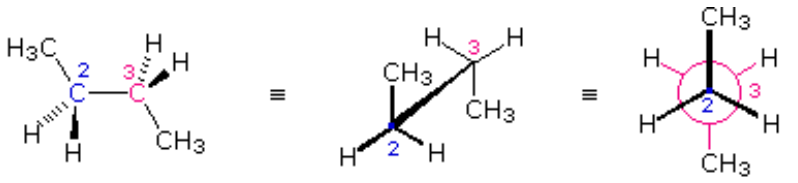
RECALL:
Isomers are compounds with the same molecular formula & a different arrangement of atoms in the molecule

- Structural (Constitutional) Isomers
- Stereoisomers
  - Diastereomers
  - Enantiomers

A molecular conformation is any spatial arrangement of atoms that can be interconverted by rotation about single bonds of the molecule

Conformation of Butane:

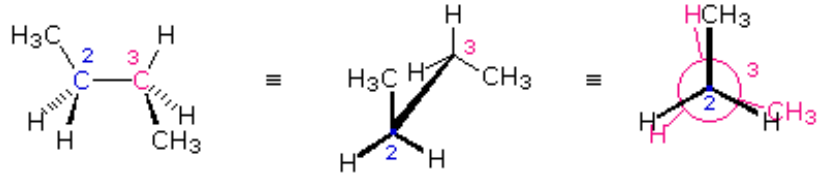
- Most stable (most populated conformation) is called anti and has groups as far away as possible
- Dihedral angle refers to angle between the two methyl groups

A 

Anti Conformation

Most stable, staggered

Dihedral angle = 180°

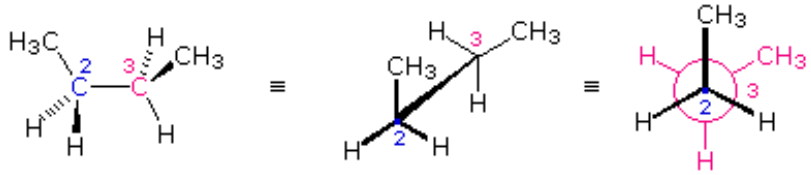
B 

Eclipsed Conformation

Dihedral angle = 120°

Repulsion = steric effect

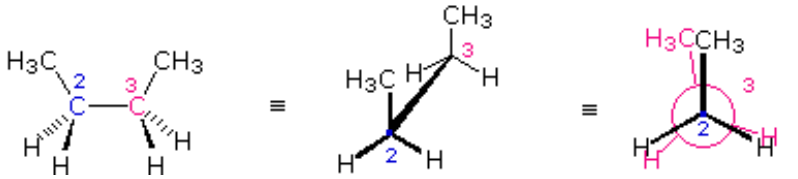
Not as stable as anti

C 

Gauche Conformation

Dihedral angle = 60°

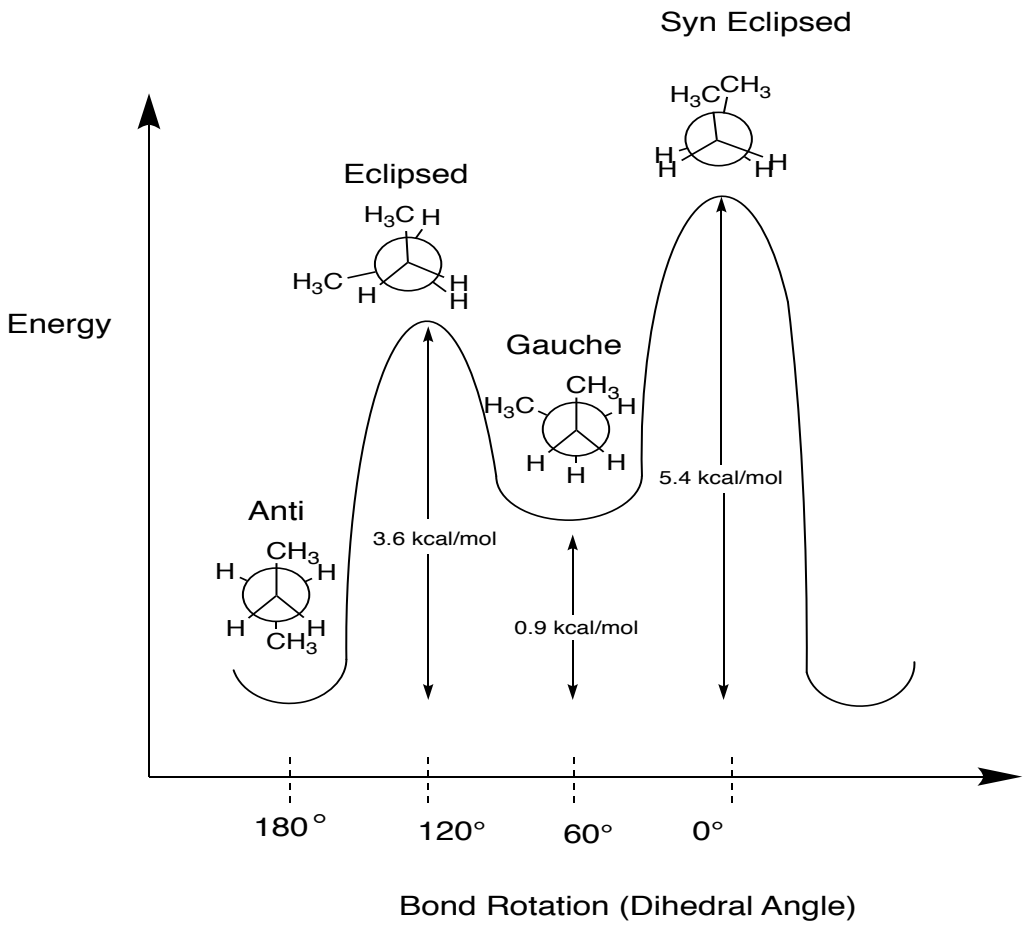
Least stable (syn) eclipsed

D 

Eclipsed Conformation

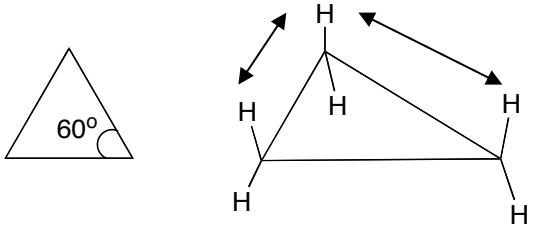
Dihedral angle = 0°

Butane Conformational Energy Diagram:

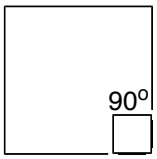


Cycloalkane Conformations:

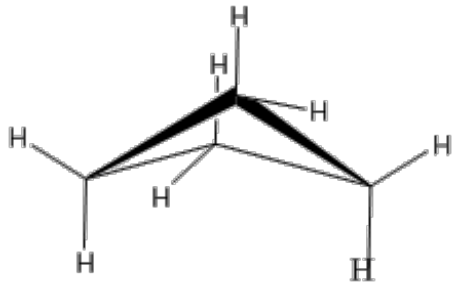
Cyclopropane –bond angle 60° – relatively rigid structure, very reactive



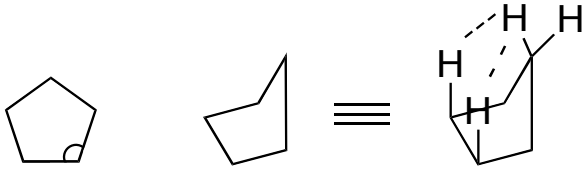
Cyclobutane – bond angle close to 90° – does have some flexibility



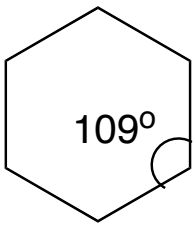
3D structure of cyclobutane:



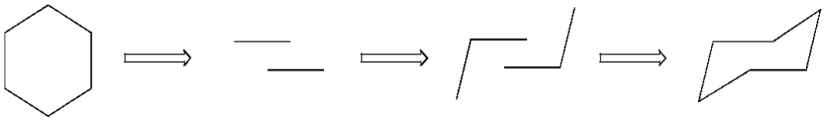
Cyclopentane – bond angles nominally 108° – more flexible than cyclobutane



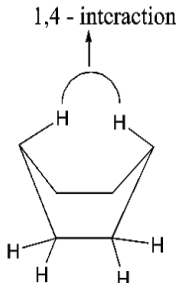
Cyclohexane – bond angles actually 109°, not 120° as in flat hexagon



Cyclohexane Conformations – How to draw:

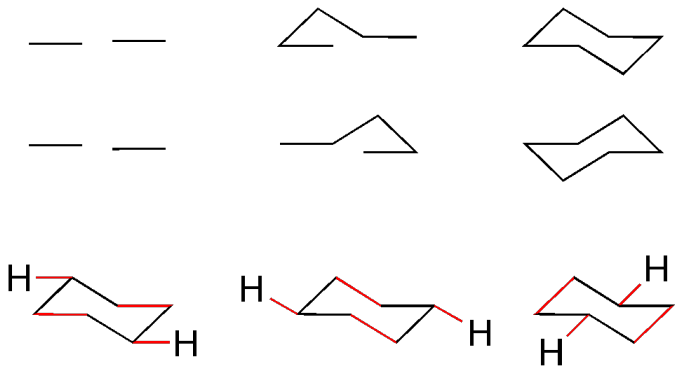


- Chair conformation (most stable)
- All adjacent hydrogen atoms are staggered

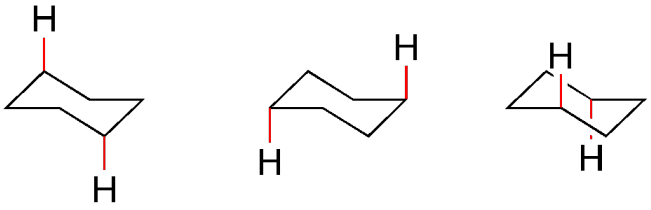


- Boat (least stable)
- many adjacent hydrogen atoms eclipsed
- 1,4 - interactions of two-hydrogens

Another way to draw cyclohexane:

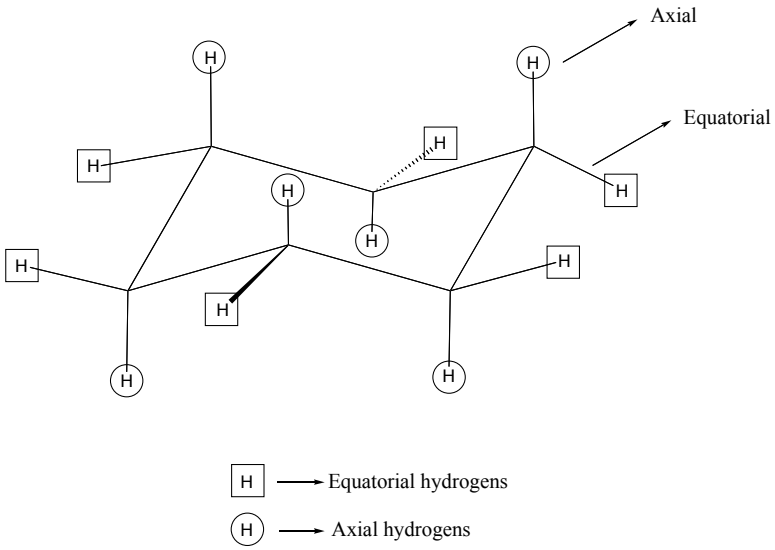


Parallel Lines in Equatorial Position

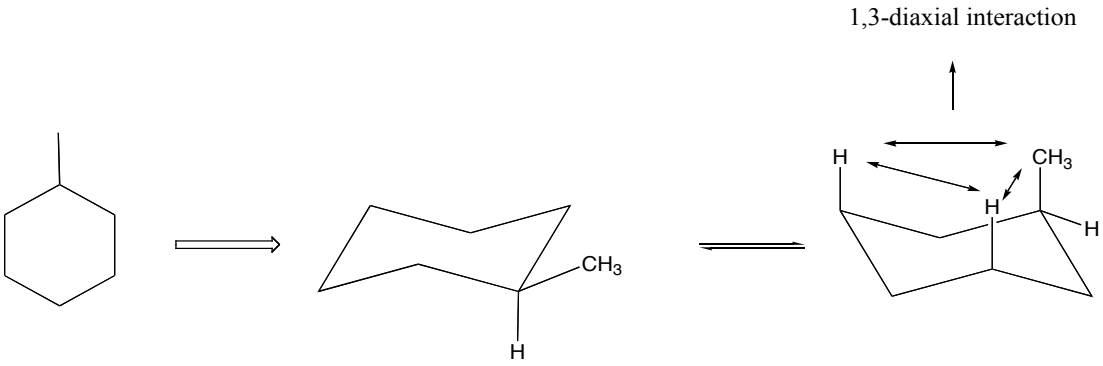


Vertical Lines in Axial Position

Cyclohexane Conformations Axial vs Equatorial Positions

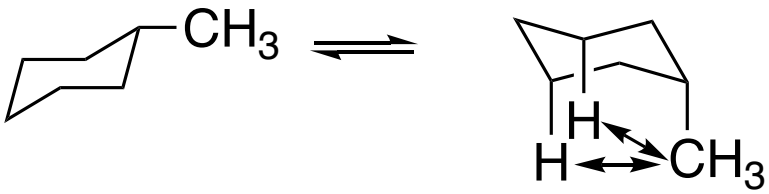


Substituted Cyclohexanes – Draw the most stable conformation



- Largest (bulkiest group close to ring) group placed equatorial – otherwise get unfavorable 1,3-diaxial interactions

- 1,3-diaxial interaction (steric effect) makes this conformation less stable.

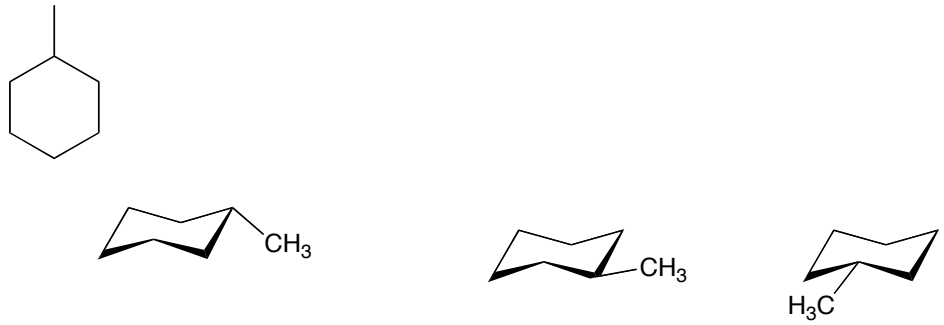


Equatorial methyl interaction
More stable

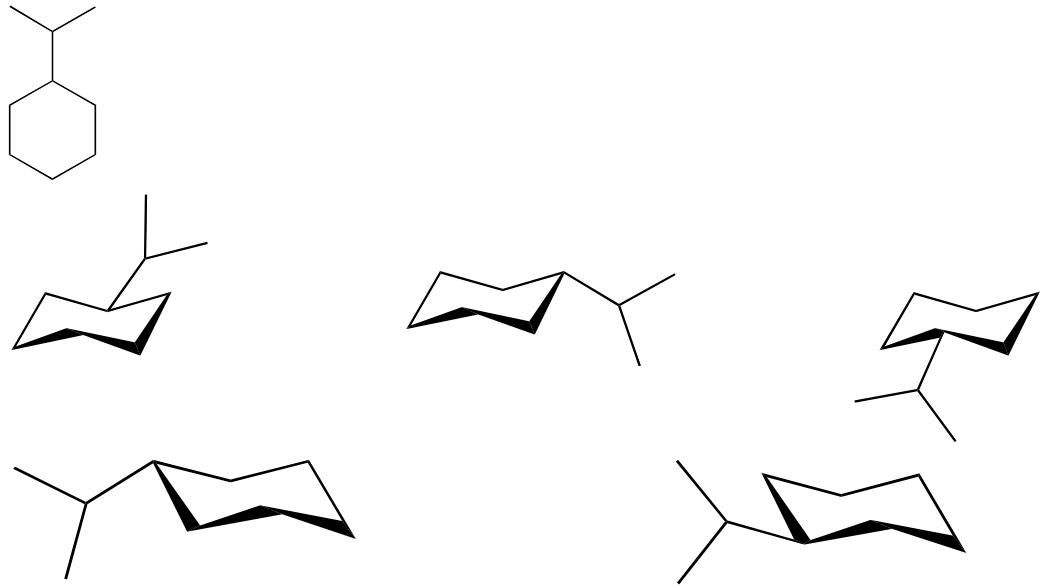
Axial methyl interaction
Less stable

Examples of Most Stable Conformation of Substituted Cyclohexanes :

1. Methylcyclohexane
   – 6 drawings of same molecule



2. Isopropylcyclohexane

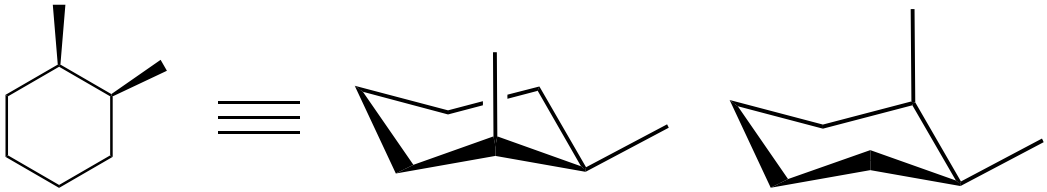


NB: For most stable conformation, largest group at equatorial position

Examples of Most Stable Conformation of Polysubstituted cyclohexanes:

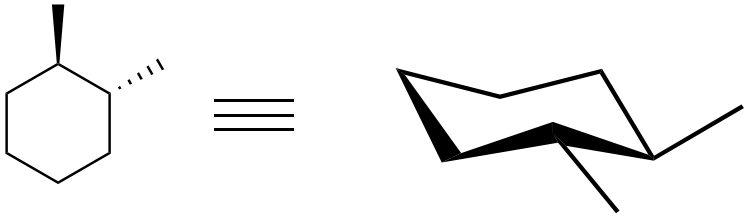
Examples:

1) cis-1,2-dimethylcyclohexane



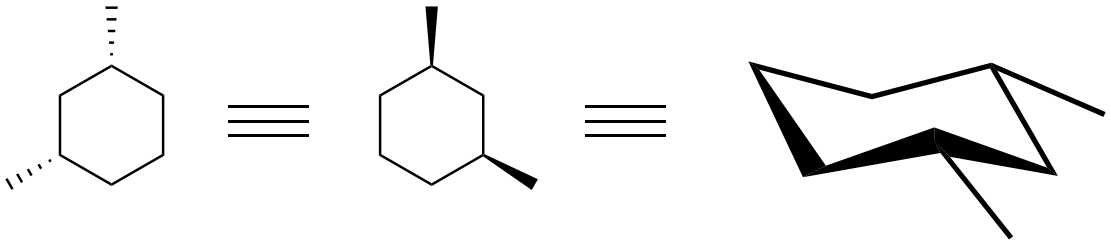
- One methyl group axial and one methyl group equatorial

2) trans-1,2-dimethylcyclohexane (a stereoisomer (diastereomer) of above structures)



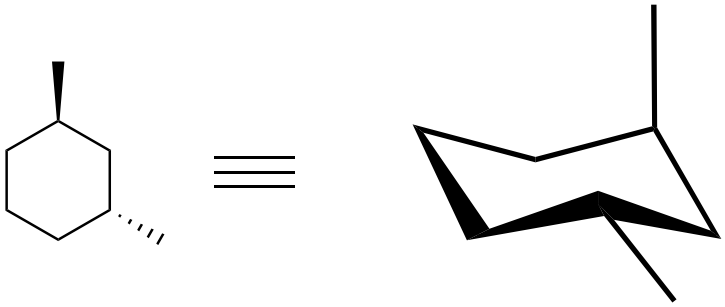
- Both methyl groups equatorial

3) cis-1,3-dimethylcyclohexane (a structural isomer of above structures)



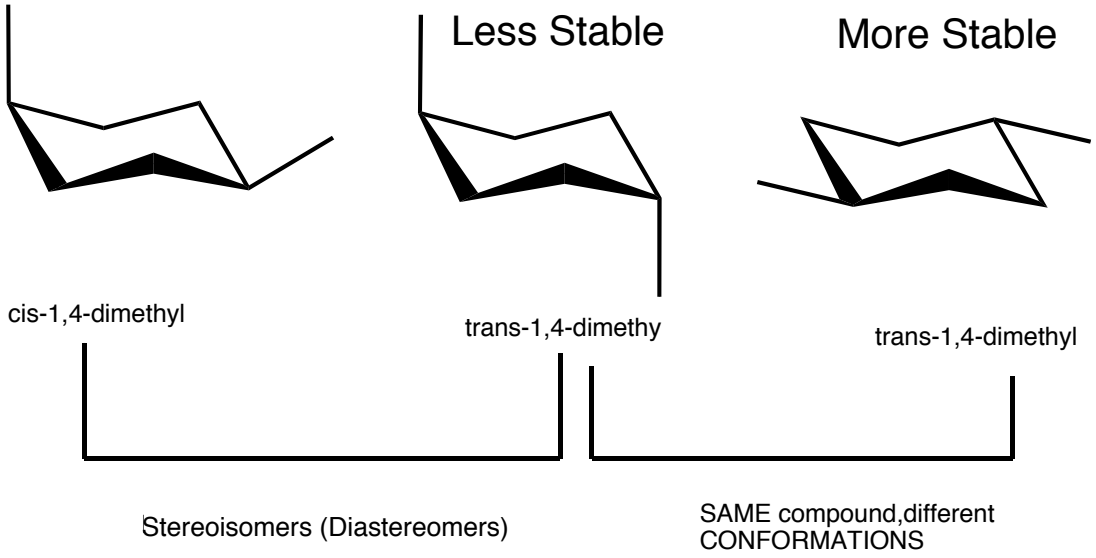
- Both methyl groups equatorial

4) trans-1,3-dimethylcyclohexane : a stereoisomer of above cis-1,3- dimethylcyclohexane

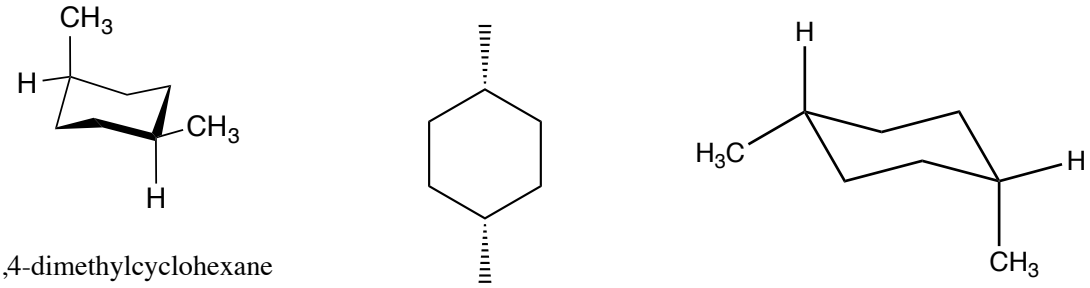


- One methyl group axial and one methyl group equatorial

5) cis-1,4-dimethylcyclohexane and trans-1,4-dimethylcyclohexane:

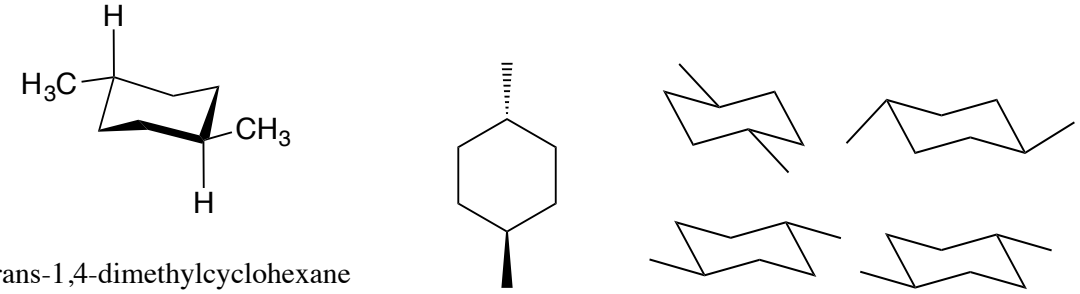


6) cis-1,4-dimethylcyclohexane:



cis-1,4-dimethylcyclohexane

7) trans-1,4-dimethylcyclohexane:

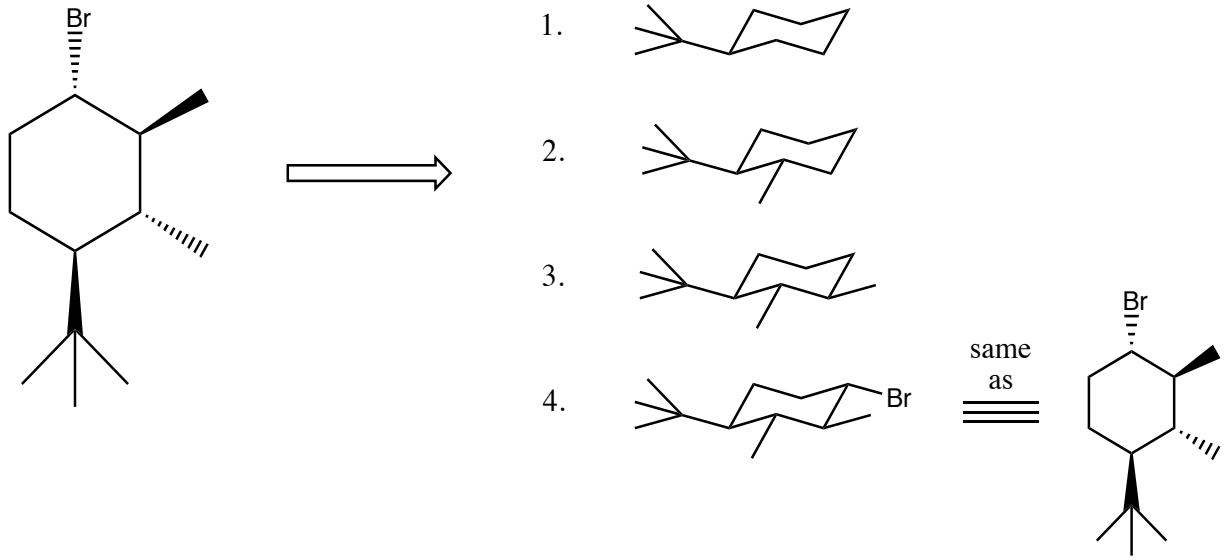


trans-1,4-dimethylcyclohexane

<u>How to draw the most stable conformation of substituted cyclohexanes:</u>

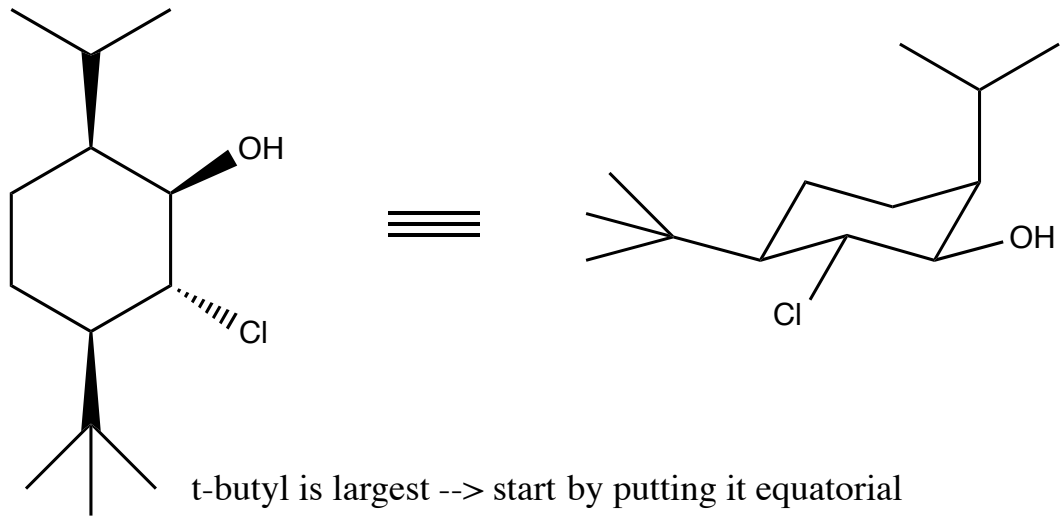
1. Start by drawing the chair conformation of cyclohexane
   Put the largest group in an equatorial position

2. Draw the next group(s) on the correct atom(s) with respect to the largest group in correct geometry



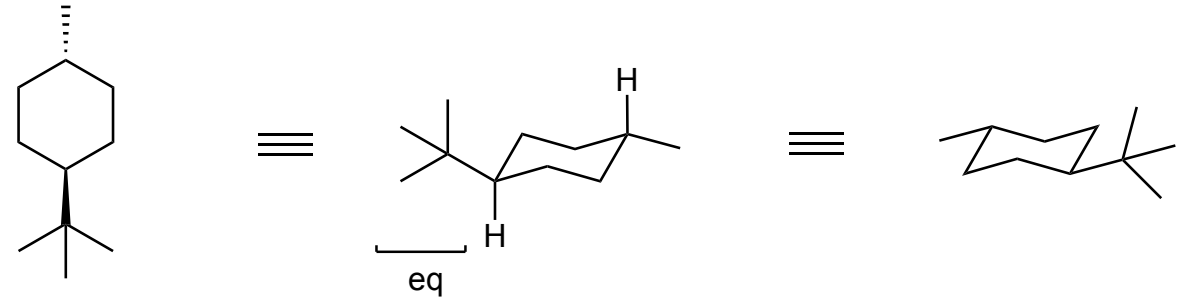
Note that the largest substituent (tertiary butyl) is placed in the equatorial position to avoid destabilizing 1,3-diaxial interactions

Another example:



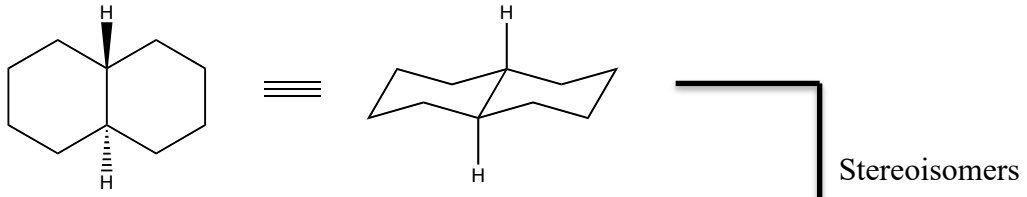
t-butyl is largest --> start by putting it equatorial

Another example:

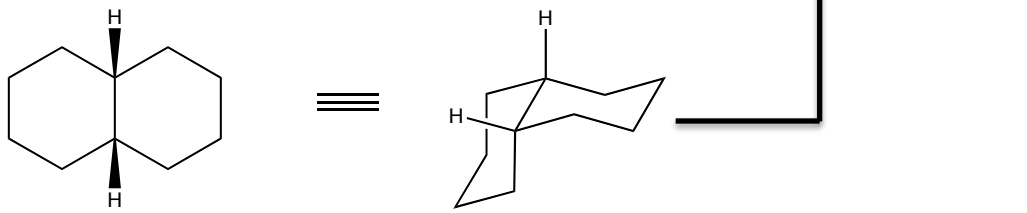


Examples of Basic Bicyclic Compounds:

trans-Decalin: ($C_{10}H_{18}$)

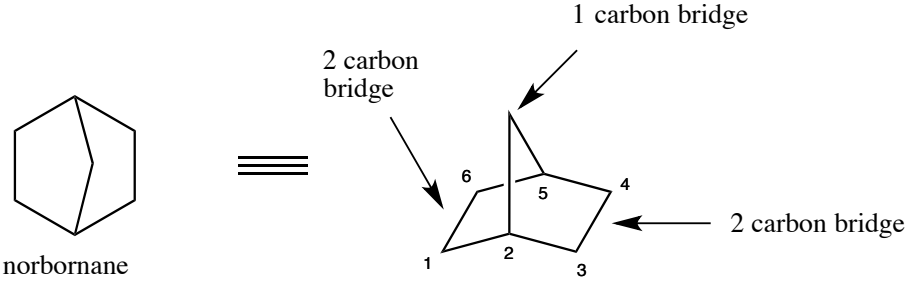


cis-Decalin:



Stereoisomers

2 degrees of unsaturation

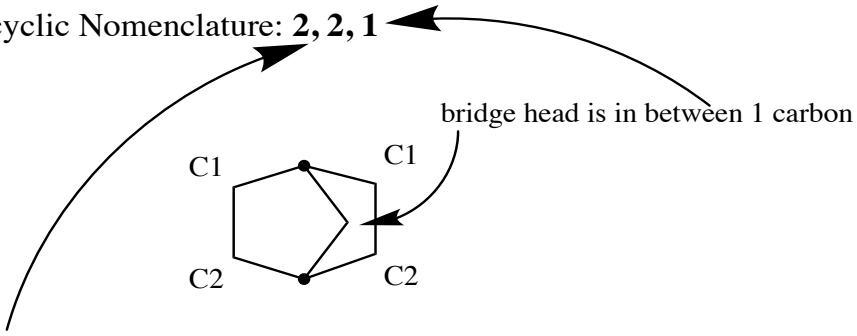


norbornane
C_7H_{12}
Degrees of unsaturation: 2

2 bridge head carbons (2 and 5)
6 membered ring in a boat conformation

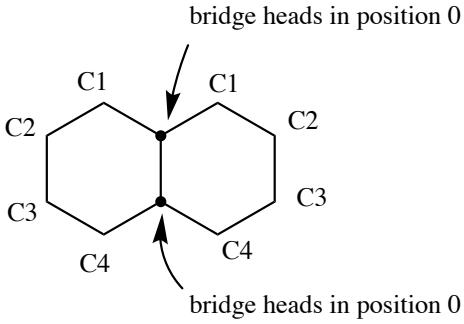
You are **not** responsible for nomenclature of bridged bicyclic compounds described below, but you should know norbornane and decalin structures above

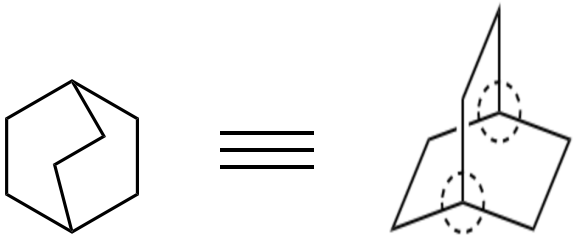
Bicyclic Nomenclature: **2, 2, 1**



there are two sets of two carbons (C1, C2) on both sides of the bridge head, hence, 2, 2

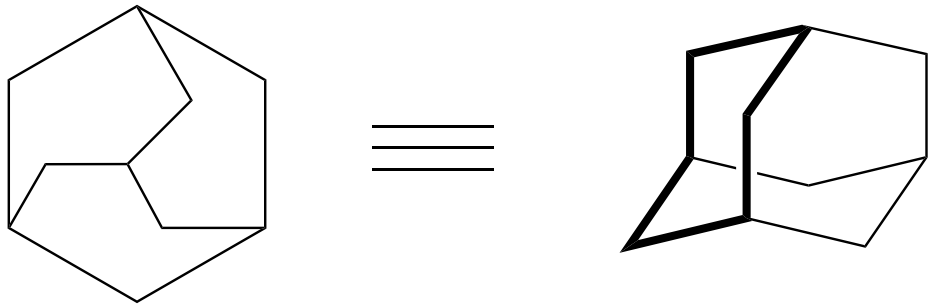
Bicyclic Nomenclature: **4, 4, 0**





2,2,2-Bicyclooctane

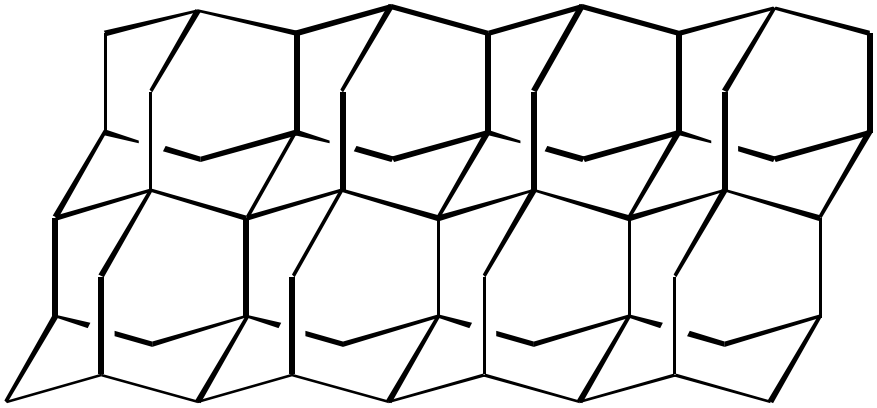
<u>A tricyclic compound:</u>



Adamantane

- This will be the basic structure of diamond

Diamond:



Steroids: