 3-bromo-2-nitrotoluene (Burton, Hammond, and Kenner, *J.*, 1926, 1802; Longo and Pirona, *Gazzetta*, 1947, **77**, 117). The crossed Ullmann reaction with 1-iodonaphthalene gave 1-(3-methyl-2-nitrophenyl)naphthalene (II). The very low yield (16%) of this compound is unusual in this type of reaction (cf. Forrest and Tucker, *J.*, 1948, 1513; Tucker and Whalley, *J.*, 1949, 632, 3213; Stubbs and Tucker, *J.*, 1951, 2936), although it has been noted that when the bromobenzene has two *ortho*-substituents (Hawkins and Tucker, *J.*, 1950, 3286) the yields in the crossed Ullmann reaction are lowered. (ii) Sorbic acid underwent a diene synthesis with acenaphthylene to give a tetrahydro-10-methylfluoranthene-13-carboxylic acid (Deno, *J. Amer. Chem. Soc.*, 1950, **72**, 4057; Kloetzel and Mertel, *loc. cit.*, used ethyl sorbate; see also Bergmann, *Nature*, 1948, **161**, 889) in which the position of the double



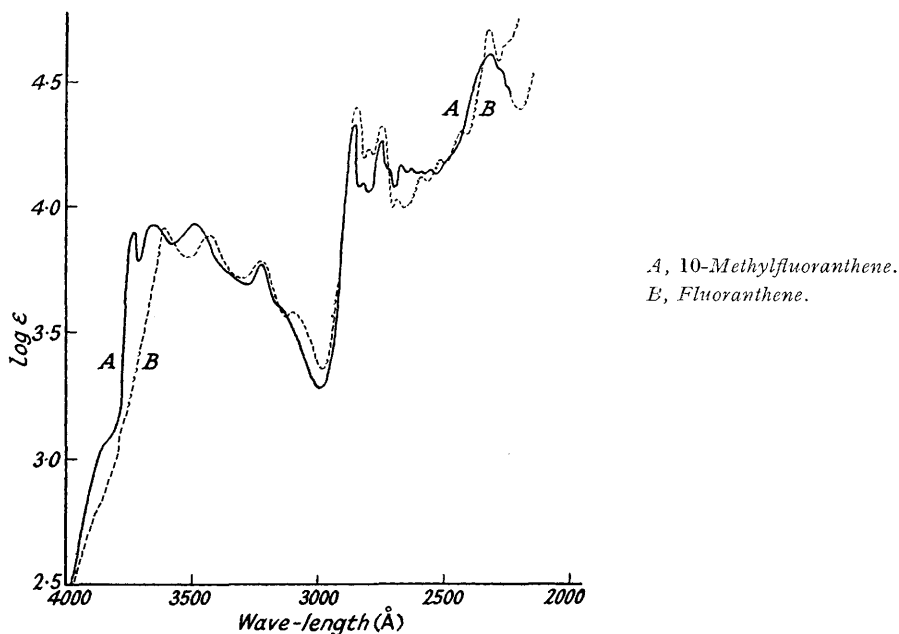
bond is unknown: it is probably not conjugated to the naphthalene ring (Deno, *loc. cit.*). It may be as indicated in (III). Heating (III) with palladium-charcoal effected dehydrogenation and decarboxylation to give 10-methylfluoranthene (cf. Wicks, Daly, and Lack, *J. Org. Chem.*, 1947, **12**, 713).

* Part IX, *J.*, 1952, 803.

Professor Kloetzel (private communication) considers the m. p. of 11-methylfluoranthene to be 90.5—91.5° (Kloetzel and Mertel, *loc. cit.*, gave 93—94°; Tucker and Whalley, *loc. cit.*, 88—90°).

EXPERIMENTAL

Repetition of Synthesis of 10-Methylfluoranthene (Tucker and Whalley, *loc. cit.*).—2-Bromo-3-nitrotoluene. Diazotisation of 2-amino-3-nitrotoluene by Hodgson and Walker's method (*J.*, 1933, 1620) proceeded more smoothly and gave a better yield of 2-bromo-3-nitrotoluene than did that of Gibson and Johnson (*J.*, 1929, 1243). Sodium nitrite (5 g.) was added with stirring to cooled concentrated sulphuric acid (40 ml.), the temperature was raised to 70° to complete solution and then lowered to room temperature, and a solution of 2-amino-3-nitrotoluene (10 g.) in glacial acetic acid (120 ml.), cooled to room temperature, was gradually added to the nitrosyl-sulphuric acid solution, the temperature being kept below 20°. The solution so obtained was run into a well-stirred solution of cuprous bromide (18 g.) in 48% hydrobromic acid solution



(150 ml.). Next morning, cold water (300 ml.) was carefully added. The precipitated solid was steam-distilled, to give 2-bromo-3-nitrotoluene as a pale yellow solid, m. p. 38—40° (9.5 g., 68%). This was of good enough quality for use in the crossed Ullmann reaction. Recrystallised from light petroleum (b. p. 40—60°), it had m. p. 41—42°. Completion of the synthesis of (I) gave the product, m. p. 105—108°, as described; but when this had been extracted with 10% potassium hydroxide solution (or when the material precipitated on the copper had been similarly treated) the residue formed a picrate (from methanol), m. p. 197—199°, which by chromatographic separation (alumina-benzene) gave a product whence crystallisation from light petroleum (b. p. 40—60°) and then from methanol gave faintly yellow, diamond-shaped plates, m. p. 132—133.5° [133—134.5° (corr.)] (Found: C, 94.3; H, 5.4. Calc. for $C_{17}H_{12}$: C, 94.4; H, 5.6%). The picrate, from methanol, has m. p. 197—199° [200—202° (corr.)] (Kloetzel and Mertel, m. p. 201—202°; Kloetzel, revised, 200—200.5°) (Found: C, 61.9; H, 3.3. Calc. for $C_{17}H_{12}, C_6H_3O_7N_3$: C, 62.0; H, 3.4%). The complex with *s*-trinitrobenzene has m. p. 218—219°; that with 2:4:7-trinitrofluorenone, m. p. 215—216° (Found: C, 67.6; H, 3.3; N, 7.8. Calc. for $C_{17}H_{12}, C_{13}H_5O_7N_3$: C, 67.8; H, 3.2; N, 7.9%). The phenolic impurity referred to above was isolated by the following modification of the cyclisation process.

1-(2-Hydroxy-6-methylphenyl)naphthalene. A mixture of 1-(2-amino-6-methylphenyl)naphthalene (0.78 g.), concentrated sulphuric acid (1.5 ml.), and water (10 ml.) was diazotised at 0° by addition of sodium nitrite (0.25 g.) in water (2 ml.). Excess of nitrite was destroyed by urea.

The solution was poured into a 33% solution of dimethylamine (*ca.* 1 g.) containing excess of sodium carbonate solution (Elks and Hey, *J.*, 1943, 441). The brick-red precipitate obtained was dissolved in acetic acid, and warmed whilst hydrogen chloride was passed in. Dilution with water gave an oil which was chromatographed (alumina-benzene). A blue-fluorescent band, on elution, gave 10-methylfluoranthene (I). The column was further eluted with benzene containing 5% of ethanol, and gave a solid (0.06 g.) which after crystallisation from light petroleum (b. p. 60—80°) gave very pale yellow monoclinic prisms of 1-(2-hydroxy-6-methylphenyl)naphthalene, m. p. 100—102° (Found: C, 87.2; H, 6.2. $C_{17}H_{14}O$ requires C, 87.2; H, 6.0%).

Synthesis of 10-Methylfluoranthene (I) from 1-Iodonaphthalene and 3-Bromo-2-nitrotoluene.—1-(3-Methyl-2-nitrophenyl)naphthalene (II). 1-Iodonaphthalene (2.54 g., 0.01 g.-mol.) and an excess of 3-bromo-2-nitrotoluene (b. p. 125—130°/8 mm.; 7.2 g.) and of copper bronze were heated at 240° for 7 hours. The black liquor was extracted with light petroleum (b. p. 60—80°), filtered from copper, and distilled, to remove unchanged liquids, up to 130°/8 mm. The residue was dissolved in light petroleum (b. p. 60—80°) and the solution chromatographed (alumina). The first eluate contained unchanged oils which on dilution with light petroleum [b. p. 40—60°; 10 parts (v/v)] and storage at 0° gave 1:1'-dinaphthyl (m. p. 156—158°). Subsequent eluates gave, even without cooling in ice, but on concentration followed by crystallisation from methanol, faintly green, long rectangular laminae of 1-(3-methyl-2-nitrophenyl)naphthalene (II), m. p. 118—119° (0.43 g., 16% calc. on 1-iodonaphthalene) (Found: C, 77.5; H, 4.95; N, 5.3. $C_{17}H_{13}O_2N$ requires C, 77.6; H, 4.9; N, 5.3%). Lower yields were obtained by heating equimolecular quantities of the reactants with excess of copper at 200° for 5 hours. In one experiment at 240° a small amount of 3:3'-dimethyl-2:2'-dinitrodiphenyl, m. p. 226—227°, was obtained from a final eluate of the column with acetone (*cf.* Longo and Pirona, *loc. cit.*).

1-(2-Amino-3-methylphenyl)naphthalene. The above nitro-compound (II) (0.36 g.) with hydrogen and Raney nickel in ethanol gave theoretical absorption of hydrogen (20 minutes), and the resulting 1-(2-amino-3-methylphenyl)naphthalene crystallised from light petroleum (b. p. 60—80°) and then from methanol in short pointed lath-like crystals, m. p. 109—110° (0.23 g., 73%) (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%). Reduction with hydrogen and 10% palladium-charcoal was very rapid.

10-Methylfluoranthene (I). The above amine (0.22 g.) in glacial acetic acid (2 ml.) was poured into a solution of sodium nitrite (0.069 g.) in acetic acid (1.5 ml.) and concentrated sulphuric acid (0.3 ml.) kept in ice. The clear yellow solution was diluted with water, and warmed on the steam-bath. Yellow crystals separated, and when the liquor became colourless (*ca.* 10 minutes) the whole was boiled, cooled, and extracted with ether, the ethereal extract was shaken with 10% potassium hydroxide solution until the alkaline extract was colourless, and then washed with water, and after removal of ether the residue was crystallised from light petroleum (b. p. 40—60°) and then from methanol to give pale yellow diamond-shaped plates (0.09 g., 45%) of 10-methylfluoranthene (I) (m. p. 132—133°). Addition of copper bronze had no facilitating influence on the cyclisation.

Synthesis of 10-Methylfluoranthene (I) from Acenaphthylene and Sorbic Acid.—9:10:13:14(?)-Tetrahydro-10-methylfluoranthene-13-carboxylic acid (0.185 g.) (Deno, *loc. cit.*) was heated at 250—270° with 10% palladium-charcoal (0.12 g.) in a current of carbon dioxide, the hydrogen evolved (in 40 minutes, *ca.* 25 ml.; theor., 31 ml.) being measured in an azotometer over 50% potassium hydroxide solution (Linstead, *J.*, 1937, 1153). Further heating for a short time at 305° caused frothing probably owing to evolution of carbon dioxide from the carboxylic acid since no evolution of hydrogen took place. A sublimate, formed on the sides of the tube, and the residue, on extraction with light petroleum (b. p. 40—60°), gave 10-methylfluoranthene (I).

Ultra-violet Absorption Spectrum of 10-Methylfluoranthene.—This was recorded by the Unicam spectrophotometer, with ethanol as solvent: maxima occurred at (λ in Å) p-bands 3740 ($\log \epsilon$ 3.90), 3660 (3.93), 3500 (3.94), 3240 (3.77); β -bands 2880 (4.34), 2770 (4.28), 2690 (4.18), 2650 (4.16), 2570 (4.17); β' -band 2350 (4.64).

We are indebted to Mr. W. C. Russell for the preparation of 2-bromo-3-nitrotoluene, to Mr. A. J. N. Hope, B.Sc., for recording the absorption spectrum of 10-methylfluoranthene, and to Miss M. W. Christie for micro-analyses.