Novel Rearrangement of the 9*H*-Fluorene System into the 1*H*- and 3*H*-Fluorene Systems

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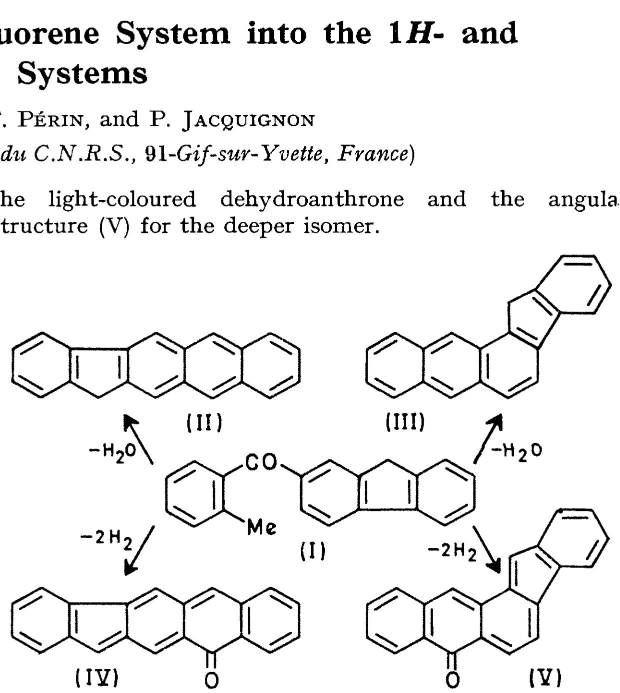
Summary Two dehydroanthrones, 11*H*-indeno[1,2-*b*]-anthracen-11-one and 7*H*-indeno[2,1-*a*]anthracen-7-one, have been obtained in the pyrolysis of 2-*o*-toluoylfluorene —a first example of a rearrangement of the ordinary 9*H*-fluorene system into the tautomeric 3*H*- and 1*H*-fluorene ones.

PYROLYSIS of 2-*o*-toluoylfluorene (I) at 380—390° and chromatographic separation (on silica column) of the pyrolysate showed that this Elbs reaction had produced four compounds: (i) two pentacyclic hydrocarbons $C_{21}H_{14}$ arising from normal dehydration, 13*H*-indeno[1,2-*b*]-anthracene (II), m.p. 319° (lit.,[1] 319°) and 13*H*-indeno[2,1-*a*]anthracene (III), m.p. 250°; and (ii) two oxygen-containing compounds $C_{21}H_{12}O$, one of them gold-yellow, m.p. 246° (absorption bands in the visible region at 406, 432, and 459 cm^{-1}), and the other crimson, m.p. 205° (bands in visible at 403, 413, 466, and 520 cm^{-1}), resulting from dehydrogenation of (I). To these isomeric dehydroanthrones we assign the 11*H*-indeno[1,2-*b*]anthracen-11-one (IV) and 7*H*-indeno[2,1-*a*]anthracen-7-one (V) structures, on the grounds of n.m.r. spectroscopy in C_6D_6 (which showed the absence of methylene protons), mass spectrometry (for both compounds, base peak *m/e* 280, and fragmentation pattern characteristic of anthrones, *i.e.* loss of carbon monoxide, to give the peak *m/e* 252), and their deep-violet halochromism in sulphuric acid indicative of highly conjugated cyclic ketones.[2] The known differences in absorption spectra between the linear and the angular dibenzofluorenones[2] suggest the linear structure (IV) for the light-coloured dehydroanthrone and the angular structure (V) for the deeper isomer.



Compounds (IV) and (V) are derivatives of, respectively, 3*H*- and 1*H*-fluorene, the hitherto unknown tautomers of fluorene itself, and their isolation demonstrates for the first time the formation of dehydroanthrones in Elbs reactions,[3] and the possibility of rearrangements of the double-bond system of 9*H*-fluorene in which the central methylene group is involved and of which the driving force is the tendency to undergo total conjugation.

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[1] E. de Barry Barnett, N. F. Goodway, and J. W. Watson, *Ber.*, 1933, **66**, 1876; O. Kruber, *ibid.*, 1937, **70**, 1556.

[2] *Cf.* R. H. Martin, *J. Chem. Soc.*, 1941, 679; *Helv. Chim. Acta*, 1947, **30**, 620; G. M. Badger, *J. Chem. Soc.*, 1941, 535.

[3] Anthrones have recently been found to be formed regularly in Elbs reactions: N.P. Buu-Hoï, C. Marie, and P. Jacquignon, *Bull. Soc. chim. France*, 1970, 1012.