The Conformation of Unsaturated Cyclodecane Derivatives. Evidence from Absence of Transannular Hydride Shifts

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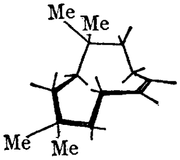
ONE of the features characteristic of medium ring compounds is that certain of their reactions involve transannular hydride shifts.[1] Processes known to proceed in this manner include, *e.g.*, the acid-catalysed hydrolysis of *cis*- and *trans*-1,2-epoxycyclodecane which gives the 1,6-diols together with other "non-classical" products;[2] similarly, ammonolysis of *cis*-1,2-epoxycyclodecane affords a mixture of bicyclic alcohols.[3] Again, bromine addition to *cis*- and *trans*-cyclodecene gives, respectively, *cis*- and *trans*-1,6-dibromocyclodecane rather than the vicinal dibromides.[4]



Suggested conformation of 5,5,8,8-*tetramethyl-*cis-*cyclodecene* (I).

We now report that in the case of 5,5,8,8-tetramethyl-*cis*-cyclodecene (I)[5] and the corresponding *cis*-epoxide (II)[5] these reactions *proceed smoothly to give the classical products.* Thus, acid-catalysed hydrolysis of (II) affords, in good yield, 5,5,8,8-tetramethylcyclodecane-*trans*-1,2-diol, m.p. 128–129° (ν_{OH} 3629, 3585 cm.$^{-1}$; very dilute CCl_4), identical with the vicinal diol obtained from 5,5,8,8-tetramethyl-*trans*-cyclodecene[5] by reaction with osmium tetroxide. Significantly, the corresponding *trans*-epoxide (III)[5] on acid hydrolysis gives no trace of vicinal diol (absence of bonded hydroxyl band in the 3μ region in the spectrum of a very dilute solution of the crude product). Ammonolysis of (II) gave a high yield of 5,5,8,8-tetramethyl-*trans*-2-aminocyclodecanol, m. p. 108–109° (ν_{OH} 3630 cm.$^{-1}$, 3498 cm.$^{-1}$, very dilute C_2Cl_4), identical with one of the stereoisomeric 2-amino-alcohols obtained by the catalytic reduction of 5,5,8,8-tetramethyl-2-hydroxycyclodecanone oxime.[5] Again, addition of bromine to (I) gives a good yield of 5,5,8,8-tetramethyl-*trans*-1,2-dibromocyclodecane, m. p. 83–84° (liberates iodine from potassium iodide solution).

The unusual character of the olefin (I) is also apparent from the fact, reported by us recently,[6] that it possesses an extremely high enthalpy of hydrogenation (28·7 kcal.mole^{-1} as compared with 20·7 kcal.mole^{-1} for *cis*-cyclodecene). The occurrence of transannular reactions (in compounds such as *cis*-cyclodecene) is a consequence of the close proximity of atoms lying on opposite sides of the ring; the absence of transannular hydride shifts in (I) and (II) leads us to suggest that the double bond in (I) and the epoxide moiety in (II) are, unlike in the corresponding derivatives of cyclodecene itself,[7] pushed far out away from the methylene chain on the "opposite" side of the ring.

These considerations, together with the fact that the four-carbon methylene chain joining the two gem-dimethyl groups will tend to exist in a near-to-staggered conformation with the methyl groups held in extra-annular positions, greatly restricts the number of possible conformations and the arrangement of the type shown schematically in the Figure is tentatively suggested for the carbon skeleton of (I).

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[1] Reviews: Sicher, in "Progress in Stereochemistry," Part 3, (ed. de la Mare and Klyne), Butterworth, London, 1962; Prelog and Traynham, in "Molecular Rearrangements" (ed. de Mayo), Wiley-Interscience, New York, 1963.

[2] Prelog and Schenker, *Helv. Chim. Acta*, 1952, **35**, 2044.

[3] Fanta, private communication.

[4] Závada and Sicher, *Proc. Chem. Soc.*, 1961, 199; Sicher, Závada, and Svoboda, *Coll. Czech. Chem. Comm.*, 1962, **27**, 1927.

[5] All new compounds gave satisfactory elemental analyses; their synthesis will be reported subsequently.

[6] Goebel, Sicher, Svoboda, and Turner, *Proc. Chem. Soc.*, 1964, 237.

[7] We have earlier suggested[6] that cyclodecene probably has a conformation essentially similar to that established by *X*-ray for the saturated hydrocarbon (Huber-Buser and Dunitz, *Helv. Chim. Acta*, 1961, **44**, 2027; Dunitz and Venkatesan, *ibid.*, p. 2033; Dunitz and Weber, *ibid.*, 1964, **47**, 951; Nowacki and Mladeck, *Chimia* (*Basel*), 1961, **15**, 631).