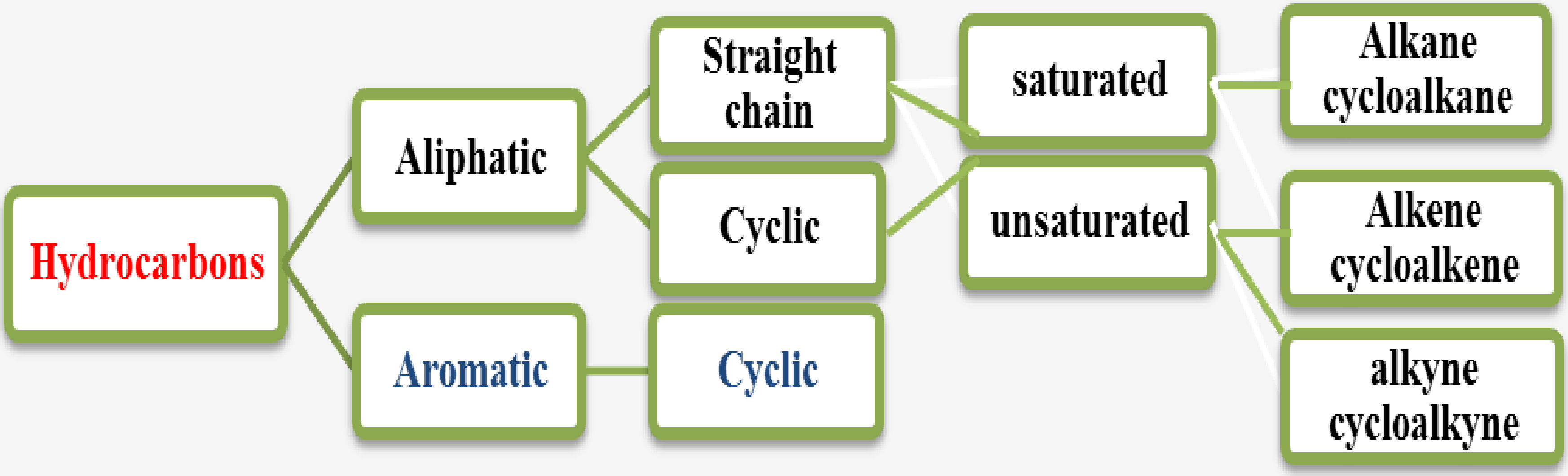
240 Chem

Saturated Hydrocarbons: Alkanes and Cycloalkanes

Chapter 2

Hydrocarbons



General Molecular Formula of Hydrocarbons (Homologous Series)

Alkanes	C_nH_{2n+2} Saturated
Cycloalkanes	C_nH_{2n} (containing a single ring)
Alkenes	C_nH_{2n} (containing one double bond)
Alkynes	C_nH_{2n-2} (containing one triple bond)

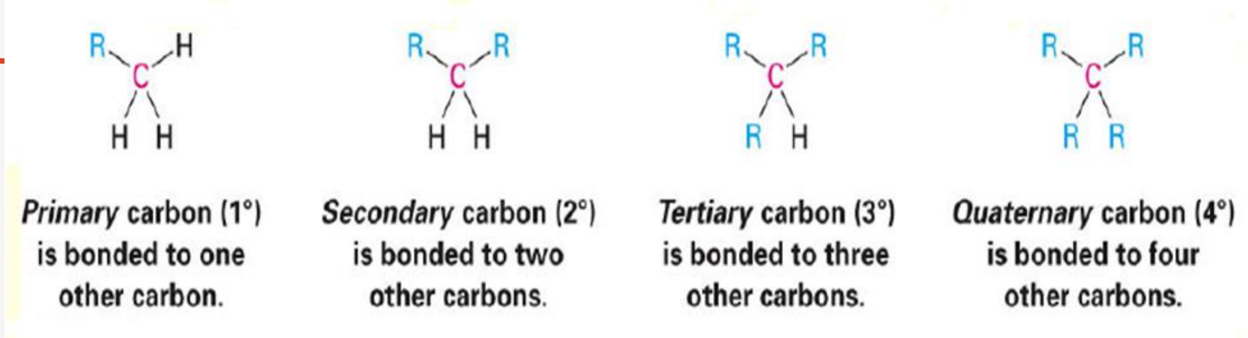
Alkanes

C_nH_{2n+2} Saturated -ane

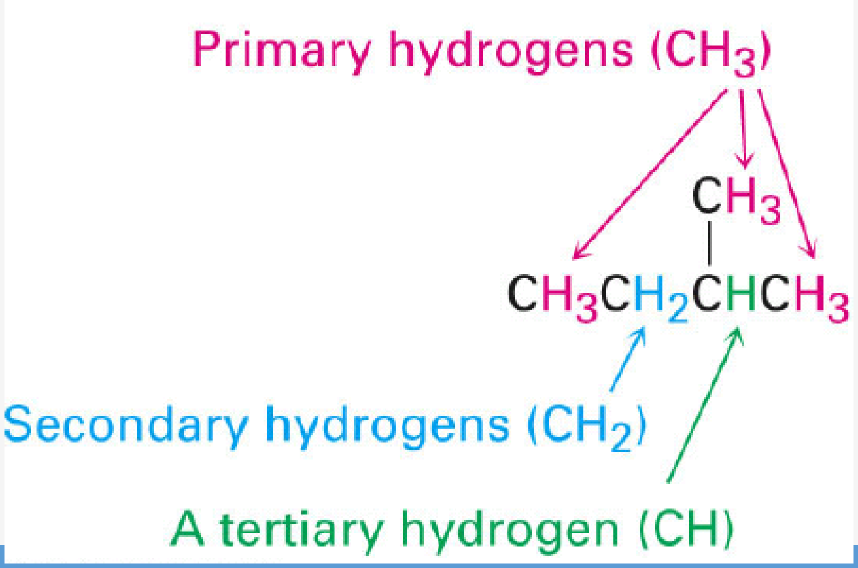
Names, Molecular Formula and Structural Formula of the first Ten Alkanes

Carbon	Name	Molecular Formula	Structural Formula
1	Methane	CH_4	CH_4
2	Ethane	C_2H_6	CH_3CH_3
3	Propane	C_3H_8	$CH_3CH_2CH_3$
4	Butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$
5	Pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$
6	Hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$
7	Heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$
8	Octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$
9	Nonane	C_9H_{20}	$CH_3(CH_2)_7CH_3$
10	Decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$

Classification of Carbon and Hydrogen Atoms



Hydrogens are also referred to as 1º, 2º or 3º according to the type of carbon they are bonded to.



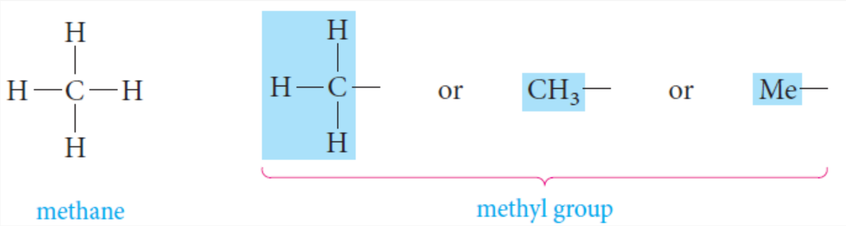
Alkyl Group

- An alkyl group is formed by loss of a hydrogen atom from the corresponding alkane.
- General formula C_nH_{2n+1}.
- The letter R is used as a general symbol for an alkyl group.
- An alkyl group is named by replacing the suffix *–ane* of the parent alkane by *–yl*.

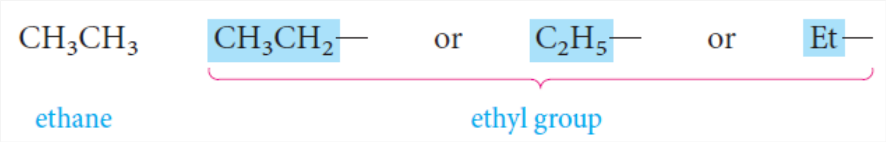
i.e. Alkane – ane + yl = Alkyl

Alkyl Group

- Examples:
  - Derived from methane by removing one of the hydrogens, a one-carbon substituent is called a methyl group.

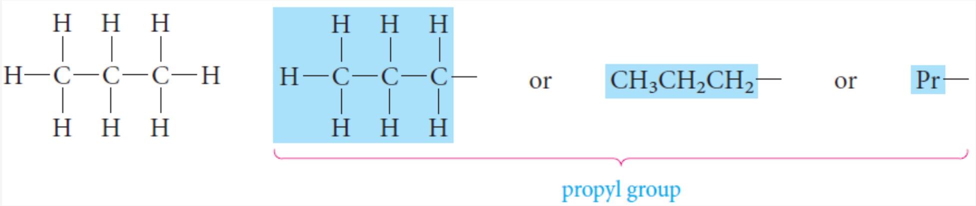


  - Thus the two-carbon alkyl group is called the ethyl group, from ethane.

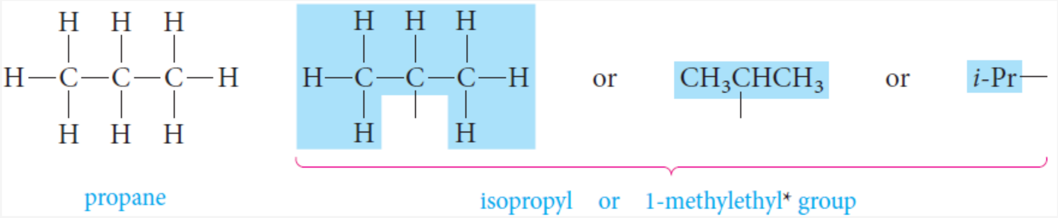


Alkyl Group — Nomenclature

- When we come to propane, there are two possible alkyl groups, depending on which type of hydrogen is removed.
  - If a *terminal* hydrogen is removed, the group is called a propyl group.



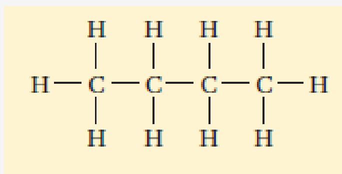
  - If a hydrogen is removed from the *central* carbon atom, we get a different isomeric propyl group, called the isopropyl group.



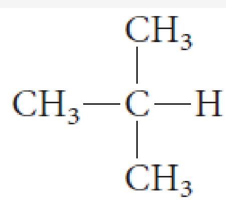
Alkyl Group

Nomenclature

- For four-carbon alkyl group, there are four different butyl groups.
  - The butyl and *sec*-butyl groups are based on *n*-butane.
  - The isobutyl and *tert*-butyl groups come from isobutane.



n-butane

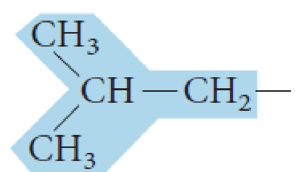


isobutane

butyl

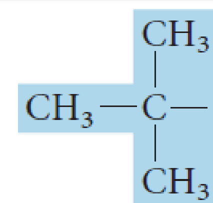
and

sec-butyl
(or 1-methylpropyl)



isobutyl
(or 2-methylpropyl)

and



tert-butyl
(or 1,1-dimethylethyl)

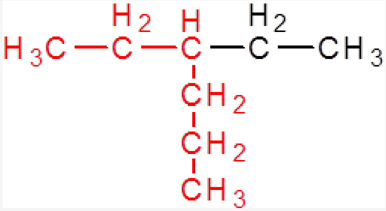
Nomenclature of Alkanes

- The older unsystematic names, (*Common names*).
- The IUPAC names.

IUPAC: International Union of Pure & Applied Chemistry

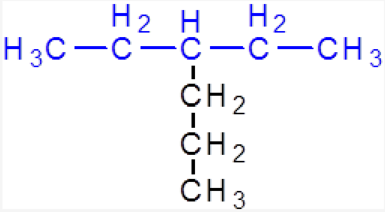
The IUPAC Rules

1) Select the parent structure; *the longest continuous chain*



Ethylhexane

not



Propylpentane X

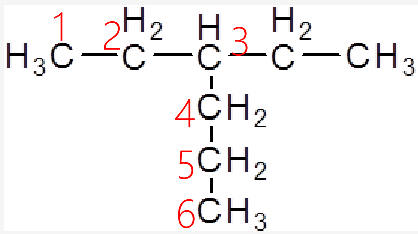
The longest continuous chain is not necessarily straight.

Nomenclature of Alkanes

Nomenclature of Saturated Hydrocarbons

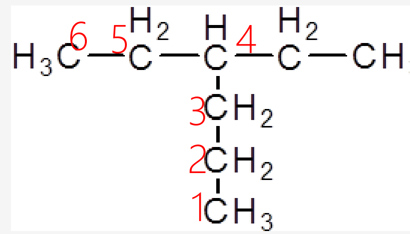
2) Number the carbons in the parent chain

starting from the end which gives the lowest number for the substituent



3-Ethyl hexane

not



4-Ethyl hexane X

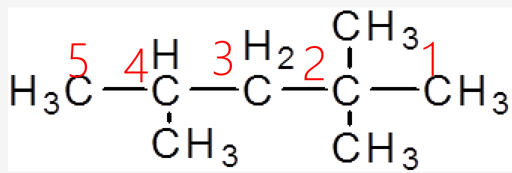
To name the compound:

1) The position of the substituent on the parent carbon chain by a number.
2) The number is followed by a hyphen (-).
3) The combined name of the substituent (ethyl).
4) The parent carbon chain (hexane).

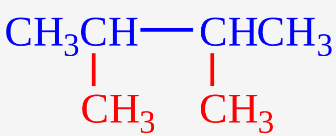
3-Ethylhexane

Nomenclature of Alkanes

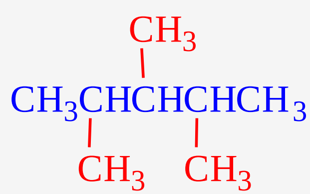
3) If the same alkyl substituent occurs more than once on the parent carbon chain, the prefixes di-, tri-, tetra-, penta-, and so on are used to indicate two, three, four, five, and so on.



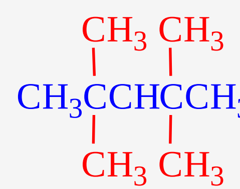
2,2,4- Tri methylpentane



2,3-Dimethylbutane



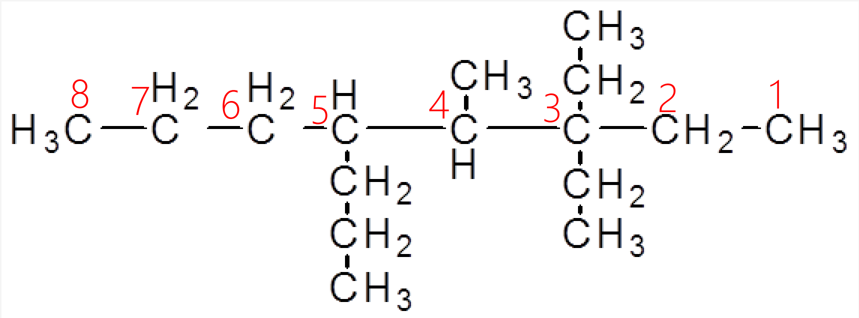
2,3,4-Trimethylpentane



2,2,4,4-Tetramethylpentane

Nomenclature of Alkanes

4) If different alkyl substituents are attached on the parent carbon chain, they are named in order of alphabetical order.



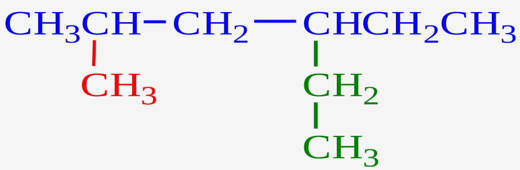
3,3-diethyl
4-methyl
5-propyl

3,3 Diethyl -4-methyl-5 -propyl octane

-

Note that

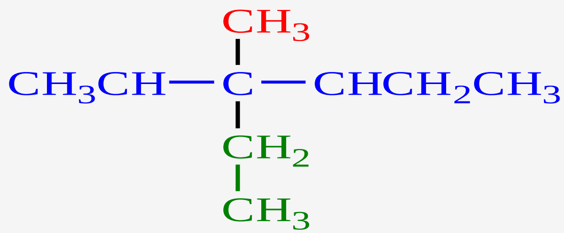
- Each substituent is given a number corresponding to its location on the longest chain.
- The substituent groups are listed alphabetically.



4-Ethyl-2-methylhexane

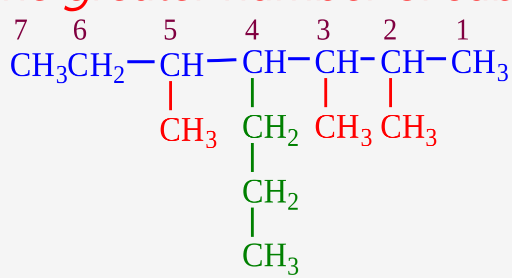
Nomenclature of Alkanes

5) When two substituent are present on the same carbon, use the number twice.



3-Ethyl-3-methylhexane

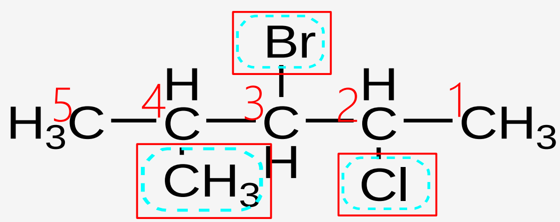
6) When two chains of equal length compete for selection as the parent chain, choose *the chain with the greater number of substituents*.



2,3,5-Trimethyl-4-*n*-propylheptane

Nomenclature of Alkanes

7) If substituents other than alky groups are also presents on the parent carbon chain; all substituents are named alphabetically.

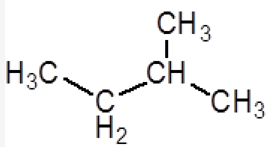
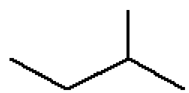
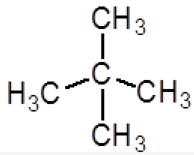
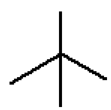


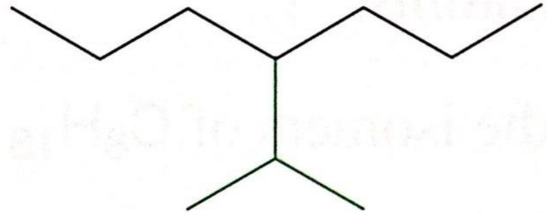
3-bromo -2-chloro -4-methyl pentane

2-chloro
3-bromo
4-methyl

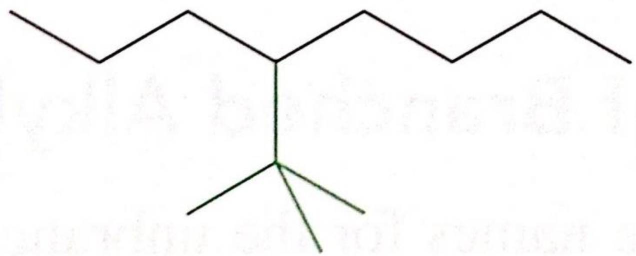
Nomenclature of Alkanes

Examples

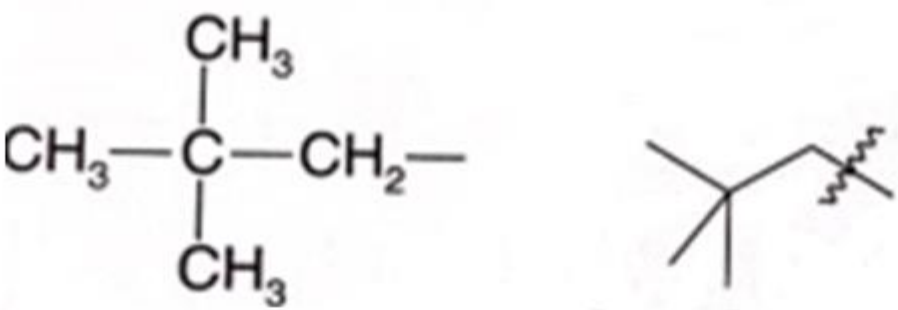
		Common name:	IUPAC name:
$CH_3CH_2CH_2CH_2CH_3$		n-Pentane	Pentane
		Isopentane	2-Methylbutane
		Neopentane	2,2-Dimethylpropane



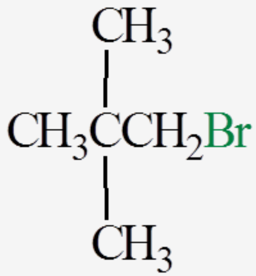
4-(1-Methylethyl)heptane or 4-isopropylheptane



4-(1,1-Dimethylethyl)octane or 4-*tert*-butyloctane



2,2-Dimethylpropyl or neopentyl group

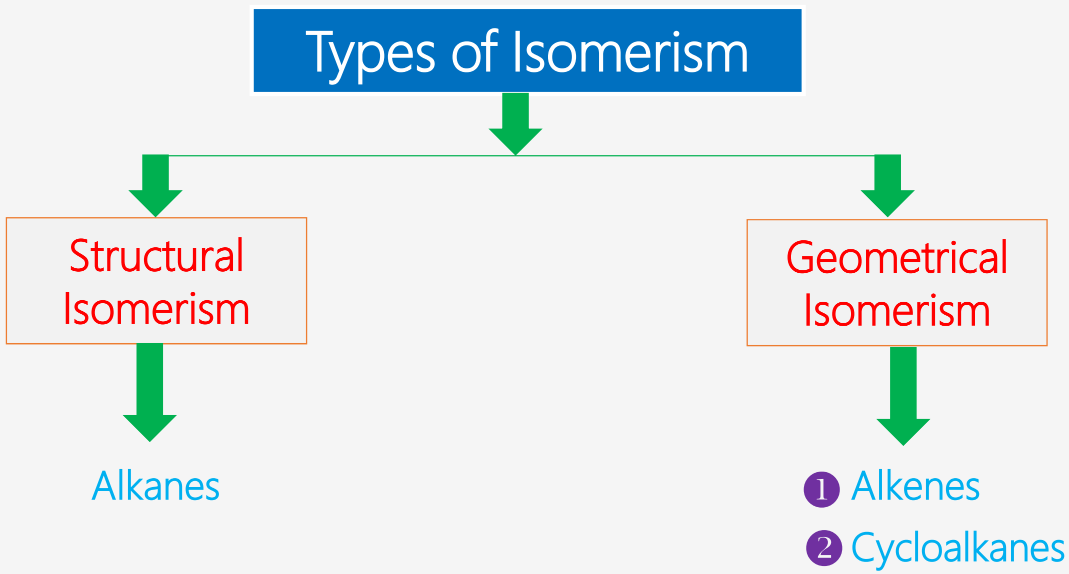


1-Bromo-2,2-dimethylpropane

Neopentyl bromide

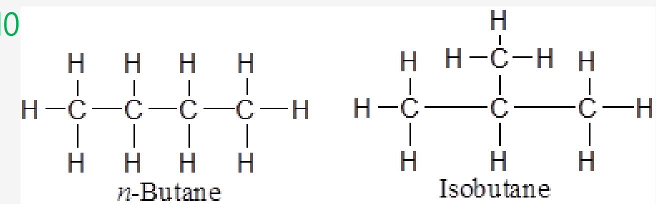
Isomerism

- **Isomers** are different compounds with identical molecular formulas.
- The phenomenon is called *isomerism*.

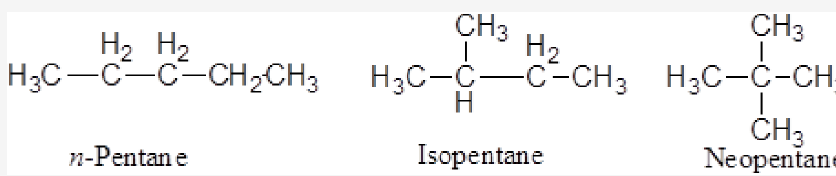


Structural Isomerism in Alkanes

- Structural or constitutional isomers are isomers which differ in the sequence of atoms bonded to each other.
  - Examples:
    - Butanes, C_4H_{10}



    - Pentanes, C_5H_{12}



Physical properties of alkanes

A Physical States and Solubilities

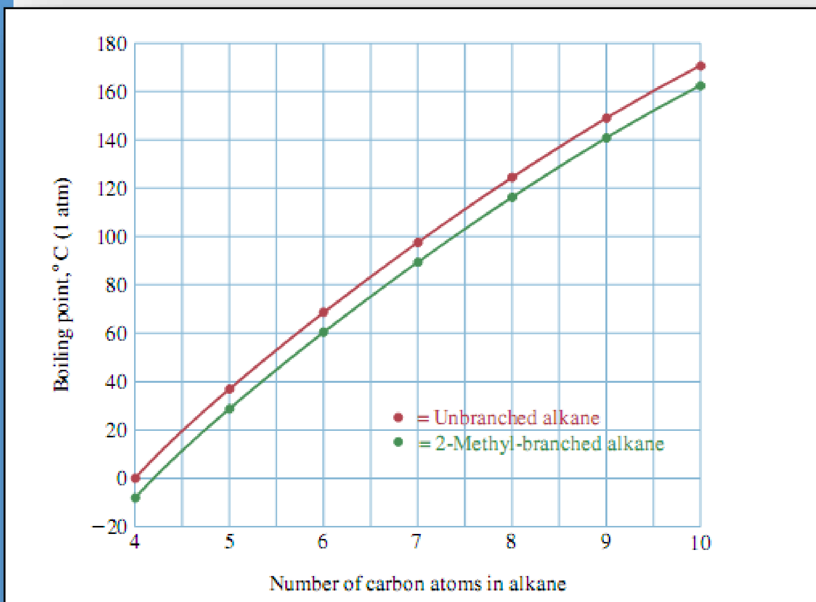
C_1-C_4	colorless gases
C_5-C_{17}	liquids with characteristic odor
C_{20} and more	odorless waxy materials

Alkanes are nonpolar compounds. Thus alkanes are soluble in the nonpolar solvents such as carbon tetrachloride (CCl_4) and benzene (C_6H_6), but they are insoluble in polar solvents such as water.

B Boiling Points

The boiling points of the normal alkanes increase with increasing molecular weight.

Branching of the alkane chain lowers the boiling point.



Example:

$CH_3CH_2CH_2CH_3$

n-Butane
(bp = 0°C)

CH_3
|
CH_3CHCH_3

Isobutane
(bp = -12°C)

C Melting Points

Generally, melting point increases as molecular weight increases, but with no particular pattern.

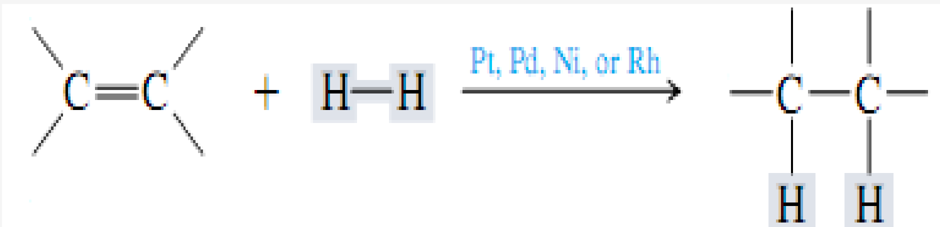
Sources of Alkanes and Cycloalkanes

The primary sources of alkanes are natural gas and petroleum.
natural gas is especially rich in methane and also contains ethane and propane, along with smaller amounts of other low-molecular-weight alkanes.
Petroleum is a liquid mixture containing hundreds of substances, including approximately 150 hydrocarbons, roughly half of which are alkanes or cycloalkanes. Distillation of crude oil gives a number of fractions such as kerosene and gas oil find wide use as fuels for diesel engines and furnaces, and the nonvolatile residue can be processed to give lubricating oil, greases, petroleum jelly, paraffin wax, and asphalt.

Preparation of alkanes

(1) From Alkenes & Alkynes

Catalytic Hydrogenation

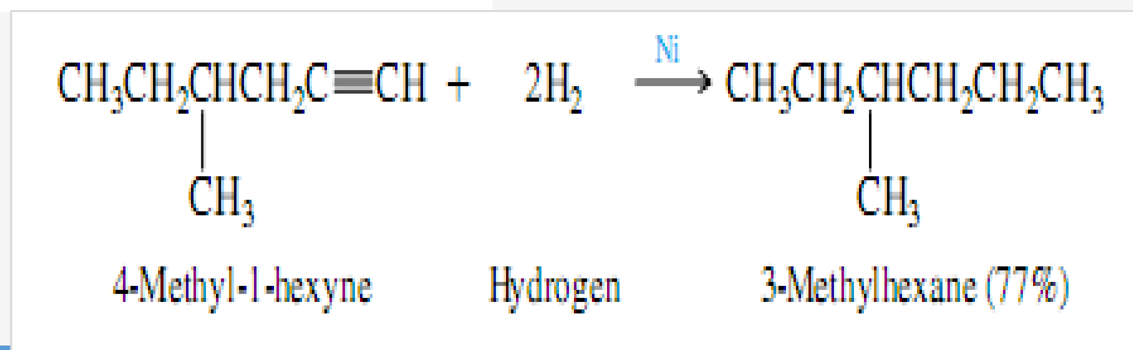


$$(CH_3)_2C{=}CHCH_3 + H_2 \xrightarrow{Pt} (CH_3)_2CHCH_2CH_3$$

2-Methyl-2-butene · Hydrogen · 2-Methylbutane (100%)

$$RC{\equiv}CR' + 2H_2 \xrightarrow{Pt,\ Pd,\ Ni,\ or\ Rh} RCH_2CH_2R'$$

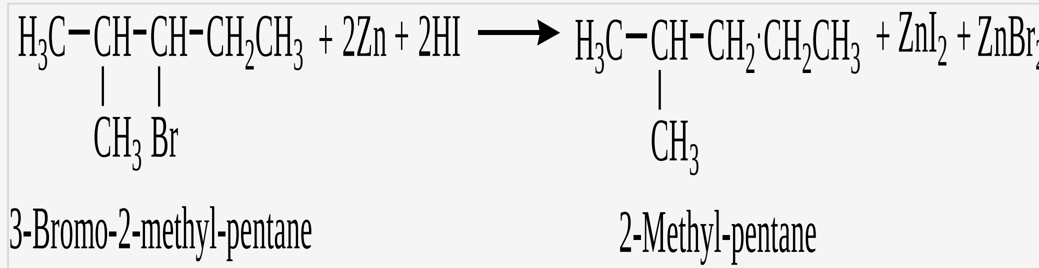
Alkyne · Hydrogen · Alkane



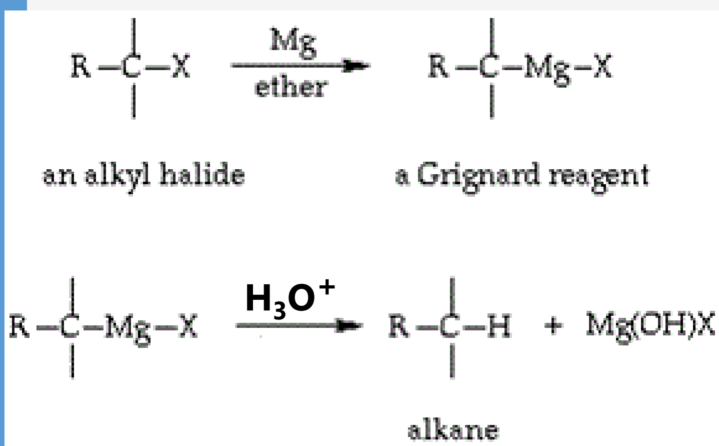
(2) From alkyl Halides

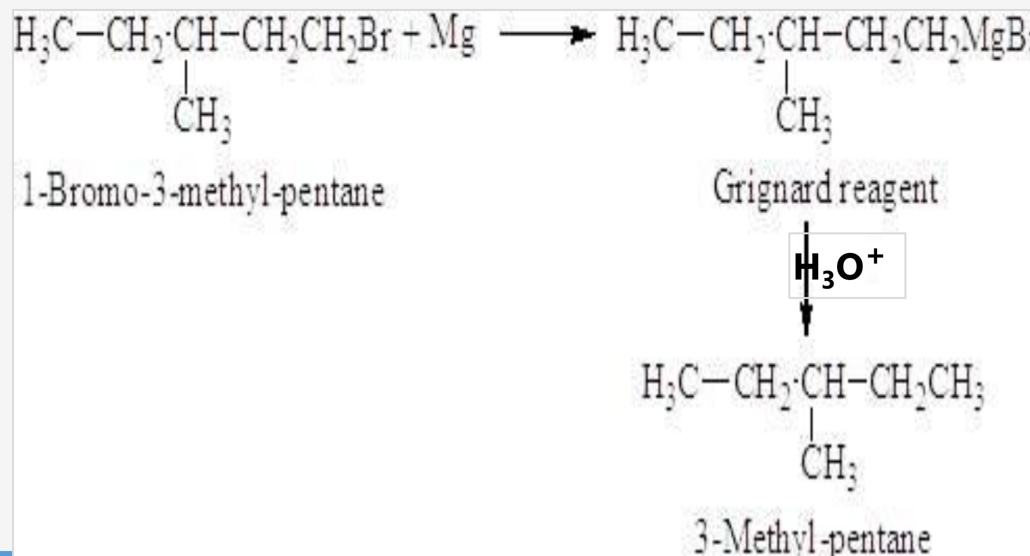
A) Reduction of alkyl halides

$$R{-}X + Zn + HX \longrightarrow R{-}H + ZnX_2$$

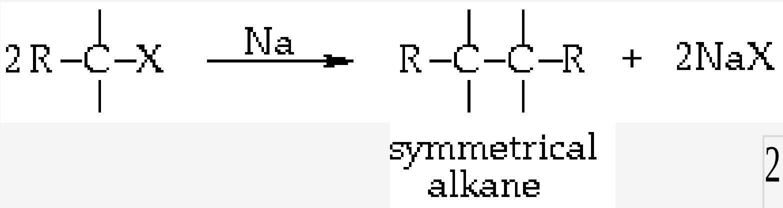


B) Hydrolysis of Grignard Reagent





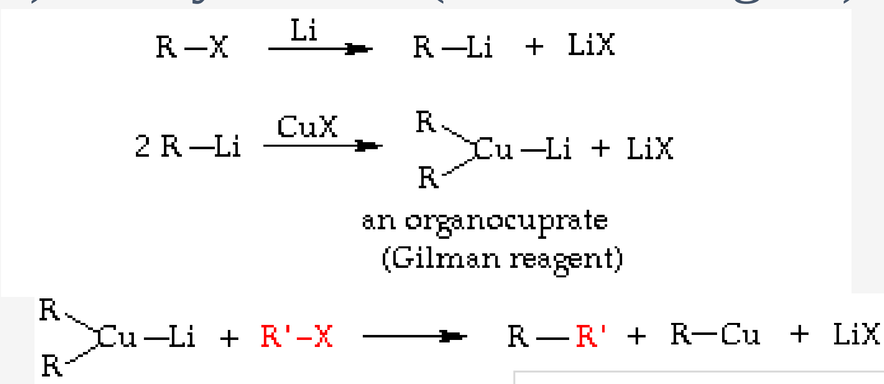
C) Wurtz-Fitting Reaction

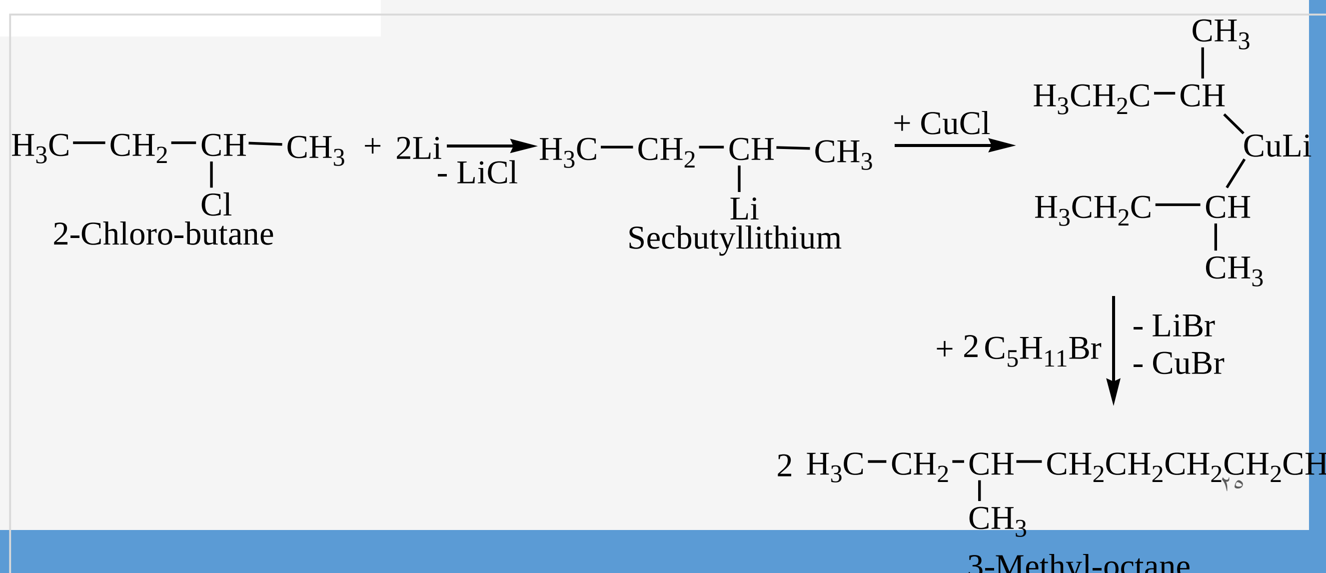


$$2\ CH_3(CH_2)_3CH_2Br + 2\ Na \longrightarrow CH_3(CH_2)_8CH_3 + 2\ NaBr$$

1-Bromo-pentane — Decane

D) Corey-House (Gilman reagent)





Reactions of alkanes

(1) Halogenation

$$R{-}H + X_2 \xrightarrow{\text{heat or light}} R{-}X + H{-}X \quad (X = Cl, Br)$$

Mechanism:

(1)	$X_2 \xrightarrow[\text{or ultraviolet light}]{250\text{–}400\ ^\circ C} 2X\cdot$	Chain-initiating step
(2)	$X\cdot + RH \longrightarrow HX + R\cdot$	Chain-propagating steps
(3)	$R\cdot + X_2 \longrightarrow RX + X\cdot$	

then (2), (3), (2), (3), *etc., until finally a chain is terminated*

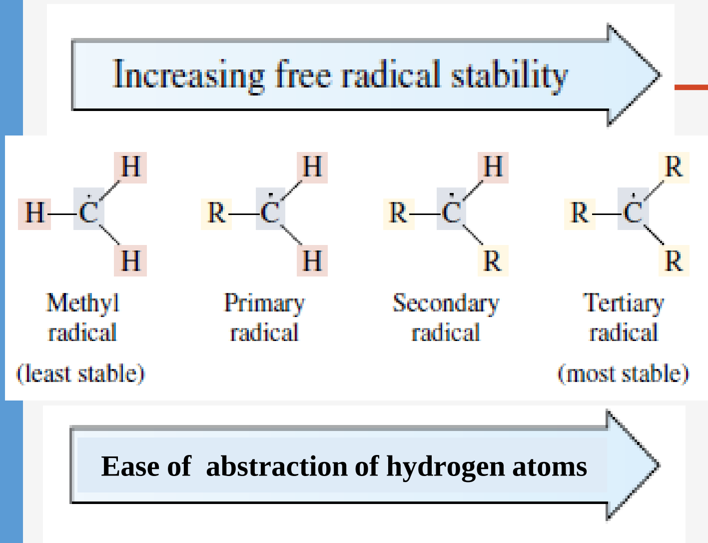
Example:

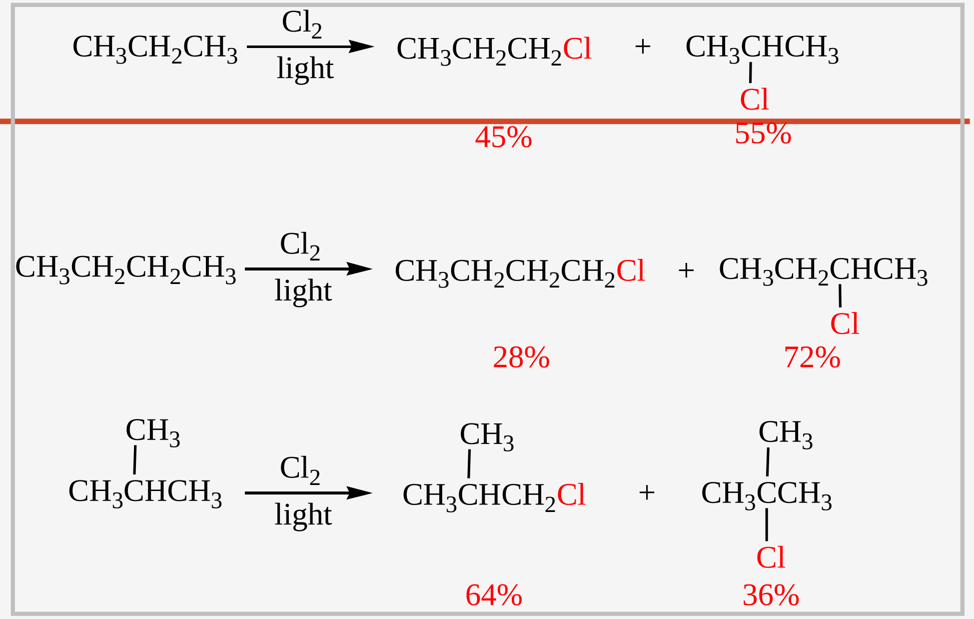
(1)	$Cl_2 \xrightarrow{\text{heat or light}} 2Cl\cdot$	Chain-initiating step
(2)	$Cl\cdot + CH_4 \longrightarrow HCl + CH_3\cdot$	Chain-propagating steps
(3)	$CH_3\cdot + Cl_2 \longrightarrow CH_3Cl + Cl\cdot$	

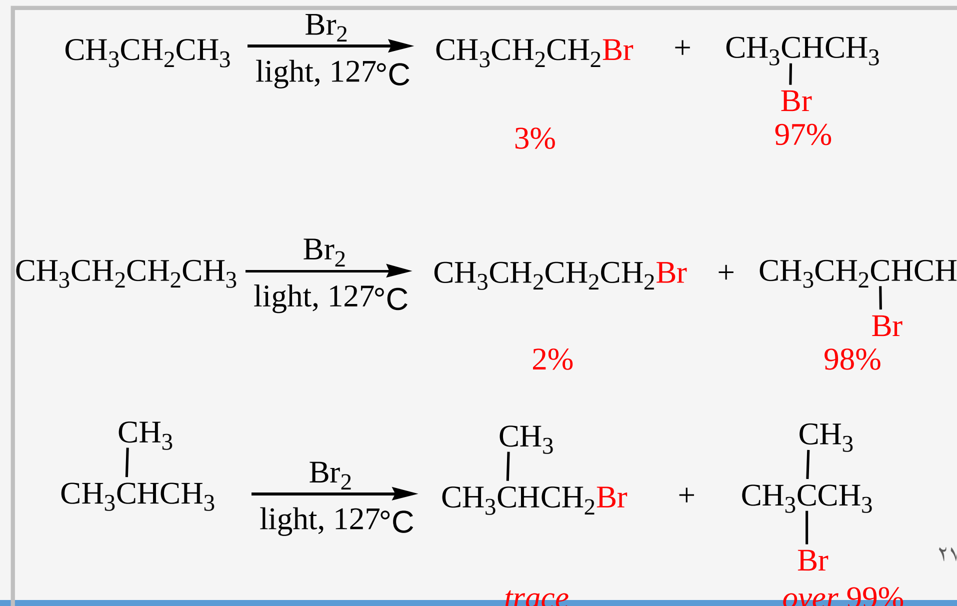
then (2), (3), (2), (3), *etc., until finally*:

(4)	$Cl\cdot + \cdot Cl \longrightarrow Cl_2$	Chain-terminating steps
	or	
(5)	$CH_3\cdot + \cdot CH_3 \longrightarrow CH_3CH_3$	
	or	
(6)	$CH_3\cdot + \cdot Cl \longrightarrow CH_3Cl$	

Selectivity in Halogenation Reactions







(2) Combustion

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O$$

Examples:

$$\underset{\text{Methane}}{CH_4} + \underset{\text{Oxygen}}{2O_2} \longrightarrow \underset{\text{Carbon dioxide}}{CO_2} + \underset{\text{Water}}{2H_2O}$$

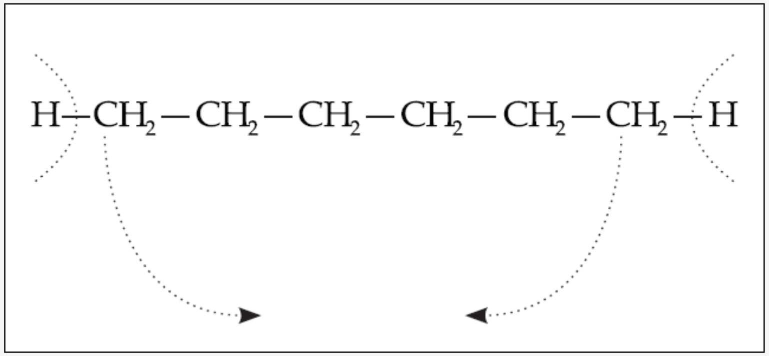
$$\underset{\text{2-Methylbutane}}{(CH_3)_2CHCH_2CH_3} + \underset{\text{Oxygen}}{8O_2} \longrightarrow \underset{\text{Carbon dioxide}}{5CO_2} + \underset{\text{Water}}{6H_2O}$$

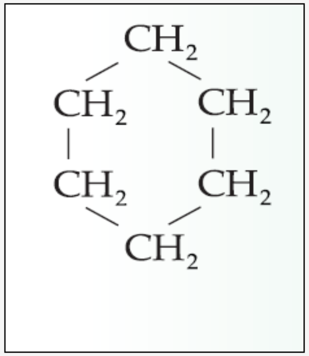
(3) Pyrolysis (cracking)

$$\text{Alkane} \xrightarrow[\text{without catalysis}]{400\text{-}600\,^\circ C\text{ ; with or}} H_2 + \text{smaller alkanes} + \text{alkenes}$$

Cycloalkanes

C_nH_{2n} containing a single ring

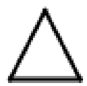




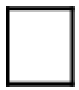
$$C_nH_{2n+2} \longrightarrow C_nH_{2n}$$

Nomenclature of Cycloalkane

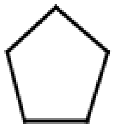
cycol-



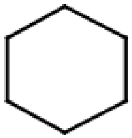
Cyclopropane



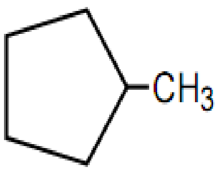
Cyclobutane



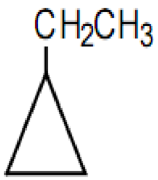
Cyclopentane



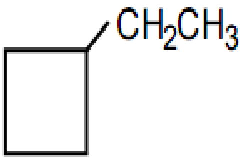
Cyclohexane



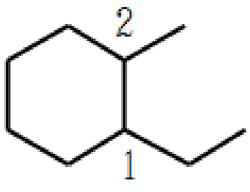
methylcyclopentane



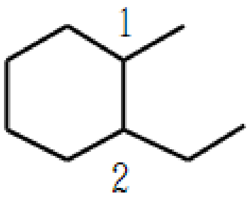
ethylcyclopropane



ethylcyclobutane

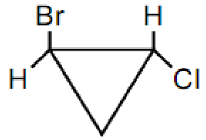


1-Ethyl-2-methylcyclohexane

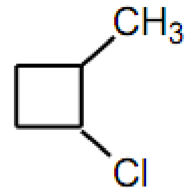


-not-

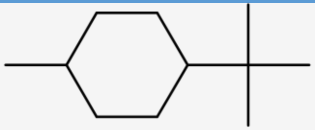
2-Ethyl-1-methylcyclohexane



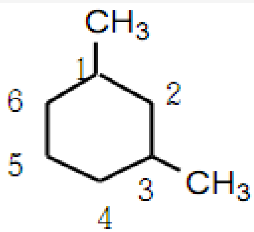
1-bromo-2-chlorocyclopropane



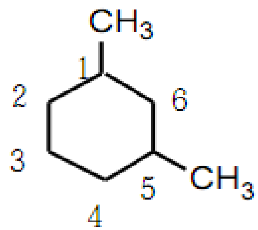
1-Chloro-2-methylcyclobutane



1-tert-Butyl-4-methylcyclohexane

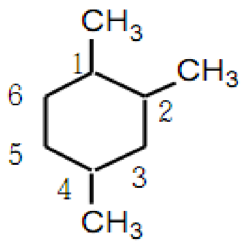


1,3-Dimethylcyclohexane



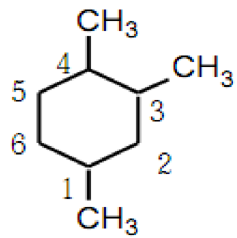
-not-

1,5-Dimethylcyclohexane



1,2,4-Trimethylcyclohexane

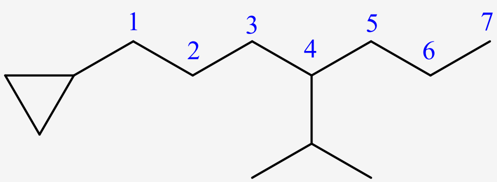
(1 + 2 + 4 = 7)



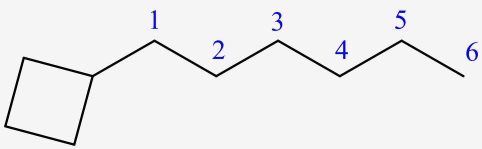
-not-

1,3,4-Trimethylcyclohexane

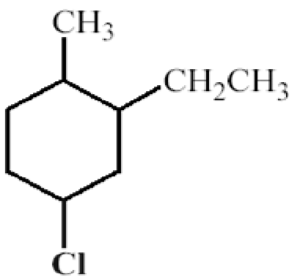
(1 +3 + 4 = 8)



4-isopropyl-1-cyclopropylheptane

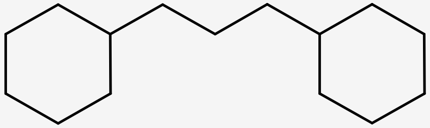


1-Cyclobutylhexane

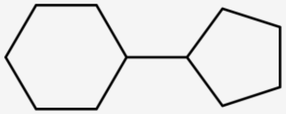


4-Chloro-2-ethyl-1-methylcyclohexane

(not **1-Chloro-3-ethyl-4-methylcyclohexane**)



1,3-Dicyclohexylpropane

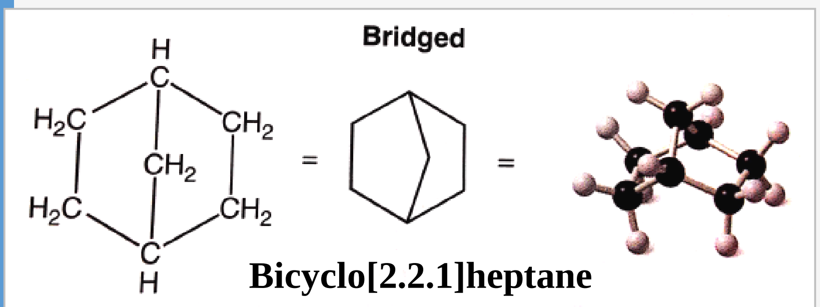


Cyclopentylcyclohexane

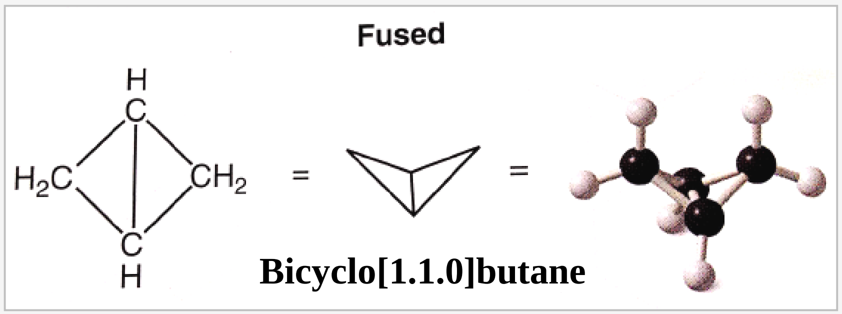
Nomenclature of Bicycloalkane

Bicycloalkanes: compounds containing two fused or bridged rings

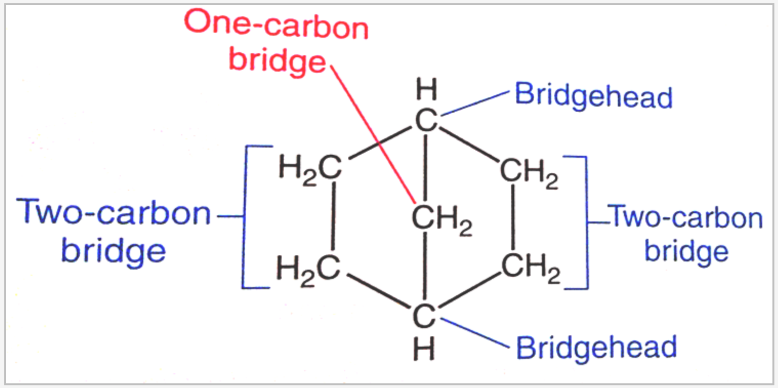
Bicyclo-



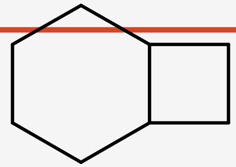
Bicyclo[2.2.1]heptane



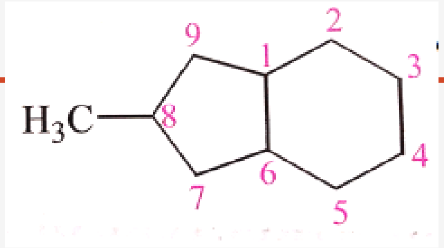
Bicyclo[1.1.0]butane



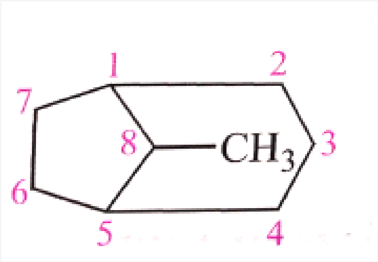
Examples:



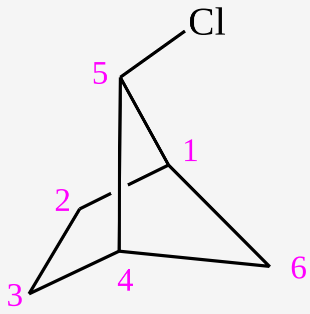
Bicyclo[4.2.0]octane



8-Methylbicyclo[4.3.0]nonane



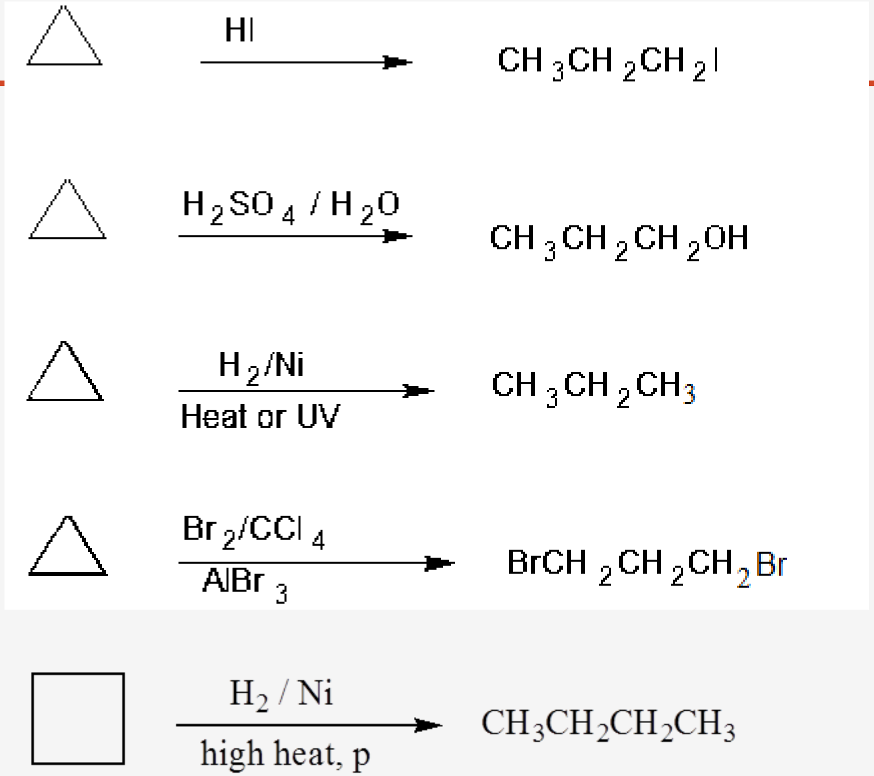
8-Methylbicyclo[3.2.1]octane



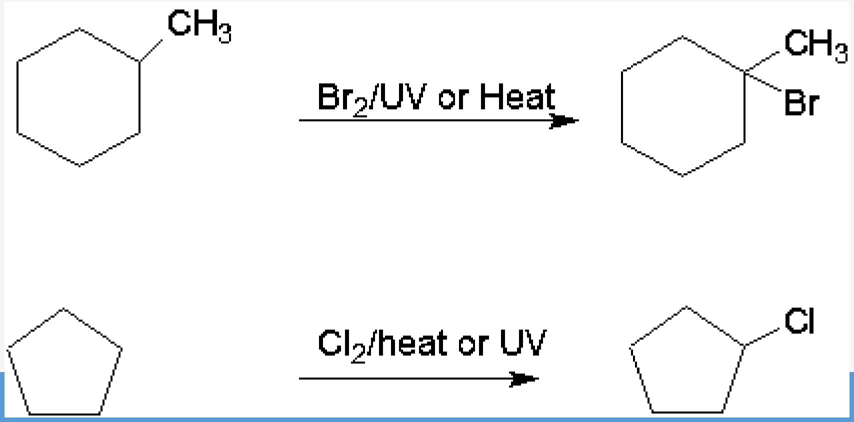
5-Chloro-bicyclo[2.1.1]hexane

Reaction of cycloalkanes

- Ring less stable 3 and 4



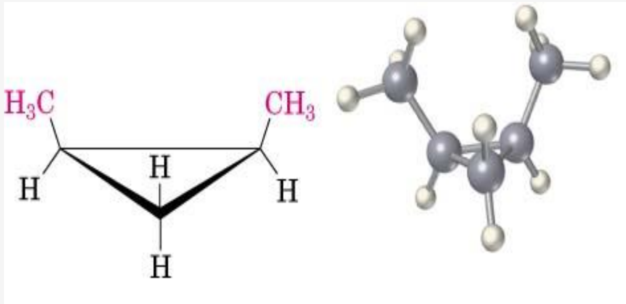
- Ring more stable 5 and 6



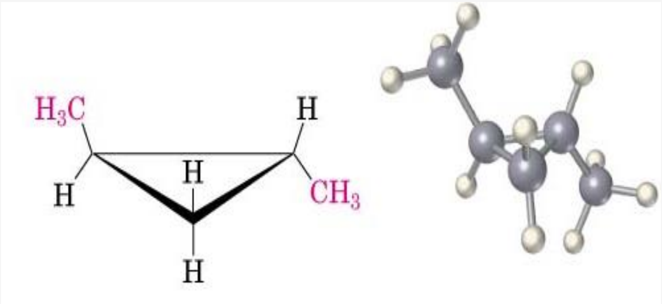
Geometric Isomerism in Cycloalkane

Cis-Trans Isomerism

- Ring structures like C=C restrict rotation and therefore can result in *cis* and *trans* isomers.
- The *trans*-isomer is the molecule with branches on OPPOSITE sides of the ring.
- The *cis*-isomer is the molecule with branches on the SAME side of the ring.
- These *cis-trans* isomers are also stereoisomers.
- The physical properties of *cis-trans* isomers are different; they have different melting points, boiling points, and so on.

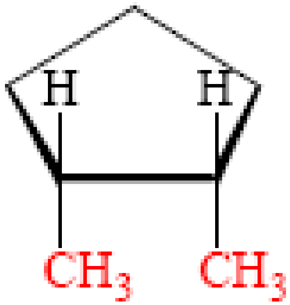


cis-1,2-Dimethylcyclopropane

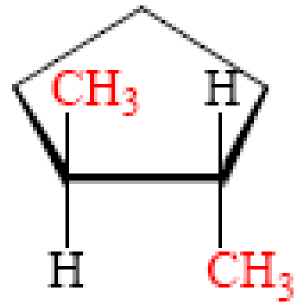


trans-1,2-Dimethylcyclopropane

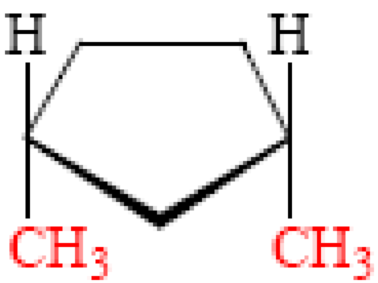
Examples:



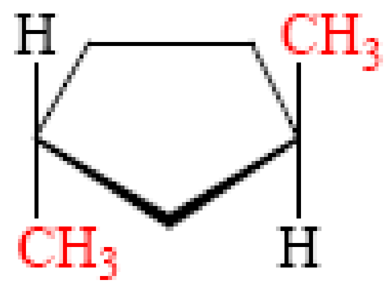
cis-1,2-Dimethylcyclopentane
bp 99.5 °C



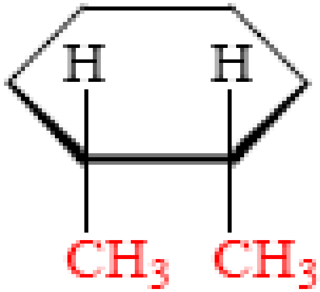
trans-1,2-Dimethylcyclopentane
bp 91.9 °C



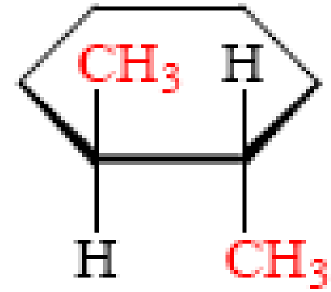
cis-1,3-Dimethylcyclopentane



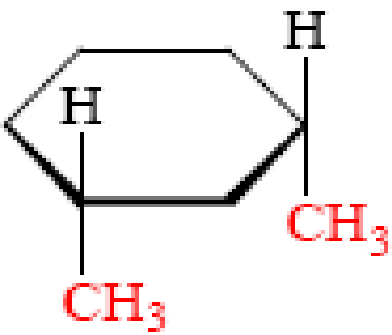
trans-1,3-Dimethylcyclopentane



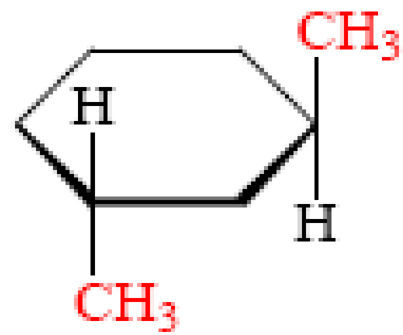
***cis*-1,2-Dimethylcyclohexane**



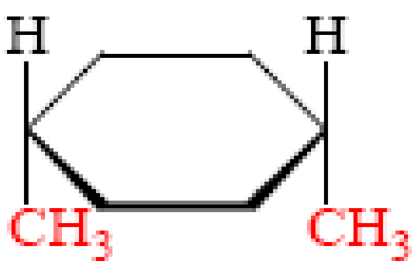
***trans*-1,2-Dimethylcyclohexane**



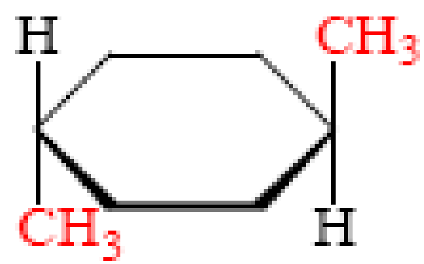
***cis*-1,3-Dimethylcyclohexane**



***trans*-1,3-Dimethylcyclohexane**



***cis*-1,4-Dimethylcyclohexane**



***trans*-1,4-Dimethylcyclohexane**

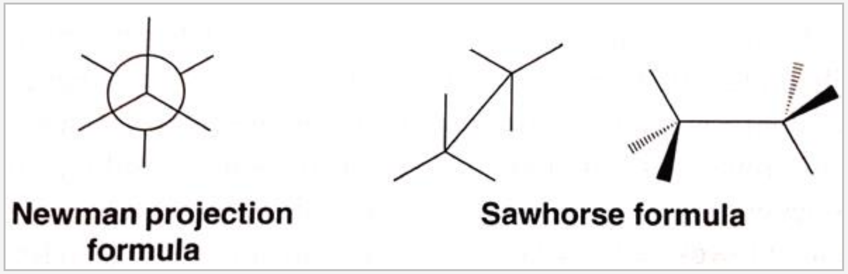
Conformations and Conformational Analysis of Alkanes

Tow groups bonded by only a single bond can undergo rotation about that bond with respect to each other.

- The temporary molecular shapes that result from such a rotation are called **conformations** of the molecule.
- Each possible structure is called **conformer**.
- An analysis of the energy changes that occur as a molecule undergoes rotations about single bonds is called a **Conformational analysis**.

- The certain types of structural formulas are:

1. Newman projection formula
2. Sawhorse formula

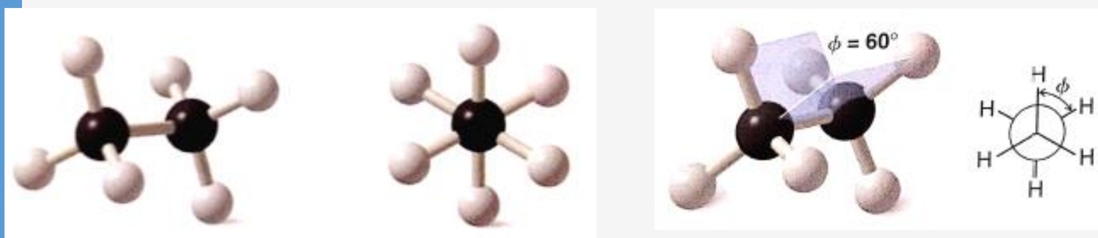


Conformational Analysis in Ethane

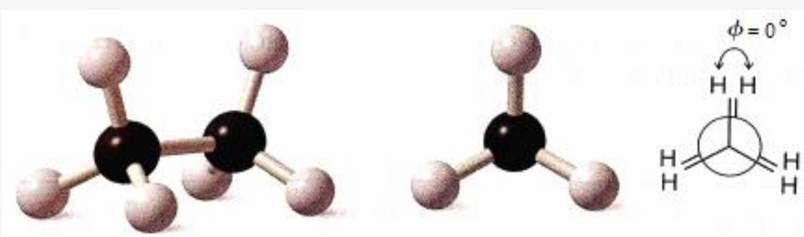
Ethane is the simplest hydrocarbon that can have distinct conformations.

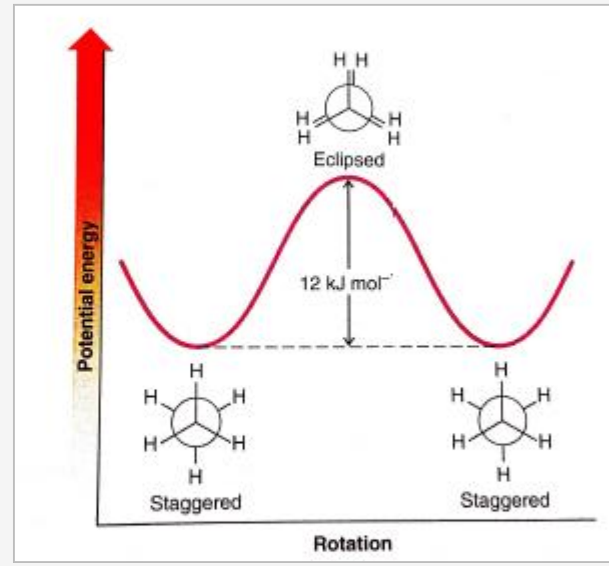
~~Two, the staggered conformation and the eclipsed conformation.~~

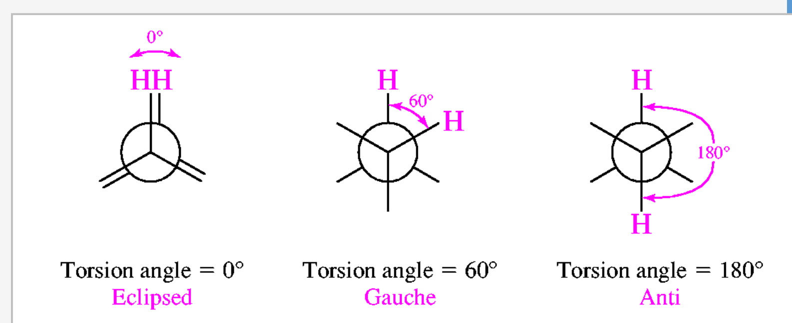
Staggered Conformation



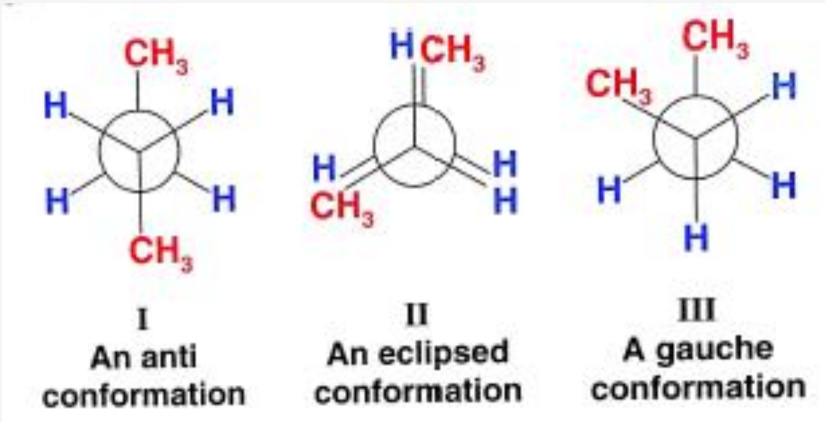
Eclipsed Conformation

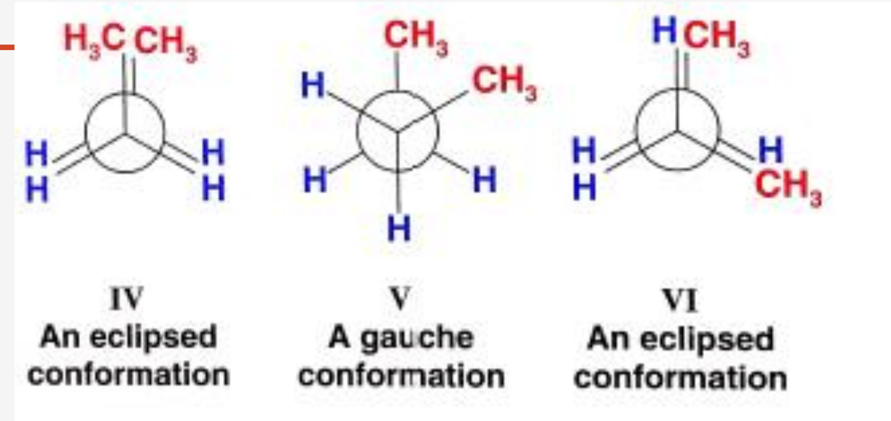


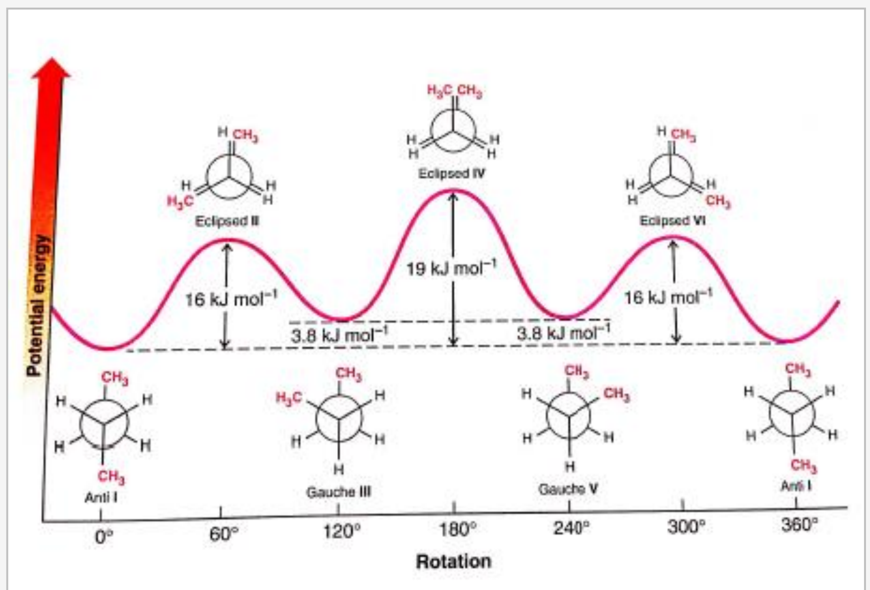




Conformational Analysis in Butane

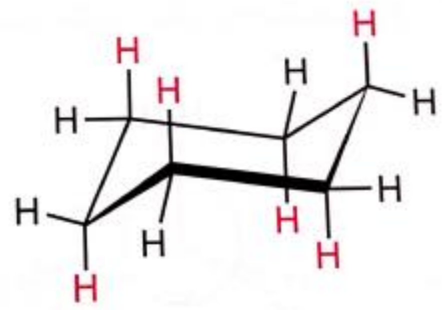






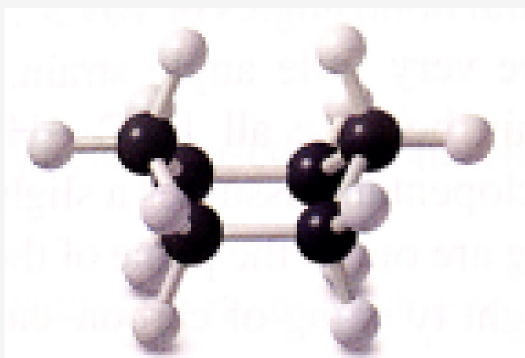
Conformational Analysis in Cyclohexane

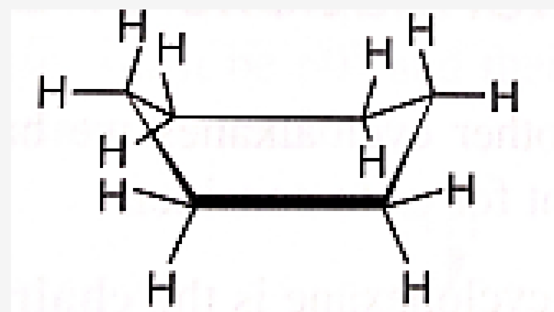
Chair conformation

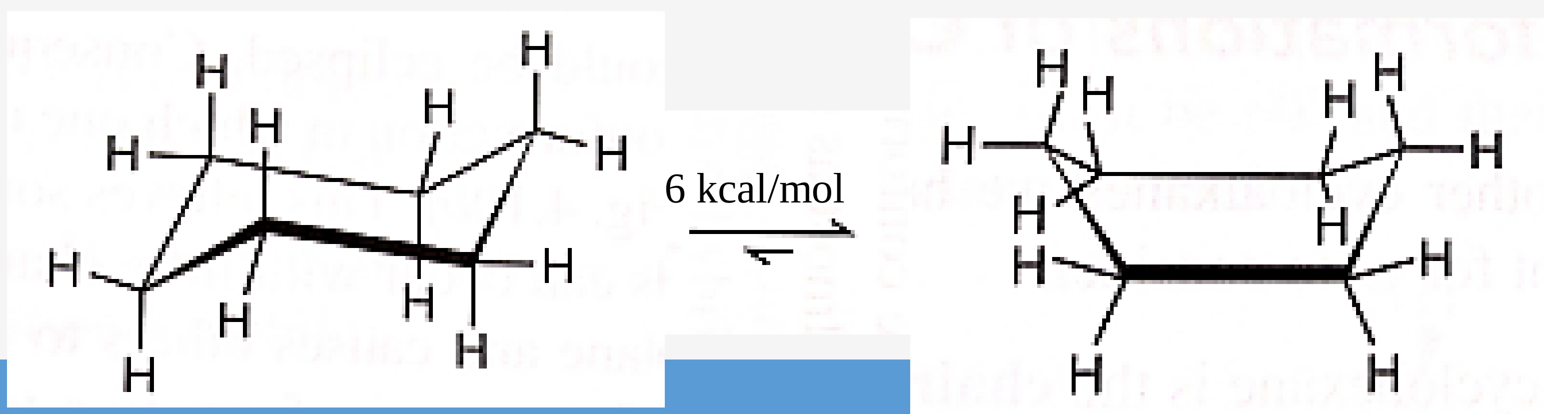


most stable

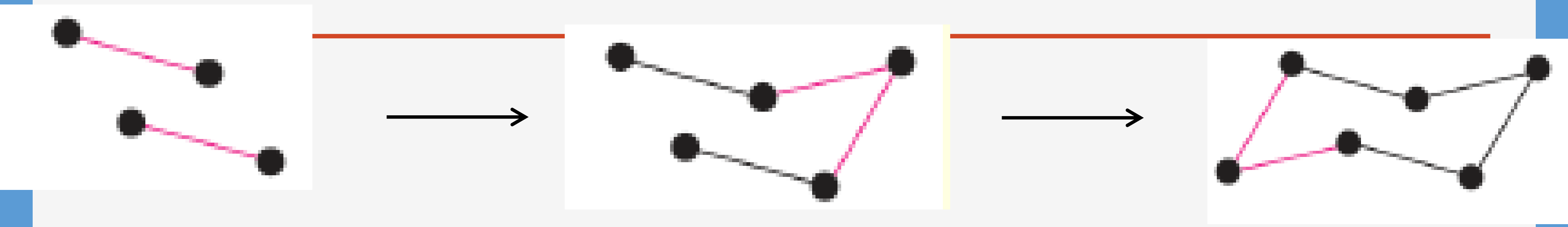
Boat conformation





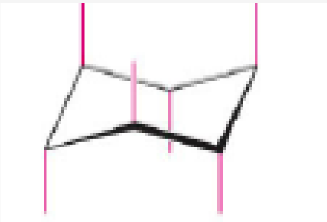


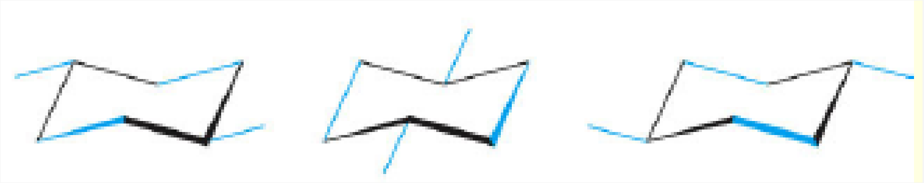
Drawing the Axial and Equatorial Hydrogens



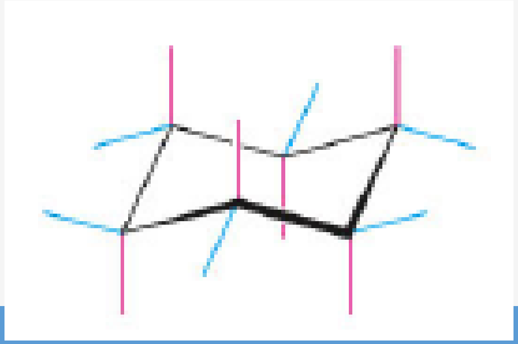
Axial bond (a)

Equatorial bond (e)



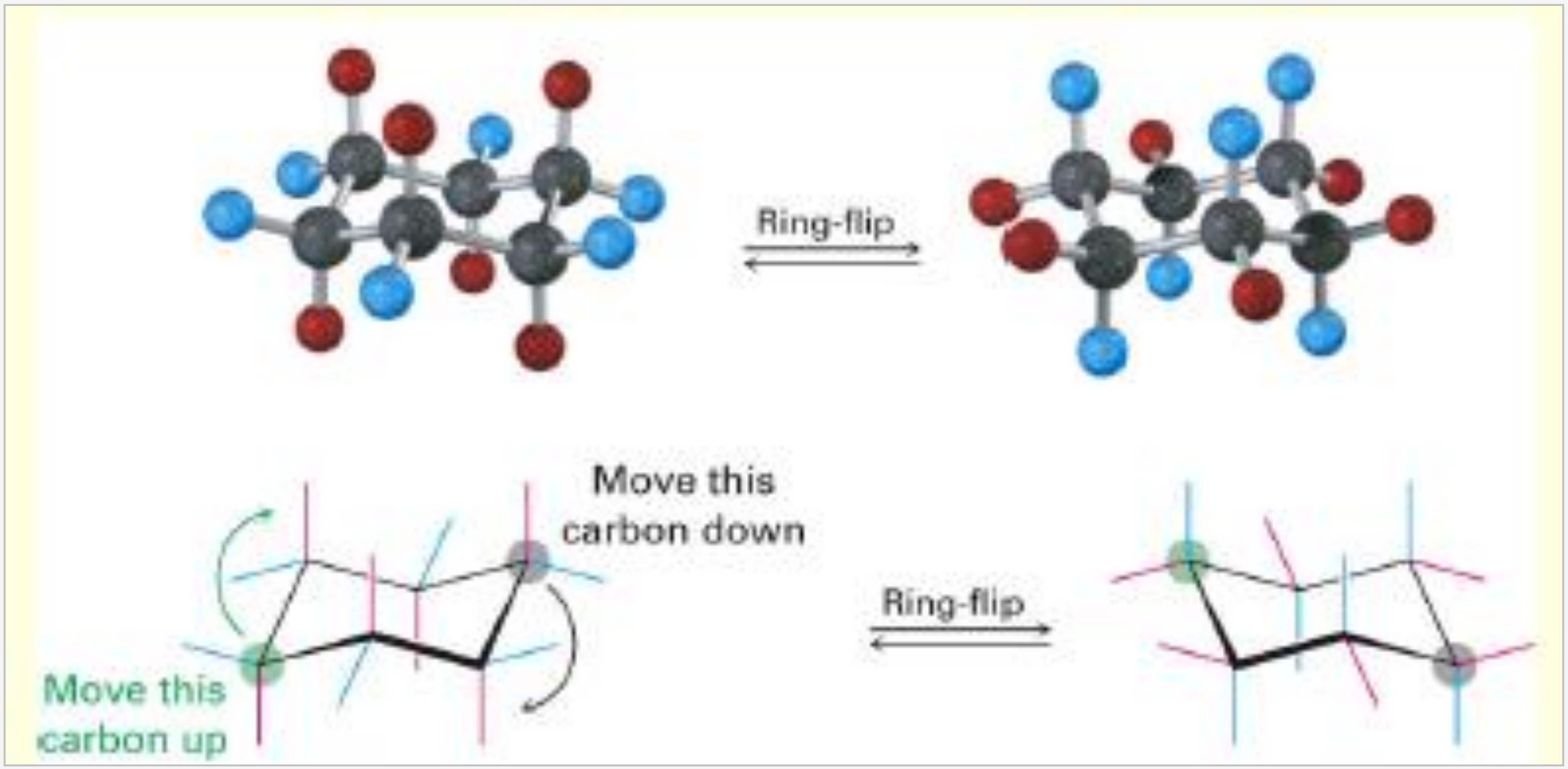


Completed cyclohexane



Conformational Mobility of Cyclohexane

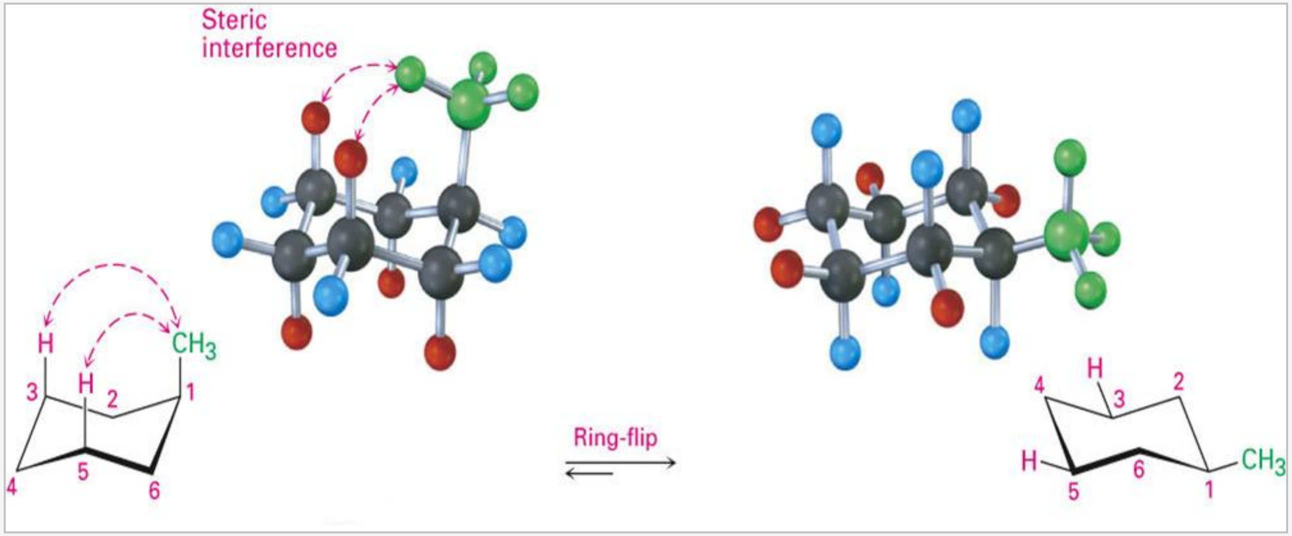
Chair conformations readily interconvert, resulting in the exchange of axial and equatorial positions by a **ring-flip**



Conformations of Monosubstituted Cyclohexanes

Determining the position of a substituent in the most stable conformer.

1,3-Diaxial Interactions



Cis-trans isomerism and Conformational Structure of Disubstituted Cyclohexane

Relationship between Substituents Carbons

	Axial - Axial	Axial - Equatorial	Equatorial - Equatorial
1 and 2	Trans	Cis	Trans
1 and 3	Cis	Trans	Cis
1 and 4	Trans	Cis	Trans
1 and 5	Cis	Trans	Cis
1 and 6	Trans	Cis	Trans

1,4-dimethylcyclohexane