Ring Inversion in Spiro-compounds. Dioxaspiro[2,5]octanes

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Summary Attaching a three-membered ring to a six-membered ring in a spiro-fashion produces a marked reduction in the barrier to inversion of the six-membered ring.

IT was recently shown[1] that the barrier to chair–chair interconversion of dioxan rings with attached spiro-rings (Ia—e), increases slightly as the spiro-ring decreases from eight- to four-membered. By contrast, it is known that the barrier to ring inversion of methylenecyclohexane (II), which may be considered formally as a spiro[1,5]heptane, is 2·5 kcal/mole lower than that of its parent cyclohexane.[2] The barriers to inversion of spiro[2,5]octanes (a cyclopropane ring attached spiro-fashion to a six-membered ring) are therefore of interest. Compounds (III)—(V) were prepared from the corresponding diol.[3] The barriers to ring inversion of these compounds as determined by n.m.r. spectroscopy are compared with reference compounds in the Table. The effect of the cyclopropane ring is the reverse of that of a cyclobutane *i.e.* the barrier to chair–chair interconversion is lowered.

The low barrier to ring inversion of methylenecyclohexane has been attributed[2] to reduced non-bonded interactions during rotation around the C-1–C-2 and C-1–C-6 bonds. This finds an analogy in the barrier to methyl-group rotation in propene (1·98 kcal/mole[4]) compared with propane (3·55 kcal/mole). The barrier to methyl-group rotation in methylcyclopropane is 2·86 kcal/mole,[4] about 1 kcal/mole lower than the barrier in its acyclic analogue, 2-methylpropane. It is thus possible to attribute the low barrier found in (III), (IV), and (V) to reduced repulsive nteractions between non-bonded hydrogen atoms in the transition state.

Ring inversion of compounds (III), (IV), and (V), *and reference compounds*

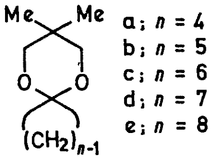
Compound	Solvent	$\delta\nu_{AB}$[a]	J_{AB}[b]	T_c[c]	$\Delta G^{\ddagger}$[d]
(III)	CH_2Cl_2	79·5	11·1	−71	9·3
(VI)	CH_2Cl_2	18·8	10·8	−54	10·5
(IV)	CH_2Cl_2	121·1	11·4	−83	8·6
(Ib)	CH_2Cl_2	20·3	10·9	−78·5	9·3
(V)	CF_2Cl_2	119·2	11·2	−80	8·7
(Ia)	CF_2Cl_2	15·1	10·7	−83·5	9·2

[a] The relative chemical shift of the O–CH_2–C hydrogens at low temperature (Hz at 100 MHz operating frequency).

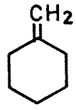
[b] Hz.

[c] Coalescence temperature.

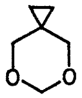
[d] Free energy of activation for ring inversion at the coalescence temperature (kcal/mole). Estimated error ±0·3 kcal/mole.



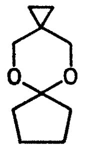
(I)



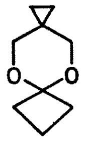
(II)



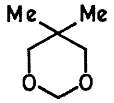
(III)



(IV)



(V)



(VI)

It seems that in both this series and in the series (I) where changes in barriers to inversion are small, while there are no doubt substantial changes in internal bond-angle in the dioxan ring, there is no reaon to invoke a substantial effect of bond-angle strain on barriers to inversion. It is not excluded that other factors are masking such an effect by changing barriers in the opposite sense but for the moment it appears that Allinger's calculation[5] of the contribution of bond-angle strain in the transition state, to the barrier to inversion of six-membered rings, 2 kcal/mole, is a better estimate than Hendrickson's, 4·1 kcal/mole.[6]

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[2] J. T. Gerig, *J. Amer. Chem. Soc.*, 1968, **90**, 1065; F. R. Jensen and B. M. Beck, *ibid.*, p. 1066.

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[4] A review of such barriers with references for the sources of individual values is given by J. P. Lowe, *Progr. Phys. Org. Chem.*, 1968 **6**, 1.

[5] N. L. Allinger, M. A. Miller, F. A. van Catledge, and J. A. Hirsch, *J. Amer. Chem. Soc.*, 1967, **89**, 4345.

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