Individual Synthesis of Rotameric (±) and *meso* Forms of a Triptycene Derivative[1]

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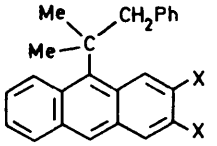
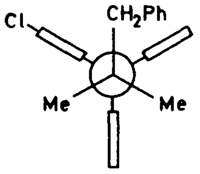
Summary Rotameric (±) and *meso* isomers of a triptycene derivative were prepared separately and the barrier to their interconversion was obtained as 33·6 kcal mol.$^{-1}$

A POSSIBILITY of the separate synthesis of (±) and *meso* forms of a compound, in which rotation about an sp^3–sp^3 carbon bond is frozen, was suggested by a report that

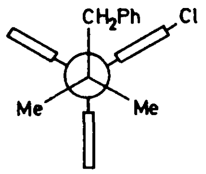
Diels–Alder reactions between dimethyl acetylenedicarboxylate and 9-(1,1-dimethyl-2-phenylethyl)anthracene derivatives (**1** and **2**) give (±) isomers only.[2] The entering dienophile approaches the anthracene derivative from the least-hindered side. Thus reaction between benzyne and (**1**) would give a (±) form (**3** and **3′**), whereas that between 4,5-dichlorobenzyne and (**2**) gives a *meso* form (**4**).



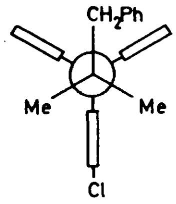
(1) X = Cl
(2) X = H



(3)



(3′)



(4)

Compound (**1**)[2] treated with benzyne,[3] generated *in situ* from anthranilic acid and isoamyl nitrite, afforded an adduct, m.p. 215·5—216·5° (83%). The n.m.r. spectral features are consistent with the (±) form (**3** and **3′**). None of the other signals attributable to the *meso* form were found.

A similar reaction between (**2**) and 4,5-dichlorobenzyne afforded another adduct, m.p. 200—201° (90%); the n.m.r. spectral data are compatible with the *meso* isomer (**4**). No other product was detected in the reaction products.

A partial explanation of this remarkable stereoselectivity derives from the conformation of the anthracene derivatives (**1** and **2**). The ^{1}H n.m.r. spectrum of the anthracene (**2**) showed 1,8-proton signals at *ca.* 8·0 p.p.m. which are at a higher field by *ca.* 0·4 p.p.m. than those of 9-t-butylanthracene. This implies that the benzyl group is folded so that the 1,8-protons are shielded by the benzene ring. Approach of the dienophile from the benzyl side is thus hindered.†

The rotamers were found to be extremely stable: no isomerisation or decomposition occurred on heating (179°) for 60 h under reflux in *o*-dichlorobenzene. However, *meso* → (±) isomerisation occurred on heating in 1-chloronaphthalene at 211°, $E_A = 33{\cdot}6$ kcal mol^{-1}, $A = 10^{11.7}$ s^{-1}, respectively, $K = 2{\cdot}0$.

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† Rotation about the C(9)–C bond is not considered to be frozen since restricted rotation involving the t-butyl groups attached to an aromatic ring has not been reported and no anomalies in the n.m.r. spectra are observed. The predominance of the said conformation can account for the stereoselectivity to some extent.

[1] For preceding papers in this series see: F. Suzuki and M. Ōki, *Tetrahedron Letters*, in the press.

[2] M. Ōki and G. Yamamoto, *Chem. Letters*, 1972, 45; G. Yamamoto and M. Ōki, *ibid.*, 1974, 67.

[3] L. F. Fieser, 'Organic Experiments.' D. C. Heath, Boston, 1964, pp. 315—317.