CHEM 261 February 2, 2023

RECALL:

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

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

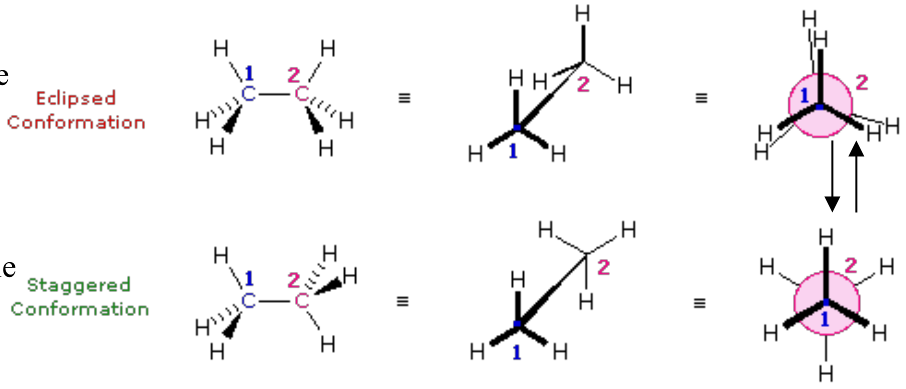
Conformation

Different 3D shapes of a single (the same) molecule obtained by rotation about single bonds
A molecular conformation is any spatial arrangement of atoms that can be interconverted by rotation about single bonds of the molecule

Example: Ethane

Less stable

Most stable



ΔG = 2.8 kcal/mol for rotation

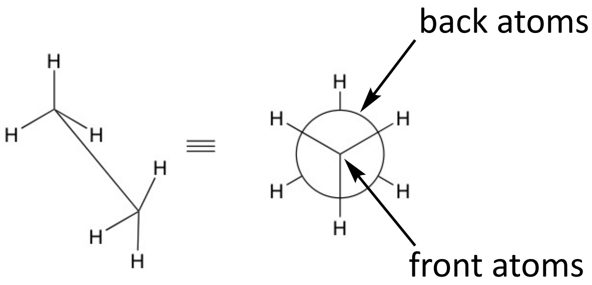
At room room temperature (20 °C): 15-20 kcal/mol of energy available. This allows for rotation around C-C to occur rapidly at room temperature. – Important to know

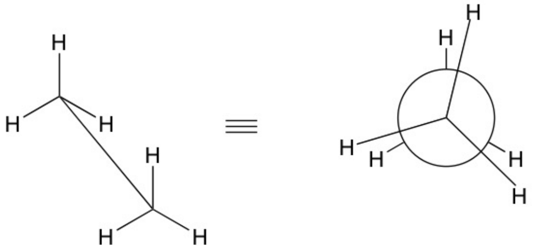
There is a **Steric effect** between neighboring bonds to hydrogens: **Repulsion of filled shells of e^-**

Newman Projections

This is a tool to examine the conformation (rotational 3D geometry) about one specific bond

- Look at one bond at a time
- Back C is a large circle and the front C is a dot





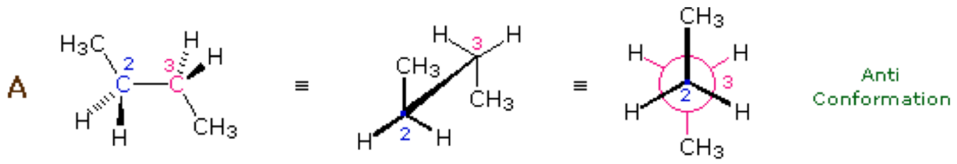
Staggered conformation (hydrogens are **anti**)
Anti means opposite side

Eclipsed conformation (hydrogens are **syn**)
Syn means same side

- Needs energy to go from one conformation to another
- Steric effect – repulsion between two filled shells of electrons
- Increased repulsion is observed as the H move closer in space. Staggered conformation has a lower energy than eclipsed conformation due to less steric repulsion between the H atoms.

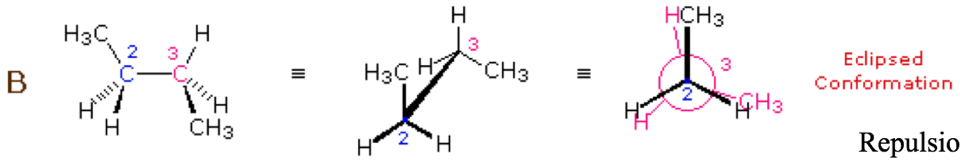
Example: n-butane (C_4H_{10})

Rotation around all bonds still very rapid.
Most stable (most populated conformation) is called anti and has groups as far away as possible.
Note: Newman Projection allows you to look at only one bond at a time. In the case of n-butane, we are looking through the central bond



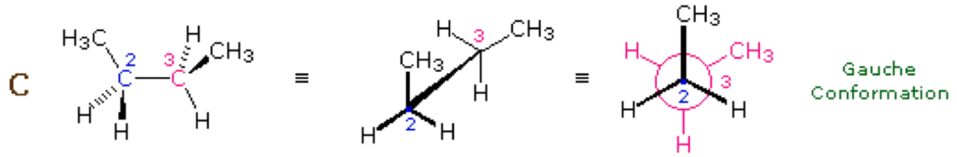
Most stable, staggered

Dihedral angle = 180°



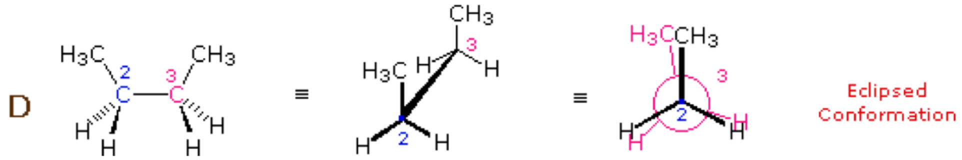
Dihedral angle = 120°

Repulsion = steric effect



Not as stable as anti

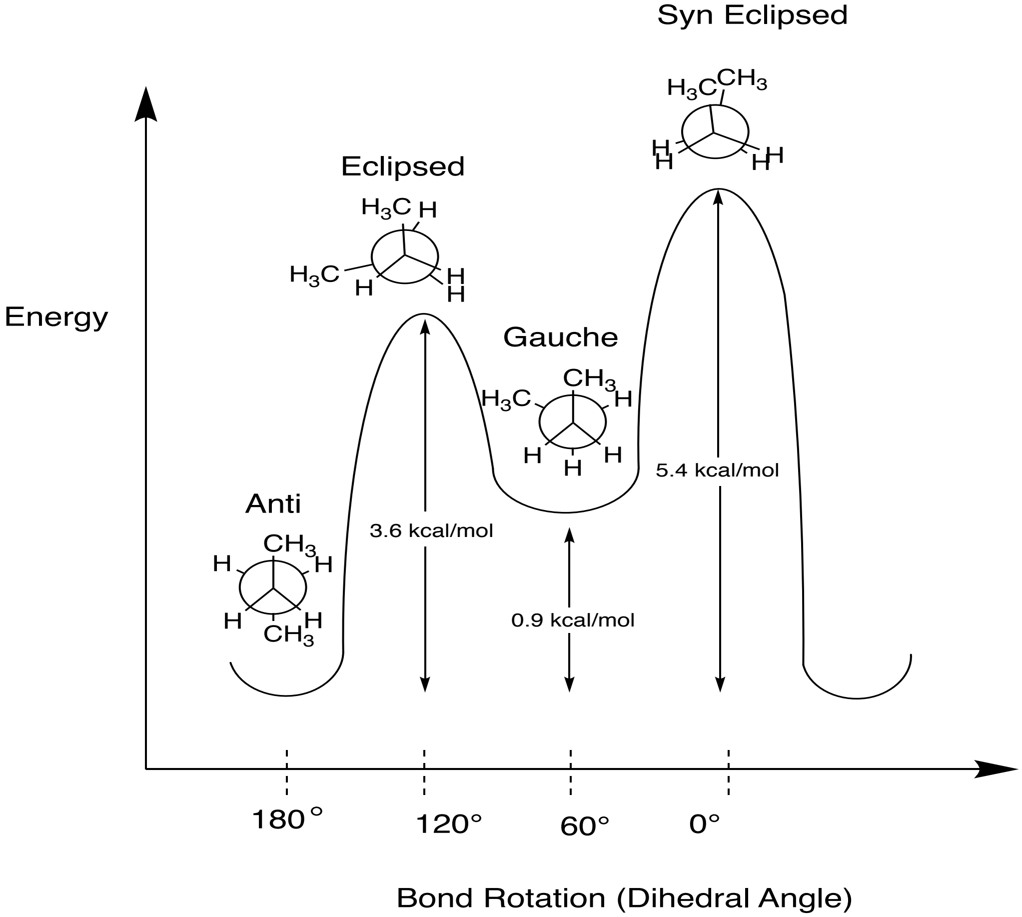
Dihedral angle = 60°



Least stable (syn) eclipsed

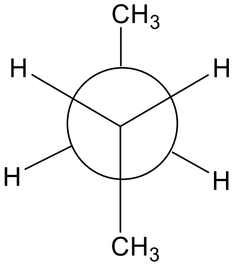
Dihedral angle = 0°

Butane Conformational Energy Diagram:

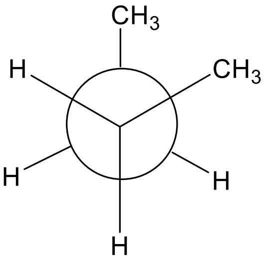


Notes:

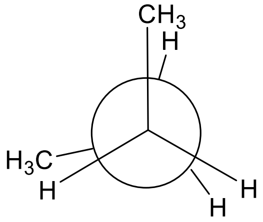
Anti Staggered – two large groups (i.e., CH_3) are as far away from each other as possible (180°) **(lowest energy, favourable)**



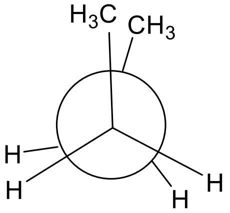
Staggered Gauche – two large groups are 60° relative to each other



Eclipsed – the groups are as close to each other as possible.

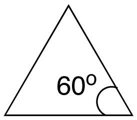


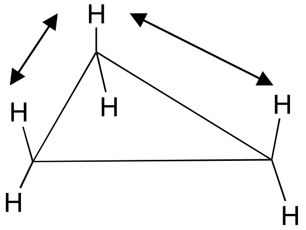
Syn Eclipsed – two large groups are as close together in space as possible. Two large groups are 0° relative to each other (**highest energy, unfavourable**)



Cycloalkane Conformations:

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

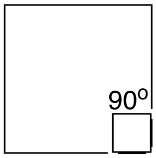




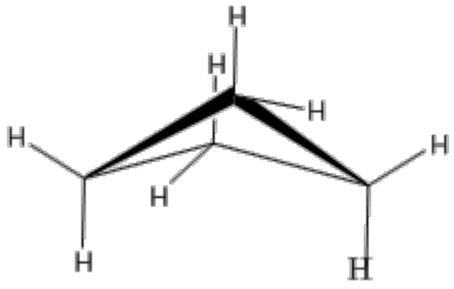
Eclipsing interactions

- High energy molecule due to the internal angle being 60° and the eclipsing interactions between the H.

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

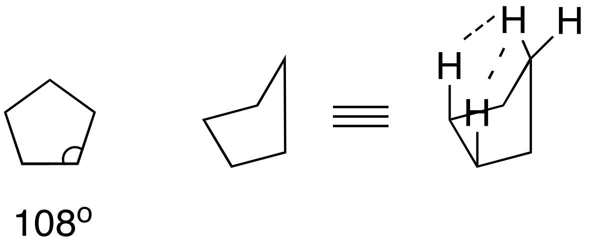


3D structure of cyclobutane:

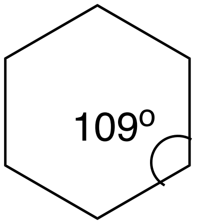


- Not completely flat and adopts a bent shape

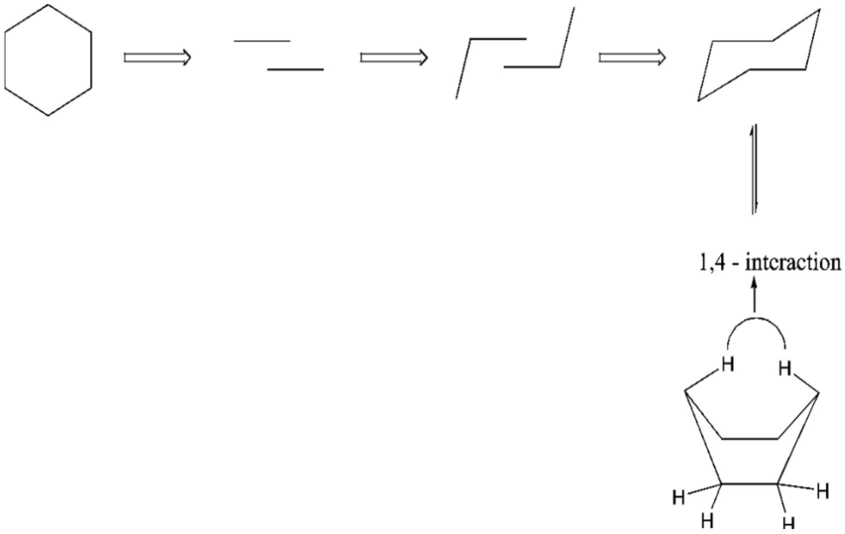
Cyclopentane – bond angles nominally 108° – more flexible than cyclobutane



Cyclohexane – bond angles actually 109°, not 120° as in flat hexagon, due to the C being sp^3 hybridized



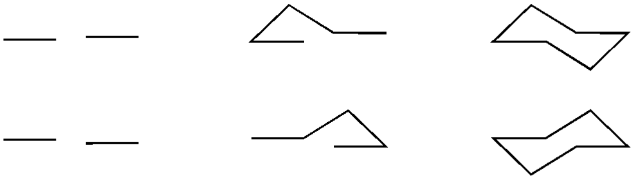
Cyclohexane Conformations – How to draw:

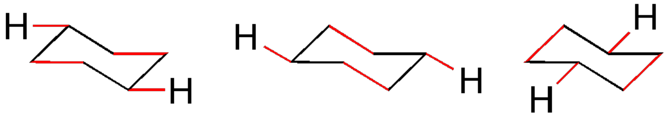


- Chair conformation (most stable)
- All adjacent hydrogen atoms are staggered

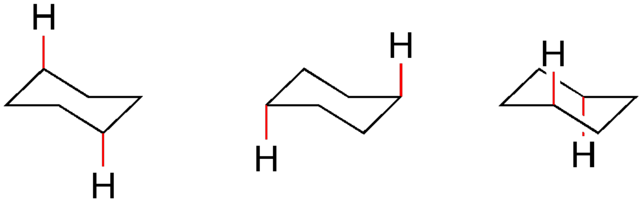
- Boat (least stable)
- many adjacent hydrogen atoms eclipsed
- 1,4 - interactions of two-hydrogens

Another way to draw cyclohexane:



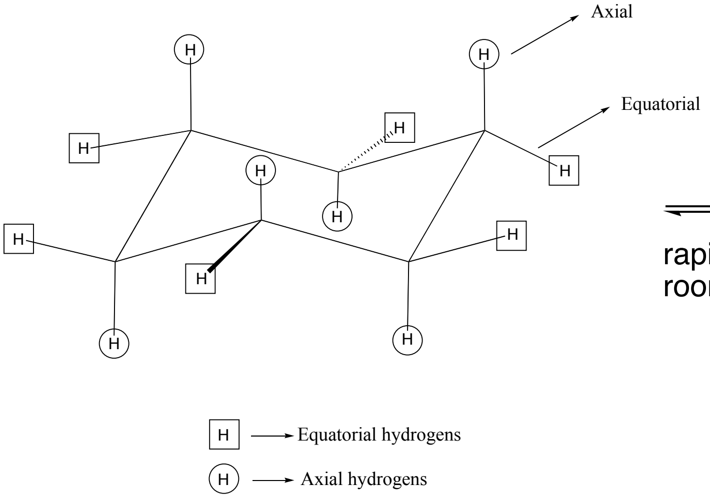


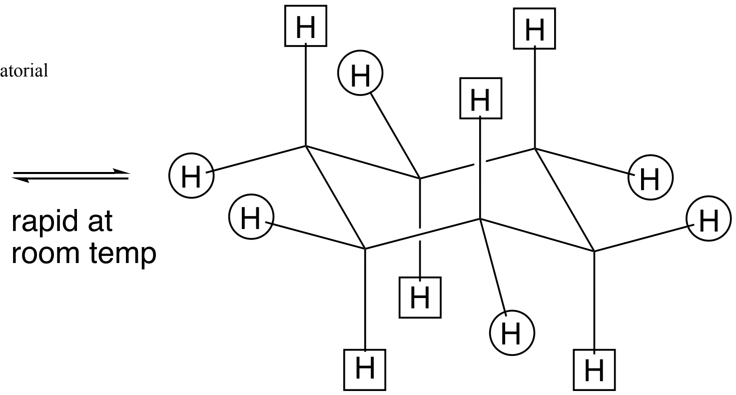
Parallel Lines in Equatorial Position



Vertical Lines in Axial Position

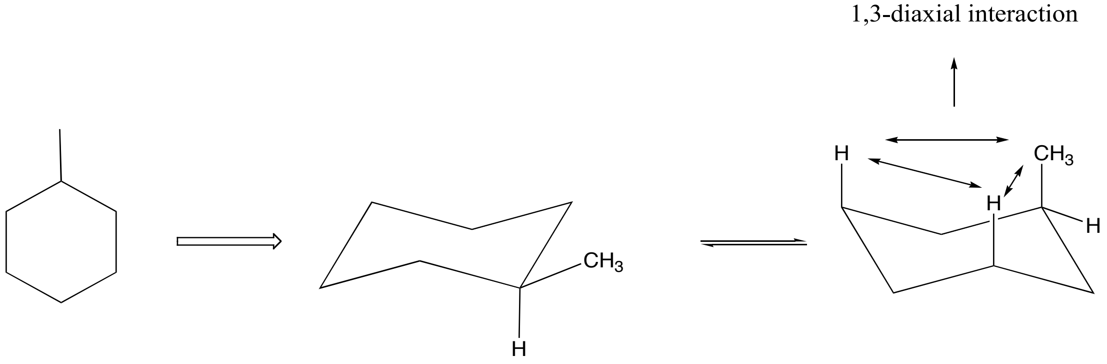
Cyclohexane Conformations Axial vs Equatorial Positions and Ring Flip





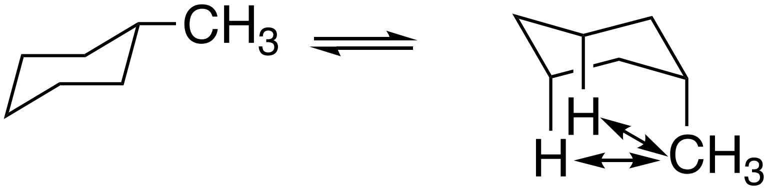
All hydrogens that were axial are now equatorial, and all that were equatorial are now axial

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.

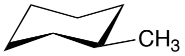


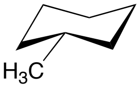
Equatorial methyl interaction
More stable

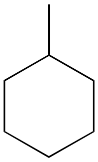
Axial methyl interaction
Less stable

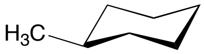
<u>Examples of Most Stable Conformation of Substituted Cyclohexanes</u> :

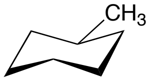
1. Methylcyclohexane
   – 6 drawings of same molecule



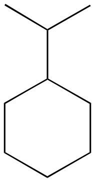


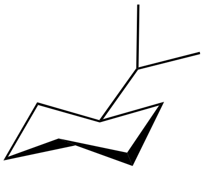


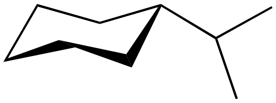


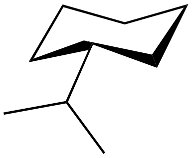


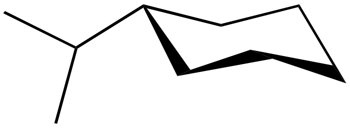
2. Isopropylcyclohexane

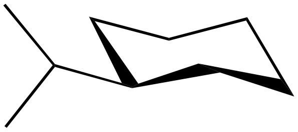










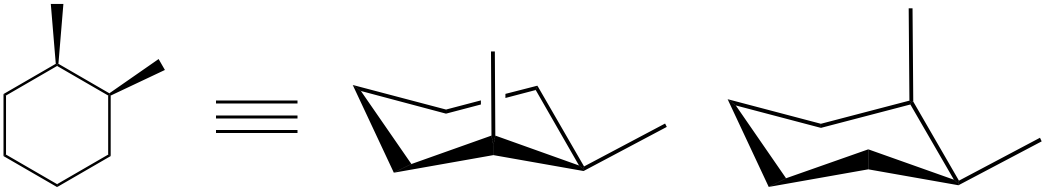


For most stable conformation, largest group at equatorial position

Examples of Most Stable Conformation of Polysubstituted cyclohexanes:

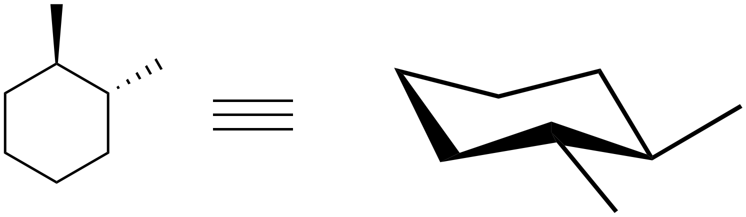
Examples:

1) cis-1,2-dimethylcyclohexane



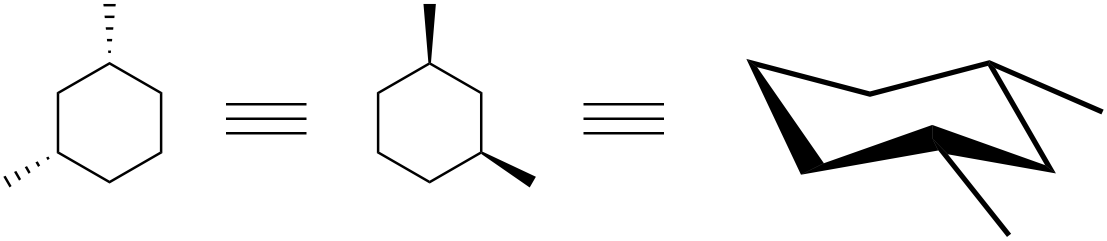
- One methyl group axial and one methyl group equatorial

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



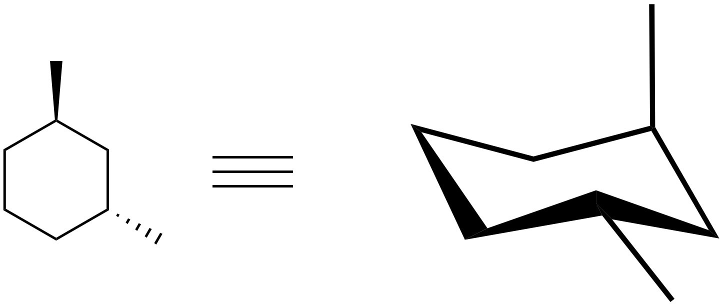
- Both methyl groups equatorial

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



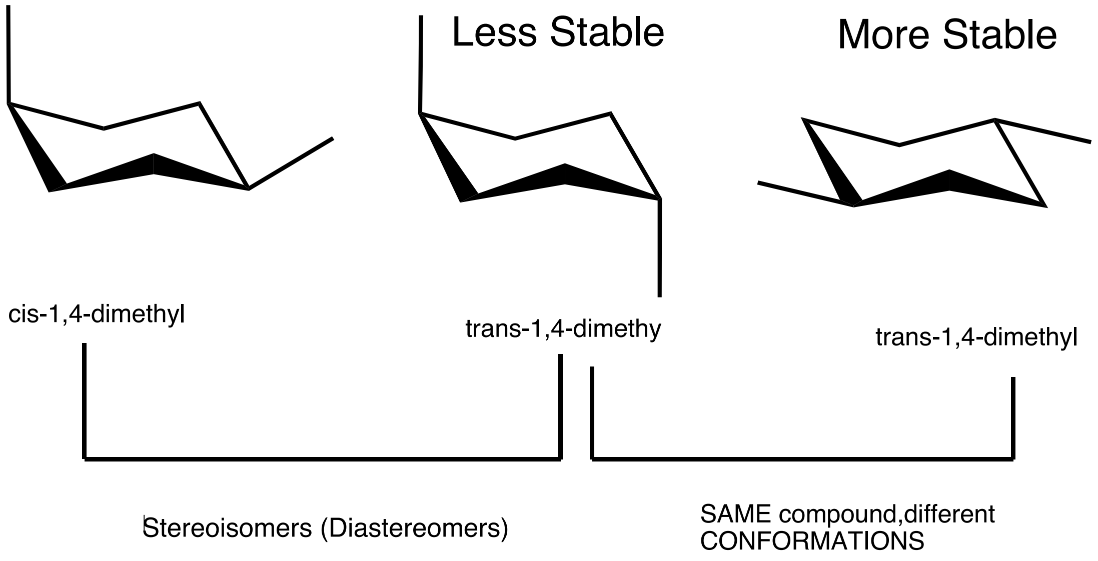
- Both methyl groups equatorial

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

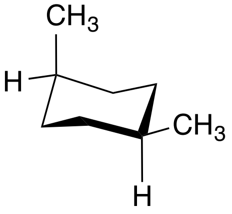


- One methyl group axial and one methyl group equatorial

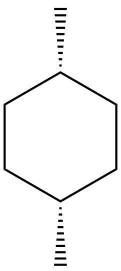
5) cis-1,4-dimethylcyclohexane and trans-1,4-dimethylcyclohexane:

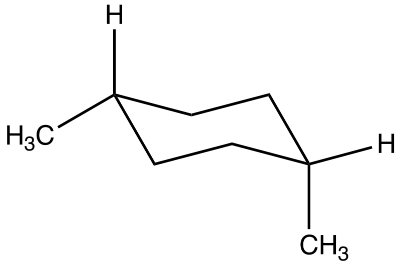


6) cis-1,4-dimethylcyclohexane:

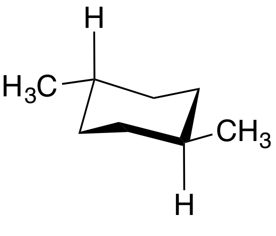


cis-1,4-dimethylcyclohexane

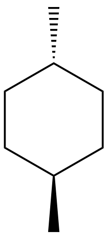


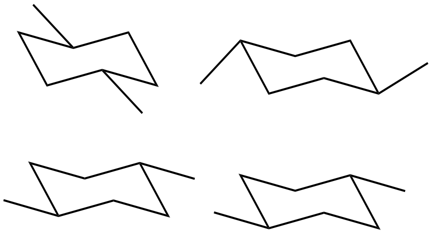


7) trans-1,4-dimethylcyclohexane:



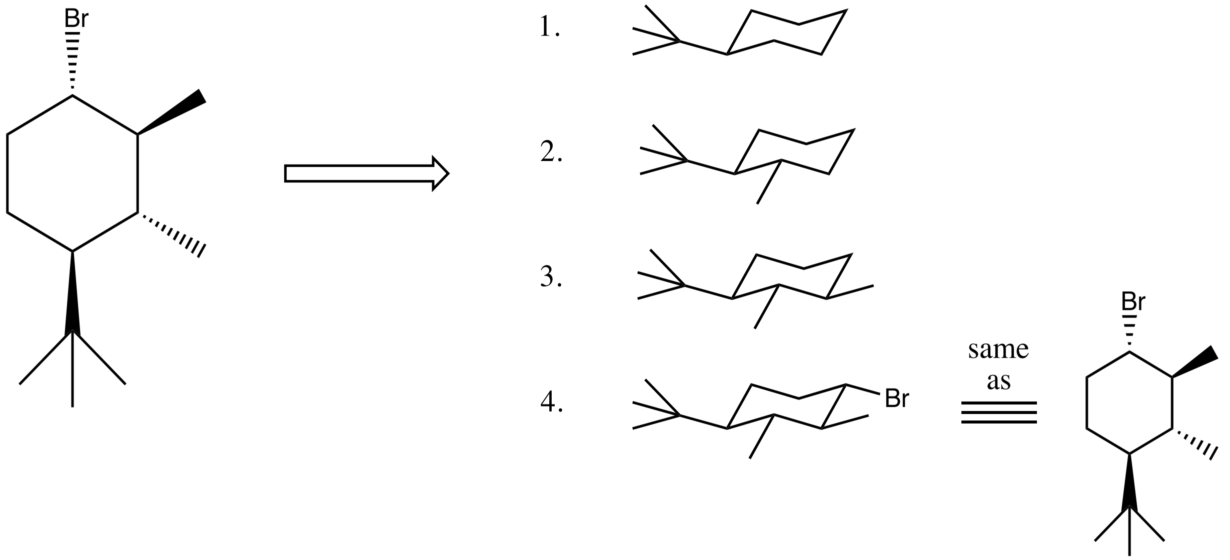
trans-1,4-dimethylcyclohexane





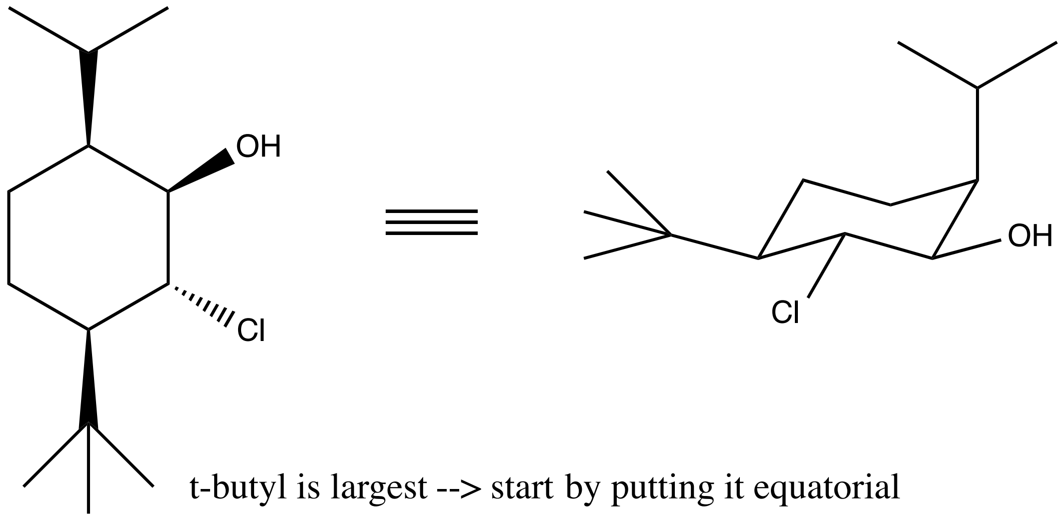
How to draw the most stable conformation of substituted cyclohexanes:

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

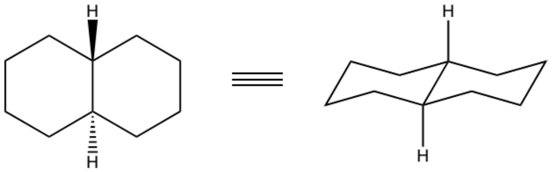
Another example:



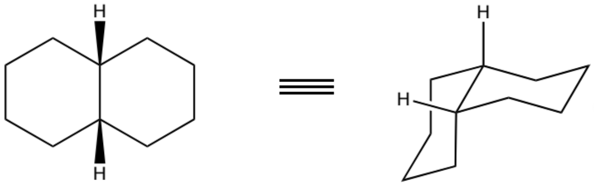
t-butyl is largest --> start by putting it equatorial

Examples of Basic Bicyclic Compounds:

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

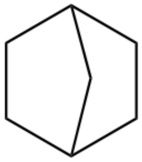


cis-Decalin:

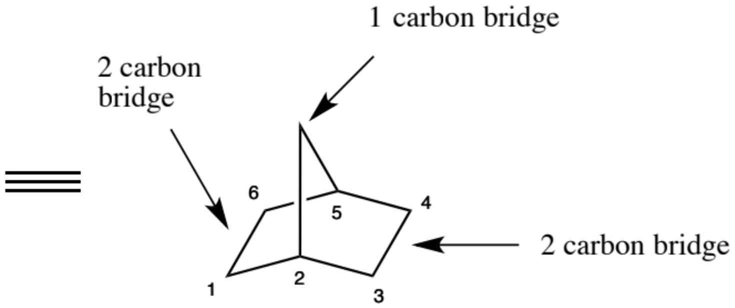


Stereoisomers

2 degrees of unsaturation



norbornane
C_7H_{12}
Degrees of unsaturation: 2

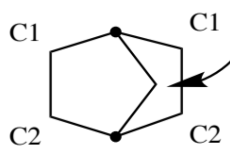


2 bridge head carbons (2 and 5)
6 membered ring in a boat conformation

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**

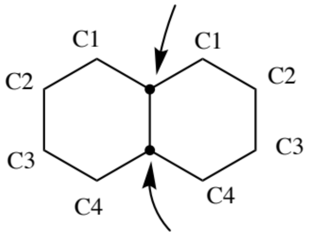
bridge head is in between 1 carbon



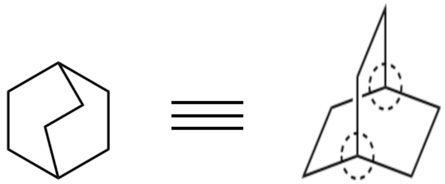
there are two sets of two carbons (C1, C2) on both sides of the bridge head, hence, 2, 2

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

bridge heads in position 0

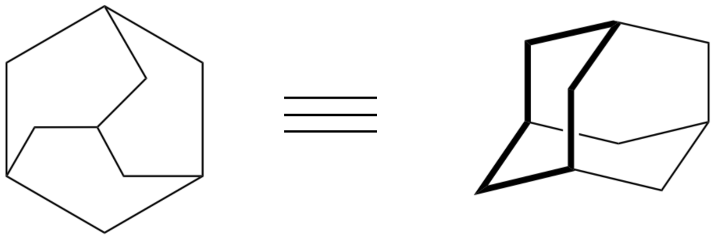


bridge heads in position 0



2,2,2-Bicyclooctane

A tricyclic compound:



Adamantane

- This will be the basic structure of diamond