

**135.** *The Condensation of Fluorene with Acetone. Part VI. Methylated Di- and Tetra-hydrofluoranthenes. Synthesis of 2 : 3 : 4-Trimethylfluoranthene.*

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4-Fluorenylidene-2-methylpent-2-ene (I) has been cyclised (a) by hydriodic acid to 2 : 4 : 4-trimethyl-1 : 2 : 3 : 4-tetrahydrofluoranthene (IIA) \* and 2 : 3 : 4-trimethylfluoranthene (III) and (b) by hydrogen bromide and stannic chloride to 2 : 4 : 4-trimethyl-1 : 4(? 3 : 4)-dihydrofluoranthene (IV).

2 : 3 : 4-Trimethylfluoranthene has been synthesised from 1 : 2 : 3-trimethylnaphthalene.

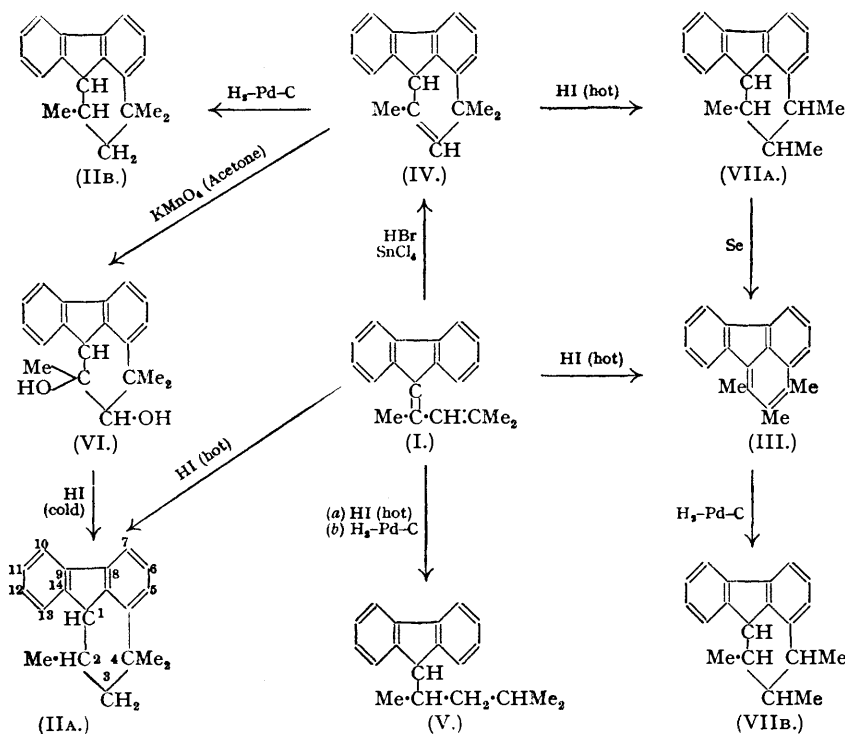
It was clearly indicated (Maitland and Tucker, Part I, *J.*, 1929, 2559; Tucker and Whalley, Part V, this vol., p. 50) that 9-fluorenylmagnesium bromide reacts with mesityl oxide to give, after dehydration, 4-fluorenylidene-2-methylpent-2-ene (I). The structure of this compound is in agreement with the following properties : (i) oxidation with sodium dichromate in acetic acid gives fluorenone; (ii) it forms a picrate; (iii) catalytic hydrogenation in presence of palladium-charcoal at atmospheric pressure shows the presence of two double bonds which are shown to be in the side chain by oxidation of the reduced product 4-(9-fluorenyl)-2-methylpentane (V) to fluorenone. It is surprising that this 1 : 3-diene (I) cannot be induced to give Diels-Alder addition products. This failure to undergo the typical diene reaction is, however, not unique : Backer and Strating (*Rec. Trav. chim.*, 1941, **60**, 391) failed to add maleic anhydride to 1-diphenylenebutadiene (assumed to be intermediately formed from 9-hydroxy-9-allylfluorene), and Bachman and Hatton (*J. Amer. Chem. Soc.*, 1944, **66**, 1513) found that 4-methyl-1 : 3-pentadiene, which is in some respects comparable with (I), failed to react with maleic anhydride and with benzoquinone even in the presence of antioxidants and at high temperatures.

Maitland and Tucker (*loc. cit.*) by the action of hydriodic acid on (I) obtained two compounds, (A), m. p. 51—55°, and (B), m. p. 103—104°. We have now established that (A) is identical with that obtained by catalytic hydrogenation of (I), *viz.*, 4-(9-fluorenyl)-2-methylpentane (V); (B) was not at first obtained in the present series of experiments but was finally obtained on one occasion only when hydriodic acid (*d* 1.50) was used instead of the more concentrated acid (*d* 1.70). The structure (IIA) has been assigned to this compound (see below). There

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

was also isolated a substance not previously obtained by this reaction, 2:3:4-trimethylfluoranthene (III), m. p. 133°. The structure of this compound was deduced by Forrest and Tucker (Part IV, *J.*, 1948, 1137) and has now been confirmed by synthesis in the following manner: 1:2:3-Trimethylnaphthalene  $\xrightarrow{KI/KIO_4/HOAc}$  1-iodo-2:3:4-trimethylnaphthalene  $\xrightarrow{o\text{-bromonitrobenzene}}$  1-(2'-nitrophenyl)-2:3:4-trimethylnaphthalene  $\xrightarrow{H_2-Ni}$  amine  $\xrightarrow{\text{cyclisn.}}$  2:3:4-trimethylfluoranthene (cf. Ullmann, *Annalen*, 1904, 332, 38; Lesslie and Turner, *J.*, 1930, 1758; 1931, 1188; Rule and Smith, *J.*, 1937, 1096; Forrest and Tucker, *loc. cit.*).

Treatment of (I) with hydrogen bromide in glacial acetic acid gave a white solid which with stannic chloride in benzene gave 2:4:4-trimethyl-1:4(?3:4)-dihydrofluoranthene (IV). This appears to be a new method of cyclisation from an aromatic ring system possessing a butadiene side chain. It has been applied successfully to the synthesis of naphthalene derivatives (future communication). The position of the double bond in (IV) cannot be proved, but the following evidence supports the constitution assigned to it. Oxidation of (IV) with sodium dichromate and acetic acid yielded fluorenone-1-carboxylic acid, proving that ring formation to the 1-position of the fluorene nucleus had occurred (see France, Tucker, and Forrest, Part III, *J.*, 1945, 7). Treatment of (IV) with selenium at 300° gave 2:4-dimethylfluoranthene, m. p. 113—115°, which had formerly been obtained by the same reaction from 2:2:4-trimethyl-1:2-dihydrofluoranthene (Forrest and Tucker, *loc. cit.*). 2:4-Dimethylfluoranthene was reduced with hydrogen and palladium-charcoal to 2:4-dimethyl-1:2:3:4-tetrahydrofluoranthene, m. p. 115—117°, and a 2:4-dimethyl-2:3(?1:2 or 3:4)-dihydrofluoranthene, m. p. 84—86°.



Catalytic hydrogenation of (IV) (with absorption of one mole of hydrogen) yielded 2:4:4-trimethyl-1:2:3:4-tetrahydrofluoranthene (IIB), m. p. 85—87°. This compound was different from (IIA), m. p. 101—103°, and was presumably its stereoisomeride.

When (IV) was oxidised with potassium permanganate in acetone solution at room temperature, it gave 2:3(?1:2)-dihydroxy-2:4:4-trimethyl-1:2:3:4-tetrahydrofluoranthene (VI), which was reduced with cold hydriodic acid in glacial acetic acid to (IIA).

Reduction of (IV) with a hot solution of hydriodic acid in glacial acetic acid gave a hydrocarbon, m. p. 102—104°; the m. p. of a mixture with (IIA), m. p. 101—103°, was

depressed. Thus, since the only other possible stereoisomer of (IIA), *viz.*, (IIB), has m. p. 85—87°, the compound, m. p. 102—104°, cannot be a 2 : 4 : 4-trimethyl-1 : 2 : 3 : 4-tetrahydrofluoranthene. Finally, since on dehydrogenation it yielded 2 : 3 : 4-trimethylfluoranthene it must be 2 : 3 : 4-trimethyl-1 : 2 : 3 : 4-tetrahydrofluoranthene (VIIA) (see Forrest and Tucker, Part IV, *loc. cit.*). Surprisingly, hydrogenation of 2 : 3 : 4-trimethylfluoranthene gave (VIIB), m. p. 107—109°, instead of (VIIA), m. p. 102—104°. It is noteworthy that whereas, as shown above, (IV) by the action of hot hydriodic acid solution gives, by migration of a methyl group, (VIIA), yet the corresponding 2 : 2 : 4-trimethyl-1 : 2-dihydrofluoranthene gives, without methyl-group migration, the normal hydrogenation product 2 : 2 : 4-trimethyl-1 : 2 : 3 : 4-tetrahydrofluoranthene (France, Tucker, and Forrest, *loc. cit.*). Migration of methyl can, however, be brought about by heating the above 2 : 2 : 4-trimethyl compound with zinc chloride or with phosphoric oxide (*loc. cit.*) to give (III).

The existence of the two pairs of isomers (IIA and IIB, m. p.s 101—103° and 85—87°, respectively; and VIIA and VIIB, m. p.s 102—104° and 107—109°, respectively) can be explained by geometrical isomerism.

(VIIB), obtained by catalytic hydrogenation of (III), presumably has all added hydrogen atoms on the same side of the ring.

A strong blue or blue-green fluorescence is exhibited by (III), (IV), (IIA), and by 2 : 4-dimethylfluoranthene when exposed to ultraviolet light. It is interesting that whilst (IIA) fluoresces strongly, its isomeride (IIB) shows no colour in ultraviolet light.

#### EXPERIMENTAL.

*Oxidation of 4-Fluorenylidene-2-methylpent-2-ene* (I).—(I) (0.5 g.), sodium dichromate (2.6 g.) and glacial acetic acid (20 ml.) were boiled together (1.5 hours); more dichromate (2.0 g.) was added, and boiling continued (1.5 hours). Fluorenone (0.26 g.; yield, 70%) was isolated. The *picrate* of (I) crystallised from ethanol as orange-red needles, m. p. 106—107° (Found: C, 63.3; H, 4.5.  $C_{19}H_{18}, C_6H_3O_7N_3$  requires C, 63.2; H, 4.4%).

4-(9-Fluorenyl)-2-methylpentane (V).—(1) (2.5 g.) was hydrogenated by means of palladium-charcoal (Cheronis and Levin, *J. Chem. Educ.*, 1944, **21**, 603) in ethanol. When absorption was complete (2 mols. of hydrogen) the filtered, evaporated solution gave from methanol needles of (V), m. p. 51—55° (1.9 g.; 76%) (Found: C, 91.1; H, 8.9. Calc. for  $C_{19}H_{22}$ : C, 91.2; H, 8.8%). By oxidation, as above, (V) gave fluorenone (0.1 g.; yield, 57%).

*Action of Hydriodic Acid on* (I).—Repetition of the work described by Maitland and Tucker (Part I, *loc. cit.*) gave 4-(9-fluorenyl)-2-methylpentane (V), m. p. 51—55° (0.2 g.; 13%), and 2 : 3 : 4-trimethylfluoranthene (III), m. p. 133° (0.19 g.; 14%), identified by mixed m. p. determination. When hydriodic acid (*d* 1.50) was used, a small quantity of white plates, m. p. 103—104°, of 2 : 4 : 4-trimethyl-1 : 2 : 3 : 4-tetrahydrofluoranthene (IIA) was obtained on one occasion only (Found: C, 91.9; H, 8.0.  $C_{19}H_{20}$  requires C, 91.9; H, 8.1%).

2 : 4 : 4-Trimethyl-1 : 4(? 3 : 4)-dihydrofluoranthene (IV).—A solution of (I) (1.0 g.) in glacial acetic acid (15 ml.) was saturated with hydrogen bromide. The precipitated white solid was filtered off, washed with glacial acetic acid, and dissolved in dry benzene (10 ml.), and the solution cooled. Stannic chloride (4 ml.) in dry benzene (10 ml.) was then added rapidly. After standing (20 minutes) in ice-water the mixture was hydrolysed with concentrated hydrochloric acid in presence of a little ether. The organic layer was separated, washed successively with dilute hydrochloric acid, water, dilute sodium hydroxide, and water, and dried ( $Na_2SO_4$ ) and evaporated to give 2 : 4 : 4-trimethyl-1 : 4(? 3 : 4)-dihydrofluoranthene (IV) which crystallised from ethanol in colourless plates, m. p. 106—107° (0.8 g.; 80%) (Found: C, 92.7; H, 7.2.  $C_{19}H_{18}$  requires C, 92.7; H, 7.3%). Oxidation of (IV), as above, but for 20 hours, gave fluorenone-1-carboxylic acid, m. p. 189—192°. Heating (IV) with selenium at 300° for 5 hours gave, from ethanol, 2 : 4-dimethylfluoranthene, m. p. 113—115°, which gave the *s*-trinitrobenzene complex, m. p. 223°.

*Catalytic Hydrogenation of 2 : 4-Dimethylfluoranthene*.—2 : 4-Dimethylfluoranthene was hydrogenated by means of twice its weight of 5% palladium-charcoal (Cheronis and Levin, *loc. cit.*) in ethanol. Absorption ceased after 4 hours when an amount of hydrogen approximately equivalent to that required for hydrogenation of one double bond had been absorbed. The filtered, evaporated ethanolic solution deposited prisms which crystallised from methanol as nacreous leaflets of 2 : 4-dimethyl-1 : 2 : 3 : 4-tetrahydrofluoranthene, m. p. 115—117° (Found: C, 92.3; H, 7.5.  $C_{18}H_{18}$  requires C, 92.3; H, 7.7%). Concentration of the alcoholic filtrate gave a very small amount of yellow plates which crystallised from methanol as pale green prisms of 2 : 4-dimethyl-1 : 2(? 1 : 4, 3 : 4)-dihydrofluoranthene, m. p. 84—86° (softening at 78°) (Found: C, 92.9; H, 6.8.  $C_{18}H_{18}$  requires C, 93.1; H, 6.9%).

*Reactions of* (IV).—(i) (IV) (0.246 g.) was hydrogenated (palladium-charcoal-ethanol) and gave, from ethanol, white needles of 2 : 4 : 4-trimethyl-1 : 2 : 3 : 4-tetrahydrofluoranthene (IIB), m. p. 85—87° (0.230 g., 93%) (Found: C, 91.5; H, 7.7.  $C_{19}H_{20}$  requires C, 91.9; H, 8.1%).

(ii) (a). (IV) (0.5 g.) was dissolved in acetone (10 ml.), potassium permanganate (0.5 g.) added in portions with frequent shaking, and the mixture left overnight, filtered, and evaporated. The residue crystallised from glacial acetic acid in white needles of 2 : 3(? 1 : 2)-dihydroxy-2 : 4 : 4-trimethyl-1 : 2 : 3 : 4-tetrahydrofluoranthene (VI), m. p. 189—193° (0.2 g., 35%) (Found: C, 81.3; H, 6.9.  $C_{18}H_{20}O_2$  requires C, 81.4; H, 7.1%).

(ii) (b). (VI) (0.2 g.), dissolved in glacial acetic acid (15 ml.), was treated with hydriodic acid (*d* 1.70, 7 ml.), and the mixture kept for 24 hours. The solid which separated was crystallised from ethanol,

giving white needles, m. p. 103—104°, of 2 : 4 : 4-trimethyl-1 : 2 : 3 : 4-tetrahydrofluoranthene (IIA). The m. p. of a mixture with the product of reaction of hot hydriodic acid on (I) (p. 634) was undepressed.

(iii) (a). (IV) (0.5 g.), glacial acetic acid (15 ml.), and hydriodic acid (*d* 1.70, 4 ml.) were heated under reflux (5 hours). The reaction mixture was poured into sodium hydrogen sulphite solution, and the oil which separated was extracted with carbon tetrachloride. After evaporation, the residue crystallised from ethanol in white needles, m. p. 102—104°, of 2 : 3 : 4-trimethyl-1 : 2 : 3 : 4-tetrahydrofluoranthene (VIIA) (Found : C, 91.8; H, 8.0.  $C_{19}H_{20}$  requires C, 91.9; H, 8.1%).

(iii) (b). (VIIA) was heated with selenium (300°, 5 hours). After extraction with ether, crystallisation from ethanol gave 2 : 3 : 4-trimethylfluoranthene (III), identified by preparation of the *s*-trinitrobenzene derivative, m. p. 228—230°.

(iii) (c). Attempts to hydrogenate (III) by means of Adams's catalyst in acetic acid showed that hydrogen was absorbed, but no product could be isolated. Microhydrogenation using palladium-black in glacial acetic acid indicated the presence of 2.07 double bonds. Hydrogenation using the Cheronis-Levin catalyst gave excellent results : 2 : 3 : 4-trimethylfluoranthene (0.122 g.) and catalyst (2 g.), in ethanol (20 ml.) which had been distilled from Raney nickel catalyst, gave practically theoretical absorption of hydrogen in 80 minutes. The solution was filtered, the palladium-charcoal *thoroughly* extracted with boiling ethanol and then with boiling ether, and the filtrates evaporated to dryness. Crystallisation of the residue first from glacial acetic acid and then from methanol gave hair-fine needles, m. p. 107—109°, of 2 : 3 : 4-trimethyl-1 : 2 : 3 : 4-tetrahydrofluoranthene (VIIb) (0.09 g., 72%) (Found : C, 91.8; H, 8.1.  $C_{19}H_{20}$  requires C, 91.9; H, 8.1%). Heated in benzene solution with 2 : 4 : 7-trinitrofluorenone, this gave an *addition product*, crystallising from benzene in dark scarlet prisms, m. p. 190—192°, decomposing at 200° (Found : C, 68.3; H, 4.3; N, 7.6.  $C_{19}H_{20}, C_{13}H_5O_7, N_3$  requires C, 68.2; H, 4.4; N, 7.5%).

*Synthesis of 2 : 3 : 4-Trimethylfluoranthene (III) from 1 : 2 : 3-Trimethylnaphthalene.*—1-Iodo-2 : 3 : 4-trimethylnaphthalene. 1 : 2 : 3-Trimethylnaphthalene (10.0 g.), prepared from 2 : 3-dimethylnaphthalene (Hewett, *J.*, 1940, 293), was dissolved in glacial acetic acid (15 ml.), and potassium iodide (6.6 g.) added, followed by potassium iodate (9.6 g.). The mixture was refluxed till it acquired a pale straw-coloured tint (~6 hours). The solution was decanted from unchanged potassium iodate, shaken with sodium hydrogen sulphite solution, and extracted with carbon tetrachloride. Evaporation gave a dark oil which crystallised from methanol (charcoal) in white needles, turning brown in air, of 1-iodo-2 : 3 : 4-trimethylnaphthalene, m. p. 110—112° (Found : C, 52.7; H, 4.3; I, 42.9.  $C_{13}H_{13}I$  requires C, 52.7; H, 4.4; I, 42.9%).

1-(2'-Nitrophenyl)-2 : 3 : 4-trimethylnaphthalene. 1-Iodo-2 : 3 : 4-trimethylnaphthalene (2.09 g.) and *o*-bromonitrobenzene (1.40 g.) were heated together at 200—215°. Copper-bronze (2.0 g.) was added at intervals, and heating continued with occasional shaking for 3 hours. The mixture was finally heated to 250° for 5 minutes, and the residue extracted with dry ether. Crystallisation of the oil obtained gave pale straw-coloured needles, m. p. 126—127°, which contained halogen but no nitrogen (Found : C, 62.3; H, 5.1%)—the nature of this compound has not been investigated—and a sticky oil which after vacuum sublimation crystallised from ethanol in yellow diamond-shaped plates, m. p. 111—114°, of 1-(2'-nitrophenyl)-2 : 3 : 4-trimethylnaphthalene (10 g., 51%) (Found : C, 78.2; H, 5.9; N, 4.9.  $C_{19}H_{17}O_2N$  requires C, 78.3; H, 5.8; N, 4.8%).

1-(2'-Aminophenyl)-2 : 3 : 4-trimethylnaphthalene. 1-(2'-Nitrophenyl)-2 : 3 : 4-trimethylnaphthalene (0.7 g.) was hydrogenated with hydrogen in the presence of Raney nickel catalyst in ethanol containing a little sodium hydroxide. When theoretical absorption had occurred, the ethanol was removed, the remaining oil extracted with dilute hydrochloric acid, the acid layer basified with sodium hydroxide, and the oil which separated extracted with carbon tetrachloride. On removal of the solvent an oil which resisted crystallisation was obtained (0.5 g., 63%).

2 : 3 : 4-Trimethylfluoranthene (III). 1-(2'-Aminophenyl)-2 : 3 : 4-trimethylnaphthalene (0.5 g.) was diazotised in dilute sulphuric acid. Excess of nitrite was destroyed by addition of a small quantity of urea, the yellow solution filtered, warmed ( $\frac{1}{2}$  hour) with copper bronze (1 g.), filtered, and the copper extracted several times with boiling ethanol. The blue fluorescent solution obtained was concentrated : 2 : 3 : 4-trimethylfluoranthene, m. p. 133°, slowly separated. A *complex* formed with 2 : 4 : 7-trinitrofluorenone, crystallised from benzene in bright scarlet needles, m. p. 208—210° (Found : C, 68.7; H, 3.9; N, 7.5.  $C_{19}H_{16}, C_{13}H_5O_7, N_3$  requires C, 68.7; H, 3.8; N, 7.5%).

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