Conformational Preference of the Oxiran Group in Cyclohexanespiro-oxiran

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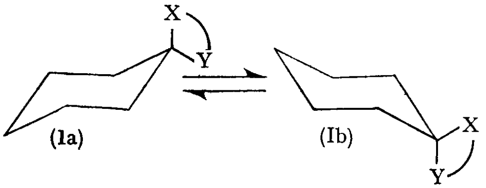
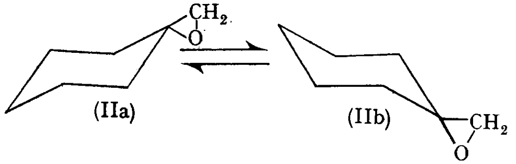
DESPITE the many functional groups whose conformational free energies ($-\Delta G_x^\circ$) have been determined by various chemical and physical techniques,[1] little is known of the conformational rivalries present in spiro systems of the type (I). The only spiro systems studied were a series of hemithioketals in which oxygen exhibited a slight preference over sulphur for the equatorial position.[2]

Whilst studying the stereochemistry of the epoxidation of methylenecyclohexanes,[3] we required an estimation of the conformational preference of the oxiran group in cyclohexanespiro-oxiran (II). Subsequent to the completion of our study, Uebel has reported a determination of the conformational preference of (II) by a kinetic method using model compounds and obtained results which indicated conformer (IIb) to be the more stable by 0·15 ± 0·1 kcal./mole.[4] We now report the direct measurement of the conformational preference of the oxiran group in (II) by low temperature n.m.r. studies.†

At room temperature the methylene protons of the oxiran group of (II) appear as a sharp singlet at δ 2·39. When a solution of (II) in carbon disulphide is cooled, the absorption for these protons gradually broadens and at −85 ± 2° the coalescence temperature is reached. Further cooling leads to the separation of the signal into two overlapping peaks separated by *ca.* 5 c./sec., the broader peak at higher field corresponding to conformer (IIa).[3] Measurement of the areas under each peak by graphical methods and calculation of -Δ*G*° by the usual method gave the results summarized in the Table indicating that conformer (IIb) is the more stable by 0·27 ± 0·04 kcal./mole.


(Ia) (Ib)


(IIa) (IIb)

TABLE

-ΔG° *Values for equilibrium* (IIa) ⇌ (IIb)

(±0·04 kcal./mole)

Temperature (±2°)	-Δ*G*°(kcal./mole)
− 94°	0·26
− 99°	0·27
−104°	0·27

This value for -Δ*G*° is considerably smaller than would be expected if the difference in conformational free energies of the -CH_2OH (-Δ*G*° = 1·4)[5] and -OMe (-Δ*G*° = 0·60)[1] groups were used as models for (II). These systems do not provide good models for (II) because in this compound neither of the substituents occupy true axial or equatorial positions. The "axial" substituent is bent downward from a true axial position by *ca.* 30° and the equatorial substituent is similarly bent upward from a true equatorial position. The hydrogens of the methylene group in conformer (IIa) are thus much farther from the *syn*-diaxial protons of the cyclohexane ring than in a molecule such as cyclohexylmethanol in which the -CH_2OH group is in a true axial position.

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† The n.m.r. spectra were determined on a Varian **HA-100** instrument equipped with a variable temperature probe.

[1] For a recent summary see J. A. Hirsch in "Topics in Stereochemistry", ed. N. L. Allinger and E. L. Eliel, Interscience, New York, vol. I, 1967, pp. 199—222.

[2] (a) E. L. Eliel and L. A. Pilato, *Tetrahedron Letters*, 1962, 103; (b) M. P. Meres, *J. Org. Chem.*, 1963, **28**, 2320; (c) E. L. Eliel, E. W. Della, and M. Rogic, *J. Org. Chem.*, 1965, **30**, 855.

[3] R. G. Carlson and N. S. Behn, *J. Org. Chem.*, 1967, **32**, 1363.

[4] J. J. Uebel, *Tetrahedron Letters*, 1967, 4751.

[5] G. W. Buchanan and J. B. Stothers, *Chem. Comm.*, 1967, 1250.