

1,4,6-Trimethylantracene and 1,4,6-Trimethylfluorene. N.m.r. Spectra of Methylfluorenes

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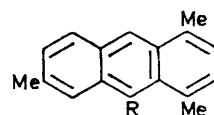
The syntheses of 1,4,6-trimethylantracene and 1,4,6-trimethylfluorene are described. N.m.r. spectroscopy has only limited use for locating the substituents in methylfluorenes, since the 1-, 2-, and 3-methyl protons have similar chemical shifts; the signal due to a 4-methyl substituent is at lower field.

A HYDROCARBON of m.p. 227 °C, regarded as 1,4,6-trimethylantracene (I; R = H) was obtained by Elbs¹ by pyrolysis of 2,2',5,5'-tetramethylbenzophenone; the quinone formed by oxidation of the hydrocarbon had m.p. 184 °C. Later, Mayer and Stark² described another quinone, m.p. 143 °C, from the cyclisation of 2,5-dimethyl-6-*p*-toluoylbenzoic acid with sulphuric acid, as 1,4,6-trimethylantraquinone and suggested that the hydrocarbon obtained by Elbs was not 1,4,6-trimethylantracene.

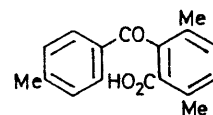
We have prepared authentic 1,4,6-trimethylantracene by reduction of the 10-acetoxy-derivative (I; R = OAc) with zinc and sodium hydroxide. The crystalline hydrocarbon had m.p. 57 °C, and on oxidation with chromium trioxide in acetic acid it furnished the corresponding quinone, m.p. 143 °C, identical (mixed m.p.) with the compound prepared as described by Mayer and Stark. The structure of the hydrocarbon was confirmed by its u.v. absorption and by the n.m.r. spectrum, which showed two singlets at τ 7.23 (6H) and 7.44 (3H) ascribable to the α - and β -methyl groups respectively, in line with the values found³ for other methylanthracenes; the slight downfield shifts observed in comparison with the signals due to the methyl substituents in 1- and 2-methylantracene are probably due to a dilution effect.⁴

The acetoxy-compound (I; R = OAc) was obtained from the trimethylbenzoylbenzoic acid (II), itself prepared from 3,6-dimethylphthalic anhydride and *p*-tolylmagnesium bromide. As in a comparable case⁵ the acid appears to exist largely in the 'pseudo' form (III; R = OH); the i.r. spectrum shows strong hydroxy-absorption at 3350 cm⁻¹ and a single carbonyl maximum at 1730 cm⁻¹, and the u.v. spectrum is similar to that of

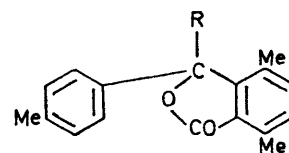
typical pseudo-esters and does not show the maximum at ca. 250 nm characteristic of the 'normal' form of *o*-benzoylbenzoic acids.⁶ Reduction of the benzoylbenzoic



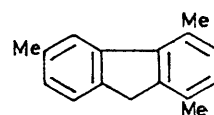
(I)



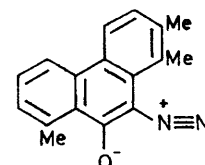
(II)



(III)



(IV)



(V)

acid with zinc and sodium hydroxide gave, not the expected benzylbenzoic acid, but the lactone (III; R = H). This was shown by the molecular weight and elemental analysis and was supported by the i.r. spectrum, which showed a sharp carbonyl peak at 1750 cm⁻¹ but no hydroxy-maximum, and by the presence in the n.m.r. spectrum of a singlet (1H) at τ 3.75. Reaction of

¹ K. Elbs, *J. prakt. Chem.*, 1890, **41** [2], 140.

² F. Mayer and O. Stark, *Ber.*, 1931, **64**, 2003.

³ Cf. W. Carruthers, H. N. M. Stewart, P. G. Hansell, and K. M. Kelly, *J. Chem. Soc. (C)*, 1967, 2607.

⁴ Cf. Foch Fu-Hsie Yew, R. J. Kurland, and B. J. Mair, *Analyt. Chem.*, 1964, **36**, 843.

⁵ W. Carruthers, *J. Chem. Soc.*, 1963, 5551.

⁶ Cf. W. Graf, E. Girod, E. Schmid, and W. G. Stoll, *Helv. Chim. Acta*, 1959, **42**, 1085; M. S. Newman and C. W. Muth, *J. Amer. Chem. Soc.*, 1951, **73**, 4627.

the lactone with zinc chloride in acetic anhydride smoothly afforded the acetoxymethylanthracene (I; R = OAc).

The identification of 1,2,7,8-tetramethylfluorene in a Kuwait mineral oil has been described by one of us⁷ and the isolation of a number of other polymethylfluorenes from mineral oils has been reported.⁸ To aid in the identification of these derivatives we have examined the n.m.r. spectra of some methylfluorenes, and to this end we have used the benzoylbenzoic acid (II) to prepare 1,4,6-trimethylfluorene (IV). Oxidative cyclisation of the acid with potassium persulphate in alkaline solution as described by Russell and Thomson⁹ gave 1,4,6-trimethylfluorenone, reduction of which with hydrogen iodide in propionic acid¹⁰ led to the trimethylfluorene.

In separate experiments an attempt was made to prepare 1,2,8-trimethylfluorene from 1,2,8-trimethylphenanthrene by the method of Süs, Steppan, and Dietrich.¹¹ Oxidation of the phenanthrene with chromic acid afforded the corresponding quinone, reaction of which with benzenesulphonohydrazide gave the diazoxide (V). However, irradiation of this compound in aqueous dioxan gave, not the expected^{7,11} trimethylfluorene-9-carboxylic acid, but a neutral compound which appears to be a trimethylfluorenone; this is supported by the molecular weight and elemental analysis and by the u.v. spectrum. Reduction with hydrogen iodide in propionic acid afforded the corresponding trimethylfluorene, presumably 1,2,8-trimethylfluorene, but until the mode of formation of the fluorenone is elucidated the orientation of the methyl groups cannot be certain.

N.m.r. spectroscopy has been of value in determining the orientation of substituents in alkyl derivatives of a number of polycyclic aromatic and heterocyclic structures.^{3,4,12,13} It has proved less useful with the methylfluorenes, however, for in this series the protons of 1-, 2-, and 3-methyl substituents have almost identical chemical shifts; only 4- (and 5-) methyl groups are easily distinguishable (see Table).¹⁴ The comparative downfield shift of the signal due to the 4-methyl protons is analogous to the shifts shown by 4-methyl derivatives in the phenanthrene^{15,16} and carbazole^{12,14} series, which have been attributed to the shielding effect of the neighbouring benzene ring. The chemical shifts of the methyl protons in the methylfluorenes are close to those of the corresponding protons in the methylcarbazoles, except for 1-methylcarbazole which shows a significant upfield shift compared with 1-methylfluorene, presumably due to the effect of the neighbouring nitrogen atom.

⁷ W. Carruthers and H. N. M. Stewart, *J. Chem. Soc. (C)*, 1967, 556.

⁸ H. N. M. Stewart, Ph.D. Thesis, University of Exeter, 1966; J. L. Martín-Picó, Ph.D. Thesis, Carnegie Institute of Technology, Pittsburgh, 1962, B. J. Mair and J. L. Martín-Picó, *Proc. Amer. Petrol. Inst.*, 1962, **42**, 173.

⁹ J. Russell and R. H. Thomson, *J. Chem. Soc.*, 1962, 3379.

¹⁰ D. C. Morrison, *J. Org. Chem.*, 1958, **23**, 1372.

¹¹ O. Süs, H. Steppan, and R. Dietrich, *Annalen*, 1958, **617**, 20.

¹² W. Carruthers, *J. Chem. Soc. (C)*, 1968, 2244.

¹³ R. J. Ouellette and B. G. van Leuwen, *J. Org. Chem.*, 1969, **34**, 62; A. D. Cross, H. Carpio, and P. Crabbé, *J. Chem. Soc.*, 1963, 5539.

It has been shown⁴ in the methylnaphthalene series that the position of the methyl proton signals is governed not only by the position of the methyl groups on the nucleus, but also by the disposition of neighbouring alkyl groups; in particular *ortho*-methyl groups shield each other. An indication that a similar effect operates in polyalkylfluorenes is given by a comparison of the methyl

Chemical shifts * (τ) of protons in methylfluorenes

	Me	Aromatic
1-Me	7.59	
2-Me	7.59	
3-Me	7.56	
4-Me	7.28	ABq (J_{AB} 7 Hz), τ_A 2.52 (5-H), τ_B 2.85 (6-H).
2-Et-1-Me	7.65	
2-Et-7-Me	7.59	br s τ 2.67 (1-H and 8-H); ABq (J_{AB} 7.5 Hz), τ_A 2.39 (4-H and 5-H), τ_B 2.85 (3-H and 6-H).
1,4,6-(Me) ₃	7.31 (4-Me) 7.55 (6-Me) 7.65 (1-Me)	τ 2.27 (5-H); overlapping AB quartets at τ 2.73 and 2.98 (J_{AB} 8 and 7.5 Hz).
1,4,5,8-(Me) ₄	7.30, 7.62	ABq (J_{AB} 8 Hz), τ_A 2.87, τ_B 2.94.
1,2,7,8-(Me) ₄	7.64	ABq (J_{AB} 8 Hz), τ_A 2.52 (4-H), τ_B 2.85 (3-H).

* Spectra were recorded with a JEOL MH-100 spectrometer (100-MHz) for 2% solutions (w/w) in deuteriochloroform containing tetramethylsilane as internal reference. All the specimens except the last three were provided by Prof. L. Chardonnens, University of Fribourg.

proton signals of 1-methyl-, 2-methyl-, and 2-ethyl-7-methylfluorene with those of 2-ethyl-1-methyl- and 1,2,7,8-tetramethylfluorene. A similar though smaller effect is observable with *para*-methyl substituents as well, as can be seen by comparing the results for 1- and 4-methylfluorene with those for 1,4,6-trimethyl- and 1,4,5,8-tetramethylfluorene. The aromatic proton regions of the spectra of the monomethylfluorenes were complex and the chemical shifts of individual protons could not be extracted from them, except in the case of 4-methylfluorene where a low-field quartet was distinguishable (see Table), the lower field doublet of which is assigned to the C-5 proton by analogy with the assignments of similarly placed protons in phenanthrene¹⁷ and carbazole.^{14,18} In the spectra of the polyalkylfluorenes studied the aromatic proton region is simplified and in these compounds it has been possible to assign chemical shifts to some of the individual aromatic protons. The signals due to the C-4 (C-5) protons again occur at lower field than those due to protons in other positions. However, in the three compounds quoted in the Table these signals appear at higher field than the signal of the C-5 proton in 4-methylfluorene, presumably owing to an effect of the alkyl substituents similar to that which has

¹⁴ Cf. also I. Puskas and E. K. Fields, *J. Org. Chem.*, 1968, **33**, 4237.

¹⁵ A. D. Cross and L. J. Durham, *J. Org. Chem.*, 1965, **30**, 3200.

¹⁶ Cf. K. D. Bartle and J. A. S. Smith, *Spectrochim. Acta*, 1967, **23A**, 1689.

¹⁷ J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High Resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959, p. 247.

¹⁸ R. E. Moore and H. Rapoport, *J. Org. Chem.*, 1967, **32**, 3335.

been observed in methyl derivatives of other aromatic hydrocarbons.¹⁶

EXPERIMENTAL

U.v. spectra, measured with a Unicam SP 800 spectrometer, refer to solutions in 95% ethanol unless otherwise stated. I.r. spectra were measured with a Perkin-Elmer Infracord and mass spectra with a Hitachi RMU 60 instrument. ¹H N.m.r. spectra were recorded on a Perkin-Elmer R10 spectrometer at 60 MHz or on a JEOL MH-100 instrument at 100 MHz, for solutions in deuteriochloroform, with tetramethylsilane as internal reference. Light petroleum refers to the fraction b.p. 60–80 °C unless otherwise stated.

3,6-Dimethyl-2-(4-methylbenzoyl)benzoic Acid (II).—A solution of *p*-tolylmagnesium bromide [from *p*-bromotoluene (5.9 g) and magnesium (0.85 g) in ether (80 ml)] was added dropwise to a stirred solution of 3,6-dimethylphthalic anhydride (6.7 g) in benzene (100 ml). Ether was distilled off and the stirred mixture was heated at 60 °C for 4 h, cooled, and decomposed with ice–hydrochloric acid. The benzene layer was separated and extracted with sodium carbonate. Acidification with acetic acid gave the benzoic acid (5.0 g), which formed blades, m.p. 180 °C (from benzene) (lit.² 180 °C) (Found: C, 75.6; H, 6.1. Calc. for C₁₇H₁₆O₃: C, 76.1; H, 6.0%); λ_{max.} (cyclohexane) 225infr and 284–292 nm (log ε 4.20 and 3.36); ν_{max.} (KBr) 3350 and 1730 cm⁻¹.

4,7-Dimethyl-3-*p*-tolylisobenzofuran-1(3H)-one (III; R = H). A solution of the foregoing benzoylbenzoic acid (2.0 g) in sodium hydroxide solution (10%; 150 ml) was boiled with zinc dust (4 g) for 72 h, filtered, and acidified to give the lactone (1.8 g) as prisms (from aqueous acetic acid), m.p. 151 °C (Found: C, 81.8; H, 6.3%; M⁺, 252. C₁₇H₁₆O₂ requires C, 80.9; H, 6.4%; M, 252).

10-Acetoxy-1,4,6-trimethylanthracene (I; R = OAc).—A solution of the preceding lactone (960 mg) and fused zinc chloride (150 mg) in acetic acid (15 ml) and acetic anhydride (10 ml) was boiled for 1 h. The hot solution was diluted with water until incipient turbidity and allowed to cool. 10-Acetoxy-1,4,6-trimethylanthracene (840 mg) was obtained as pale yellow needles, m.p. 128 °C (from light petroleum–benzene) (Found: C, 82.2; H, 6.6%; M⁺, 278. C₁₉H₁₈O₂ requires C, 82.0; H, 6.5%; M, 278); λ_{max.} (cyclohexane) 240infr, 253infr, 261, 320infr, 337, 354, 373, and 393 nm (log ε 4.27, 4.85, 5.13, 3.17, 3.41, 3.68, 3.82, and 3.77).

1,4,6-Trimethylanthracene (I; R = H).—A mixture of the foregoing acetoxy-compound (700 mg) and zinc dust (4 g) in sodium hydroxide (10%; 50 ml) was boiled under nitrogen for 48 h, cooled, and extracted with benzene. The recovered material was filtered through alumina. Elution with light petroleum gave 1,4,6-trimethylanthracene (500 mg) as prisms, m.p. 57 °C (from methanol) (Found: C, 92.5; H, 7.6%; M⁺, 220. C₁₇H₁₆ requires C, 92.7; H, 7.3%; M, 220); λ_{max.} 239infr, 250infr, 257, 330, 343infr, 348, 364, and 385 nm (log ε 4.39, 4.92, 5.18, 3.44, 3.63, 3.69, 3.78, and 3.73); τ 1.53 (1H, s) and 1.59 (1H, s) (*meso*-protons), 2.24br (1H, s, 5-H), 2.41 (q, J_{AB} 8 Hz, 7-H and 8-H), and 2.85 (2H, s, 2-H and 3-H). Oxidation of the hydrocarbon (60 mg) with chromium trioxide (200 mg) in acetic acid (10 ml) on a water-bath for 1 h gave 1,4,6-trimethylanthraquinone, yellow prisms (from ethanol–benzene), m.p. 142–143 °C, not

depressed when mixed with the quinone, m.p. 143 °C, obtained by cyclisation of the benzoylbenzoic acid (II) with sulphuric acid as described by Mayer and Stark.²

1,4,6-Trimethylfluorene.—A solution of potassium persulphate (2.4 g) in water (30 ml) was added to a hot (boiling water-bath) stirred solution of the benzoylbenzoic acid (II) (2.0 g) in 0.5M-sodium hydroxide (50 ml). The hot solution was stirred for 3 h and small amounts of sodium hydroxide were added from time to time to keep the solution alkaline. The cooled solution was extracted with ether and the recovered product was chromatographed on alumina. Elution with benzene–light petroleum (3:4) gave 1,4,6-trimethylfluorenone (80 mg) as yellow needles, m.p. 98 °C (from methanol) (Found: C, 86.7; H, 6.2%; M⁺, 222. C₁₆H₁₄O requires C, 86.5; H, 6.4%; M, 222). Reduction of the fluorenone (70 mg) with red phosphorus (2 mg) and hydriodic acid (*d* 1.94; 2 ml) in propionic acid (12 ml) under reflux for 60 h gave 1,4,6-trimethylfluorene (30 mg) as silky needles, m.p. 105 °C (from methanol) (Found: C, 92.4; H, 7.6%; M⁺, 208. C₁₆H₁₆ requires C, 92.3; H, 7.7%; M, 208); λ_{max.} 258infr, 263, 268, 272, 278infr, 288, 292infr, and 299 nm (log ε 5.51, 5.20, 5.22, 5.20, 5.06, 4.91, 4.86, and 4.87).

1,2,8-Trimethylphenanthrenequinone.—A solution of 1,2,8-trimethylphenanthrene (300 mg) and chromium trioxide (400 mg) in acetic acid (15 ml) and water (1 ml) was heated on a water-bath for 1 h. The recovered neutral material was chromatographed on alumina. Elution with benzene–ether (20:1) gave the quinone (110 mg) as orange needles, m.p. 202–203 °C (from benzene) (Found: C, 81.4; H, 5.5. C₁₇H₁₄O₂ requires C, 81.6; H, 5.6%).

1,2,8-Trimethylfluorene.—A mixture of 1,2,8-trimethylphenanthrenequinone (80 mg) and benzenesulphonylhydrazide (70 mg) in ethanol (2 ml) was stirred at 60 °C for 6 h; the orange colour of the quinone was gradually replaced by the yellow of the diazo-oxide. The mixture was cooled to 0 °C and the diazo-oxide was collected and washed with a little cold methanol. A solution in dioxan (60 ml), water (30 ml), and acetic acid (2 ml) was irradiated through Pyrex at 0 °C with light from a medium-pressure mercury lamp for 4 h. Solvents were evaporated off under reduced pressure and the residue, in ether, was extracted with aqueous sodium carbonate. Only a trace of acidic material was recovered. The neutral fraction (30 mg) was chromatographed on alumina; elution with light petroleum–benzene (4:1) gave 1,2,8-trimethylfluorenone (16 mg) as yellow plates, m.p. 152–153 °C (from ethanol–benzene) (Found: C, 86.8; H, 6.3%; M⁺, 222. C₁₆H₁₄O requires C, 86.5; H, 6.4%; M, 222); λ_{max.} 251, 266, 295, 309, 323, 341, and 412 nm (log ε 4.96, 5.13, 3.57, 3.63, 3.63, 3.64, and 3.04). The fluorenone (16 mg) was reduced with red phosphorus (20 mg) and hydriodic acid (0.2 ml) in propionic acid (1.5 ml) as described for 1,4,6-trimethylfluorenone. The recovered neutral product was filtered through alumina; elution with light petroleum–benzene (5:1) gave 1,2,8-trimethylfluorene (5 mg) as plates, m.p. 147–148 °C (from methanol) (Found: C, 92.6; H, 7.2%; M⁺, 208. C₁₆H₁₆ requires C, 92.3; H, 7.7%; M, 208); λ_{max.} 226infr, 262infr, 266infr, 271, 284, 293, 297infr, and 305 nm (log ε 4.29, 4.27, 4.32, 4.36, 4.19, 3.88, 3.72, and 3.87).