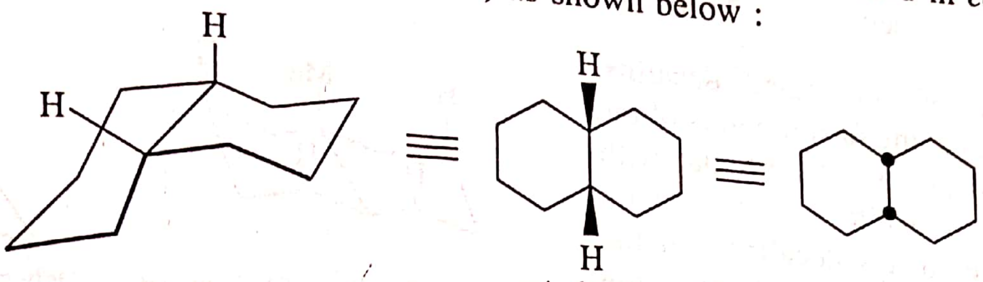
Thus, the β-anomer is more stable than the α-anomer, and so it predominates in the equilibrium mixture.

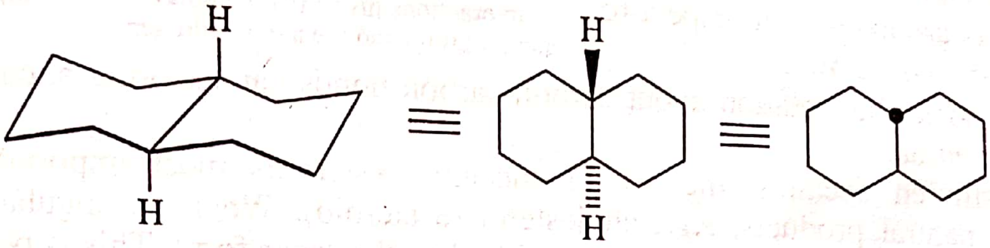
2.29 CONFORMATIONS OF FUSED RINGS : DECALINS

Decalin (bicyclo[4,4,0]decane) exists in two diastereoisomeric forms *cis* and *trans* decalins, depending on the way in which the two cyclohexane rings are fused together. In both the diastereoisomers of decalin, the two cyclohexane rings are joined together in the chair conformation.

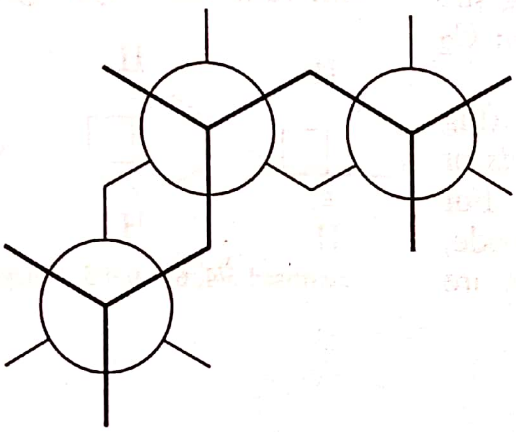
Since the decalin is analogous to a 1,2-disubstituted cyclohexane, in the *cis* isomer the two cyclohexane rings are fused together in *ea* form (*i.e.*, the equatorial bond of one ring is fused with the axial bond of the other), while in the *trans* isomer the two rings are fused in *ee* form (*i.e.*, each ring is fused with other ring by equatorial bonds) as shown below :



cis-decalin

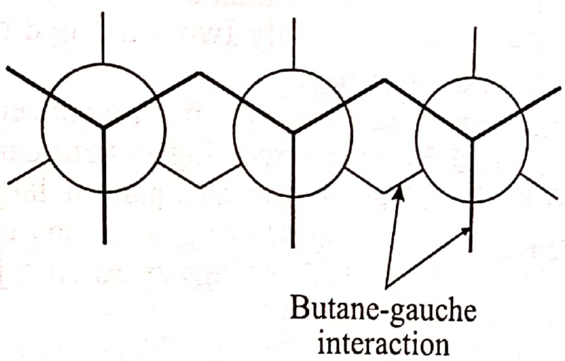


trans-decalin



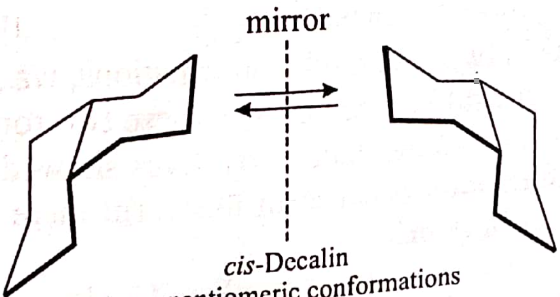
cis-Decalin

2.7 kcal/mole less stable
than the *trans*-isomer
has three more gauche, butane-
like interactions than *trans*-decalin



trans-Decalin

The *trans* decalin is more stable than the *cis* by 2.7 kcal/mole. Thus, *cis* decalin can be smoothly pyrolysed to the *trans* isomer irreversibly. In *cis*-decalin the ring fusion involves *ae* bonds, hence it is flexible and exists in two forms which are interconvertible as a result of conformational flipping similar to that of the chair conformation of monocyclic cyclohexane as shown below :

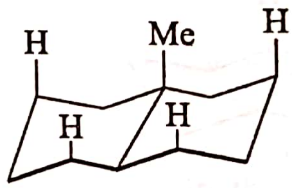


cis-Decalin
two enantiomeric conformations

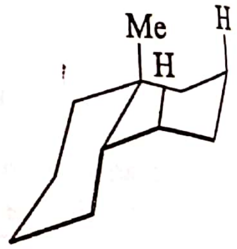
Since, *trans* decalin involves two equatorial bonds for the ring fusion, it is a rigid molecule and cannot undergo conformational flipping, *i.e.*, it cannot be converted into *aa* conformation which also does not exist in decalin type of fused-ring compounds.

Any substituent attached to the *cis* decalin system is free to adopt the equatorial orientation. *Cis* decalain is chiral in both the conformations which are nonsuperimposable mirror images of each other. Because of rapid interconversions of the two *cis* conformations, *cis* decalin exists as a nonresolvable enantiomeric pair. On the other hand, *trans* decalin has a centre of symmetry and is therefore, optically inactive.

In the case of substituted decalins, substituents located at the fusion points of the two rings (angular positions) are axial with respect to one ring, while equatorial with respect to the other in *cis* decalins. On the other hand, in the case of *trans* decalins the angular substituents are axial with respect to both the rings as shown below :



There are four sets of 1, 3-diaxial interactions involving the bulky methyl group and the axial hydrogens

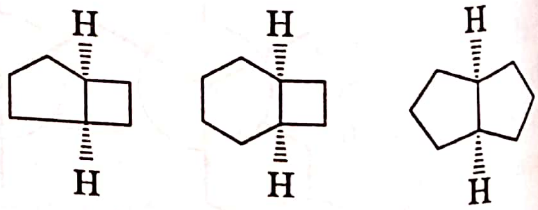


Only two sets of 1, 3-diaxial interactions with the methyl group

It should be noted that rotation about carbon-carbon bonds cannot bring about interconversions of *cis* and *trans* decalins.

Among substituted decalins, the 9-methyldecalin system is most important because of its presence in many natural products, *e.g.*, cholesterol (a steroid). When an angular methyl group is introduced, the *cis* form becomes slightly more stable than the *trans* form. This is because in the *trans* form the methyl group has 1,3-diaxial interaction (causing strain) with four axial hydrogens (on C_2, C_4, C_5 and C_7), while with only two axial hydrogens (on C_2 and C_4) in the case of *cis* isomer.

As far as other fused ring systems are concerned, the ring junction of a fused 5/6-membered ring system can have *cis* or *trans* stereochemistry and so can any pair of large rings. For smaller rings, *trans* 5/5- and 4/6-ring junctions can be made, with difficulty, but with smaller rings *trans* ring junctions are essentially impossible.



***cis*-fused 5/4, 6/4 and 5, 5 bicyclic rings**

2.30 CONFORMATIONS OF OTHER RINGS

Three membered rings must be planar, thus cyclopropane exists as a planar structu[re]. Cyclobutane is not planar. In cyclobutane the conformational eclipsing strain can be reli[eved to some] extent by deviation ...