

Synthesis of a 1,2,3,6b,7,8,12b,12c-Octahydrobenzo[*j*]fluoranthene

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One of the four isomeric 1,2,3,6b,7,8,12b,12c-octahydrobenzo[*j*]fluoranthenes and benzo[*j*]fluoranthene have been synthesised from 2a,3,4,5-tetrahydro-2-phenylacenaphthen-1-one by way of 2a,3,4,5-tetrahydro-2-phenyl-acenaphthene-1-acetic acid.

THE structures of the octahydrobenzo[*j*]fluoranthenes isolated by von Braun and Kirschbaum¹ (m.p. 93°) and Dansi and Ferri² (m.p. 150°), have been the subject of much comment.³⁻⁵ Campbell and Gorrie,⁶ by synthesis, showed that the latter isomer was a 4,5,6,6a,6b,-

7,8,12b-octahydrobenzo[*j*]fluoranthene, probably that with the *cis*-6b*H*,12b*H*-configuration since these hydrogen atoms were introduced by catalytic hydrogenation. No indication of the stereochemistry at position 6a was

¹ J. von Braun and G. Kirschbaum, *Ber.*, 1921, **54**, 597.

² A. Dansi and G. Ferri, *Gazzetta*, 1941, **71**, 648.

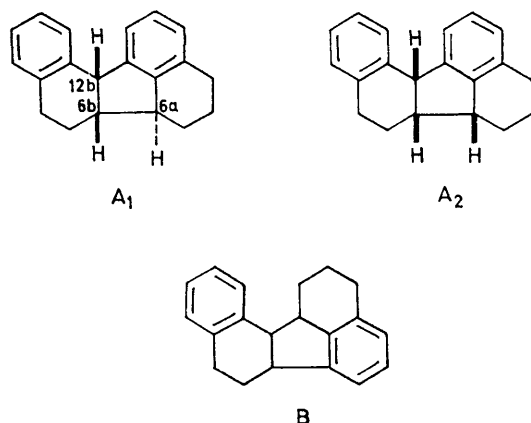
³ C. D. Nenitzescu and M. Avram, *J. Amer. Chem. Soc.*, 1950, **72**, 3486.

⁴ N. Campbell, N. M. Khanna, and A. Marks, *J. Chem. Soc.*, 1951, 2511.

⁵ M. Crawford and V. R. Supanekar, *J. Chem. Soc. (C)*, 1968, 2328.

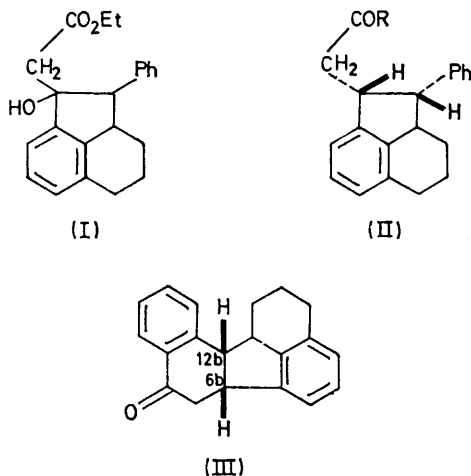
⁶ N. Campbell and J. R. Gorrie, *J. Chem. Soc. (C)*, 1968, 1887.

obtained. Recently (and in conformity with these findings), on the basis of n.m.r. studies⁷ and mass spectral fragmentation patterns,⁸ the hydrocarbons have been assigned the absolute structures A_1 and A_2 , respectively. We now report the synthesis of a



1,2,3,6b,7,8,12b,12c-octahydrobenzo[*j*]fluoranthene (B), a structure previously assigned³ to the hydrocarbon of von Braun and Kirschbaum.

Treatment of 2a,3,4,5-tetrahydro-2-phenylacenaphthen-1-one⁹ with zinc and ethyl bromoacetate yielded the hydroxy-ester (I); dehydration, hydrogenation of the resulting double bond, and hydrolysis gave the acid (II; R = OH). Ring closure of the acid chloride



(II; R = Cl) by the inverse Friedel-Crafts reaction with tin(IV) chloride yielded the ketone (III), and this on Wolff-Kishner reduction gave a 1,2,3,6b,7,8,12b,12c-octahydrobenzo[*j*]fluoranthene (B) of m.p. 122–123°. Dehydrogenation by heating with an excess of sulphur gave benzo[*j*]fluoranthene.

Since the 6b- and 12b-hydrogen atoms were introduced by catalytic hydrogenation their configuration is probably *cis*, but our synthesis gives no indication of the stereochemistry at position 12c. In the n.m.r. spectra⁷ of the hydrocarbons A_1 and A_2 , the resonance

⁷ D. V. Hertzler, E. J. Eisenbraun, and P. W. K. Flanagan, *Chem. and Ind.*, 1969, 877.

of the 12b-proton is a doublet [τ 5.2 (J 6 Hz)] owing to coupling with the 6b-proton. As expected, our product (B) gave no resonance in this region.

EXPERIMENTAL

I.r. spectra were recorded on a Unicam SP 200 instrument for liquid films or Nujol mulls. U.v. spectra were recorded on a Unicam SP 800 instrument for solutions in ethanol solution. Mass spectra were obtained on an A.E.I. MS 902 double-focussing instrument. ¹H N.m.r. data were recorded on a Varian HA100 (100 MHz) instrument at 28° for solutions (5–10%) in carbon tetrachloride, with tetramethylsilane as internal reference. M.p.s were determined on a Kofler hot-stage apparatus.

Ethyl 2a,3,4,5-Tetrahydro-1-hydroxy-2-phenylacenaphthene-1-acetate (I).—2a,3,4,5-Tetrahydro-2-phenylacenaphthen-1-one (3.0 g), ethyl bromoacetate (5 ml), activated zinc wool (5 g), dry benzene (100 ml), and a crystal of iodine were boiled (2 h). Benzene was decanted from the cooled mixture and the residual yellow solid was dissolved in methanol–water–acetic acid (100 ml; 1:1:1 v/v) and added to the benzene. Ether was added and the ether–benzene extract was washed successively with dilute sodium hydroxide solution and water, dried, and evaporated. The residual gum (4.1 g) gave the *ester* (I) (3.5 g, 87%) as prisms (from ethanol), m.p. 105–106° [Found: C, 78.1; H, 7.3%; ($M - H_2O$)⁺, 318. $C_{22}H_{24}O_3$ requires C, 78.55; H, 7.2%; $M - H_2O$, 318], ν_{\max} 3550m (OH) and 1720s cm^{-1} (CO₂Et), τ (CCl₄) 8.9–9.1 (3H, t, O-CH₂-CH₃), 6.2–8.5 (10H, m), 5.9–6.15 (2H, q, O-CH₂-CH₃), 5.0–5.2 (1H, s, OH), and 2.6–3.4 (8H, m, ArH). Dehydration of the ester (5.0 g) with 90% formic acid (130 ml) gave the crude unsaturated ester (4.3 g) as a yellow oil, ν_{\max} 1740s (CO₂Et) and 1605m cm^{-1} (C=C). Hydrolysis of this oil (4.0 g) with potassium hydroxide (5.0 g) in aqueous ethanol gave 2a,3,4,5-tetrahydro-2-phenylacenaphthylene-1-acetic acid (46%) as needles (from methanol), m.p. 197–198° (Found: C, 83.6; H, 6.4%; M^+ , 290. $C_{20}H_{18}O_2$ requires C, 82.7; H, 6.3%; M , 290), λ_{\max} 221, 230, 237, and 302 nm (log ϵ 4.13, 4.10, 4.10, and 4.32), ν_{\max} 1685s (CO₂H) and 1605m cm^{-1} (C=C), τ 8.8–8.0 (8H, m), 5.8–5.5 (1H, d, J 10 Hz, ArCH=C=C), 3.1–2.8 (2H, m, ArH), and 2.8–2.5 (6H, m, ArH).

2a,3,4,5-Tetrahydro-2-phenylacenaphthene-1-acetic Acid (II; R = OH).—The foregoing unsaturated ester (3.9 g) was hydrogenated in ethyl acetate (200 ml) over palladium-charcoal (10%; 200 mg) at 60° and 100 atm for 12 h to give the saturated ester (3.7 g) as an orange oil. Hydrolysis with potassium hydroxide gave the crude acid (2.7 g). Crystallisation from ethanol–water and benzene–petroleum (b.p. 60–80°) gave the *acid* (0.46 g), m.p. 180.5–181.5° (Found: C, 82.3; H, 6.7%; M^+ 292. $C_{20}H_{20}O_2$ requires C, 82.2; H, 6.9%; M , 292), λ_{\max} 220 nm (log ϵ 4.16), ν_{\max} 1695s cm^{-1} (CO₂H), τ 9.0–5.8 (11H, m), 3.2–2.9 (3H, m, ArH), and 2.9–2.7 (5H, m, ArH).

2,3,6b,7,12b,12c-Hexahydrobenzo[*j*]fluoranthene-8(1H)-one (III).—The acid (II; R = OH) (0.20 g) with thionyl chloride (1.0 ml) at room temperature gave the acid chloride, which was dissolved in dry *s*-tetrachloroethane (2 ml) and added slowly to anhydrous tin(IV) chloride (1 ml) in the same solvent (1 ml). After 1 h at 95° the mixture was

⁸ M. C. Hamming and G. W. Keen, *Internat. J. Mass Spectrometry Ion Phys.*, 1969, **3**, App. 1.

⁹ E. Buchta and H. Maar, *Chem. Ber.*, 1962, **95**, 1826; *Annalen*, 1964, **674**, 129.

cooled and the complex decomposed with cold dilute hydrochloric acid. An ether-benzene (20 ml; 1:1) extract was then washed successively with dilute hydrochloric acid, dilute sodium hydroxide, and water, dried, and evaporated. The residual gum was chromatographed on alumina. The benzene eluate afforded *prisms* (from benzene-light petroleum) (63%), m.p. 193–194° (Found: C, 87.3; H, 6.6%; M^+ , 274. $C_{20}H_{18}O$ requires C, 87.6; H, 6.6%; M , 274), ν_{\max} 1680s cm^{-1} (six-membered-ring ketone), τ 8.6–6.1 (11H, m), 3.1–2.4 (6H, m, ArH), and 2.0–1.8 (1H, d, J 7 Hz, ArH).

1,2,3,6b,7,8,12b,12c-Octahydrobenzo[*j*]fluoranthene (B).—The ketone (III) (0.27 g), potassium hydroxide (1.2 g), bis(2-methoxyethyl) ether (20 ml) and hydrazine hydrate (3 ml; 99%) were heated at 130° for 2 h. Some distillate was removed and the residual mixture was then boiled under reflux for a further 3 h, cooled, diluted with water, and extracted with benzene-ether (1:1; 20 ml). The extract

was washed with water, dried, and evaporated to give a gum that was purified by chromatography. The benzene eluate yielded a solid that was twice crystallised from benzene-light petroleum to give the *hydrocarbon* (62%), m.p. 122–123° (Found: C, 92.2; H, 7.7%; M^+ , 260. $C_{20}H_{20}$ requires C, 92.2; H, 7.7%; M , 260), τ 8.8–6.7 (13H, m) and 3.3–2.7 (7H, m, ArH) [no (Ar)₂CH doublet at τ 5.8]. The hydrocarbon (50 mg) and sulphur (0.5 g) were heated together at 230° for 1 h, then cooled. The residue was dissolved in benzene. Chromatographic separation on alumina and elution with light petroleum removed the excess of sulphur. Elution with benzene gave a yellow solid. Crystallisation from benzene-light petroleum gave benzo[*j*]fluoranthene (20 mg), yellow needles, m.p. 163–164° (lit.,³ 165°); picrate, red-brown needles, m.p. 195° (lit.,³ 195°), both identical (mixed m.p.) with authentic samples.

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