

## Friedel–Crafts Acetylation of 3-Methylfluoranthene

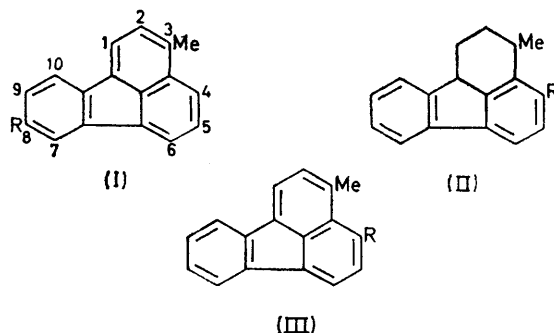
By Neil Campbell \* and N. H. Wilson, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

3-Methylfluoranthene reacts with acetyl chloride and aluminium chloride to yield 4-acetyl- (4%) and 8-acetyl-3-methylfluoranthene (92%), and possibly a third isomer. 2-Acetyl- and 10-acetyl-3-methylfluoranthene have been synthesised.

3-METHYLFLUORANTHENE (I; R = H) undergoes nitration at the 8- (55%), the 2- (20%), the 4- (20%), and probably the 10-position (5%).<sup>1</sup> To discover if this is the general pattern of electrophilic attack on the hydrocarbon we have investigated its reaction with acetyl chloride at  $-5^{\circ}$  in methylene chloride in the presence of aluminium chloride.<sup>2</sup> The crude product was shown by g.l.c. to contain mainly monoacetyl-3-methylfluoranthenes, 92% of which consisted of 8-acetyl-3-methylfluoranthene (I; R = Ac). The identification of this compound was confirmed by treatment with hydrazoic acid to give 8-acetamido-3-methylfluoranthene (I; R = NHAc), from which 8-amino-3-methylfluoranthene (I; R = NH<sub>2</sub>) was obtained. The amine was oxidised by peroxyacetic acid to 3-methyl-8-nitrofluoranthene (I; R = NO<sub>2</sub>), identical with a sample obtained previously.<sup>1</sup>

G.l.c. showed the presence in the crude acetylation

mixture of a second acetylmethylfluoranthene (4%) and a third product which may also be an acetyl-3-methylfluoranthene. T.l.c. and fluorescence studies



showed the former to be the 4-acetyl compound and proved that the unknown is certainly not 2- or 10-acetyl-3-methylfluoranthene.

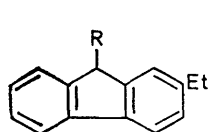
<sup>1</sup> H. F. Andrew, N. Campbell, and N. H. Wilson, *J.C.S. Perkin I*, 1972, 755.

<sup>2</sup> Cf. N. Campbell, W. K. Leadill, and J. F. K. Wilshire, *J. Chem. Soc.*, 1951, 1404.

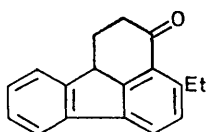
The substitution pattern of 3-substituted fluoranthenes is not as simple as was first thought,<sup>3</sup> but the tendency of 3-alkyl groups, like other *ortho,para*-directing groups, to direct further substitution into the 8-position is confirmed by our results. These also show that acetylation differs from nitration in yielding overwhelmingly the 8-substituted product and no 2-isomer. It is perhaps relevant that 1-methylfluorene is nitrated in the 2-position, but undergoes acetylation in the 7-position.<sup>4</sup>

4-Acetyl-3-methylfluoranthene (III; R = Ac) was prepared by Friedel-Crafts acetylation of 1,2,3,10b-tetrahydro-3-methylfluoranthene (II; R = H) and dehydrogenation of the product (II; R = Ac). The structure was assigned by analogy with reactions of 1,2,3,10b-tetrahydrofluoranthene,<sup>5</sup> and was confirmed by reduction of the acetylmethylfluoranthene to 4-ethyl-3-methylfluoranthene (III; R = Et), identical with a sample prepared by the following method. 2-Ethylfluorene (IV; R = H) was metallated with phenyllithium and then carboxylated with solid carbon dioxide to give 2-ethylfluorene-9-carboxylic acid (IV; R = CO<sub>2</sub>H). Treatment of the methyl ester of the acid with

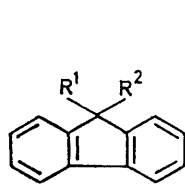
2-Acetyl-3-methylfluoranthene was synthesised by condensing fluorene-9-carbaldehyde (VI; R<sup>1</sup> = H, R<sup>2</sup> = CHO) with acetylacetone. In benzene in the presence of piperidinium acetate a low yield of the desired product (VII) was obtained, the main product being 9-piperidinomethylenefluorene (VI; R<sup>1</sup>R<sup>2</sup> = :CH·NC<sub>5</sub>H<sub>10</sub>).<sup>7</sup> With acetic acid as solvent, however, a high yield of compound (VII) was obtained. The position of the double bond follows from the n.m.r. spectrum, which lacks a signal at  $\tau$  ca. 6.2, characteristic of C-9 protons (see also Experimental section). The u.v. spectrum is very similar to that of the product (VI; R<sup>1</sup>R<sup>2</sup> = :CH·CH<sub>2</sub>Ac) which is obtained by the interaction of acetoacetic ester and the aldehyde in the presence of piperidine and acetic acid, condensation being accompanied by decarboxylation. Here, the position of the double bond is established conclusively by the n.m.r. spectrum. Hydrogenation of the ketone (VII) followed by cyclisation with PPA gave 2-acetyl-



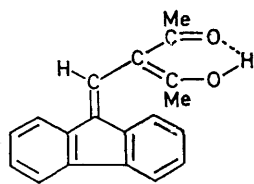
(IV)



(V)



(VI)

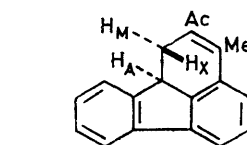


(VII)

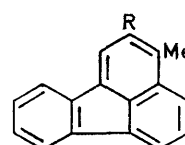
vinyl cyanide in the presence of base followed by use of standard procedures<sup>6</sup> gave 3-(2-ethylfluoren-9-yl)-propionic acid (IV; R = [CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>H). Cyclisation of this acid with polyphosphoric acid (PPA) gave the ketone (V), which was converted into 3-ethylfluoranthene, thus showing that the ring closure had occurred on the ethyl-substituted ring. The ketone (V) with methylmagnesium iodide yielded a product, dehydration of which followed by dehydrogenation gave 4-ethyl-3-methylfluoranthene (III; R = Et). The n.m.r. signal of the methine 3-proton in the hydrocarbon (II; R = H) underwent a downfield shift of 1.2 p.p.m. when the 4-acetyl group was introduced, owing to deshielding by the neighbouring carbonyl group.

<sup>3</sup> N. Campbell and N. H. Keir, *J. Chem. Soc.*, 1955, 1233; M. C. Kloetzel, W. King, and J. H. Menkes, *J. Amer. Chem. Soc.*, 1956, **78**, 1165.

<sup>4</sup> E. O. Arene and D. A. H. Taylor, *J. Chem. Soc. (C)*, 1966, 481.



(VIII)



(IX)

1,10b-dihydro-3-methylfluoranthene (VIII). The structure of this compound was confirmed by its AMX-type n.m.r. spectrum (Table I), which may advantageously be compared with that of 1,10b-dihydro-3-methylfluoranthene-2(3*H*)-one,<sup>1</sup> which likewise contains a rigid half-chair non-aromatic ring.

TABLE I

N.m.r. data for 2-acetyl-1,10b-dihydro-3-methylfluoranthene ( $\tau$  values;  $J$  in Hz)

		Solvent	
		CDCl <sub>3</sub>	C <sub>6</sub> H <sub>6</sub>
C-10b	H <sub>A</sub> quasialxial	6.15 (2 × d)	6.5
C-1	H <sub>M</sub> quasiequatorial	6.9 (2 × d)	7.4, $J_{AM}$ 7.5
C-1	H <sub>X</sub> quasialxial	7.85 (m)	8.3, $J_{AX}$ 16.0
C-3	Me	7.65 (d)	7.8 (d), $J_{MX}$ 15.0
Ac	Me	7.7 (s)	8.2 (s)

The H<sub>A</sub> and H<sub>M</sub> signals present no difficulties, but the axial H<sub>X</sub> signal at a higher field, due to the proton lying above the plane of the aromatic nucleus,<sup>1</sup> is not so simple. Instead of the expected double doublet it appears as a 'triplet,' since  $J_{MX}$  and  $J_{AX}$  have nearly the same value, the lower peak of the triplet being obscured by the methyl signals. The signals of the two methyl groups appear as a single peak, but with benzene as solvent the peaks become separated, the acetyl methyl peak being shifted upfield to  $\tau$  8.2.<sup>8</sup> Expansion of the spectrum showed that each of the three H<sub>X</sub> peaks is a quartet

<sup>5</sup> N. Campbell and W. W. Easton, *J. Chem. Soc.*, 1949, 340; J. von Braun and G. Manz, *Annalen*, 1932, **466**, 170.

<sup>6</sup> A. Campbell and S. H. Tucker, *J. Chem. Soc.*, 1949, 2625.

<sup>7</sup> F. D. Miller and E. C. Wagner, *J. Org. Chem.*, 1951, **16**, 279.

<sup>8</sup> N. S. Bhacca and D. H. Williams, 'Applications of N.M.R. in Organic Chemistry,' Holden Day, San Francisco, 1964, p. 170.

with a coupling constant ( $J$  2.5 Hz) identical with that of the C-3 methyl protons, thus indicating homoallylic couplings between  $H_X$  and the C-3 methyl protons.<sup>9</sup> This is not surprising, since the C- $H_X$  bond lies at an angle of about  $90^\circ$  to the plane containing C-1, C-2, C-3, and the C-3 methyl group. The homoallylic coupling was confirmed by spin decoupling. Irradiation at the frequency of the C-3 methyl protons converted the  $H_X$  quartets into singlets, and irradiation at the  $H_X$  frequency converted the  $H_A$  and  $H_M$  double doublets into doublets.

The dihydro-compound (VIII) was aromatised to give 2-acetyl-3-methylfluoranthene (IX;  $R = \text{Ac}$ ), which with hydrazoic acid yielded 2-acetamido-3-methylfluoranthene (IX;  $R = \text{NHAc}$ ); hence 2-amino-3-methylfluoranthene (IX;  $R = \text{NH}_2$ ) was obtained. Oxidation of the amine with peroxymaleic acid<sup>10</sup> gave 3-methyl-2-nitrofluoranthene (IX;  $R = \text{NO}_2$ ). This synthesis is to be preferred to that reported.<sup>1</sup> Replacement of the peroxymaleic acid by peroxytrifluoroacetic or peroxyacetic acid yielded only intractable products.

10-Acetyl-3-methylfluoranthene was synthesised from 1-chlorofluorene, a compound mentioned in one or two papers, but whose preparation and properties have not been reported. This chloro-derivative was converted into the 9-methoxycarbonyl compound, which was condensed with methyl vinyl ketone to give 4-(1-chlorofluoren-9-yl)butan-2-one. Reduction of the carbonyl group followed by ring closure with sulphuric acid yielded 10-chloro-1,2,3,10b-tetrahydro-3-methylfluoranthene, dehydrogenation of which gave 10-chloro-3-methylfluoranthene. This compound reacted with copper(I) cyanide in *N*-methylpyrrolidone to give the 10-cyano-compound, which on treatment with methyl-lithium followed by hydrolysis yielded 10-acetyl-3-methylfluoranthene.

## EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus. Alumina (Spence type H) was used in the chromatographic separations. I.r. spectra were measured for Nujol mulls or for films on an SP 200 instrument, and u.v. spectra for solutions in methanol on an SP 800 spectrometer. N.m.r. instruments used were a Perkin-Elmer R10 (60 MHz) and a Varian HA 100 (100 MHz). Molecular weights were determined from mass spectra, obtained with an A.E.I. MS 902 spectrometer. G.l.c. was effected with a Pye 104 instrument (OV1 Silicone Oil on Chromosorb; column  $6 \times \frac{3}{8}$  in).

**8-Acetyl-3-methylfluoranthene** (I;  $R = \text{Ac}$ ).—3-Methylfluoranthene (1.0 g) and acetyl chloride (0.40 g) were stirred in methylene chloride (8 ml) at  $-5^\circ\text{C}$ . Aluminium trichloride (0.80 g) was added in portions during 45 min and the mixture was stirred overnight at  $0^\circ$ . Ice and hydrochloric acid were added and the product was extracted with methylene chloride; the extract was washed with water, dried ( $\text{MgSO}_4$ ), and evaporated to yield 8-acetyl-3-methylfluoranthene, greenish yellow prisms (from acetic acid and then from ethanol) (0.61 g), m.p.  $121\text{--}123^\circ$  (Found: C, 88.2; H, 5.1.  $\text{C}_{19}\text{H}_{14}\text{O}$  requires C, 88.3;

H, 5.5%),  $\nu_{\text{max}}$  (film)  $1675\text{ cm}^{-1}$  (CO),  $\lambda_{\text{max}}$  229, 242infr, 254infr, 264infr, 299, 326.5, 358, and 374 nm ( $\log \epsilon$  4.58, 4.48, 4.36, 4.28, 4.53, 3.95, 4.15, and 4.17).

**8-Amino-3-methylfluoranthene** (I;  $R = \text{NH}_2$ ).—Sodium azide (1.0 g) was added to the foregoing ketone (2.58 g), which was stirred in trichloroacetic acid (15 g) at  $60^\circ$ . After 4 h water (75 ml) was added and the solution made alkaline with ammonia. 8-Acetamido-3-methylfluoranthene separated and crystallised from acetic acid or ethanol in dark yellow prisms (2.18 g), m.p.  $210\text{--}213^\circ$  (after sublimation at  $190^\circ$  to give needles) (Found: C, 83.5; H, 5.8; N, 5.4.  $\text{C}_{19}\text{H}_{15}\text{NO}$  requires C, 83.5; H, 5.8; N, 5.1%),  $\nu_{\text{max}}$  (Nujol)  $1655$  (CO) and  $3300\text{ cm}^{-1}$  (NH). The compound (1.0 g) was hydrolysed by boiling (15 min) with 60% aqueous sulphuric acid (10 ml). The mixture was poured into water and basified ( $\text{NaOH}$ ). The amine was extracted with ether; the extract was washed with saturated sodium chloride solution, dried ( $\text{MgSO}_4$ ), and evaporated to give yellow needles (74%) (from benzene-light petroleum and then aqueous ethanol), m.p.  $137\text{--}142^\circ$  (Found: C, 88.3; H, 5.65; N, 6.35.  $\text{C}_{17}\text{H}_{13}\text{N}$  requires C, 88.3; H, 5.6; N, 6.05%).

**3-Methyl-8-nitrofluoranthene** (I;  $R = \text{NO}_2$ ).—The amine (0.61 g) was mixed with acetic acid (8 ml) containing hydrogen peroxide (98%; 5 ml) and conc. sulphuric acid (0.1 ml); the mixture was warmed on a water-bath (3 min), then poured into water and extracted with benzene. The benzene solution was chromatographed on a short column from which a yellow band was eluted giving 3-methyl-8-nitrofluoranthene, yellow needles (from acetic acid) (0.22 g), m.p. and mixed m.p.  $178\text{--}179^\circ$ .<sup>1</sup>

**4-Acetyl-1,2,3,10b-tetrahydro-3-methylfluoranthene** (II;  $R = \text{Ac}$ ).—Aluminium chloride (0.48 g) was added during 2 h to 1,2,3,10b-tetrahydro-3-methylfluoranthene (0.73 g) and acetyl chloride (0.33 ml) in methylene chloride (5 ml) at  $-10^\circ$ . After a further 2 h the temperature was slowly raised to  $10^\circ\text{C}$  and stirring was continued for 30 h. The mixture was worked up as already described, but the product was purified by chromatographing the product in benzene to give 4-acetyl-1,2,3,10b-tetrahydro-3-methylfluoranthene (0.51 g crude), m.p.  $124\text{--}125^\circ$  (from ethanol) (Found: C, 86.9; H, 6.9.  $\text{C}_{19}\text{H}_{18}\text{O}$  requires C, 87.0; H, 6.9%),  $\nu_{\text{max}}$  (film)  $1675\text{ cm}^{-1}$  (CO),  $\tau$  2.2—2.8 (6H, m, Ar), 5.9 (1H, quintet, 3-H), 6.3 (1H,  $2 \times \text{d}$ , 10b-H), 7.4 (3H, s, Ac), 7.4—8.8 (4H, m,  $2 \times \text{CH}_2$ ), and 9.0 (3H, d, Me) (n.m.r. data similar to those of 1,2,3,10b-tetrahydro-3-methylfluoranthene).

**4-Acetyl-3-methylfluoranthene** (III;  $R = \text{Ac}$ ).—The foregoing compound (0.5 g) was heated (1 h) with *o*-chloranil (1.6 g) in benzene and the filtered solution was chromatographed to give 4-acetyl-3-methylfluoranthene, yellow plates (0.34 g) (from benzene-light petroleum and then acetic acid), m.p.  $186\text{--}187^\circ$  (Found: C, 88.2; H, 5.3%;  $M^+$ , 258.  $\text{C}_{19}\text{H}_{14}\text{O}$  requires C, 88.3; H, 5.5%;  $M$ , 258),  $\nu_{\text{max}}$  (Nujol)  $1677\text{ cm}^{-1}$  (CO),  $\lambda_{\text{max}}$  214, 240, 270, 282infr, 286, 292m, 315infr, 332, 349, and 366 nm ( $\log \epsilon$  4.57, 4.52, 4.18, 4.29, 4.32, 4.45, 3.65, 3.89, 4.00, and 4.03).

**4-Ethyl-3-methylfluoranthene** (III;  $R = \text{Et}$ ).—(a) The foregoing ketone (0.33 g), powdered potassium hydroxide (0.15 g), and 85% hydrazine hydrate (2 ml) were heated in digol (5 ml) for 2 h. The condenser was removed and the temperature raised to  $210^\circ$ . After 4 h the cooled mixture was poured into water and the product extracted

<sup>9</sup> S. Sternhell, *Quart. Rev.*, 1969, **236**, 266.

<sup>10</sup> W. D. Emmons and R. H. White, *Tetrahedron*, 1961, **17**, 31.

with benzene. Chromatography of the solution gave 4-ethyl-3-methylfluoranthene, yellow-green plates (from ethanol) (0.22 g), m.p. 104–105° (Found: C, 93.3; H, 6.25.  $C_{19}H_{16}$  requires C, 93.4; H, 6.6%); picrate, orange rods from ethanol, m.p. 154–156°.

(b) 2-Ethylfluorene (14 g) was metallated with phenyllithium and then carboxylated with solid carbon dioxide to give 2-ethylfluorene-9-carboxylic acid (82%); methyl ester, b.p. 204–210° at 11–12 mmHg (Found: C, 81.1; H, 6.0.  $C_{17}H_{16}O_2$  requires C, 80.05; H, 6.35%). The ester was condensed with vinyl cyanide and the resulting Michael product with alkali gave 3-(2-ethylfluorene-9-yl)propionic acid, crystals (from light petroleum containing a few drops of benzene) (80%), m.p. 95–99° (Found: C, 81.2; H, 6.6.  $C_{18}H_{18}O_2$  requires C, 81.2; H, 6.8%). The acid was cyclised with polyphosphoric acid at 100° to give as sole isolable product 4-ethyl-1,10b-dihydrofluoranthene-3(2H)-one (V), yellow plates (from ethanol) (76%), m.p. 91–93° (Found: C, 87.45; H, 6.6.  $C_{18}H_{16}O$  requires C, 87.1; H, 6.5%). Sodium borohydride reduction of the product followed by dehydration and dehydrogenation with *o*-chloranil gave 3-ethylfluoranthene, m.p. and mixed m.p. 75°. The Grignard reagent from magnesium (0.45 g) and methyl iodide (2.5 g) in ether was added in portions to the ketone (V) (2 g) in ether. The mixture was boiled (30 min) and worked up in the usual way, and the crude product was dehydrated by boiling (2 h) with formic acid (100 ml). The mixture was poured into water and the product was dissolved in benzene; the solution was washed with saturated sodium hydrogen carbonate solution, dried ( $MgSO_4$ ), and evaporated. 4-Ethyl-1,10b-dihydro-3-methylfluoranthene, after being passed through a chromatographic column in benzene, was obtained in plates (from methanol) (1.3 g), m.p. 70–72° (Found: C, 92.4; H, 7.3.  $C_{19}H_{18}$  requires C, 92.6; H, 7.4%). The dihydro-compound (1.0 g) was boiled (1 h) in benzene with *o*-chloranil. Chromatography of the product in benzene gave a single band with a bright blue fluorescence from which 4-ethyl-3-methylfluoranthene was eluted; square plates (from ethanol) (0.63 g), m.p. and mixed m.p. 104–105°.

3-(Fluorene-9-ylidenemethyl)pentane-2,4-dione (VII).—Fluorene-9-carbaldehyde (25.0 g), acetylacetone (15 ml), acetic acid (100 ml), and piperidine (4 ml) were boiled (2 h). The mixture was diluted with ether, washed with sodium hydrogen carbonate, and then water, dried ( $MgSO_4$ ), and evaporated to give a red oil which was dissolved in boiling ethanol. The dione (VII) separated and was washed with light petroleum; it formed rods (from light petroleum) (20.6 g), m.p. 130–132° (Found: C, 82.2; H, 5.8%;  $M$ , 276.  $C_{19}H_{16}O_2$  requires C, 82.6; H, 5.8%;  $M$ , 276),  $\nu_{max}$  1610  $cm^{-1}$  (broad chelated CO),  $\tau$  2.2–3.0 (9H, m, 8 Ar and 1 olefinic H), 7.9 (6H, s, 2  $\times$  Me), and –7.0 (1H, chelated OH). Chelation is possible only if the compound has the structure (VII) assigned.

Fluorene-9-carbaldehyde (10 g), acetylacetone (5 ml), piperidine (2.5 ml), acetic acid (2.5 ml), and benzene (50 ml) were boiled until no more water separated (Dean-Stark apparatus) and yielded 9-piperidinomethylenefluorene<sup>6</sup> (6.1 g), m.p. 109.5–110.5° (from ethanol). The filtrate

on evaporation yielded the dione (VII) (1.4 g), m.p. 130–132° (from ethanol and then from light petroleum).

Hydrogenation of the dione in methoxyethanol over 10% palladium-carbon at room temperature and atmospheric pressure gave 3-(fluorene-9-ylmethyl)pentane-2,4-dione, prisms (from ethanol) (92%), m.p. varying from 111 to 120° depending on the rate of heating (Found: C, 81.9; H, 6.4.  $C_{19}H_{18}O_2$  requires C, 82.0; H, 6.5%),  $\tau$  2.2–3.0 (8H, m, Ar), 6.2 (1H, t, 9-H,  $J$  8.0 Hz), 7.5 (2H, d,  $CH_2$ ,  $J$  8.0 Hz), and 8.1 (6H, s, 2  $\times$  Me).

2-Acetyl-1,10b-dihydro-3-methylfluoranthene (VIII).—The foregoing diketone (2.0 g) was heated with PPA (100 g) under dry nitrogen at 65° for 50 min. The mixture was poured into water and the product in benzene was chromatographed. A small bright blue fluorescing band was followed by the main greenish blue fluorescing zone, which on elution yielded 2-acetyl-1,10b-dihydro-3-methylfluoranthene, white rods (from ethanol) (0.81 g), m.p. 127–129° (Found: C, 87.7; H, 6.1%;  $M$ , 260.  $C_{19}H_{16}O$  requires C, 87.7; H, 6.2%;  $M$ , 260),  $\nu_{max}$  1660  $cm^{-1}$  (CO). The dihydro-compound (2.0 g) with *o*-chloranil (3.0 g) in benzene gave 2-acetyl-3-methylfluoranthene, m.p. 75–77° (Found: C, 88.5; H, 5.4.  $C_{18}H_{14}O$  requires C, 88.3; H, 5.4%). The acetyl compound with sodium azide and trichloroacetic acid gave 2-acetamido-3-methylfluoranthene (88%), pale yellowish green needles (from ethanol), m.p. 272–274° (Found: C, 83.2; H, 5.2; N, 4.9.  $C_{19}H_{15}NO$  requires C, 83.5; H, 5.5; N, 5.1%). Hydrolysis yielded the amine as an oil which with peroxymaleic acid yielded 3-methyl-2-nitrofluoranthene,<sup>1</sup> m.p. and mixed m.p. 165–167° (22%).

10-Acetyl-3-methylfluoranthene.—Aminofluorenone<sup>12</sup> was converted into 1-chlorofluorenone, m.p. 140–141° (lit.<sup>12</sup> 137–138°), after chromatographic purification in benzene. Wolff-Kishner reduction with no alkali present<sup>13</sup> yielded 1-chlorofluorene (90%), plates (from ethanol), m.p. 67–68° (Found: Cl, 17.65.  $C_{13}H_9Cl$  requires Cl, 17.65%)\*. It was converted by standard procedures, some already described, into the following substances: slightly impure 1-chlorofluorene-9-carboxylic acid, plates (from aqueous ethanol) (68%), m.p. 217–222° (Found: Cl, 13.7. Calc. for  $C_{14}H_9ClO_2$ : Cl, 14.5%), methyl ester, prisms (from methanol), m.p. 76–77° (Found: Cl, 13.6.  $C_{15}H_{11}ClO_2$  requires Cl, 13.6%); methyl 1-chloro-9-(3-oxobutyl)fluorene-9-carboxylate, prisms (from methanol) (5.7 g), m.p. 136–138° (Found: Cl, 10.2.  $C_{18}H_{17}ClO_3$  requires Cl, 10.8%). Alkaline hydrolysis was accompanied by decarboxylation to yield 4-(1-chlorofluorene-9-yl)butan-2-one, yellow oil, reduction of which with sodium borohydride followed by ring closure with sulphuric and acetic acids<sup>14</sup> gave 10-chloro-1,2,3,10b-tetrahydro-3-methylfluoranthene, yellow oil, which with *p*-chloranil yielded 10-chloro-3-methylfluoranthene, pale yellow plates (from benzene) (2.8 g), m.p. 167–168° (Found: Cl, 13.65%;  $M$ , 250.  $C_{17}H_{11}Cl$  requires Cl, 14.1%;  $M$ , 250). The chloro-compound (1.0 g) was heated (30 h) in *N*-methylpyrrolidone with copper(I) cyanide to give 3-methylfluoranthene-10-carbonitrile, needles (from ethanol) (0.64 g), after chromatographic separation from unchanged material, m.p. 181–182° (subliming in plates) (Found: C, 89.4; H, 4.8; N, 5.8%;  $M$ , 241.  $C_{18}H_{11}N$  requires C, 89.6; H, 4.6; N, 5.8%).

\* This compound is merely mentioned in *Chem. Abs.*, e.g. 1970, 17,346.

<sup>11</sup> N. P. Buu-Hoi, P. Mabile, and Do Cao Thang, *Bull. Soc. chim. France*, 1968, 981.

<sup>12</sup> N. Kharasch and T. C. Bruice, *J. Amer. Chem. Soc.*, 1951, **73**, 3242.

<sup>13</sup> H. F. Andrew and N. Campbell, *Proc. Roy. Soc. Edinburgh*, 1965, **66A**, 252.

<sup>14</sup> E.g. H. France, S. H. Tucker, and J. Forest, *J. Chem. Soc.*, 1945, 7.



5.8%; *M*, 241), which on treatment with methyl-lithium followed by hydrolysis yielded 10-acetyl-3-methylfluoranthene (0.32 g), m.p. 150—152° (Found: C, 88.3; H, 5.65%; *M*, 258.  $C_{19}H_{14}O$  requires C, 88.3; H, 5.5%; *M*, 258).

4-Fluorene-9-ylidenebutan-2-one.—Heating (6 h) fluorene-9-carbaldehyde with ethyl acetoacetate, acetic acid, and a little piperidine as before yielded 4-fluorene-9-ylidenebutan-2-one (25%), yellow rods (from ethanol), m.p. 127—128° (Found: C, 87.2; H, 5.9.  $C_{17}H_{14}O$  requires C, 87.15; H, 6.0%),  $\nu_{\max}$  (Nujol) 1710s  $cm^{-1}$  (CO),  $\tau$  2.2—2.9 (8H, m, Ar), 3.1 (1H, t, olefinic *J* 8.0 Hz), 6.2 (2H, d,  $CH_2$ , *J* 8.0 Hz), and 7.8 (3H, s, Me). The n.m.r. spectrum establishes the position of the double bond.

*T.l.c.* of  $\alpha$ -Acetyl-3-methylfluoranthenes.—The behaviour

of the crude acetylation product and of synthetic samples was studied in benzene on Kieselgel G nach Stahl (Merck) (Table 2).

TABLE 2

<i>x</i>	Fluorescence in 360 nm u.v. light	<i>R<sub>F</sub></i>
2	Greenish yellow	0.25
4	Orange-yellow	0.24
8	Bright blue	0.18
10	Bright blue	0.33
Unknown	Bright blue	0.23
3-Methyl fluoranthene	Bright blue	0.74

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