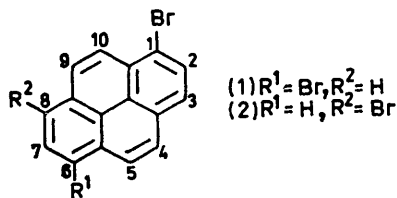


Characterisation of 1,6- and 1,8-Dibromopyrenes

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Treatment of pyrene or 1-bromopyrene with limited amounts of bromine affords 1,6-dibromopyrene and 1,8-dibromopyrene (not isolated pure by previous workers). Further bromination of either dibromide gives 1,3,6-tribromopyrene.

1,6- AND 1,8-DIBROMOPYRENES, (1) and (2), are apparently well characterised,^{1,2} and are reported to have m.p. 221—222 and 176—177°, respectively. Recently doubt has been cast on the homogeneity of the isomer of lower m.p.³ We have found that the crude less soluble '1,6-dibromide' described in the literature



can be separated by fractional crystallisation into two components, each with characteristic i.r. and ¹H n.m.r. spectra. The crude more soluble 'dibromide' is a mixture of mono-, di-, and tri-bromopyrenes from which we were unable to isolate any pure component. The two pure dibromopyrenes were also isolated from the bromination products of 1-bromopyrene.

Structures can be assigned to the pure dibromopyrenes from their n.m.r. spectra (220 MHz). The isomer of m.p. 210—211° must be 1,8-dibromopyrene (2). Its spectrum shows two singlets (area one unit each) due to protons 4 and 5 and protons 9 and 10, respectively, and an AB quartet (total area two units) due to the 2-, 3-, 6-, and 7-protons. The spectrum of the isomer of m.p. 230—231° is more complex (see

Experimental section); we interpret this as two overlapping AB quartets of equal total intensity. This leads to the assignment of structure (1) (1,6-dibromopyrene) and to coupling constants $J_{2,3}$ 8.4 and $J_{4,5}$ 9.6 Hz. These coupling constants fall into the ranges ($J_{2,3}$ 8—8.4 and $J_{4,5}$ 9.2—9.5 Hz) found for a series of 1-substituted pyrenes.⁴ In the spectrum⁴ of 1-bromopyrene the 10-proton signal appears at lower field than that of the 2-proton and the line positions which we assign to the spectra of the dibromopyrenes are in accord with this influence of a 1-bromo-group.

Further bromination of either dibromopyrene gave the same 1,3,6-tribromo-pyrene, m.p. 271—272°. Clar⁵ isolated this tribromide by direct bromination of pyrene and reported m.p. 259—260°. His product was probably not absolutely pure since we find (mass spectral analysis) that removal of the last traces of di- and tetra-bromide is difficult.

EXPERIMENTAL

¹H N.m.r. spectra were determined for solutions in [²H₆]dimethyl sulphoxide at 146° to overcome solubility difficulties (Varian HR-220 instrument). Hexamethyldisilane was used as internal lock. The line positions are quoted in τ values, obtained by combining the data recorded with the average τ values obtained at 60° in [²H₆]dimethyl sulphoxide with a 100 MHz instrument. Mass spectra (A.E.I. MS902 instrument) were used to monitor the separation of polybromopyrenes.

Dibromopyrenes.—(a) Bromine (10 ml) in carbon tetrachloride (500 ml) was added during 5 h with stirring to a

⁴ R. H. Martin, N. Defay, F. Geerts-Evard, and H. Figeys, *Bull. Soc. chim. Belges*, 1964, **73**, 199; R. H. Martin, R. Flam-mang, and M. Arbaoui, *ibid.*, 1965, **74**, 418.

⁵ E. Clar, *Ber.*, 1936, **69**, 1671.

¹ G. Lock, *Ber.*, 1937, **70**, 926.

² H. Vollmann, H. Becker, M. Corell, and H. Streeck, *Annalen*, 1937, **531**, 1.

³ M. de Clercq and R. H. Martin, *Bull. Soc. chim. belges*, 1955, **64**, 367.

solution of pyrene (20 g) in carbon tetrachloride (500 ml). The precipitate (14 g) was collected after 12 h and resolved by fractional crystallisation from toluene into two components. The less soluble 1,6-dibromopyrene (1) crystallised as needles (from toluene or benzene-hexane), m.p. 230—231° (Found: C, 53.3; H, 2.2; Br, 44.8. $C_{16}H_8Br_2$ requires C, 53.4; H, 2.2; Br, 44.4%), τ (a) 1.49 (d, H-5 + H-10), (b) 1.54 (d, H-2 + H-7), (c) 1.62 (d, H-4 + H-9), and (d) 1.67 (d, H-3 + H-8), $J_{2,3}$ 8.4, $J_{4,5}$ 9.6 Hz; the upfield line from doublet (a) coincides, at 220 MHz, with the downfield line from doublet (b) so that (a) + (b) appears as a triplet; similarly (c) + (d) appears as a triplet. The more soluble 1,8-dibromopyrene (2) crystallised from benzene-hexane as needles, m.p. 210—211° (Found: C, 53.1; H, 2.1; Br, 45.0%), τ 1.40 (s, H-9 + H-10), 1.52 (d, H-2 + H-7), 1.65 (d, H-3 + H-6), 1.70 (s, H-4 + H-5), $J_{2,3}$ 8.5 Hz; there are no line coincidences at 220 MHz. The two dibromopyrenes show different i.r. spectra (CS_2). Evaporation of the original reaction filtrate gave a solid (15 g) from which small quantities only of the foregoing two dibromides could be separated.

(b) 1-Bromopyrene (8 g) in carbon tetrachloride (250 ml) was treated with bromine (3.3 g) in carbon tetrachloride (100 ml) and the product was worked up as in (a) to yield the same two dibromopyrenes.

1,3,6-Tribromopyrene.—(a) Bromine (24 g) in carbon tetrachloride (100 ml) was added to a solution of pyrene (10 g) in carbon tetrachloride (400 ml) and the mixture was stirred at room temperature for 4 days. The precipitate (18 g), m.p. 210—230°, was collected and extracted with boiling carbon tetrachloride and the residue was recrystallised many times from toluene. The final product (7.5 g), m.p. 271—272°, was shown by mass spectroscopy to be 1,3,6-tribromopyrene contaminated with traces of dibromo- and tetrabromo-pyrenes (Found: C, 43.6; H, 1.6; Br, 54.7. Calc. for $C_{16}H_7Br_3$: C, 43.8; H, 1.6; Br, 54.6%).

(b) 1,8-Dibromopyrene (0.20 g) was dissolved in warm nitrobenzene (5 ml) and a solution of bromine (0.088 g) in nitrobenzene (1 ml) was added. After 12 h the precipitate (0.21 g) was collected (m.p. 258—272°) and crystallised from toluene to give 1,3,6-tribromopyrene, m.p. 265—270°. 1,6-Dibromopyrene (0.20 g) was brominated similarly to give a crude product (0.21 g; m.p. 260—275°) which crystallised from toluene to yield 1,3,6-tribromopyrene, m.p. 265—270°. The three samples of tribromopyrene showed identical i.r. spectra (KBr) and did not show mixed m.p. depression.

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