

Reactions of 4-Fluoren-9-ylidene-2-methylpent-2-ene and 2-Fluoren-9-yl-2-methylpentan-4-one

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The photochromic title hydrocarbon undergoes a photochemical 1,5-H shift to 4-fluoren-9-yl-2-methylpenta-1,3-diene and photocyclisation to red 3,3a-dihydro-1,3,3-trimethylfluoranthene; the latter undergoes a thermal 1,9-H shift in toluene and a photochemical 1,7-H shift in ethanol. The title ketone (17) cyclises in the presence of hydrogen bromide in acetic acid to yield 1,10b-dihydro-1,1,3-trimethylfluoranthene which, on catalytic hydrogenation, yields the same tetrahydrofluoranthene derivative as is obtained when 2-fluoren-9-yl-2-methylpentan-4-ol (20) is cyclised with sulphuric acid. On treatment with PCl_5 , the ketone (17) yields 4-chloro-2-fluoren-9-yl-2-methylpent-4-ene, which reacts with sodium in xylene to give *trans*-2-fluoren-9-yl-2-methylpent-3-ene, obtained also when the alcohol (20) is heated at 180 °C with KHSO_4 .

In 1929, Maitland and Tucker¹ obtained a small quantity of a colourless photochromic hydrocarbon, m.p. 80–82 °C, from the reaction of fluorenylmagnesium bromide with 2-hydroxy-2-methylpentan-4-one. Twenty years later, Tucker and Whalley² prepared this hydrocarbon by vacuum distillation of the product from the reaction, of fluorenylmagnesium bromide with 2-methylpent-2-en-4-one (1), and reported that the colourless crystals turned pink in sunlight and that the colour faded in the dark at ambient temperatures. The authors suggested that the photochromic hydrocarbon was 4-fluoren-9-ylidene-2-methylpent-2-ene (4) but offered no explanation for the photochromic properties. They reported³ that the hydrocarbon (4) gave 4-fluoren-9-yl-2-methylpentane (6), 1,2,3-trimethylfluoranthene (12), and a hydrocarbon A, $\text{C}_{19}\text{H}_{20}$, m.p. 103–104 °C, when boiled with hydroiodic acid in acetic acid; it also reacted with hydrogen bromide in acetic acid to give a bromo compound B, which, on treatment with tin(IV) chloride in benzene, gave hydrocarbon C, $\text{C}_{19}\text{H}_{18}$, m.p. 106–107 °C. The latter, on catalytic hydrogenation in the presence of palladium on charcoal, gave a hydrocarbon D, $\text{C}_{19}\text{H}_{20}$, m.p. 85–87 °C. The structures of compounds A–D were not established.

The observation^{1,2} that the hydrocarbon (4) became coloured in sunlight indicates a high quantum yield for colouring with u.v. light compared to the quantum yield for bleaching of the coloured form by white light. These properties, its thermal stability, and the fast thermal fade of its coloured form at ambient temperatures are characteristics required for a plastic sunglass application. The preparation, reactions, and photochromic properties of the hydrocarbon (4) have been reinvestigated and the structure and stereochemistry of products elucidated. Because of irreversible side reactions, the photochromic hydrocarbon (4) does not appear to be of commercial interest.

Fluorenylmagnesium bromide undergoes 1,2-addition to 2-methylpent-2-en-4-one (1) to give, after treatment with ice-cold aqueous ammonium chloride, 2-fluoren-9-yl-4-methylpenta-1,3-diene (3), presumably *via* dehydration of the alcohol (2). 1-Fluoren-9-yl-1-phenylethanol (14) undergoes a similar acid-catalysed dehydration to yield quantitatively 1-fluoren-9-yl-1-phenylethene (15).⁴ The hydrocarbon (3) isomerises to hydrocarbon (4) on boiling with (a) iodine in xylene, (b) a catalytic amount of toluene-*p*-sulphonic acid in benzene or (c) potassium hydroxide in ethanol. The hydrocarbon (4), in turn,

undergoes an acid-catalysed cyclisation to yield quantitatively, 2,3-dihydro-1,3,3-trimethylfluoranthene (2,3-DHF) (9) but shows no rearrangement when heated with iodine in xylene or with ethanolic potassium hydroxide.

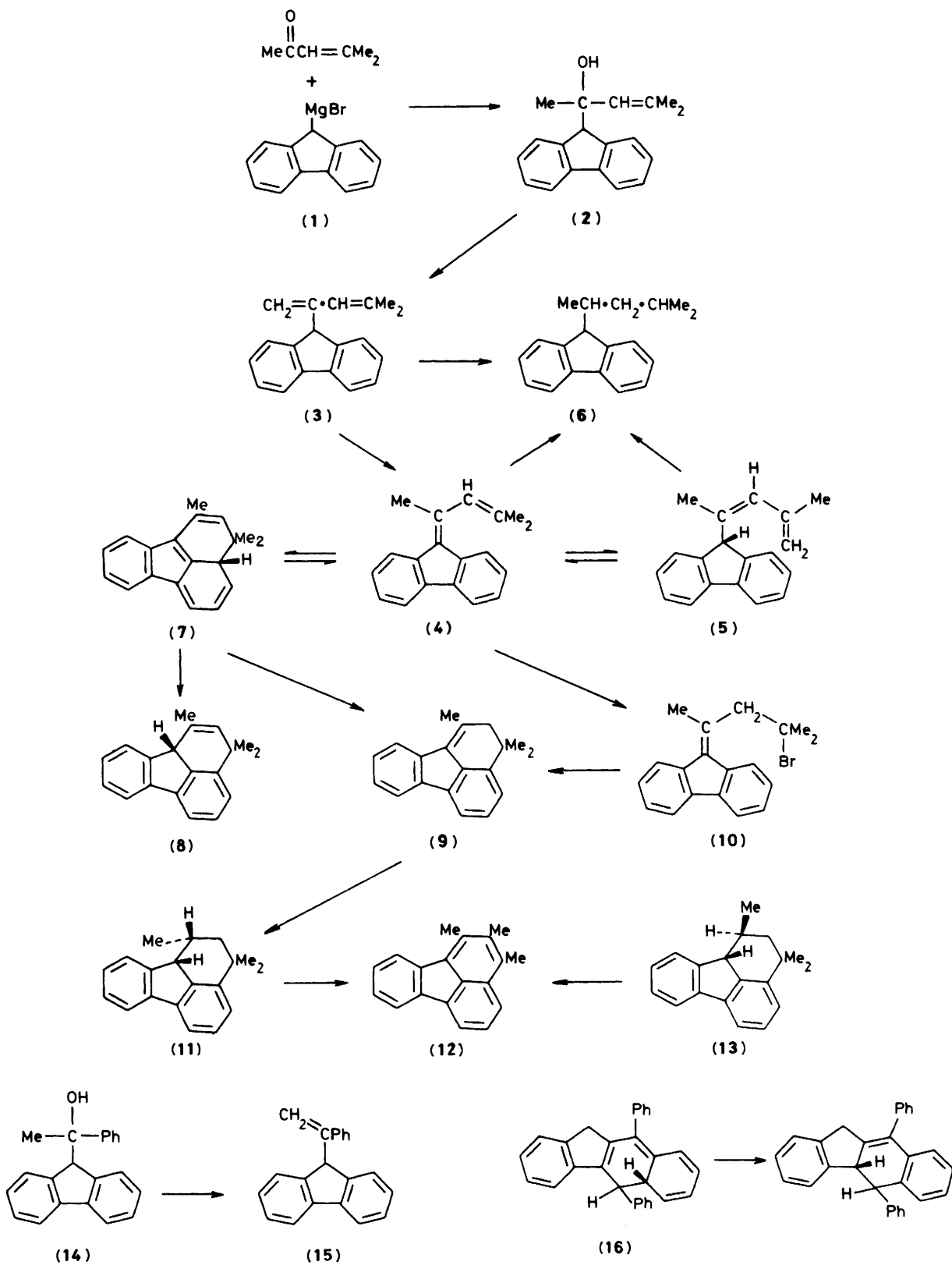
The hydrocarbon (4) is thermally stable up to 300 °C but, on irradiation at 254 or 366 nm, either in the crystalline state or in an appropriate organic solvent, shows a reversible colourless to red colour change.

On prolonged irradiation of the hydrocarbon (4) in toluene, the red colour disappeared and two photoproducts were obtained in approximately equal amounts. One was 2,3-DHF (9), believed to be formed by photocyclisation of the hydrocarbon (4) to the red 3,3a-dihydro-1,3,3-trimethylfluoranthene (3,3a-DHF), (7), followed by a thermal suprafacial 1,9-H shift. This shift is slower than for comparable systems [e.g. for the 10,10a-dihydrobenzofluorene derivative (16)⁵], presumably because the five-membered ring of the fluoranthene (7) causes distortion of the ring system over which the hydrogen shift must occur.

The second component is 4-fluoren-9-yl-2-methylpenta-1,3-diene (5) from its n.m.r. spectrum and because it gave 4-fluoren-9-yl-2-methylpentane (6) on catalytic hydrogenation [identified by comparison of its n.m.r. spectrum with an authentic sample prepared by catalytic hydrogenation of the hydrocarbon (3) or (4)], and because it isomerised to the hydrocarbon (4) when boiled with ethanolic potassium hydroxide.

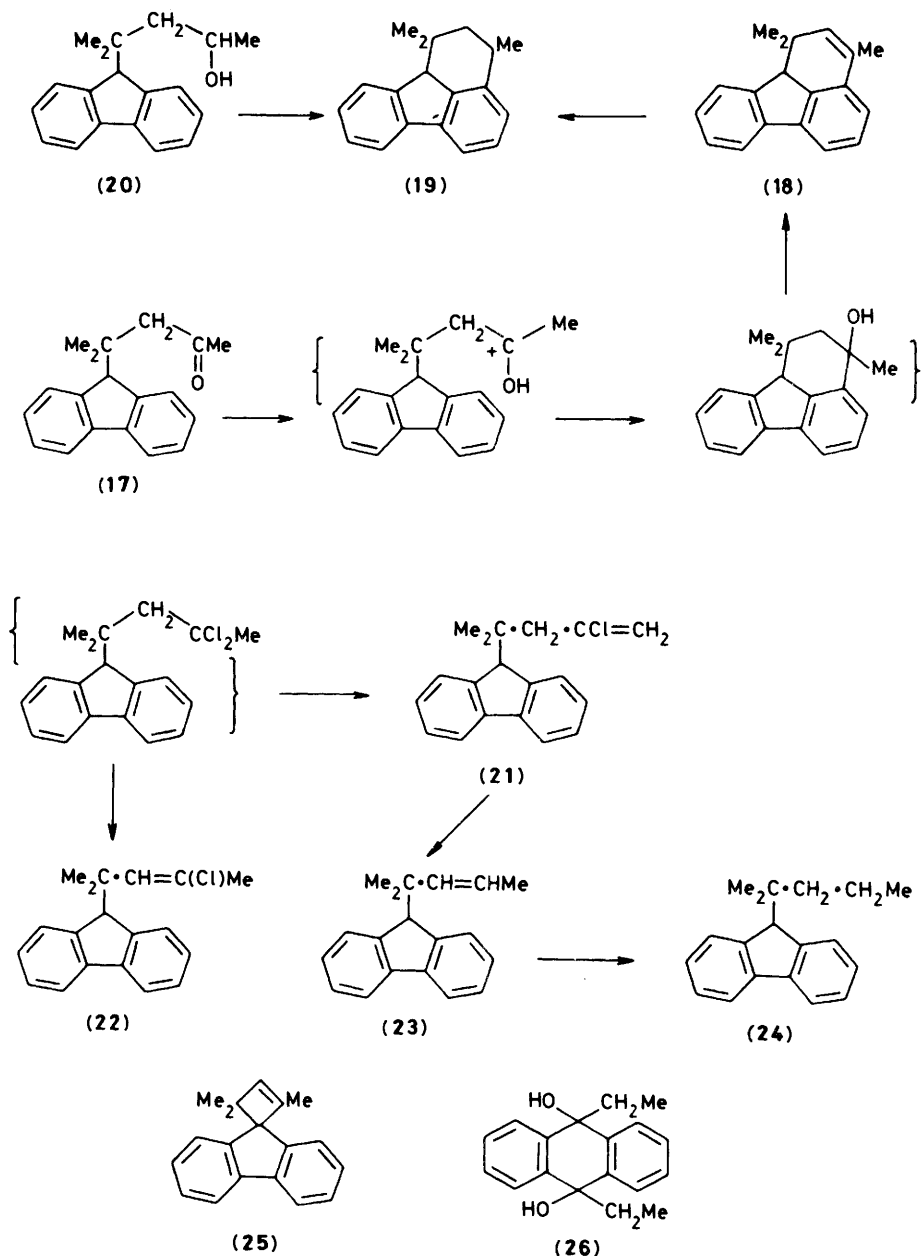
While thermal suprafacial 1,5- and 1,9-H shifts are well-documented, photochemical (presumably antarafacial) 1,5- and 1,9-H shifts are less common.⁶ We suggest that the photorearrangement of the hydrocarbon (4) into the hydrocarbon (5) is such a reaction. Molecular models show that the hydrocarbon (4) can adopt readily the helical conformation required for the antarafacial hydrogen shift. Irradiation of the hydrocarbon (4) in toluene containing 1% benzophenone as sensitizer, in hexane, or in hexane containing 1% naphthalene as quencher, showed no significant change in photoproduct distribution. On irradiation at 366 nm, the hydrocarbon (4) in ethanol, photocyclises and undergoes a 1,7-H shift to give, 3,10b-dihydrotrimethylfluoranthene (8) the structure of which was assigned from its n.m.r. spectrum. Tucker and Whalley³ suggested that hydrocarbon C might have this structure. Following their paper,³ the hydrocarbon (4) was treated with hydrogen bromide in acetic acid to yield the bromo compound B, which proved to be 2-bromo-4-fluoren-9-ylidene-2-methylpentane (10). On treatment with tin(IV) chloride in benzene, it gave the 2,3-dihydrofluoranthene derivative (9), which had been obtained by acid-catalysed rearrangement and photorearrange-

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ment of the hydrocarbon (4). It follows that hydrocarbon (9) is compound C. Catalytic hydrogenation of compound (9) gave *cis*-1,2,3,10b-tetrahydro-1,3,3-trimethylfluorene (11) (compound D).³ The hydrocarbon A,³ from reduction of hydrocarbon (4) with hydroiodic acid, is presumably its *trans* isomer (13).

Between 1929 and 1949^{1,3} Tucker and co-workers published a series of six papers on 'the condensation of fluorene with acetone'. In part II,⁷ they established that fluorene reacted with acetone in the presence of ethanolic potassium hydroxide to yield 2-fluorene-9-yl-2-methylpentan-4-one (17). It was assumed that acetone underwent self-condensation to give 2-methylpent-



2-en-4-one (1) to which 1,4-addition of fluorene occurred under basic conditions.

Parts III⁸ and IV⁹ were concerned mainly with the preparation of fluoranthene derivatives from the ketone (17). These reactions have been reinvestigated and the structures and stereochemistry of products assigned, confirmed, or corrected using ¹H n.m.r. spectroscopy.

It was reported⁸ that when the ketone (17) was treated with hydrogen bromide in acetic acid, 1,10b-dihydro-1,1,3-trimethylfluoranthene (1,10b-DHF) (18) was obtained which, on catalytic hydrogenation, gave a tetrahydro-1,1,3-trimethylfluoranthene (19), obtained also by (a) boiling ketone (17) with hydroiodic acid, (b) reducing ketone (17) to the corresponding alcohol (20) and cyclising the latter with concentrated sulphuric acid, and (c) converting the ketone (17) into a chloro derivative E by reaction with phosphorus pentachloride and boiling compound E with hydroiodic acid. Further, it was reported that compound E reacted with sodium in xylene to yield a

hydrocarbon F, m.p. 92–94 °C which was tentatively assigned structure (25).

Part IV⁹ recorded that when 1,10b-DHF (18) was heated with anhydrous zinc chloride, 1,2,3-trimethylfluoranthene (12) and the tetrahydrofluoranthene derivative (19) was formed. We found that n.m.r. studies could not be used to establish the stereochemistry of (19) but could be used to show that the same geometrical isomer was obtained in all the reactions indicated.

Fluoranthene derivatives (19), (18), and (11) all show exceptionally high field signals (δ 0.30, 0.42, 0.45 respectively) as a result of the quasi-axial 1-methyl groups being heavily shielded by the aromatic system; 9,10-diethylanthracene-9,10-diol (26) shows a high field methyl signal at δ 0.20 for the same reason.¹⁰

The chloro-compound E was synthesised by reaction of the ketone (17) with phosphorus pentachloride.⁸ Its n.m.r. spectrum established conclusively that it was (21) containing a small quantity of (22). When boiled with finely divided sodium in

xylene, compound (21) was converted into a *cis* and *trans* mixture of 2-fluoren-9-yl-2-methylpent-3-enes (23). On attempted catalytic hydrogenation in ethyl acetate using 5% palladium on charcoal, only *cis-trans* isomerisation took place. *trans*-Isomer (23), m.p. 94–95 °C, is hydrocarbon F, which can be obtained by dehydration of the alcohol (20) by heating the latter at 180 °C with KHSO₄. 2-Fluoren-9-yl-2-methylpentane (24) was obtained when the catalytic hydrogenation of the isomers (23) was carried out in acetic acid.

Experimental

U.v. spectra were measured in hexane on a Unicam SP 1700 spectrometer; n.m.r. spectra were obtained with a Perkin-Elmer R32 (90 MHz) spectrometer (tetramethylsilane as internal standard). Photoreactions were carried out by irradiation (366 nm) using a 250-W mercury discharge lamp (type ME/D, Thorn Lighting) with a filter (type OX1 chance Pilkington) focussed on the reaction cuvette. Petroleum refers to the fraction b.p. 60–80 °C. Reagents and solvents were purified before use and extracts were dried over anhydrous MgSO₄ and filtered.

4-Fluoren-9-ylidene-2-methylpent-2-ene (4).—Ethylmagnesium bromide [from ethyl bromide (68.3 g) and magnesium (15 g) in ether (150 cm³)] was added to fluorene (41.5 g) in xylene (130 cm³). Ether was distilled off and 2-methylpent-2-en-4-one (1) (24.5 g) was added to the resulting fluorenylmagnesium bromide in xylene. The reaction mixture was heated (2.5 h) at 125 °C, cooled, and poured onto ice and aqueous ammonium chloride. The organic layer was separated, dried, and solvent removed, leaving an orange oil (40 g), which contained mainly 2-fluoren-9-yl-4-methylpenta-1,3-diene (3), δ 1.15 (3 H, d, *J* 2 Hz, 4-Me, shielded by fluorene ring), 1.92 (3 H, s, 4-Me), 4.36 (1 H, s, 9'-H), * 4.89 and 5.00 (2 H, s, 1-Hs), 6.20 (1 H, br, 3-H), and 7.75–6.90 (m, ArH). Double resonance at δ 6.20 caused the doublet at 1.15 to collapse to a singlet. The diene (3) (5 g) was boiled (1 h) with ethanolic potassium hydroxide (80 cm³), cooled, and acidified. Ethanol was removed and the residue dissolved in ether and dried. Removal of ether left an oil which gave 4-fluoren-9-ylidene-2-methylpent-2-ene (4) (1.8 g), colourless needles from methanol, m.p. 82–83 °C (lit.,¹ 81–82 °C), δ 1.66 (3 H, s, Me shielded by fluorene ring), 1.97 (3 H, s, Me), 2.53 (3 H, s, Me), 6.31 (1 H, s, =CH), and 7.95–7.15 (8 H, m, ArH); λ_{\max} . 234, 251, 260, and 319 nm (log ϵ 4.65, 4.42, 4.44, and 4.20).

2,3-Dihydro-1,3,3-trimethylfluoranthene (2,3-DHF) (9).—Compound (3) or (4) was boiled (2 h) in benzene containing a few crystals of toluene-*p*-sulphonic acid. The solution was washed with water, dried, reduced in volume, and chromatographed on basic alumina with petroleum as eluant. In both cases, the only product isolated was 2,3-DHF (9), colourless crystals from ethanol, m.p. 106–107 °C (lit.,³ 106–107 °C), δ 1.34 (6 H, s, 3-Me), 2.36 (3 H, s, 1-Me), 2.60 (2 H, s, CH₂), and 7.95–7.15 (7 H, m, ArH).

Photoreactions.—The hydrocarbon (4) (60 mg) in toluene or hexane (2 cm³) in a cuvette (10-mm path length) was irradiated (366 nm) with stirring until the solution became colourless. Solvent was removed and the residue dissolved in CDCl₃. The 1,3-diene (5) showed absorptions at δ 1.11 (3 H, d, *J* 1.5 Hz, 4-Me), 2.06 (3 H, br s, 2-Me), 5.38 (1 H, s, 9'-H), 5.07 and 5.18 (2 H, 2 \times s, 1-H), and 6.12 (1 H, br s, 3-H) in its n.m.r. spectrum. Double resonance irradiation at δ 6.12 caused the doublet at

1.11 to collapse to a singlet and at 5.07 or 5.18 caused the broad absorption at 2.06 to sharpen or *vice versa*.

Irradiation of the hydrocarbon (4) (60 mg) in ethanol (2 cm³) gave a third product, believed to be 3,10b-DHF (8); δ 1.39 and 1.47 (6 H, 2 \times s, 3-Me's), 2.17 (3 H, d, *J* 2 Hz, 1-Me), 4.40 (1 H, s, 10b-H), and 5.60 (1 H, broad peak of unresolved quartet, 2-H).

Hydrogen bromide gas was passed into the diene (4) (1 g) in acetic acid (15 cm³). A solid separated, which was filtered off and recrystallised from petroleum, giving colourless crystals of 2-bromo-4-fluoren-9-ylidene-2-methylpentane (10) (0.8 g), m.p. 121–122 °C, δ 1.98 (6 H, s, gem Me's), 2.69 (3 H, s, Me), 3.71 (2 H, s, CH₂), and 8.15–7.25 (8 H, m, ArH). The bromo compound (10) in benzene (5 cm³) was stirred with stannic chloride (2 g) in benzene (5 cm³) for 0.5 h. The reaction mixture was treated with hydrochloric acid and the organic layer washed with water, dried, and the solvent removed. The residue crystallised from ethanol, giving 2,3-DHF (9), m.p. 106–107 °C.

Hydrogenation of 2,3-DHF (9) (50 mg) in acetic acid (15 cm³) using a PtO₂ catalyst (10 mg) gave *cis*-1,2,3,10b-tetrahydro-1,3,3-trimethylfluoranthene (11), m.p. 85–87 °C, colourless crystals from ethanol (lit.,³ 85–87 °C), δ 0.45 (3 H, d, *J* 7 Hz, 1-Me), 1.35 and 1.45 (6 H, 2 \times s, 3-Me's), 1.79 (1 H, q, *J*_{gem} 14 Hz, *J*_{vic} 6 Hz, CH₂), 2.27 (1 H, q, *J*_{gem} 14 Hz, *J*_{vic} 4 Hz, CH₂), 3.0 (1 H, m, 1-H), 3.93 (1 H, d, *J* 6 Hz, 10b-H), and 7.95–7.15 (7 H, m, ArH). Catalytic hydrogenation of the hydrocarbons (3) or (4) gave 4-fluoren-9-yl-2-methylpentane (6),³ δ 0.62 (3 H, d, *J* 7 Hz, 5-Me), 0.92 (6 H, d, *J* 6 Hz, gem-Me's), 1.29 (2 H, m, CH₂), 2.50 (1 H, m, 4-H), 3.30 (1 H, m, 2-H), 3.98 (1 H, d, *J* 3 Hz, 9'-H), and 7.7–7.1 (8 H, m, ArH).

2-Fluoren-9-yl-2-methylpentan-4-one (17).—Finely powdered potassium hydroxide (100 g) was added to fluorene (20 g) in warm acetone (120 cm³) in a large beaker. The mixture turned deep blue and a vigorous exothermic reaction took place. Water (120 cm³) was added and the mixture carefully acidified with 50% sulphuric acid and extracted with ether. The ether layer was washed with water, dried, solvent removed, and the residue crystallised from ethanol, giving ketone (17), colourless needles (18.6 g), m.p. 77–78 °C (lit.,⁷ 77–78 °C), δ 1.12 (6 H, s, 2 Me's), 2.12 (3 H, s, MeCO), 2.41 (2 H, s, CH₂), 4.25 (1 H, s, 9'-H), and 7.85–7.10 (8 H, m, ArH).

1,10b-Dihydro-1,1,3-trimethylfluoranthene (18).—Hydrogen bromide was passed into the ketone (17) (2 g) in acetic acid (20 cm³). After 3 h, solvent was removed and the residue recrystallised from methanol, giving 1,10b-DHF (18) (0.43 g), m.p. 78–79 °C (lit.,⁸ 77–79 °C), δ 0.42 (3 H, s, 1_{ax}-Me), 1.63 (3 H, s, 1_{eq}-Me), 2.13 (3 H, d, *J* 2 Hz, 3-Me), 3.80 (1 H, s, 10b-H), 5.60 (1 H, q, *J* 2 Hz, 2-H), and 7.85–7.10 (8 H, m, ArH).

1,2,3,10b-Tetrahydro-1,1,3-trimethylfluoranthene (19).—1,10b-DHF (0.13 g) was hydrogenated in acetic acid using 5% palladium on charcoal (40 mg) as catalyst. The product (19) crystallised from methanol as colourless needles, m.p. 104–105 °C (lit.,⁸ 103–104 °C), δ 0.30 (3 H, s, 1_{ax}-Me), 1.35 (3 H, d, *J* 7 Hz, 3-Me), 1.52 (3 H, s, 1-Me), 1.80 (1 H, d, *J*_{gem} 14 Hz, 2-H), 2.18 (1 H, q, *J*_{gem} 14 Hz, *J*_{vic} 7 Hz, 2-H), 3.15 (1 H, quint, *J*_{vic} 7 Hz, 3-H), 3.52 (1 H, s, 10b-H), and 7.90–7.10 (7 H, m, ArH).

2-Fluoren-9-yl-2-methylpentan-4-ol (20).—The ketone (17) (3 g) in ether (25 cm³) was added with stirring to LiAlH₄ (0.4 g) in ether (25 cm³). Work-up gave the alcohol (20), colourless plates (1.84 g) from petroleum, m.p. 86 °C (lit.,⁸³ 83–85 °C), δ 1.07 and 1.17 (2 \times 3 H, 2 \times s, gem-Me's), 1.17 (3 H, d, *J* 6 Hz, 5-Me), 1.30 (1 H, s, OH), 1.45 (2 H, m, 3-H_s), 4.00 (1 H, s, 9'-H), 4.10 (m, 4-H), and 7.85–7.20 (8 H, m, ArH).

Treatment of the alcohol (20) (0.5 g) in acetic acid (3 cm³) with a 1:1 mixture of concentrated sulphuric acid and acetic

* Throughout, the primed numbers refer to positions on the fluorene nucleus.

acid (3 cm³) gave the tetrahydrofluoranthene derivative (**19**), colourless needles (0.28 g) from methanol, m.p. 104–105 °C.

2-Chloro-4-fluoren-9-yl-4-methylpent-1-ene (21) and *Pent-2-ene (22)*. The ketone (**17**) (10 g) in chloroform (100 cm³) was boiled (1 h) with phosphorus pentachloride (40 g). The solution was decanted onto crushed ice and the organic layer separated and dried. Solvent was removed and the residue crystallised from ethanol giving colourless crystals of the chloropent-1-ene derivative (2.52 g) (**21**), m.p. 76–77 °C (lit.,⁶ 76–78 °C), δ 1.18 (6 H, s, 2 Me's), 2.29 (2 H, s, CH₂), 4.00 (1 H, s, 9'-H), 5.05 (1 H, s, =CH), 5.29 (1 H, s, =CH), and 7.85–7.20 (8 H, m, ArH). The n.m.r. spectrum of the crude product showed weak additional signals attributed to the chloropent-2-ene (**22**) which was not isolated; δ 1.09 (6, 2 Me's), 2.24 (d, *J* 1.5 Hz, =CMe), 4.67 (s, 9'-H), and 5.64 (q, 1.5 Hz, =CH).

cis- and trans-2-Fluoren-9-yl-2-methylpent-3-ene (23).—The chloropent-1-ene derivative (**21**) (2.37 g) was added to finely divided sodium (0.5 g) in xylene (5 cm³) and boiled (1 h). On cooling, a purple solid was deposited. The solution was decanted off and the purple solid treated first with a small quantity of ethanol and then with water, and finally extracted with ether. The ether layer was dried, filtered and combined with the xylene layer. Solvent was removed and the residue chromatographed on basic alumina using petroleum as eluant. The main band, on evaporation, left a solid which gave colourless crystals of a mixture of *cis-* and *trans*-pentene derivative (**23**), from which part of the n.m.r. spectrum of the *cis* isomer was assigned; δ 0.97 (6 H, s, 2 Me's), δ 2.15 (d, *J* 7 Hz, =CMe), 3.90 (1 H, s, 9'-H), and 6.05 (1 H, m, 3-H).

When the mixture was shaken with palladium on charcoal in ethyl acetate *cis-trans* isomerisation occurred to give the pure *trans*-alkene (**23**); this was also obtained by heating the alcohol (**20**) (1 g) with KHSO₄ (1 g) at 180 °C for 10 min; colourless

needles (0.22 g) from methanol, m.p. 94–95 °C (lit.,⁸ 92–94 °C), δ 0.89 (6 H, s, 2 Me's), 1.78 (3 H, d, *J* 6 Hz, =CMe), 3.82 (1 H, s, 9'-H), 5.33 (1 H, octet, *J* 6 Hz, *J* 16 Hz, 3-H), 5.83 (1 H, d, *J* 16 Hz, 4-H), and 7.85–7.10 (8 H, m, ArH).

2-Fluoren-9-yl-2-methylpentane (24).—Catalytic hydrogenation (Pd/C) of *cis-* and *trans*-pent-3-enes (**23**) in acetic acid gave the pentane (**24**) as colourless needles from methanol, m.p. 84 °C (lit.,⁸ 84–85 °C), δ 0.87 (6 H, s, 2 Me's), 9.90–1.60 (7 H, m), 3.92 (1 H, s, 9'-H), and 7.92–7.12 (8 H, m, ArH).

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