Thermal Valence-bond Isomerisation of an Aromatic Compound to its *para*-Bonded Form; Preparation of Hexakis(pentafluoroethyl)bicyclo[2,2,0]hexa-2,5-diene

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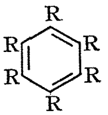
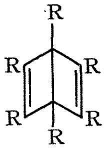
Summary A *para*-bonded valence isomer (Dewar benzene) (IIb) has been prepared for the first time by pyrolysis of the corresponding aromatic compound (Ib), thus affording a ready, quantitative route to (IIb).

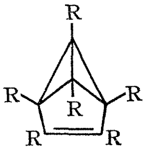
THE photolysis of hexakis(trifluoromethyl)benzene (Ia) in perfluoro-n-pentane solution[1] or, more recently, in the gas phase[2] has been reported to give mixtures of the three valence isomers of (Ia), *viz.* the Dewar or *para*-bonded benzene (IIa), the benzvalene (IIIa), and the prismane (IVa). Prolonged photolysis of hexakis(pentafluoroethyl)-benzene (Ib) in solution gives high yields of the prismane (IVb) or the *para*-bonded benzene (IIb) depending on the conditions used.[1,3]



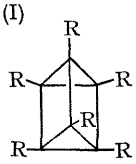
(I)



(II)



(III)



(IV)

a; R=CF_3
b; R=C_2F_5

It has now been found that when (Ib) is subjected to flow pyrolysis at low pressure (*ca.* 1 mm. Hg) in platinum at 400° with a contact time of 1 sec. or less, followed by rapid freezing, it is quantitatively converted into the *para*-bonded benzene (IIb) which is uncontaminated (n.m.r. spectroscopy) by other isomers.

Hexakis(pentafluoroethyl)bicyclo[2,2,0]hexa-2,5-diene (IIb), m.p. 122—124° (sealed tube), is a waxy white solid which readily sublimes. It has ν_{max} 1665 cm.$^{-1}$ (C:C str.) and its mass spectrum exhibits an intense molecular ion. The ^{19}F n.m.r. spectrum (relative to external $CF_3\cdot CO_2H$ in C_6F_6) shows two absorptions for the CF_3 groups at +1·3 (6F) and +5·4 p.p.m. (12F), and two areas of absorption for the CF_2 groups at +26·0 (4F) and +34·5 p.p.m. (8F; AB system, J_{AB} 266 Hz, F_A +33·0 and F_B 36·0 p.p.m.).

The *para*-bonded benzene (IIb) reverts quantitatively to its aromatic isomer (Ib) when heated in a sealed tube at 140° for 65 hr. The reversal of the order of the thermodynamic stability of the two isomers with increase in temperature is presumably due to the decreased barrier to the rotation of the pentafluoroethyl groups in the *para*-bonded benzene (IIb). Studies are in progress on other highly substituted fluoro-aromatic systems to determine the scope of this novel isomerisation.

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[1] M. G. Barlow, R. N. Haszeldine, and R. Hubbard, *Chem. Comm.*, 1969, 202.
[2] D. M. Lemal, J. V. Staros, and V. Austel, *J. Amer. Chem. Soc.*, 1969, **91**, 3373.
[3] M. G. Barlow, R. N. Haszeldine, and R. Hubbard, unpublished results.