Pharmaceutical Organic Chemistry-1

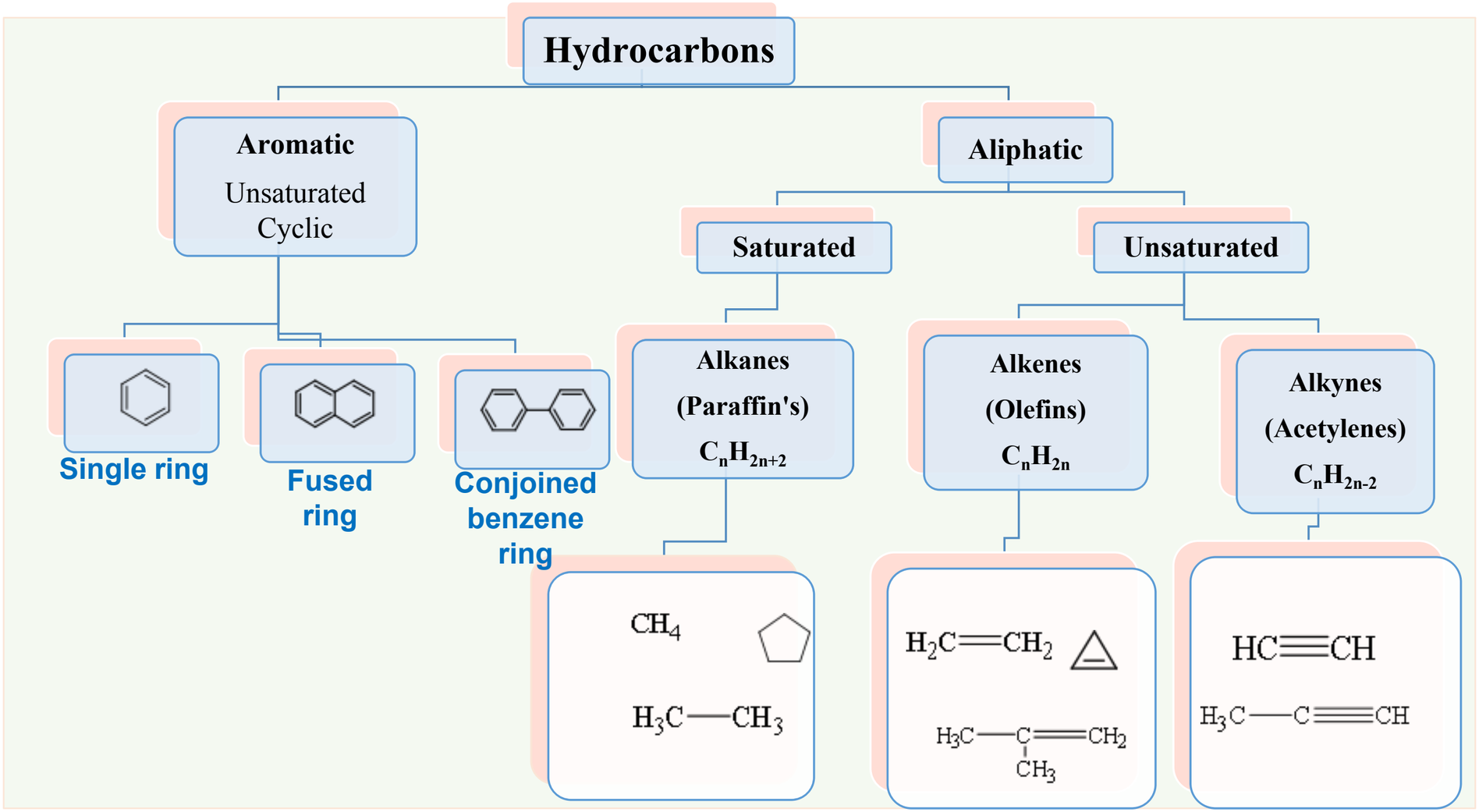
Chapter-2: Aliphatic Hydrocarbon

Hydrocarbons

- **Hydrocarbons are Organic Compounds, which contain only the two elements carbon and hydrogen.**
- **Aliphatic hydrocarbons are subdivided into:**
  - ***Saturated hydrocarbons***
    - **Alkanes; C_nH_{2n+2}** (*contain carbon-carbon single bond*)
    - **Cycloalkanes: C_nH_{2n}** (***contain carbon-carbon single bond in a single ring***)

    Alkanes and cycloalkanes are so similar that many of their properties can be considered side by side.
  - ***Unsaturated hydrocarbons***
    - **Alkenes : C_nH_{2n}** **(contain *carbon-carbon double bond)***
    - **Alkynes : $C_n H_{2n-2}$** **(contain *carbon-carbon triple bond)***

Hydrocarbons



Saturated Hydrocarbons
1. Alkanes

- General formula is C_nH_{2n+2}
- In alkanes, the four sp^3 orbitals of carbon repel each other into a TETRAHEDRAL arrangement with bond angles of 109.5º like in CH_4.
- Each sp^3 orbital in carbon overlaps with the 1s orbital of a hydrogen atom to form a C-H bond.

Saturated Hydrocarbon
1. Alkanes

Names, Molecular formulas and Number of Isomers of the first ten Alkanes

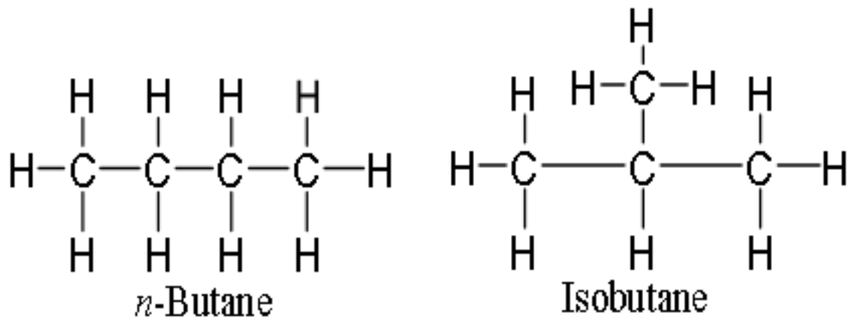
Name	Molecular Formula	Number of isomers
Methane	CH_4	1
Ethane	C_2H_6	1
Propane	C_3H_8	1
Butane	C_4H_{10}	2
Pentane	C_5H_{12}	3
Hexane	C_6H_{14}	5
Heptane	C_7H_{16}	9
Octane	C_8H_{18}	18
Nonane	C_9H_{20}	35
Decane	$C_{10}H_{22}$	75

Saturated Hydrocarbons
1. Alkanes

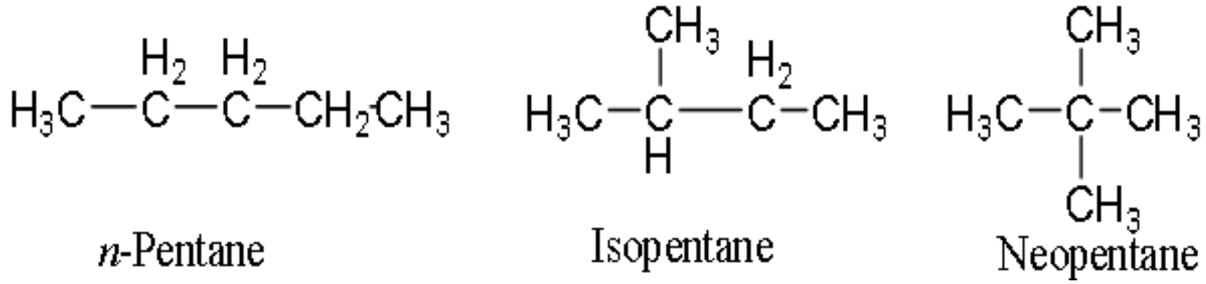
Structural Isomerism

- **Isomers** are different compounds with identical molecular formulas. The phenomenon is called ***isomerism***.
- **Structural** or **constitutional isomers** are isomers which differ in the sequence of atoms bonded to each other.
- **Examples:**

➤ **Butanes, C_4H_{10}.**



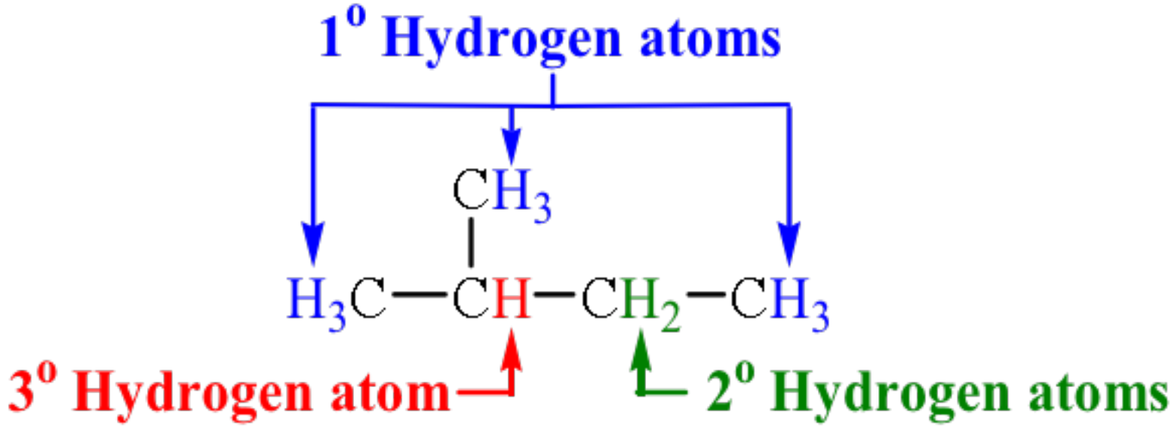
➤ **Pentanes, C_5H_{12}.**



Saturated Hydrocarbons
1. Alkanes

Classes of Carbons and Hydrogen

- **A primary (1°) carbon** is one that is bonded to only one other carbon.
- **A secondary (2°) carbon** is one that is bonded to two other carbons.
- **A tertiary (3°) carbon** is one that is bonded to three other carbons.
- **A quaternary (4°) carbon** is one that is bonded to four other carbons.



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

Saturated Hydrocarbons
1. Alkanes

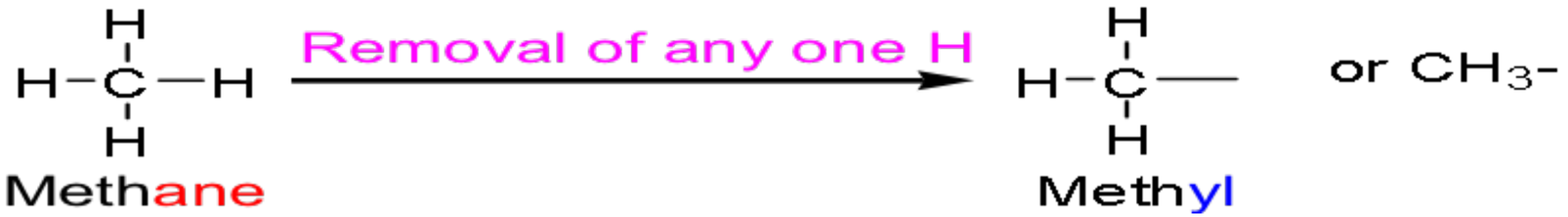
Alkyl Groups

- An **alkyl group** is an alkane from which a hydrogen has been removed.
- General formula C_nH_{2n+1}.
- **Alky group** is represented by **R**.
- **Nomenclature of alkyl groups by**

  replacing the suffix *– ane* of the parent alkane by *–yl*.

  i.e. Alkane – ane + yl = Alkyl

- **Examples:**
  - ***Methane***

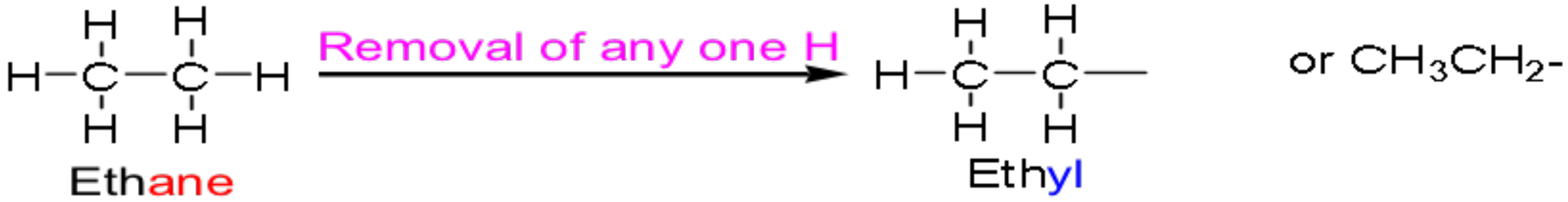


CH_3- (Methane – ane + yl) = methyl

Saturated Hydrocarbons
1. Alkanes

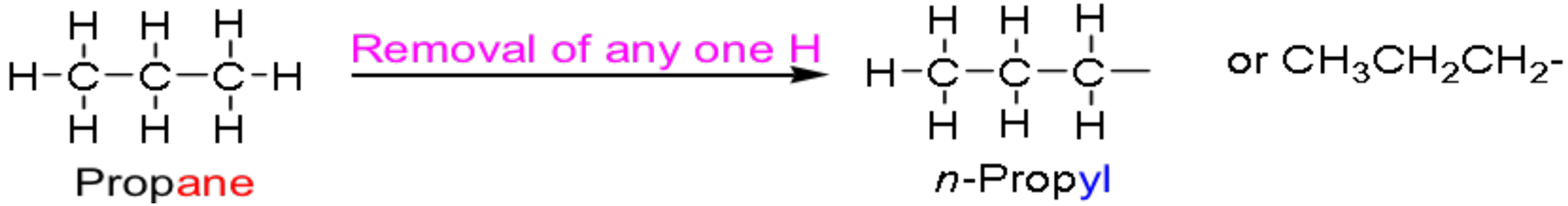
Alkyl Groups

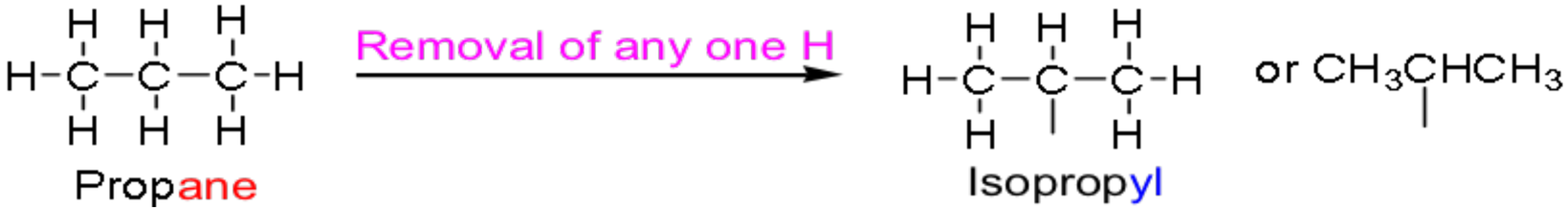
- ***Ethane***



CH_3CH_2- (Ethane – ane + yl) = ethyl

- ***Propane***



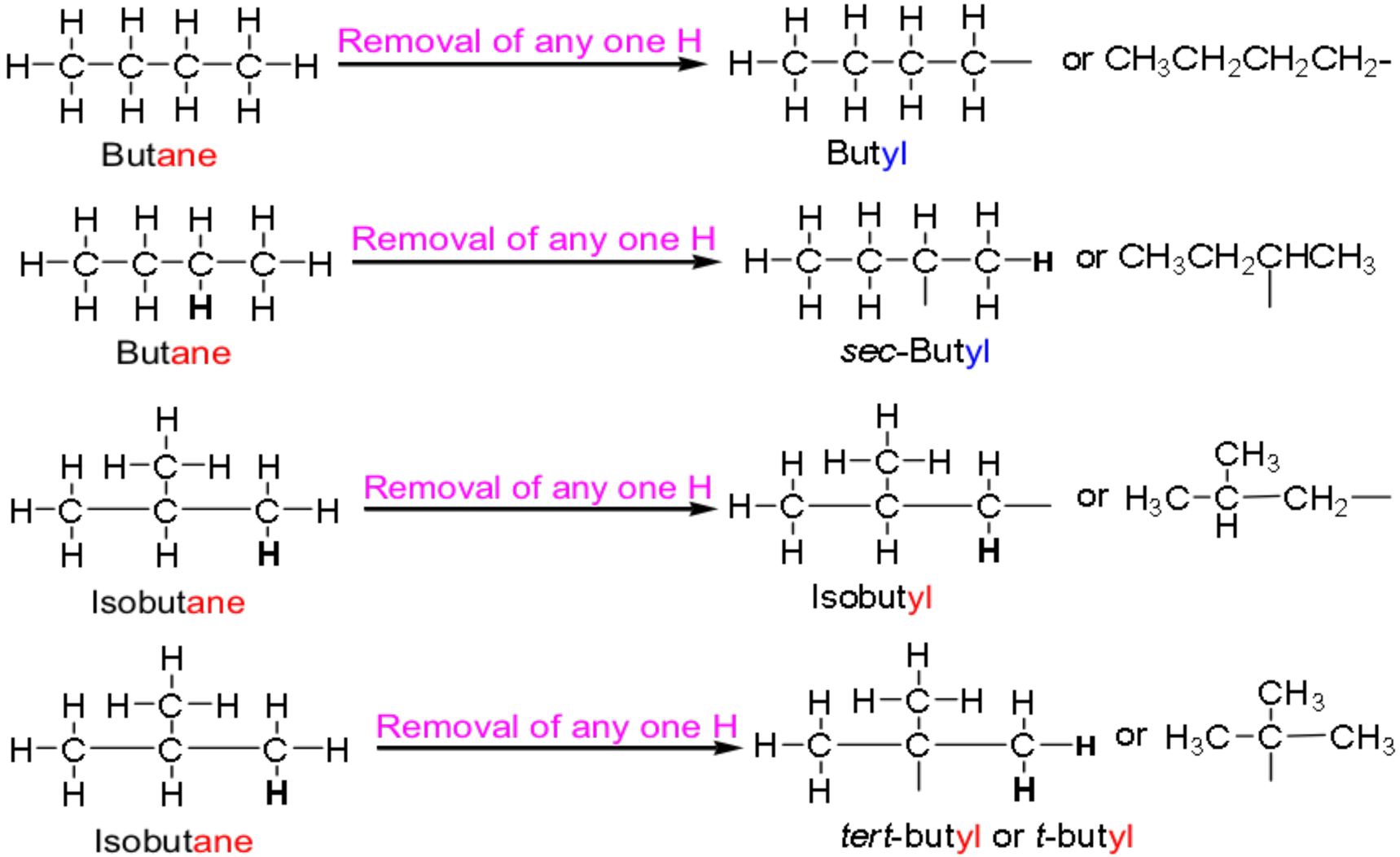


Propane – ane + yl = *n*-propyl or isopropyl

Saturated Hydrocarbons
1. Alkanes

Alkyl Groups

- *Butane*



Saturated Hydrocarbons
1. Alkanes

Alkyl Groups

Alkane		Alkyl Group	Abbreviation
CH_3—**H** **Methane**	becomes	CH_3— **Methyl**	Me–
CH_3CH_2—**H** **Ethane**	becomes	CH_3CH_2— **Ethyl**	Et–
$CH_3CH_2CH_2$—**H** **Propane**	becomes	$CH_3CH_2CH_2$— **Propyl**	Pr–
$CH_3CH_2CH_2CH_2$—**H** **Butane**	becomes	$CH_3CH_2CH_2CH_2$— **Butyl**	Bu–

Saturated Hydrocarbons
1. Alkanes

Nomenclature

- **Most organic compounds are known by two or more names:**
  - **The older unsystematic names, (*Common names*).**
  - **The IUPAC names.**

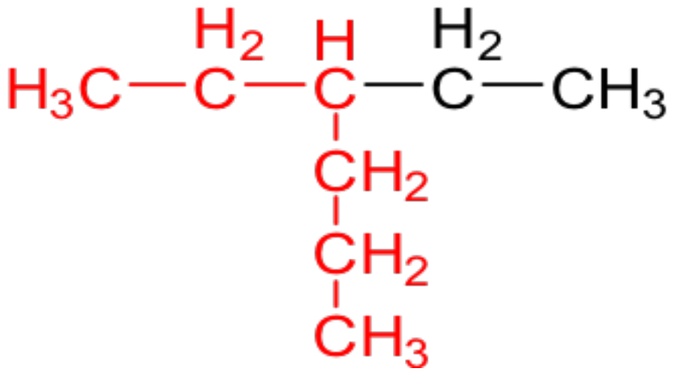
    International Union of Pure & Applied Chemistry

Saturated Hydrocarbons
1. Alkanes

Nomenclature

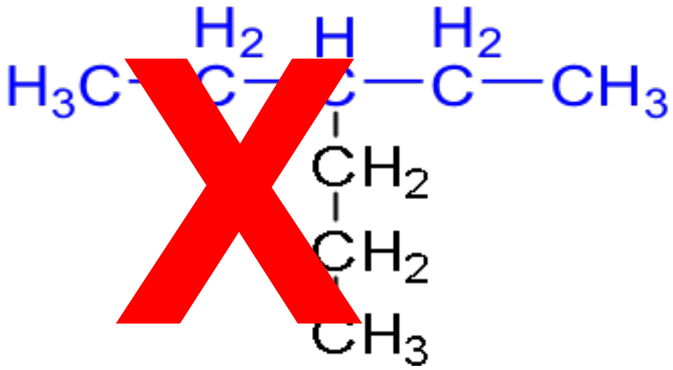
The IUPAC Rules

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



Ethyl hexane

not



Propyl pentane

The longest continuous chain is not necessarily straight.

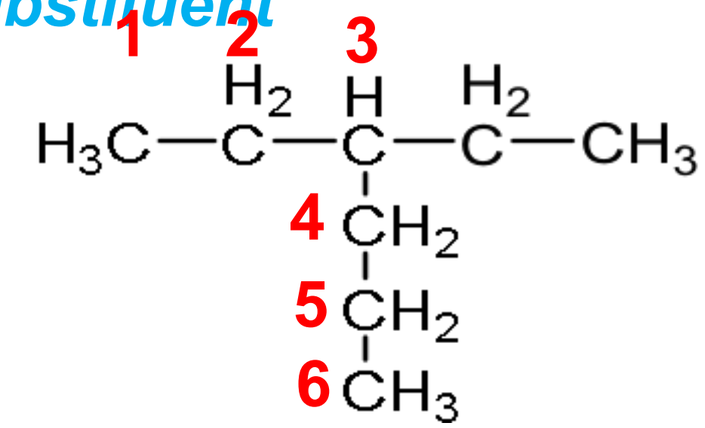
Saturated Hydrocarbons
1. Alkanes

Nomenclature

The IUPAC Rules

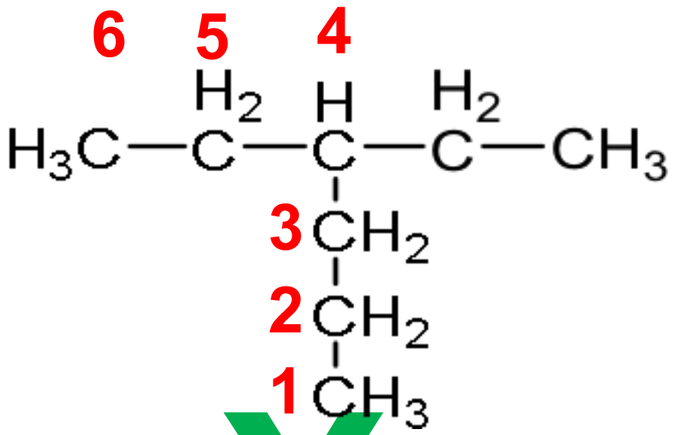
2) Number the carbons in the parent chain

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



3-Ethylhexane

not



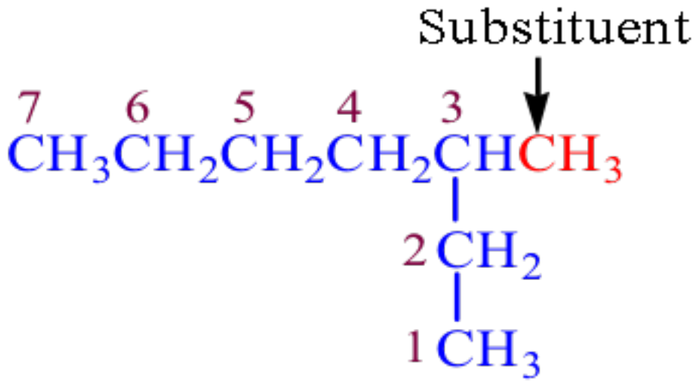
4-Ethylhexane

Saturated Hydrocarbons
1. Alkanes

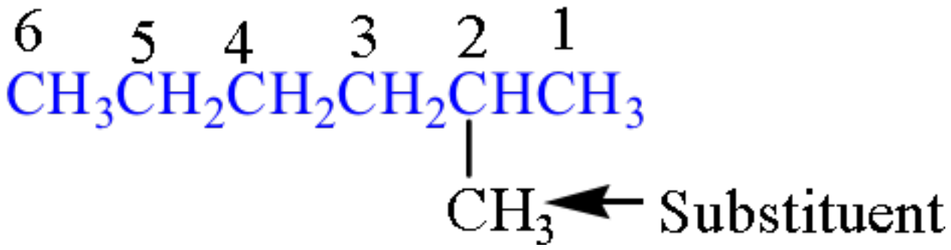
Nomenclature

The IUPAC Rules

2) Number the carbons in the parent chain



3-Methylheptane



2-Methylhexane

Saturated Hydrocarbons
1. Alkanes

Nomenclature

The IUPAC Rules

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 - Ethyl hexane

Saturated Hydrocarbons
1. Alkanes

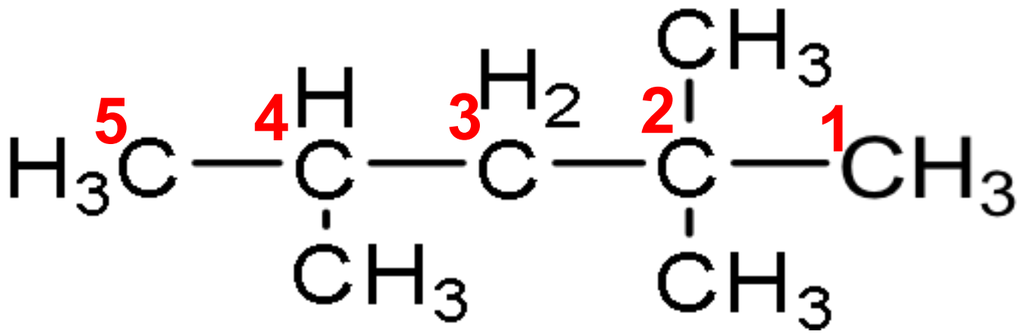
Nomenclature

The IUPAC Rules

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.

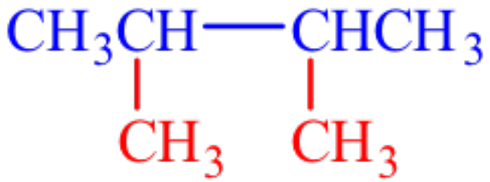


2,2,4-Trimethylpentane

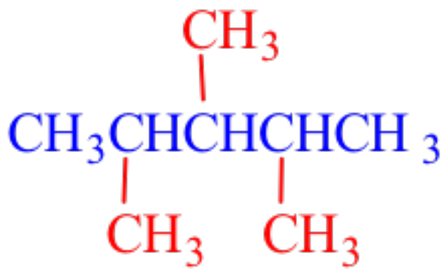
Saturated Hydrocarbons
1. Alkanes

Nomenclature

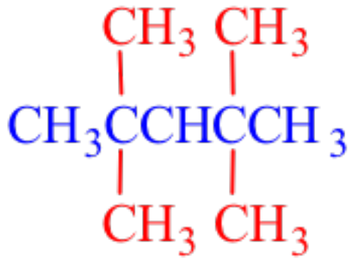
The IUPAC Rules



2,3-Dimethylbutane



2,3,4-Trimethylpentane



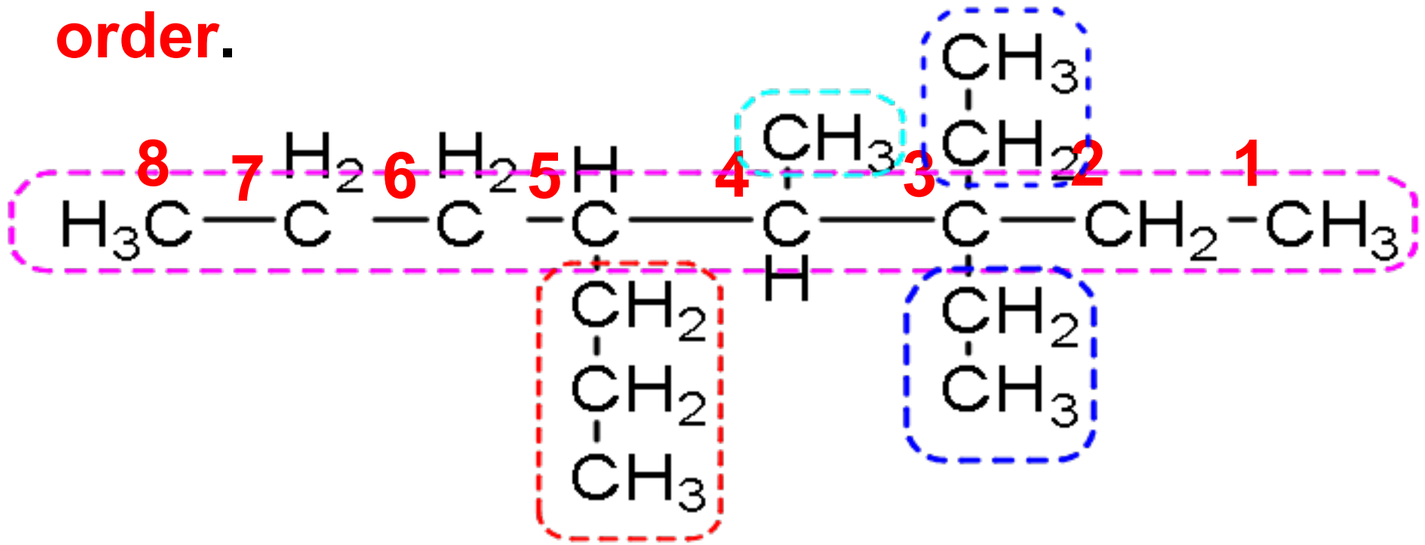
2,2,4,4-Tetramethylpentane

Saturated Hydrocarbons
1. Alkanes

Nomenclature

The IUPAC Rules

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



3,3-diethyl
4- methy
5- propyl

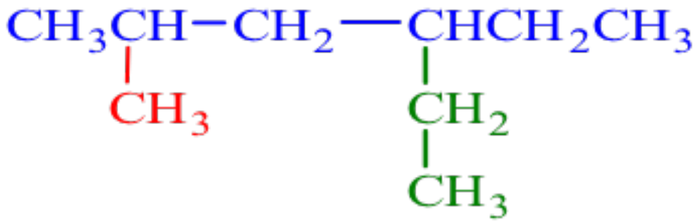
3,3-Diethyl-4-methyl-5-propyloctane

Saturated Hydrocarbons
1. Alkanes

Nomenclature

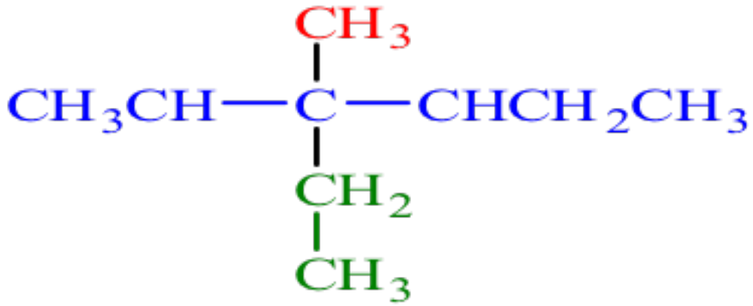
The IUPAC Rules

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

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



3-Ethyl-3-methylhexane

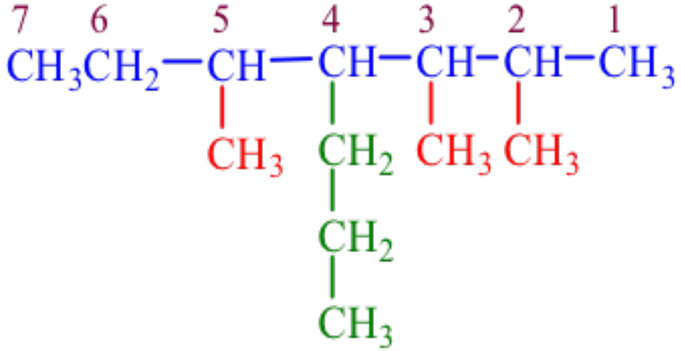
Saturated Hydrocarbons
1. Alkanes

Nomenclature

The IUPAC Rules

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

Saturated Hydrocarbons
1. Alkanes

Nomenclature

The IUPAC Rules

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

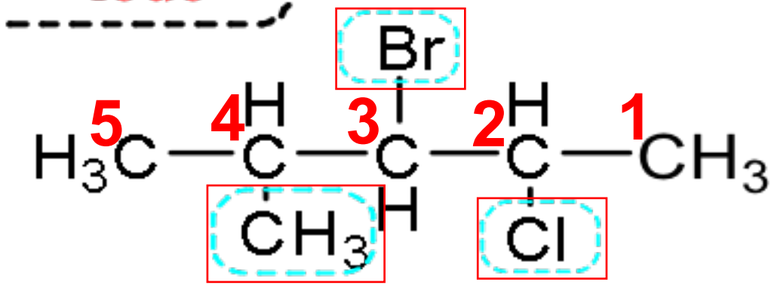
-F fluoro

-Cl chloro

-Br bromo

-I iodo

$-NO_2$ nitro



3-brom-2-chloro-4-methylpentan

2-chloro
3-brom
4-methyl

Saturated Hydrocarbons
1. Alkanes

Sources of Alkanes

- The two principal sources of alkanes are petroleum and natural gas.

  Petroleum and natural gas constitute the chief sources of

  - Alkanes up to 40 Carbons
  - Alicyclic (Cyclic aliphatic hydrocarbons)
  - Aromatic
  - Heterocyclic

Saturated Hydrocarbons
1. Alkanes

Sources of Alkanes

Petroleum Refining

Some components of refined

Fraction	Boiling range (°C)	Caron content
Gas	Below 20	C1 – C4
Petroleum ether	20 – 60	C5 – C6
Naphtha	60 – 100	C6 – C7
Gasoline	40 – 200	C5 – C10
Kerosine	175 – 325	C11 – C18
Gas oil	300 – 500	C15 – C40
Lubricating oil, asphalt, petroleum coke and paraffins	Above 400	C15 – C40

Saturated Hydrocarbons
1. Alkanes

Physical Properties

Physical Properties of Alkanes, Alkenes and Alkynes

Those properties that can be observed without the compound undergoing a chemical reaction.

A. Physical States

- C1 (C2) to C4 are gases,
- C5 to C17 are liquids,
- C18 and larger alkanes are wax –like solids.

B. Solubility

- Alkanes, Alkenes and Alkynes are nonpolar compounds.
- Their solubility " Like dissolve Like"
- Alkanes, Alkenes and Alkynes are soluble in the nonpolar solvents; carbon tetrachloride, CCl_4 and benzene.
- Alkanes, Alkenes and Alkynes are insoluble in polar solvents like water.

Intermolecular Forces and Liquids and Solids

Intermolecular Forces

Intermolecular forces are attractive forces **between** molecules.

Intramolecular forces hold atoms together in a molecule.

Intermolecular vs Intramolecular

- 41 kJ to vaporize 1 mole of water (**inter**)
- 930 kJ to break all O-H bonds in 1 mole of water (**intra**)

Generally, **inter**molecular forces are much weaker than **intra**molecular forces.

"Measure" of intermolecular force

boiling point

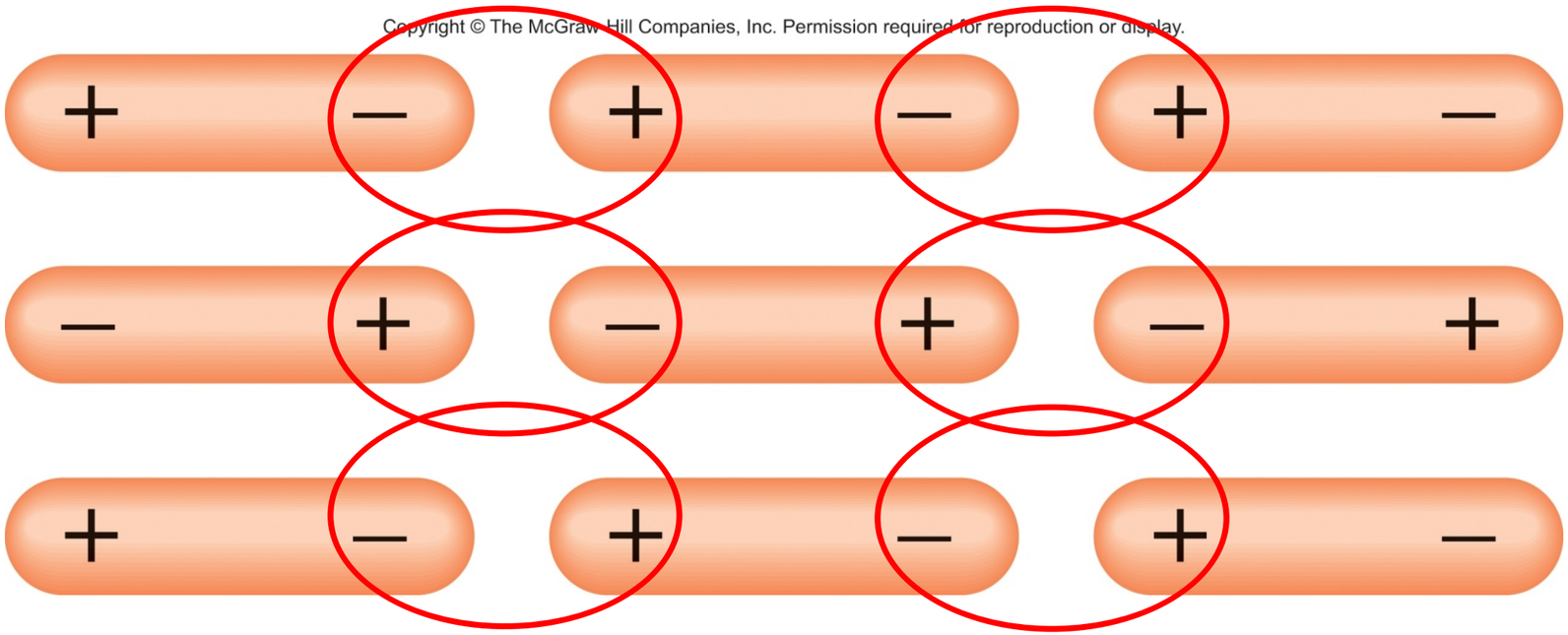
melting point

Intermolecular Forces

Dipole-Dipole Forces

Attractive forces between **polar molecules**

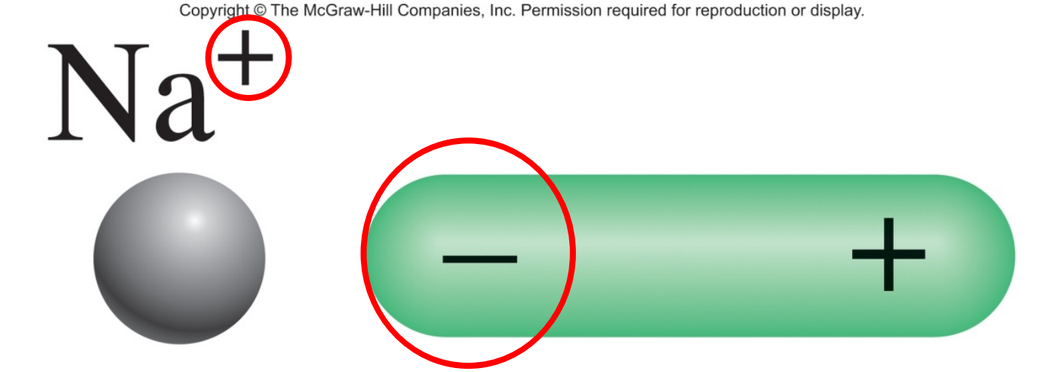
Orientation of Polar Molecules in a Solid

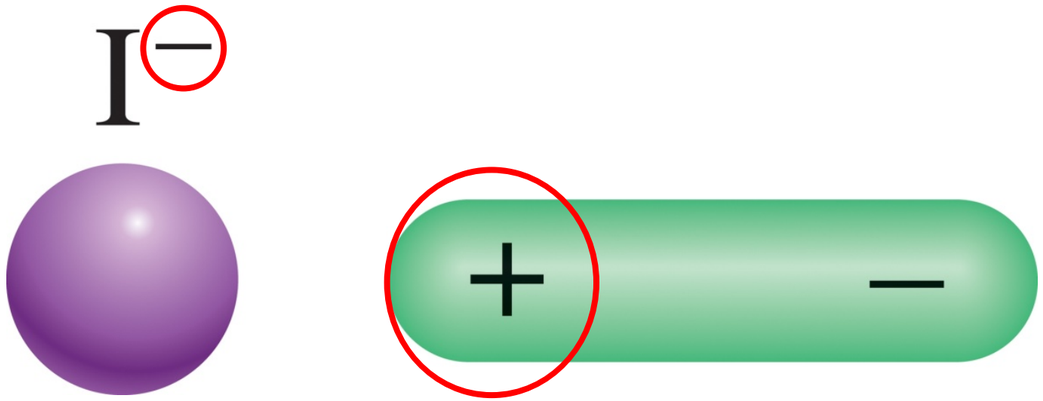


Intermolecular Forces

Attractive forces between an **ion** and a **polar molecule**

Ion-Dipole Interaction





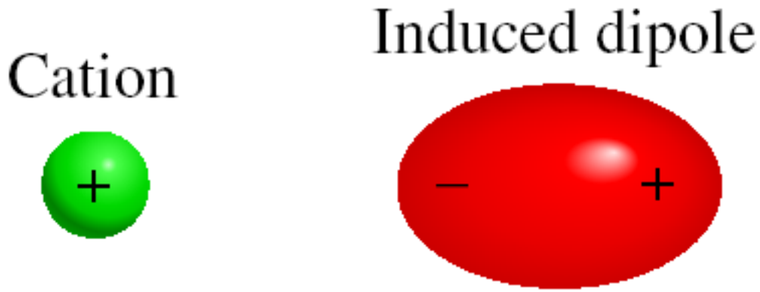
London forces (dipole-induced dipole attraction)

- Non-polar molecules do not have dipoles like polar molecules. How, then, can non-polar compounds form solids or liquids?
- London forces (also called van der Waal forces) are due to small dipoles that exist in non-polar molecules
- Because electrons are moving around in atoms there will be instants when the charge around an atom is not symmetrical
- The resulting tiny dipoles cause attractions between atoms/molecules **(the greater the mass, the greater the London forces)**

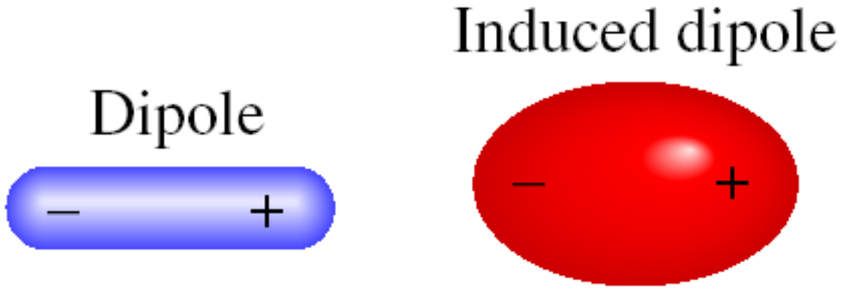
Intermolecular Forces

Dispersion Forces

Attractive forces that arise as a result of **temporary dipoles induced** in atoms or molecules

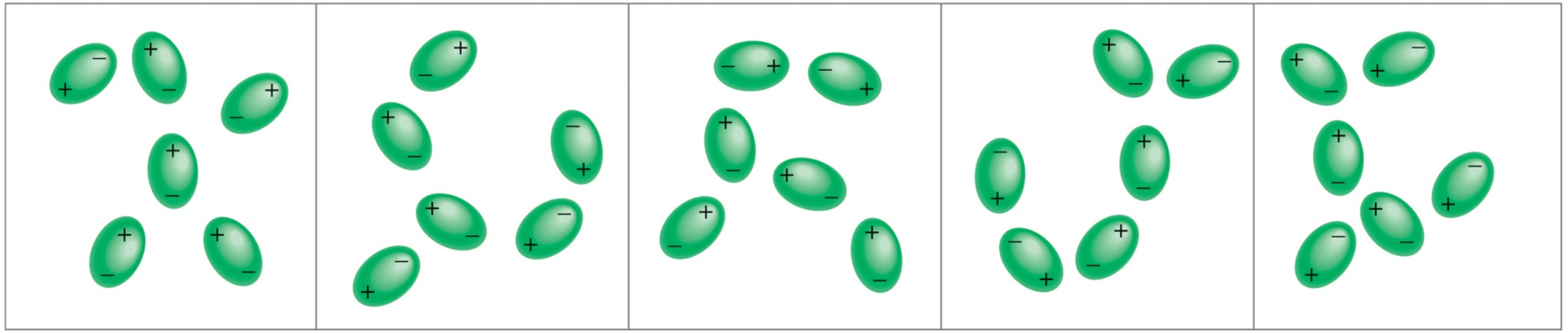


ion-induced dipole interaction



dipole-induced dipole interaction

Induced Dipoles Interacting With Each Other



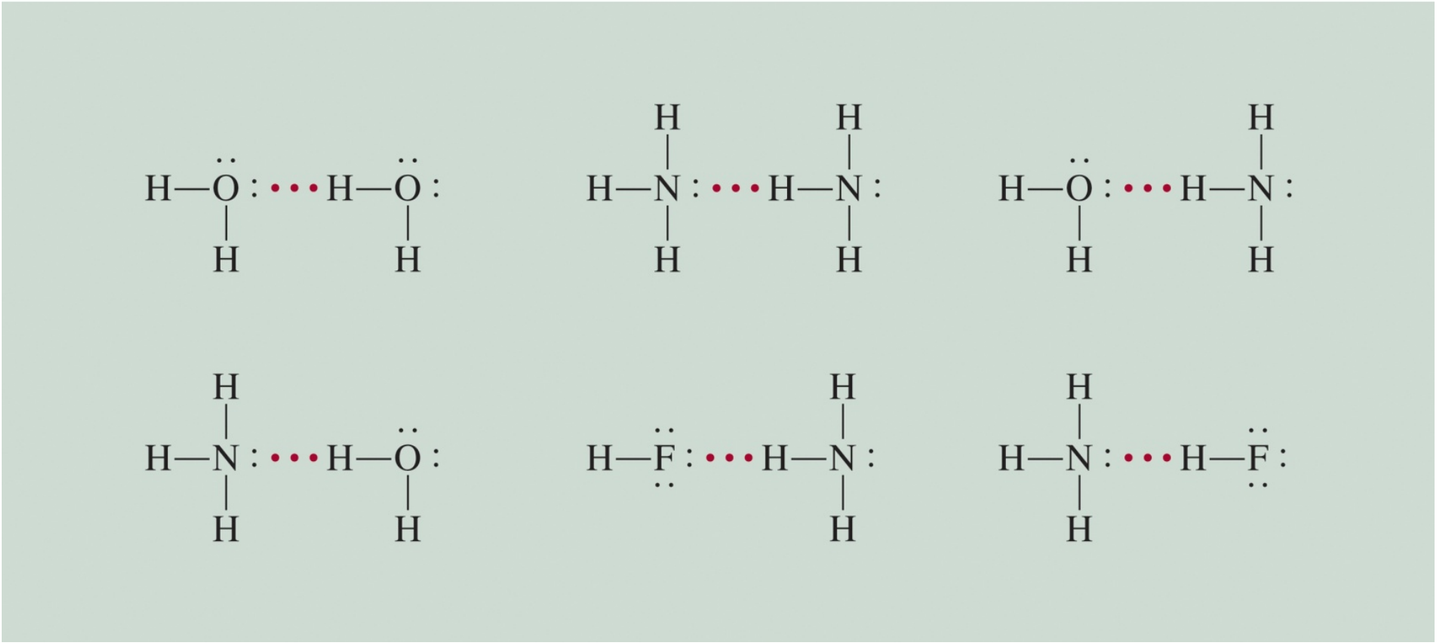
Intermolecular Forces

Hydrogen Bond

The ***hydrogen bond*** is a special dipole-dipole interaction between the hydrogen atom in a polar N-H, O-H, or F-H bond and an electronegative O, N, or F atom.

$$A — H \cdots B \qquad \text{or} \qquad A — H \cdots A$$

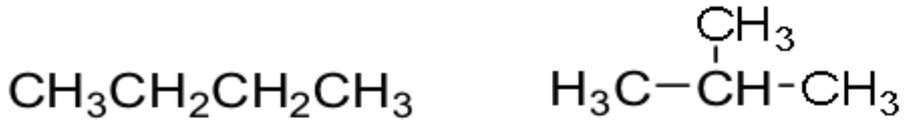
A & B are N, O, or F



Saturated Hydrocarbons
1. Alkanes

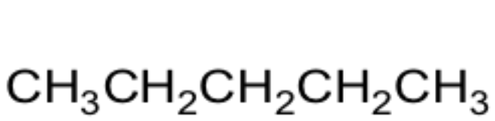
Physical Properties

C. Boiling Points

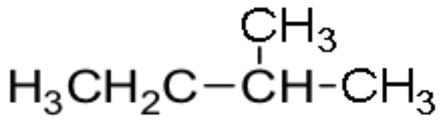


n-Butane
b.p.=0°C

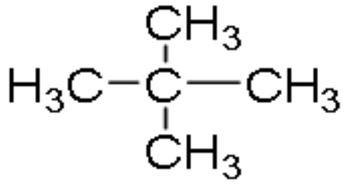
Isobutane
b.p.=-12°C



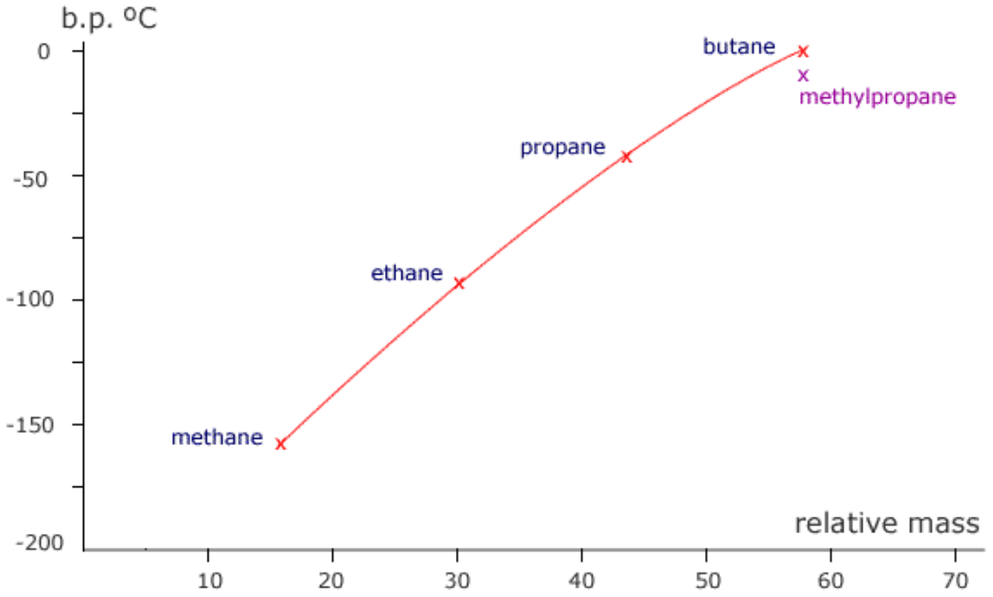
n-Pentane
b.p.=36°C



Isopentane
b.p.=28°C



Neopentane
b.p.=9.5°C

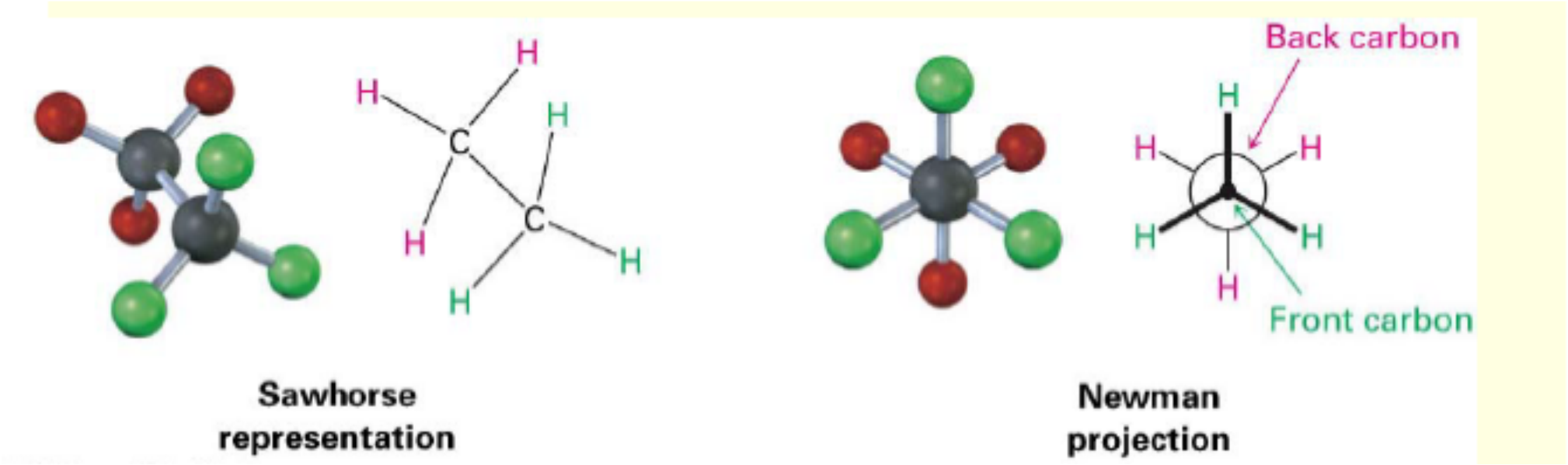


Graph showing boiling point of the alkanes against relative mass

- Boiling point decreases with increasing branches
- Boiling point increases with increasing molecular weight.

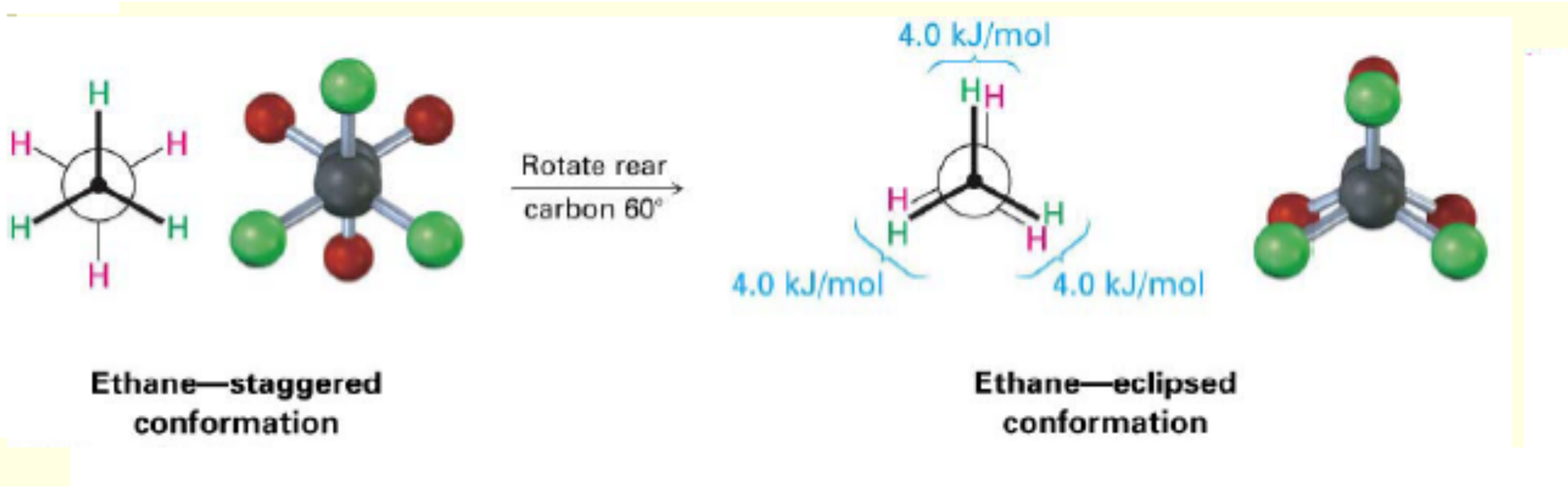
Conformational Isomers of Alkanes

Isomers that differ as a result of sigma bond Isomers that differ as a result of sigma bond rotation of C-C bond in alkanes



Bond Rotation and Newman Projections

As carbon As carbon -carbon bond rotates, interconvert carbon bond rotates, interconvert between staggered and eclipsed conformers

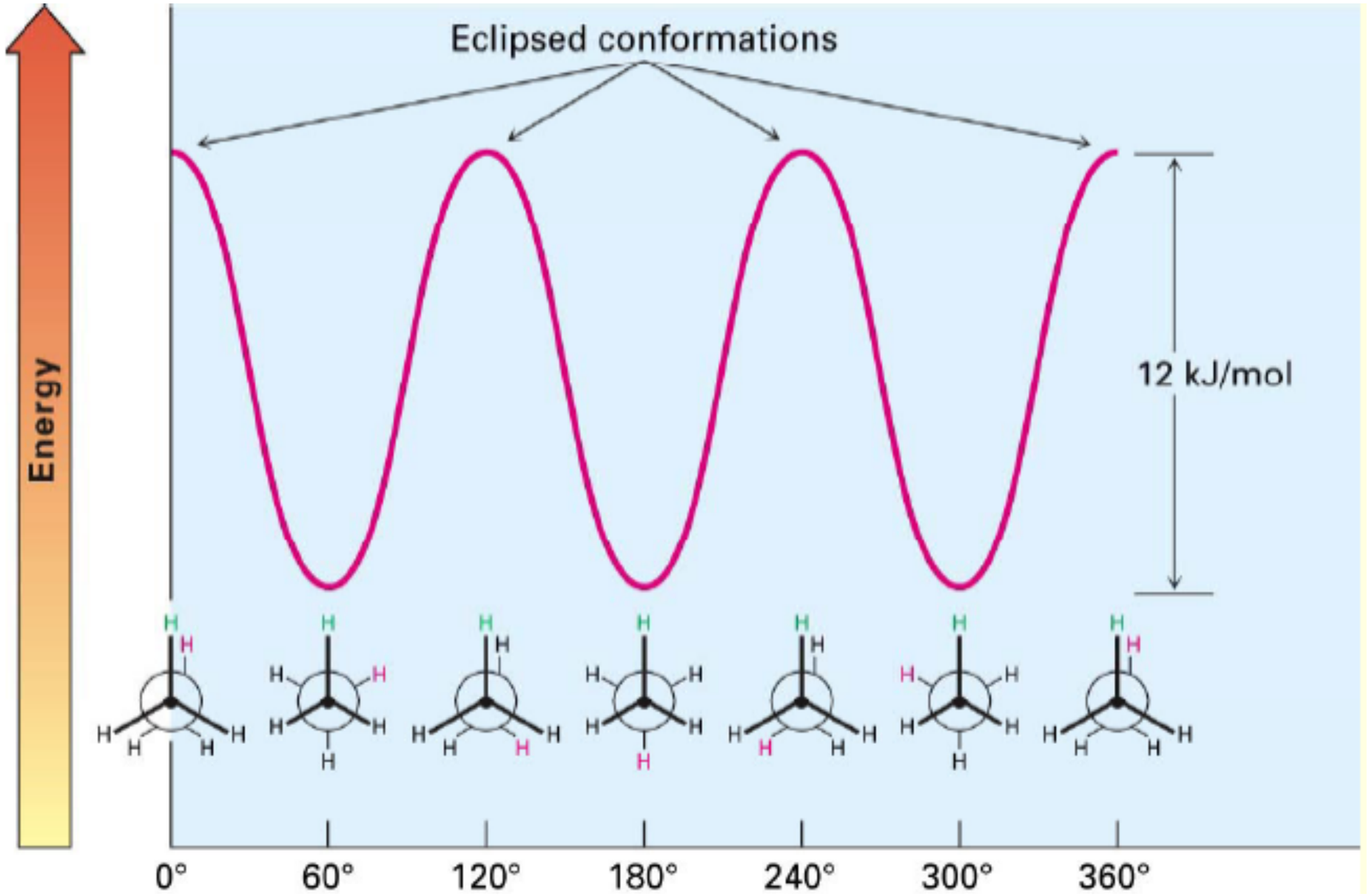


Eclipsed conformer is 12.0 kJ/mol higher in energy ('free' rotation at room temperature)

Torsional Strain Energy

Force that opposes rotation due to the repulsion Force that opposes rotation due to the repulsion of bonding electrons

- We do not observe perfectly free rotation
- There is a barrier to rotation, and some conformers are more stable than others
- Small energy barrier easily overcome at RT
- Each eclipsed H-H costs 4 kJ/mol of Torsional Energy


Energy
Eclipsed conformations
12 kJ/mol
0°
60°
120°
180°
240°
300°
360°

Strain Energy in Alkanes

Torsional Strain

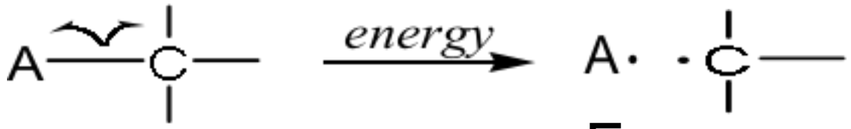
Steric strain- repulsive interaction occurring between atoms that are forced closer together than their at far from each other.

Table 3.5 | Energy Costs for Interactions in Alkane Conformers

Interaction	Cause	Energy cost (kJ/mol)	Energy cost (kcal/mol)
H⟷H eclipsed	Torsional strain	4.0	1.0
H⟷CH_3 eclipsed	Mostly torsional strain	6.0	1.4
CH_3⟷CH_3 eclipsed	Torsional and steric strain	11	2.6
CH_3⟷CH_3 gauche	Steric strain	3.8	0.9

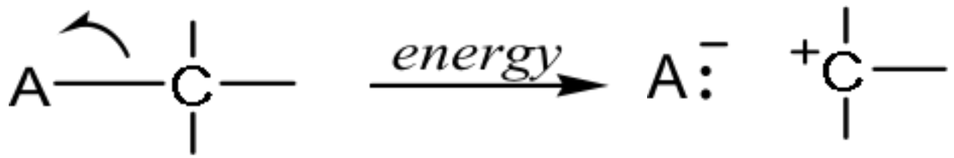
Notations for bond breaking and bond making

- **A covalent bond can be broken in either two ways,**
  - **Homolytic cleavage.**

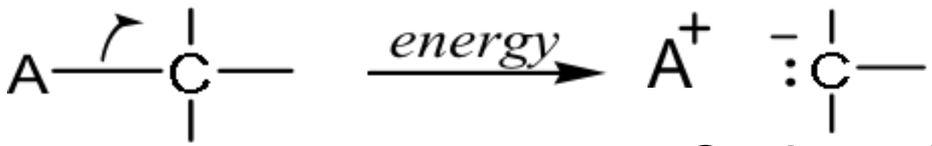


Free radicals

  - **Heterolytic cleavage.**



Carbocation



Carboanion

Preparation of Alkanes

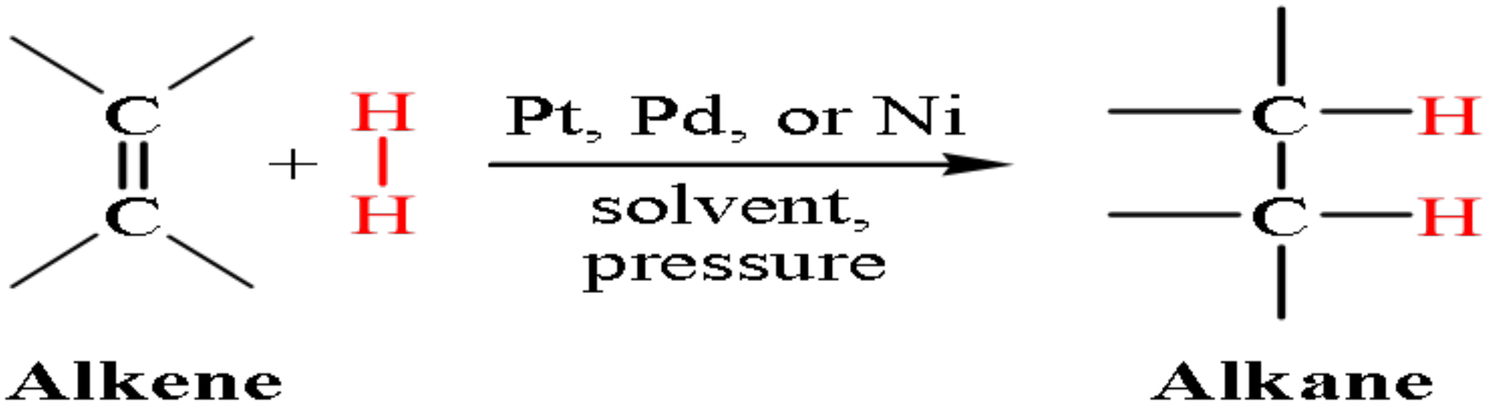
1) Hydrogenation of Alkenes and Alkynes

A great number of alkanes can be obtained by fractional distillation of crude petroleum and subsequent reactions as follows:

1. Catalytic hydrogenation:

Alkenes and alkynes react with hydrogen in the presence of metal catalysts such as nickel, palladium, and platinum to produce alkanes.

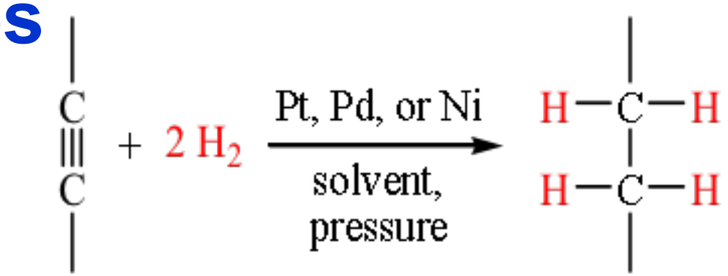
General Reaction



Alkene **Alkane**

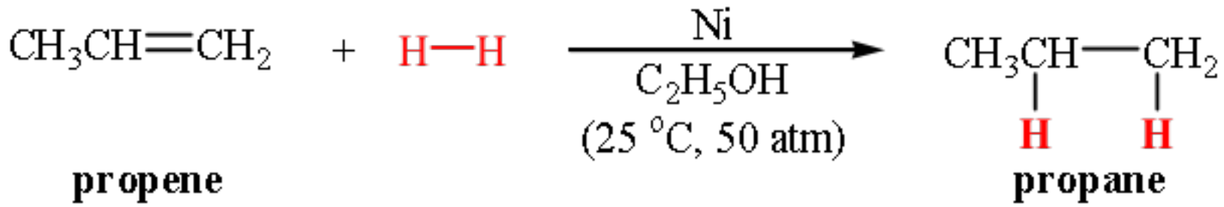
Preparation of Alkanes

1) Hydrogenation of Alkenes and Alkynes

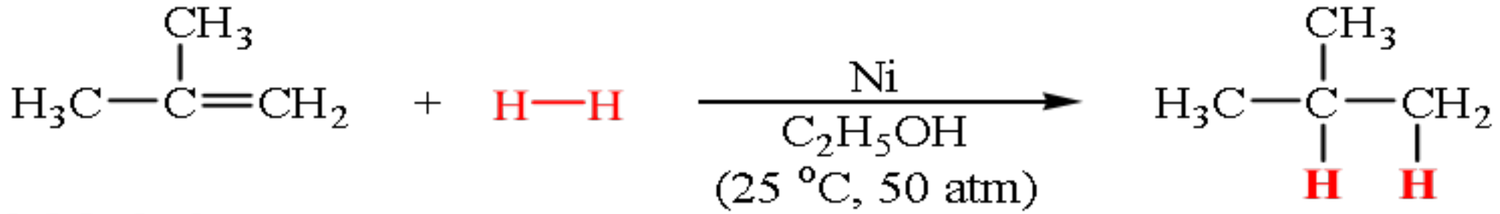


Alkyne **Alkane**

- ***Specific Examples***



propene **propane**



2-Methylpropene **Isobutane**

Preparation of Alkanes

2) Hydrolysis of Grignard Reagent

$$R{-}MgX + HOH \longrightarrow RH + MgX(OH)$$

Alkyl magnesium halide (Grignard reagent)

- ***Grignard reagents*** **react readily with any source of protons to give hydrocarbons.**

$$CH_3CH_2Br + Mg \xrightarrow{\text{Dry Ether}} CH_3CH_2MgBr$$

Ethyl bromide → Ethyl magnesium bromide (Grignard reagent)

$$CH_3CH_2MgBr + HOH \longrightarrow CH_3CH_3 + MgBr(OH)$$

Ethane

3) By coupling of alkyl halides with dialkyl cuprate (all kinds of alkanes)

$$(CH_3CH_2)_2CuLi \xrightarrow{CH_3Br} CH_3CH_2CH_3$$

Reactions of Alkanes

Saturated hydrocarbons undergo very few reactions, so they are called Paraffinic hydrocarbons. (Latin *parum*, little; *affinis*, affinity)

Halogenation

The halogenation of an alkane appears to be a simple free radical substitution in which a C-H bond is broken and a new C-X bond is formed

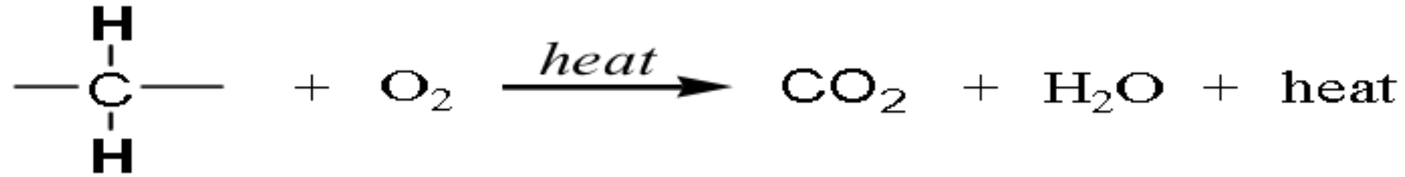
$$RH + X_2 \xrightarrow[\text{or UV light}]{\text{Heat}} RX + HX \quad X = Cl \text{ or } Br$$

Alkyl halide

Reactivity X_2: $Cl_2 > Br_2$

H: $3^0 > 2^0 > 1^0 > CH_3\text{-}H$

Combustion



An alkane

Reactions of Alkanes

A. Halogenation

- **Substitution reaction of alkanes**
  i.e. **replacement of hydrogen by halogen**,
  usually **chlorine or bromine**, giving alkyl chloride or alkyl bromide.

- **Flourine reacts explosively with alkanes**
  It is unsuitable reagent for the preparation of the alkyl flourides.

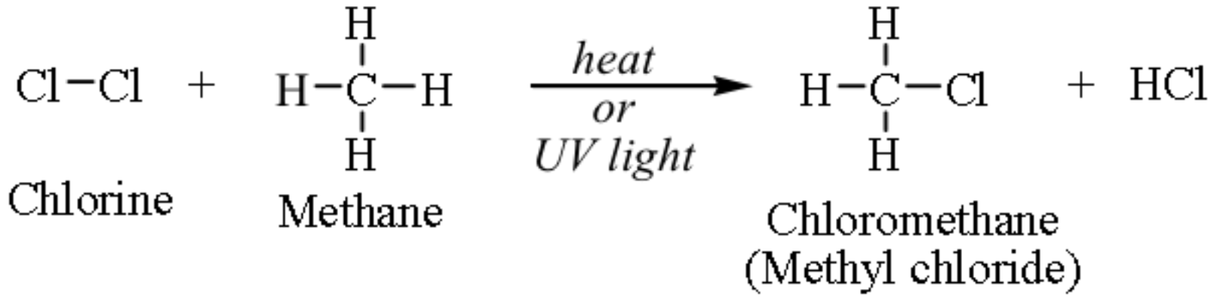
- **Iodine is too unreactive**
  It is not used in the halogentaion of alkanes.

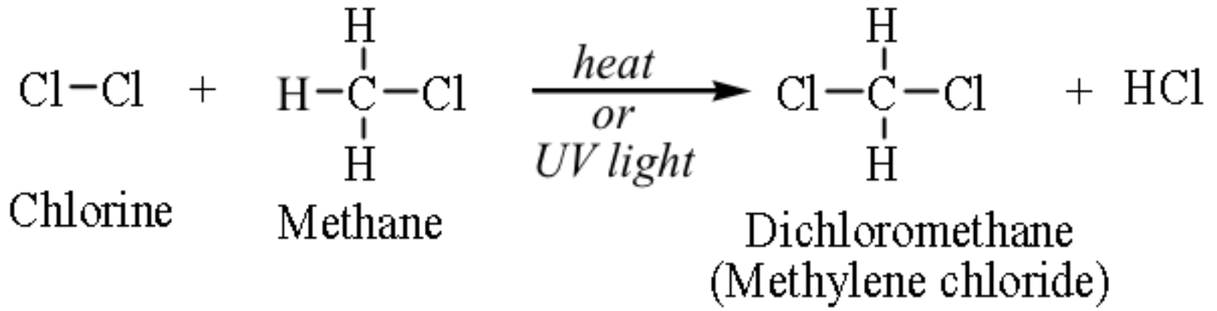
- Halogenation of alkanes take place at **high temperatures** or under the influence of **ultraviolet light**

Reactions of Alkanes

A. Halogenation

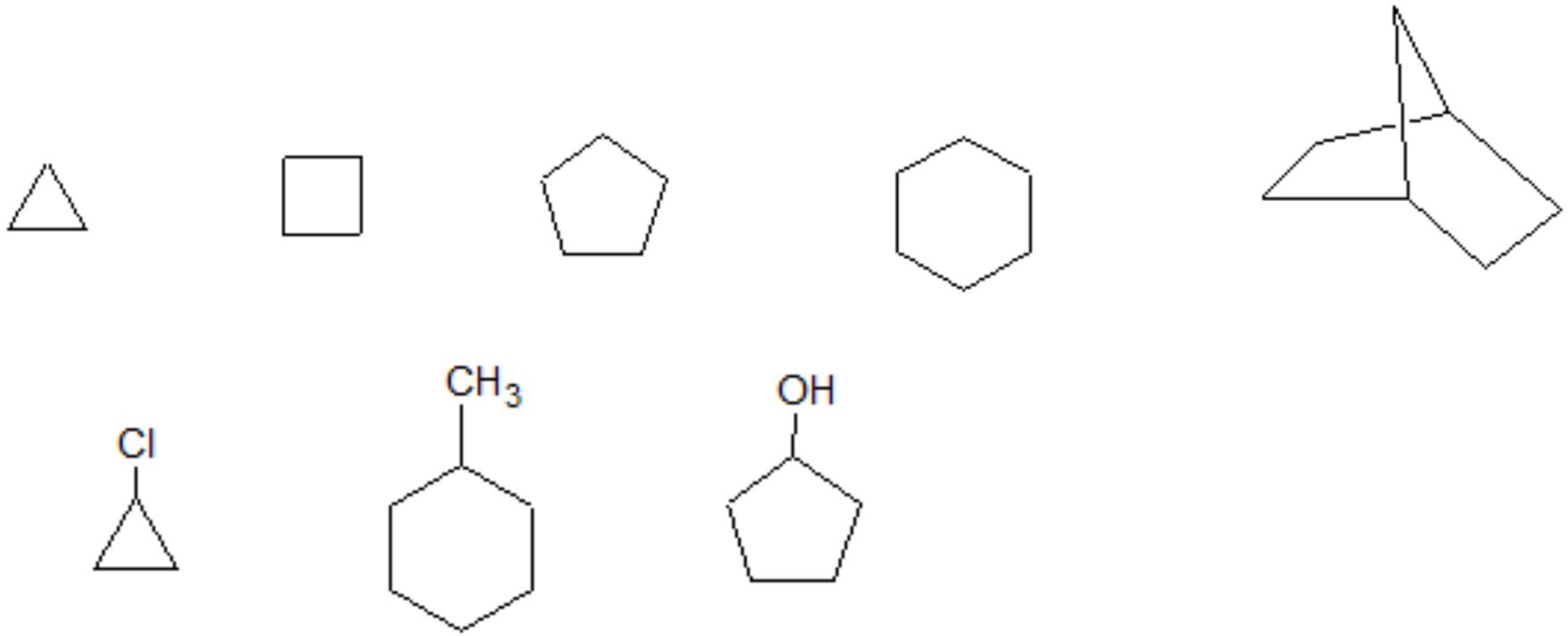
- **Chlorination of an alkane usually gives a mixture of products**





2-Alicyclic Alkanes

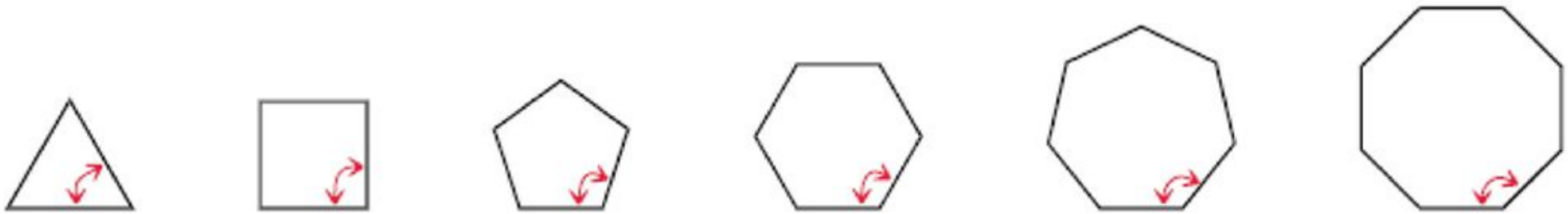
Cycloalkanes: C_nH_{2n} (***contain carbon-carbon single bond in a single ring***)



Saturated Hydrocarbons
2. Alicyclic Alkanes

Cyclic Alkanes

- Carbon atoms in alkanes are sp^3 hybridized

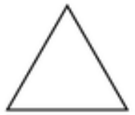


- To optimize the bond angles, most cycloalkanes are NOT flat in their most stable conformation

Nomenclatu re

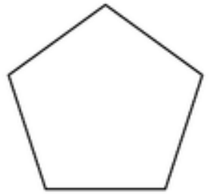
Cycloalkanes

- Alkanes with closed ring(s) of C atoms
- General formula: C_nH_{2n} (C_3H_6, C_4H_8, C_5H_{10}, etc.)
- Naming: use cyclo- prefix before alkane name

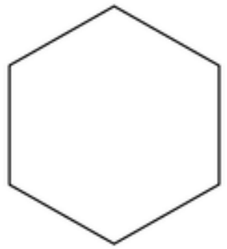


cyclopropane
n = 3
C_3H_6

cyclobutane
n = 4
C_4H_8



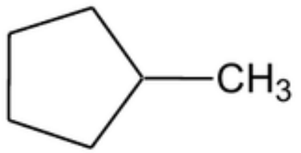
cyclopentane
n = 5
C_5H_{10}



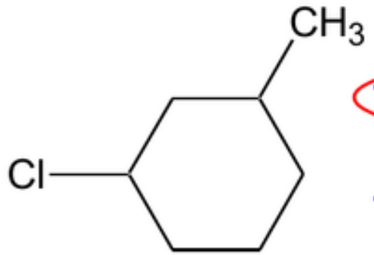
cyclohexane
n = 6
C_6H_{12}

Naming substituted cycloalkanes:

- 1 substituent: no numbering necessary
- 2 or more substituents: highest alpha priority on C #1



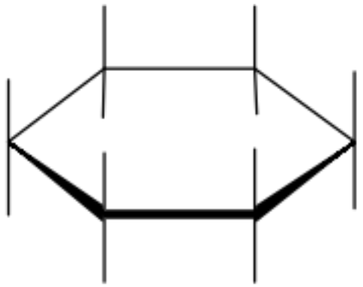
methylcyclopentane



1-chloro-5-methylcyclohexane

1-chloro-3-methylcyclohexane

Conformations of Cyclohexane

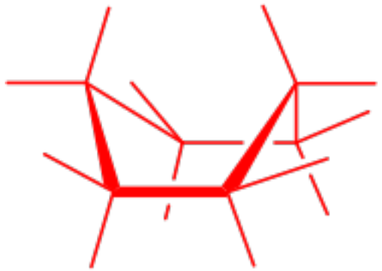


Cyclohexane does not have any angle strain! It isn't a flat molecule. By rotating about the carbon-carbon bonds, it can achieve 109.5^{o} bond angles.

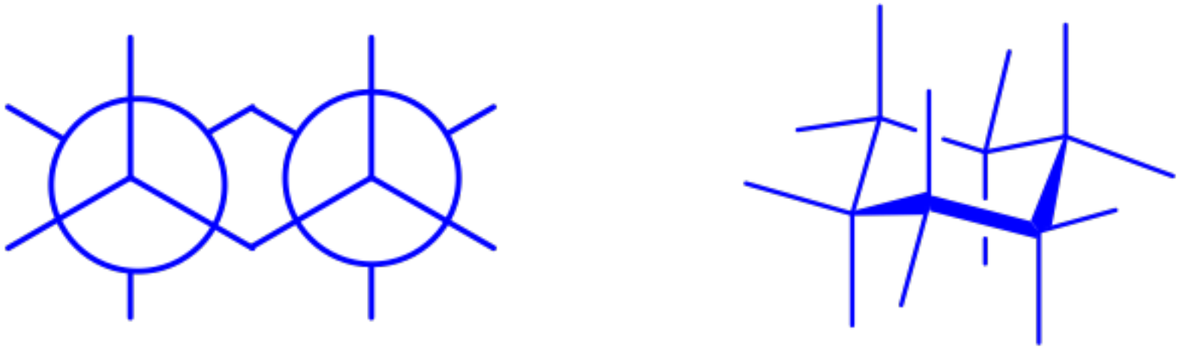
conformations of cyclohexane

chair

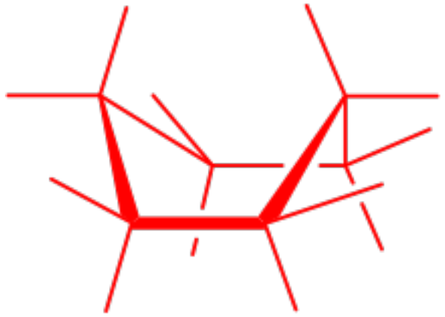
twist boat

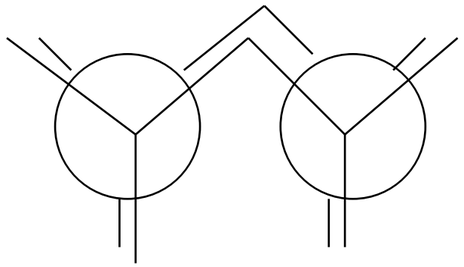


boat

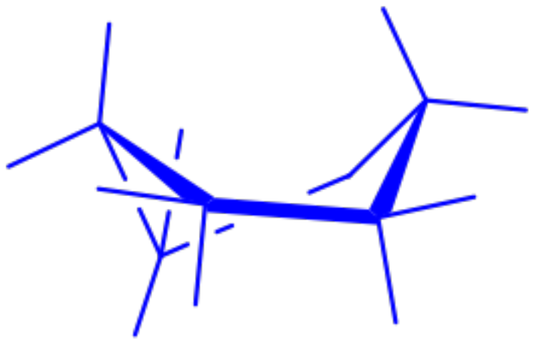


The **chair** conformation of cyclohexane is free of both angle strain and torsional strain (deviation from staggered). This is the **most** stable conformation.

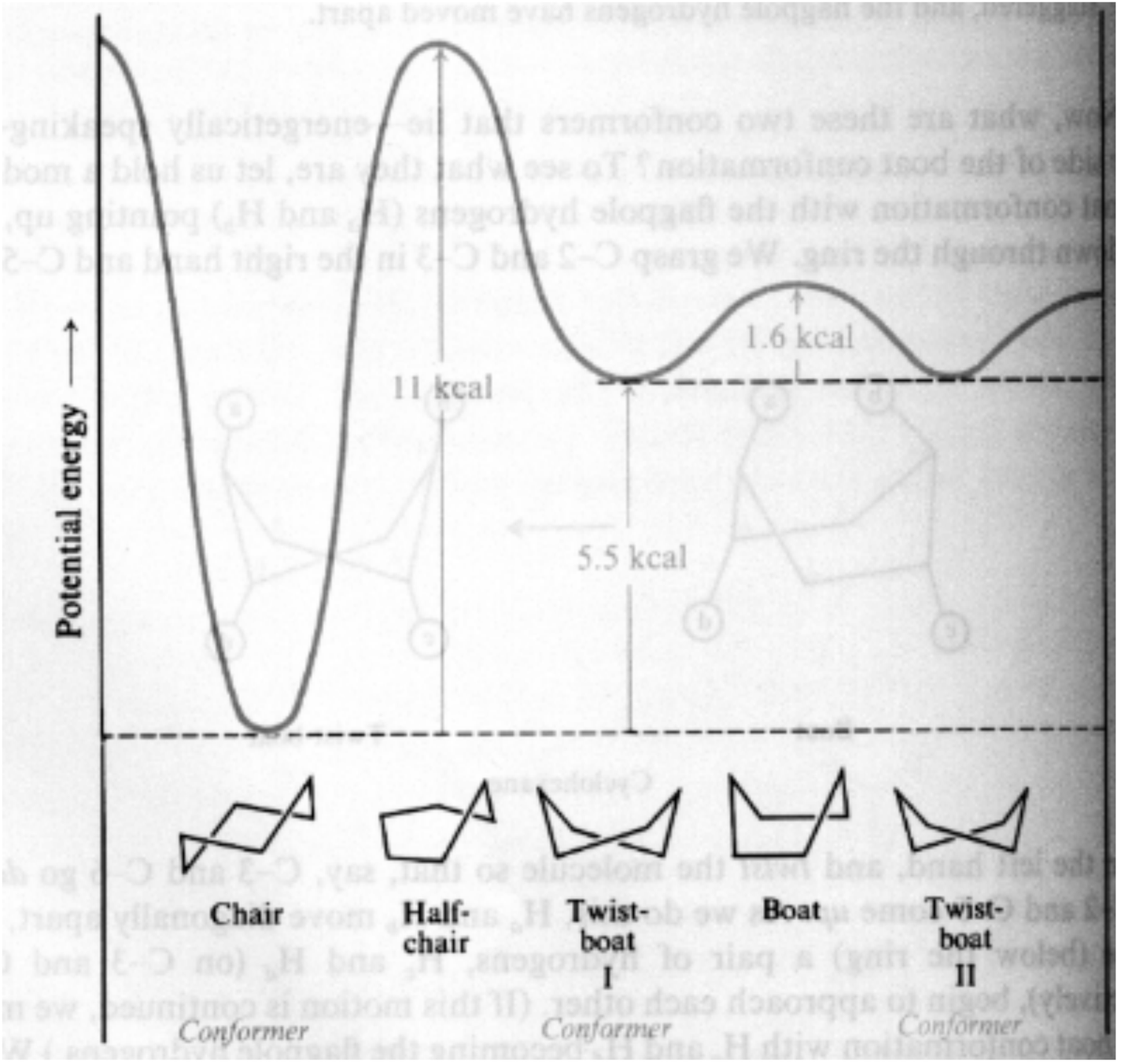


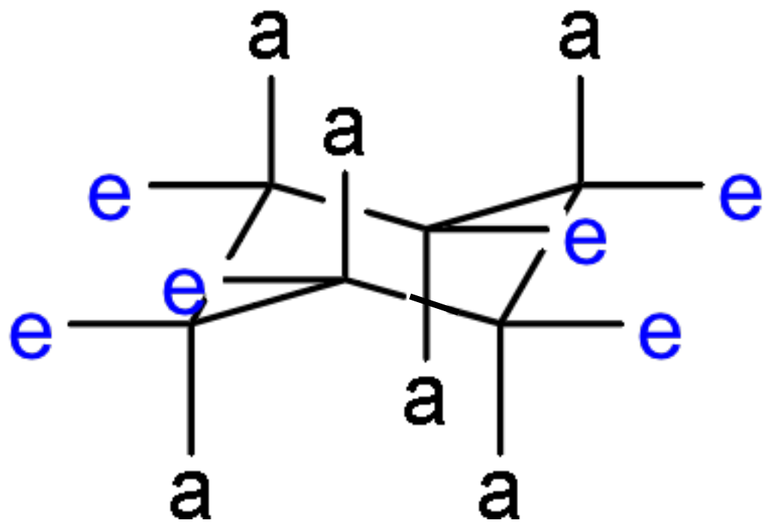


The boat conformation is free of angle strain, but has a great deal of torsional strain (eclipsed). To relieve the strain, it twists slightly to form the twist boat:



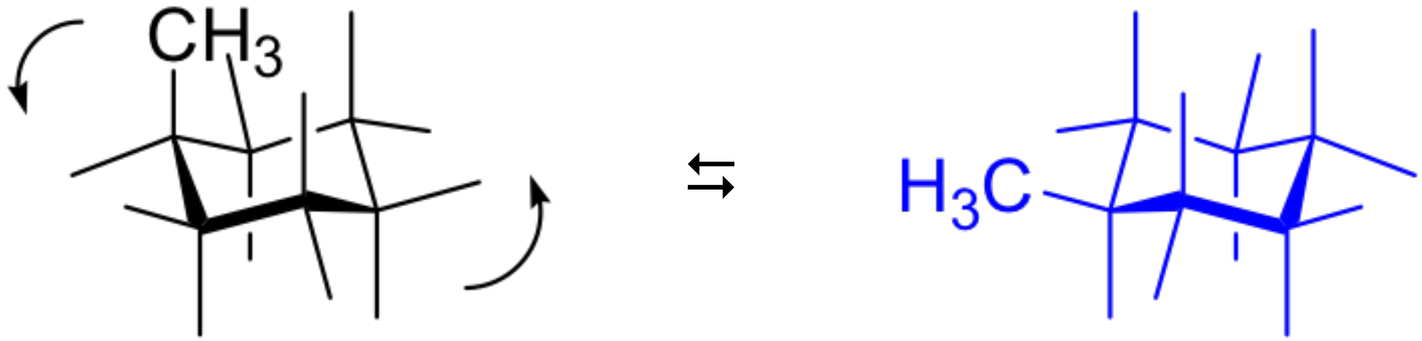
conformations of cyclohexane





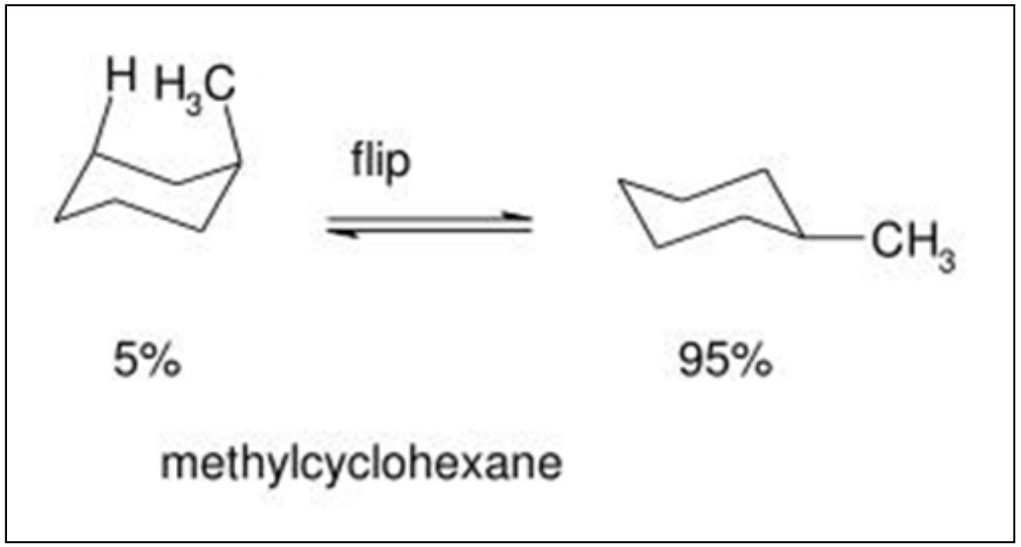
a = axial positions in the chair conformation

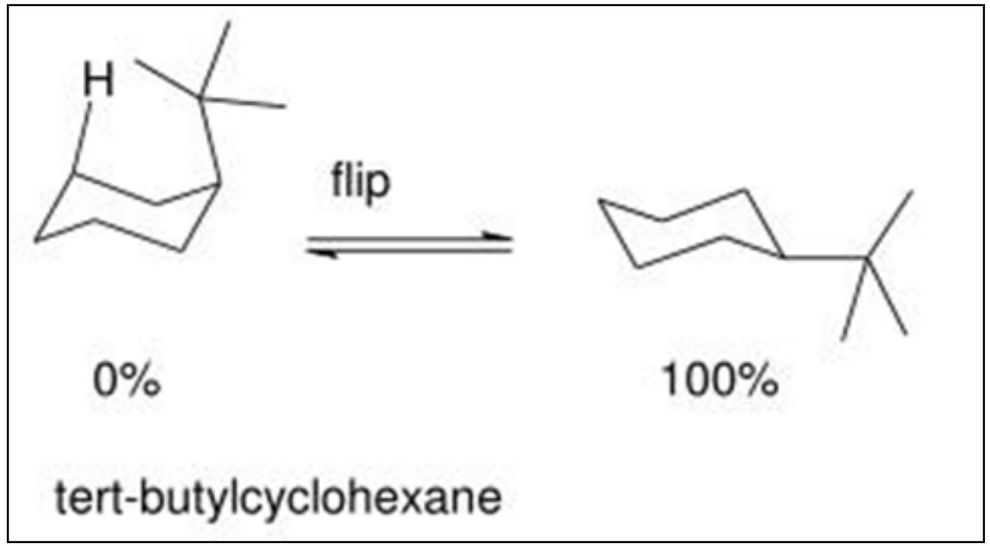
e = equatorial positions



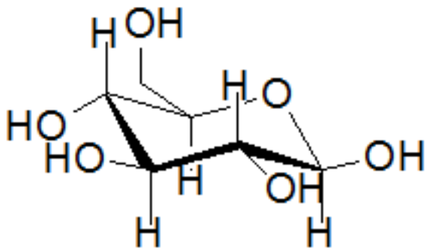
CH_3 in axial position

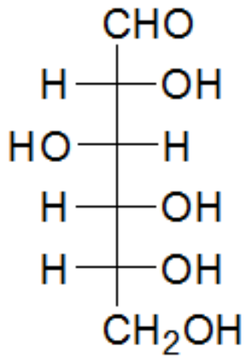
CH_3 in equatorial position is more stable

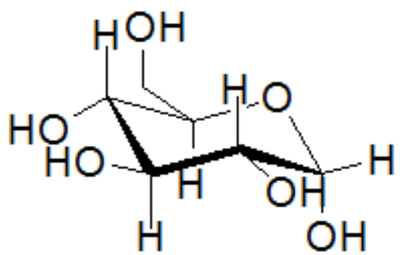




Glucose molecule







beta-D-glucose

all OH groups equatorial

more stable

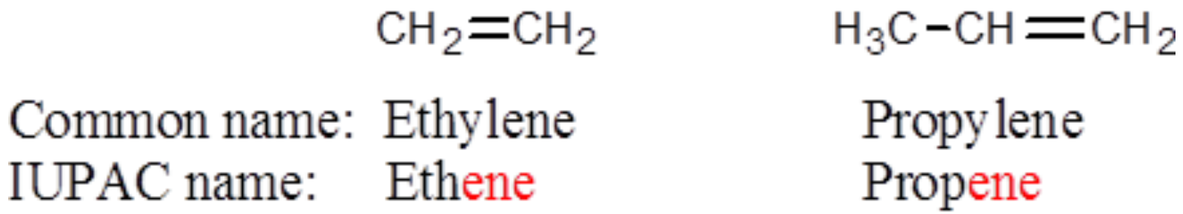
alpha-D-glucose

one group forced to be axial

2. ALKENES

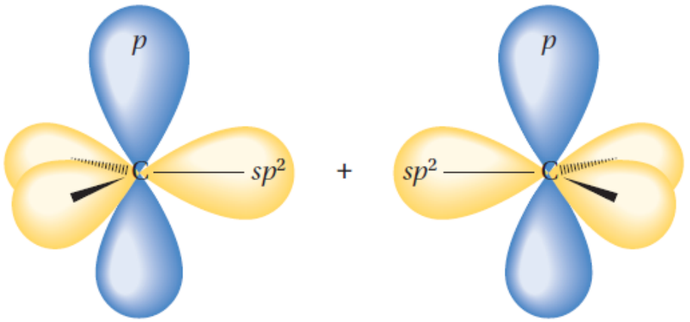
The Structure of Alkenes

- **Alkenes are hydrocarbons that contain a *carbon–carbon double bond*.**
- **Alkenes are also *Olefins*.**
- **General formula is C_nH_{2n}**
- **The simplest members of the Alkenes series are C_2 & C_3**

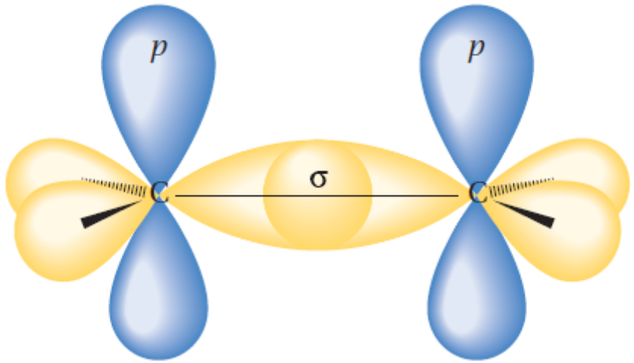


The Structure of Alkenes

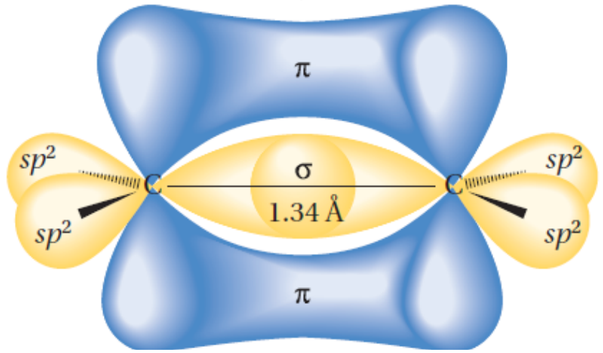
- Hybridization; sp^2-hybridized orbitals
- The angle between them is 120° and bond length C=C (1.34 Å).
- A trigonal planar.



two sp^2-hybridized carbons with p orbitals parallel



the σ bond is formed by two electrons in overlapping sp^2 orbitals

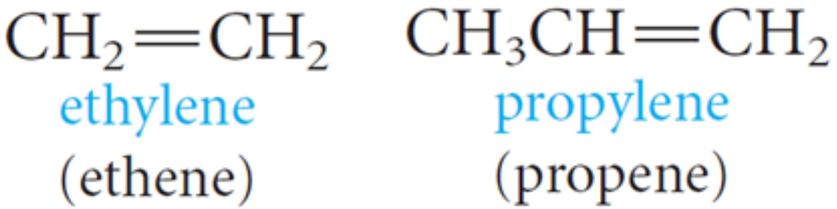


the π bond is formed by two electrons in overlapping parallel p orbitals

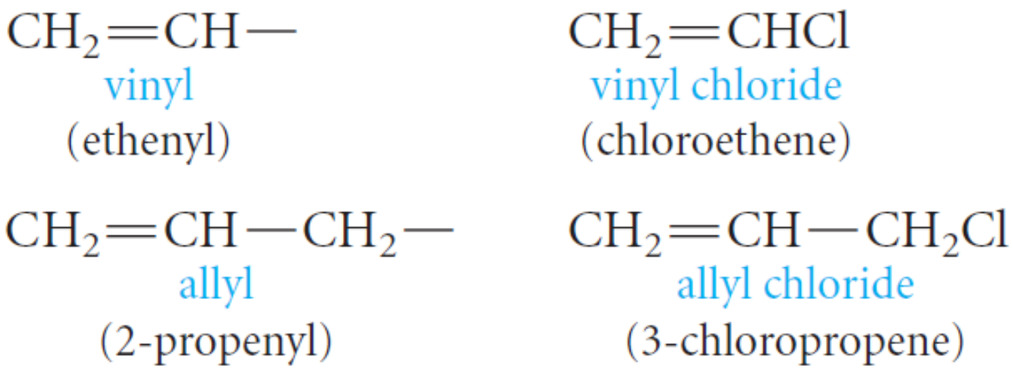
Nomenclature of Alkenes

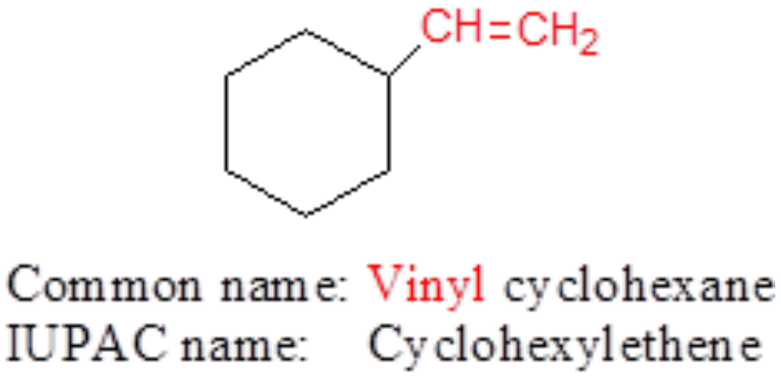
Common Names

- The simplest members of the alkene series are frequently referred to by their older common names, ethylene, and propylene.



- Two important groups also have common names; They are the vinyl and allyl groups.
- These groups are used in common names.



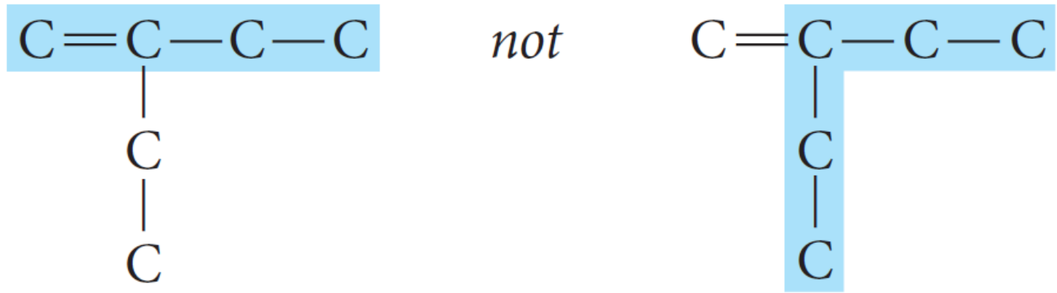


Nomenclature of Alkenes

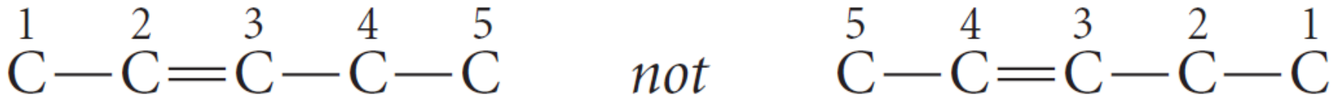
The IUPAC Rules

The IUPAC rules for naming alkenes are similar to those for alkanes, but a few rules must be added for naming and locating the multiple bonds.

1. The ending ***-ene*** is used to designate a carbon–carbon double bond.
2. Select the **longest chain that includes *both carbons of the double bond***.

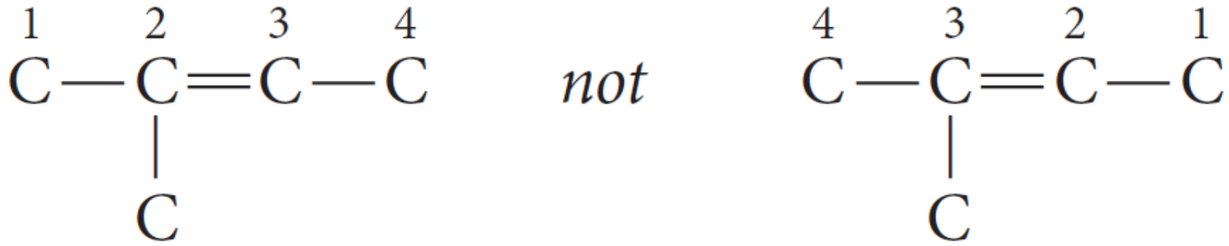


3. **Number the chain from the end nearest the double bond** so that the carbon atoms in that bond have the lowest possible numbers.

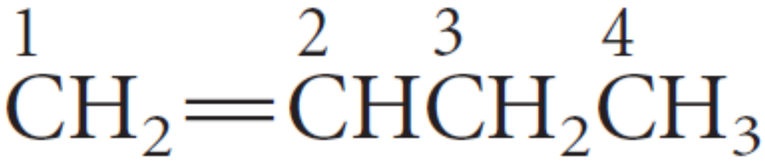


Nomenclature of Alkenes

If the multiple bond is equidistant from both ends of the chain, number the chain from the end nearest the first branch point.



4. Indicate the **position of the multiple bond using the *lower numbered carbon atom*** of that bond.



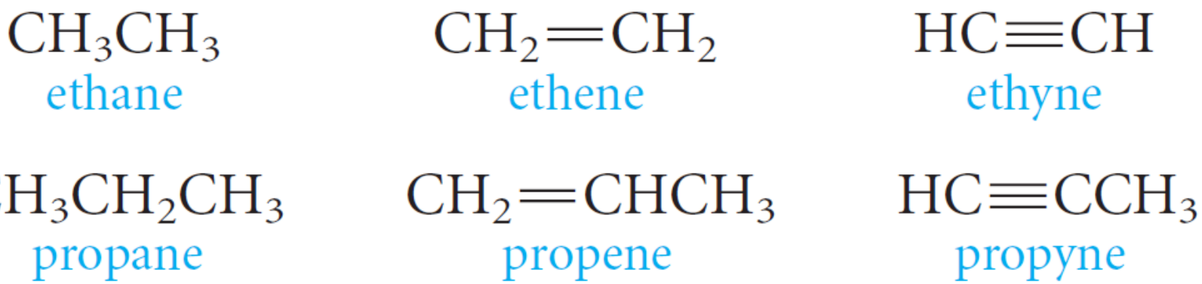
1-butene, *not* 2-butene

Nomenclature of Alkenes

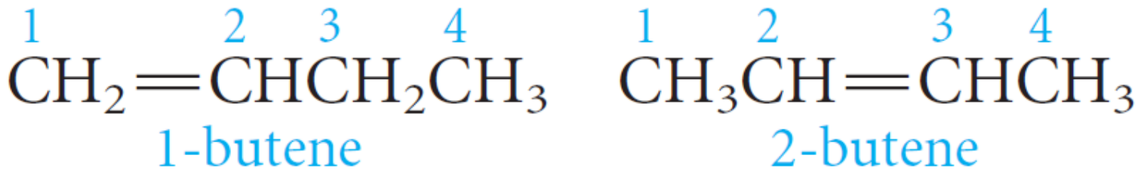
NOTES

The root of the name (*eth-* or *prop-*) tells us the number of carbons, and the ending (*-ane, -ene,* or *-yne*) tells us whether the bonds are single, double, or triple.

No number is necessary in these cases, because in each instance, only one structure is possible.

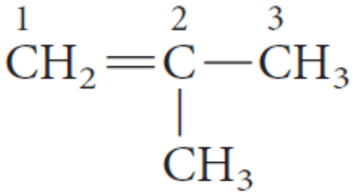


With four carbons, a number is necessary to locate the double bond.

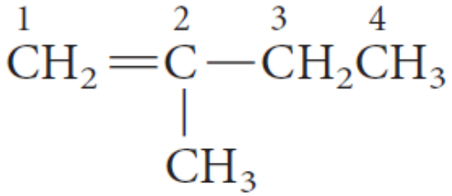


Nomenclature of Alkenes

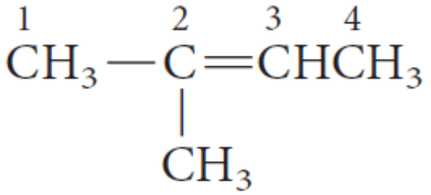
- Branches are named in the usual way.



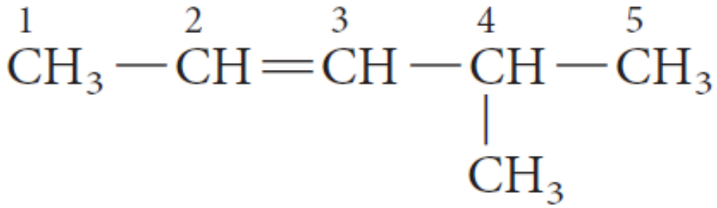
methylpropene
(isobutylene)



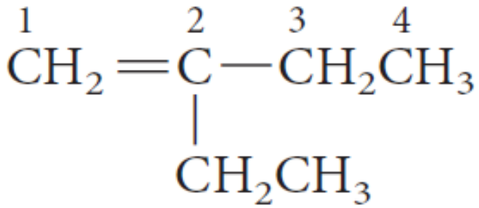
2-methyl-1-butene



2-methyl-2-butene



4-methyl-2-pentene
(*Not* 2-methyl-3-pentene; the chain is numbered so that the double bond gets the lower number.)

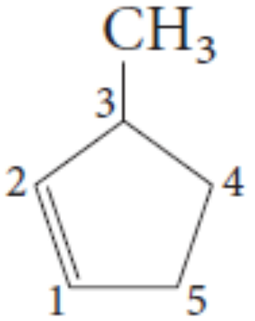


2-ethyl-1-butene
(Named this way, even though there is a five-carbon chain present, because that chain does not include both carbons of the double bond.)

Nomenclature of Alkenes

- **With cyclic hydrocarbons, we start numbering the ring with the carbons of the double bond.**

cyclopentene
(No number is necessary, because there is only one possible structure.)



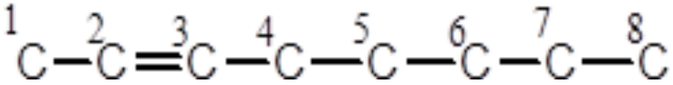
3-methylcyclopentene
(Start numbering at, and number through the double bond; 5-methylcyclopentene and 1-methyl-2-cyclopentene are incorrect names.)

Nomenclature of Alkenes

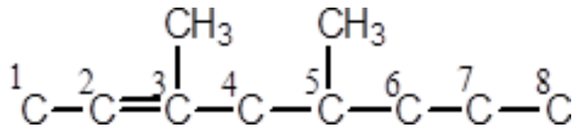
Example: Write the structural formula of 4-Isopropyl-3,5-dimethyl-2-octene.

1) The parent carbon chain is an Octene.

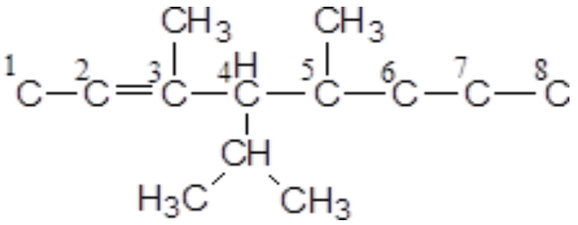
The double bond is located between the 2nd and 3rd carbons.



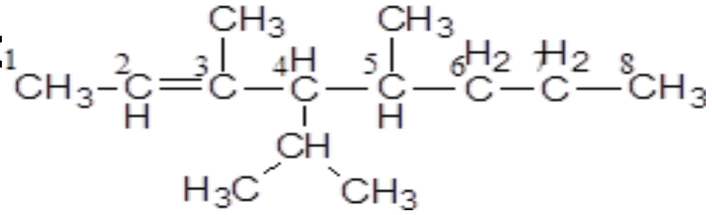
2) Two methyl groups are attached on the parent carbon chain, one on carbon 3 and the other on carbon 5.



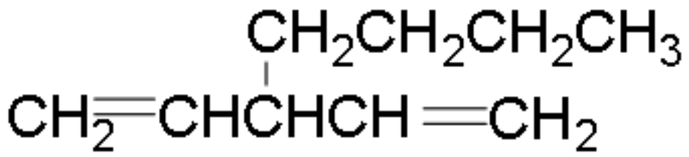
3) An isopropyl group is attached on carbon 4.



4) Put the missing hydrogens to get the correct struc

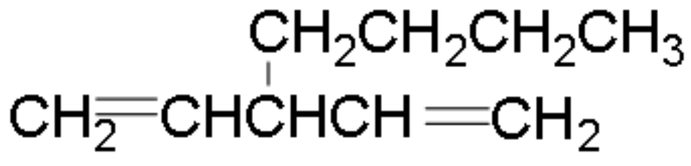


Diene compounds: are alkenes with two π bonds



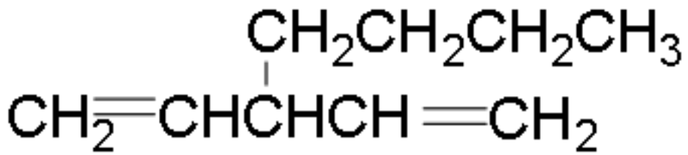
Nomenclature of Dienes

1. Find the longest chain containing both double bonds



3-butyl-1,4-pentadiene

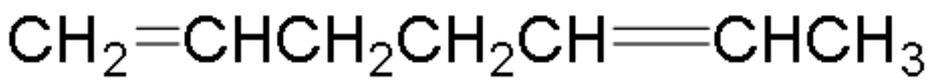
2. Use corresponding alkane name but replace the "*ne*" ending with "*diene*"



3-butyl-1,4-pentadiene

"pentane" changed to "pentadiene"

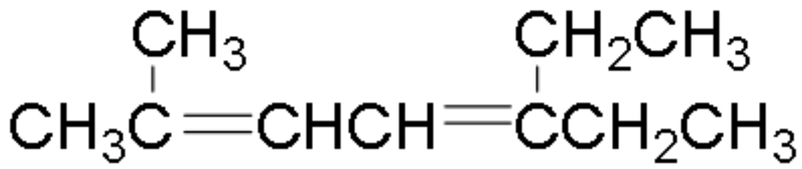
3. Number in the direction that gives the lowest number to a double bond



1,5-heptadiene

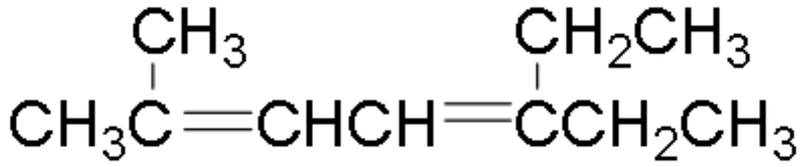
not 2,6-heptadiene

4. List substituents in alphabetical order



5-ethyl-2-methyl-2,4-heptadiene

5. Place numbers indicating the double bond positions either in front of the parent compound or in the middle of the name immediately before the *diene* suffix

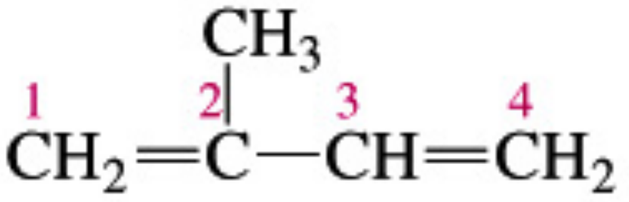


5-ethyl-2-methyl-2,4-heptadiene

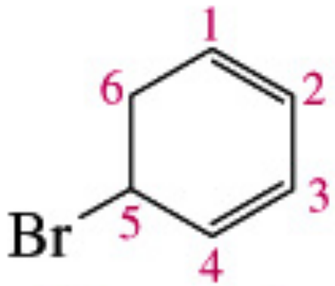
or 5-ethyl-2-methyl-hepta-2,4,-diene

Example:

systematic: propadiene
common: allene



2-methyl-1,3-butadiene
isoprene



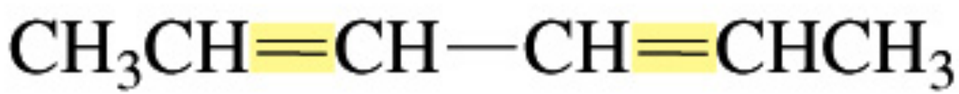
5-bromo-1,3-cyclohexadiene

Types of Dienes

- When double bonds are separated by at least one sp^3 carbon, **isolated diene**

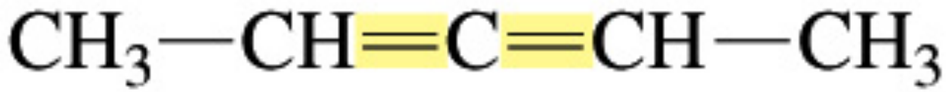
an isolated diene

- When double bonds are separated by only one single bond (i.e. four sp^2 carbons in a row), **conjugated diene**



a conjugated diene

- When both sets of double bonds emanate from the same carbon, **cumulated diene**

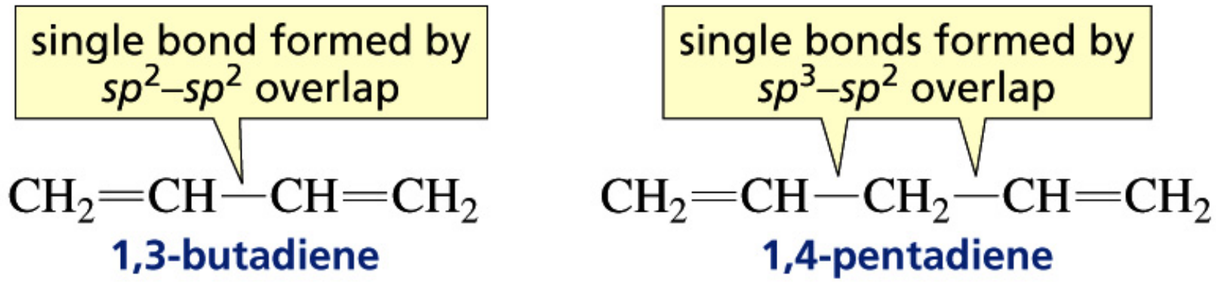


a cumulated diene

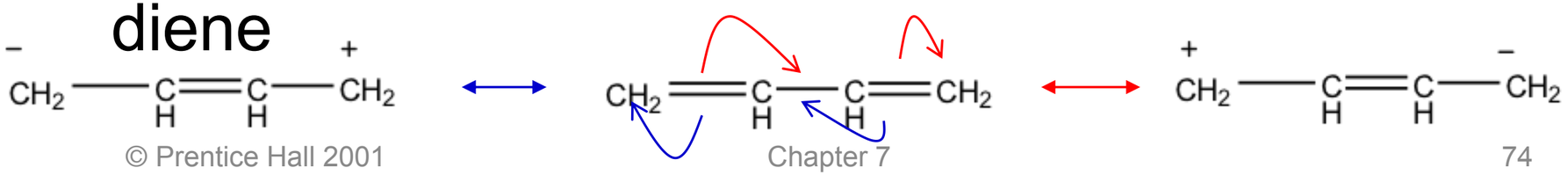
an allene

Relative Stabilities of Dienes

- Conjugated dienes are more stable than isolated dienes because
  - An sp^2-sp^2 single bond is shorter and stronger than a sp^3-sp^2 single bond

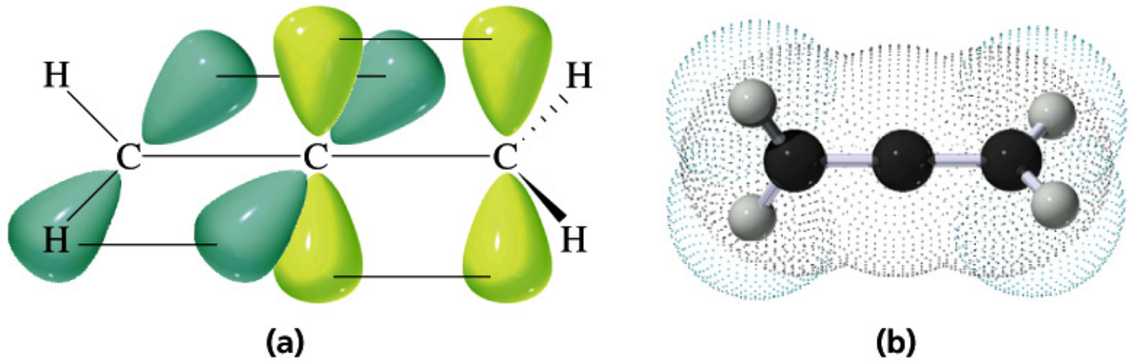


- Resonance also stabilizes the conjugated diene

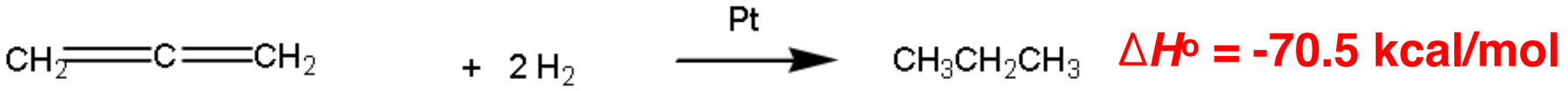


Relative Stabilities of Dienes

- Doubly-bonded carbons in isolated and conjugated dienes all are *sp*^{2} hybridized
- The central carbon in a cumulated diene is *sp* hybridized



Relative Stabilities of Dienes



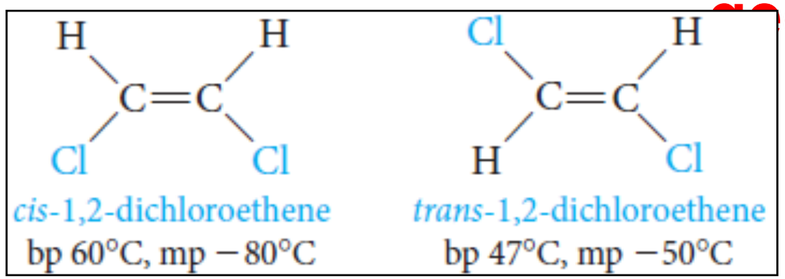
- The heat of hydrogenation of allene is similar to that of 1-butyne; both have at least one *sp* carbon
- Additional reactivity of cumulated dienes will not be considered in this course

Geometric Isomerism in Alkenes

- In alkenes, geometric isomerism is due to restricted rotation about the carbon - carbon double bond.

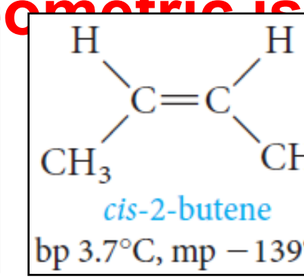
Geometric isomers

A) when W differs from X and Y from Z, Alkenes exist as geometric isomers

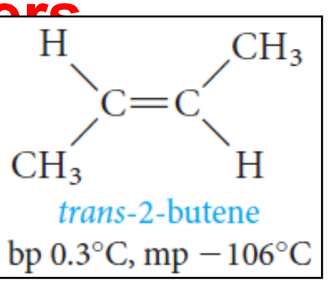


cis-1,2-dichloroethene
bp 60°C, mp −80°C

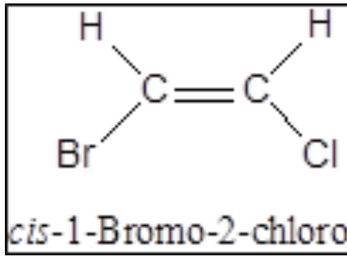
trans-1,2-dichloroethene
bp 47°C, mp −50°C



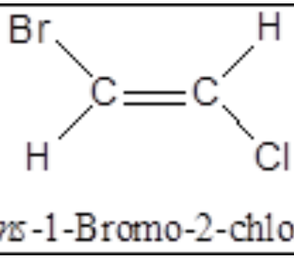
cis-2-butene
bp 3.7°C, mp −139°C



trans-2-butene
bp 0.3°C, mp −106°C



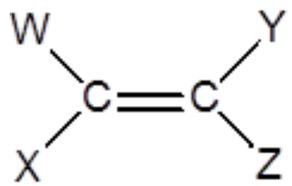
cis-1-Bromo-2-chloroethene

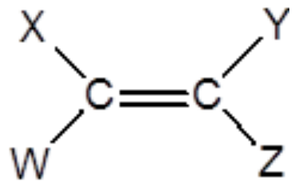


trans-1-Bromo-2-chloroethene

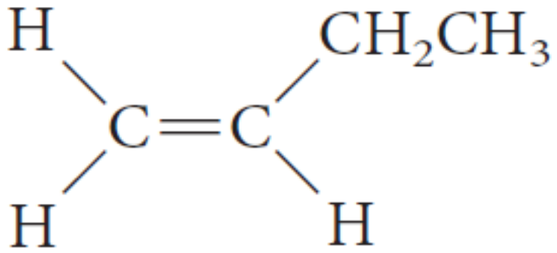
- ***cis* isomer; when two similar groups are on the same side of the double bond.**
- ***trans* isomer; when two similar groups are on the opposite sides of the double bond.**
- **They have different physical properties and can be separated by fractional crystallization or distillation.**

Geometric Isomerism in Alkene



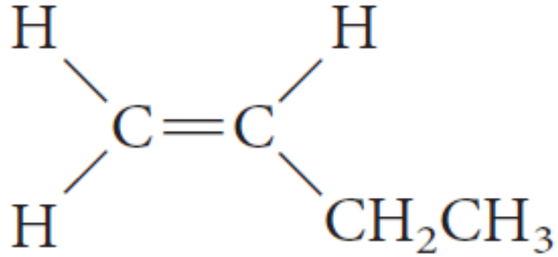


B) If (W = X or Y = Z), geometric isomerism is not possible.

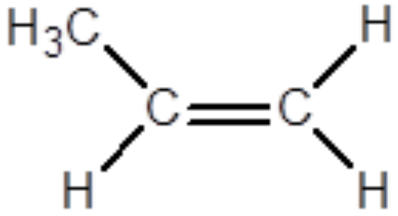


1-butene

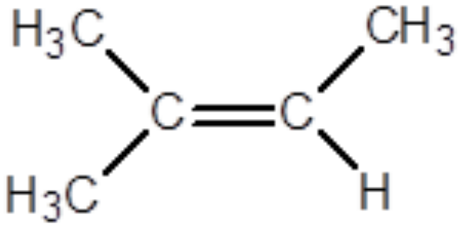
is identical to



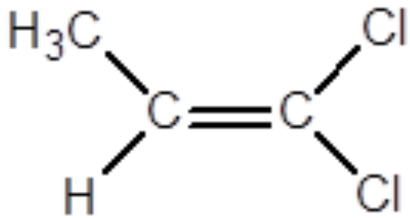
1-butene



Propene



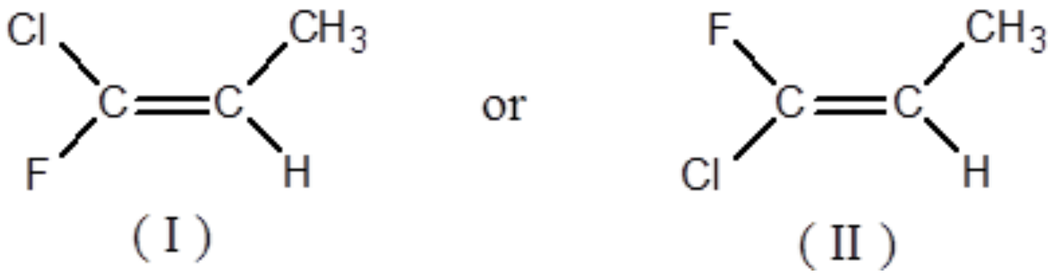
2-Methyl-2-butene



1,1-Dichloropropene

Geometric Isomerism in Alkene

- For alkenes with four different substituent such as



(I) (II)

Another system, the *E, Z* system

- Basically, the E,Z system works as follows;

  Arrange the groups on each carbon of the C=C bond in order of priority

- The priority depends on atomic number;

  The higher the atomic number of the atom directly attached to the double-bonded carbon, the higher the priority.

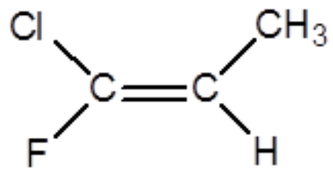
Thus, in structure (I),

Cl > F, and CH_3 > H.

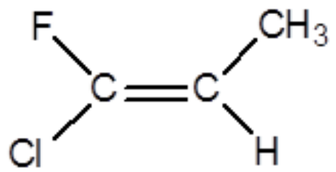
Geometric Isomerism in Alkene

- If the two groups of **higher priority** are on the **same side** of the C=C plane, ***the*** **isomer is labeled *Z;*** **(from the German *zusammen*, together).**
- **If the two groups of higher priority are on opposite sides of the C=C plane, *the isomer is labeled E; (from the German entgegen, opposite).***

Priority: Cl > F, CH_3 > H

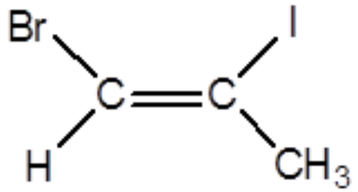


Z-1-Chloro-1-fluoropropene
(Cl and CH_3 on same side)



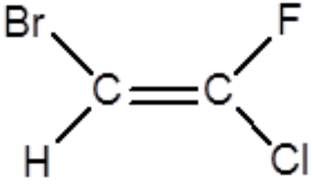
E-1-Chloro-1-fluoropropene
(Cl and CH_3 on opposite side)

Priority: Br > H, I > CH_3



Z-1-Bromo-2-iodopropene

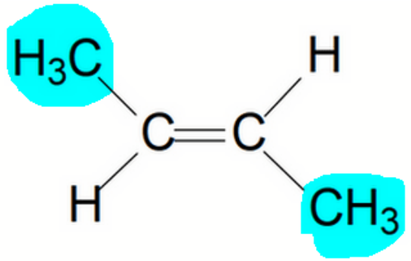
Priority: Br > H, Cl > F



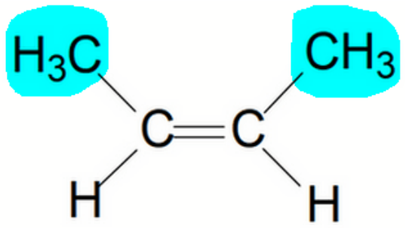
E-1-Brfomo-2-chloro-2-fluoroethene

Geometric Isomerism in Alkene

B



and



trans isomer
less polar
lower bp

cis isomer
more polar
higher bp

The bulky groups for cis isomers are on the same side of the alkene.
This makes the cis isomer less symmetrical and the electron cloud distribution is more unequal.
Therefore the cis isomer is more polar than the trans isomer and has a slight permanent dipole - permanent dipole attraction between molecules.
Thus the cis isomer has a higher boiling point than the trans isomer.
Interestingly the cis isomer has a lower melting point than the trans isomer, even though it is more polar.

Preparation of Alkenes

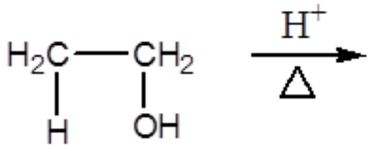
- **Alkenes** are prepared by ***Elimination*** of an atom or group of atoms from adjacent carbons to form ***carbon-carbon double bond.***

+ AB

(A=H or halogen;
B=OH or halogen)

1) Dehydration of Alcohols

- ***When an alcohol is heated in the presence of a mineral acid catalyst, It readily loses a molecule of water to give an alkene.***



$H_2C{=}CH_2$ + H_2O

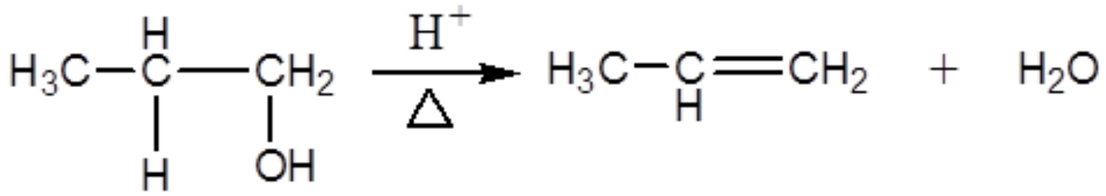
IUPAC name:	Ethanol	Ethene
Common name:	Ethyl alcohol	Ethylene

- **The acid *catalysts* most commonly used are sulfuric acid, H_2SO_4, and phosphoric acid, H_3PO_4.**

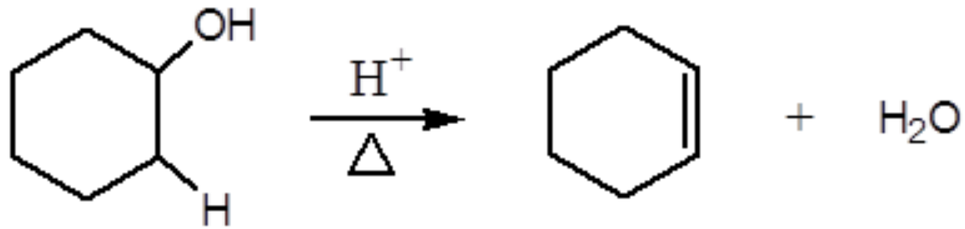
Preparation of Alkenes

1) Dehydration of Alcohols

Removal of OH group and a proton from two adjacent carbon atoms using mineral acids such as H_2SO4 or H_3PO_4



IUPAC name: 1-Propanol — Propene
Common name: *n*-Propyl alcohol — Propylene



IUPAC name: Cyclohexanol — Cyclohexene
Common name: Cyclohexyl alcohol

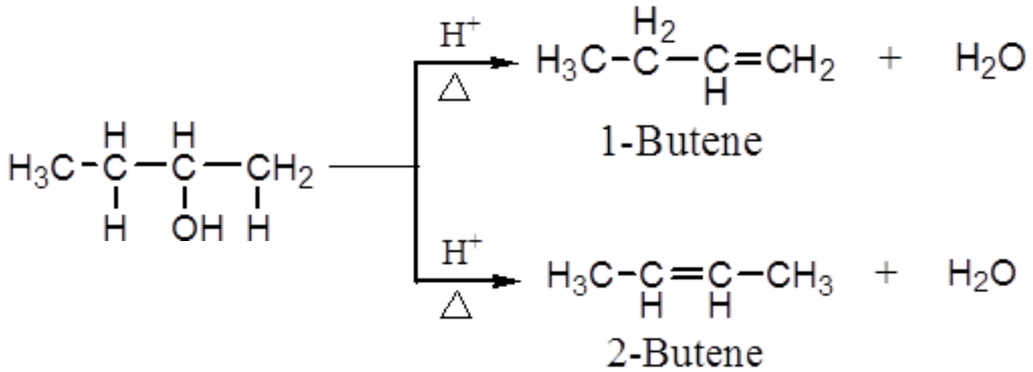
1) Dehydration of Alcohols

Which Alkene Predominates?;

Saytzeff's Rule

The loss of water from adjacent carbon atoms, can give rise to more than one alkene.

Example: the dehydration of 2-butanol.



2-butene is the major (with two alkyl substituents attached to C=C)

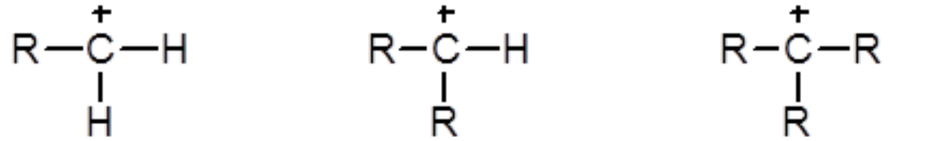
Saytzeff's Rule applies

In every instance in which more than one Alkene can be formed

The major product is always the alkene with the most alkyl substituents attached on the double-bonded carbons.

1) Dehydration of Alcohols

- **Classes of Carbocations**



according to the number of carbon atoms attached to the positively charged carbon

The ease of formation and the stabilities of carbocations follow the order

$$3^\circ > 2^\circ > 1^\circ$$

Ease of formation and stabilities of carbocations

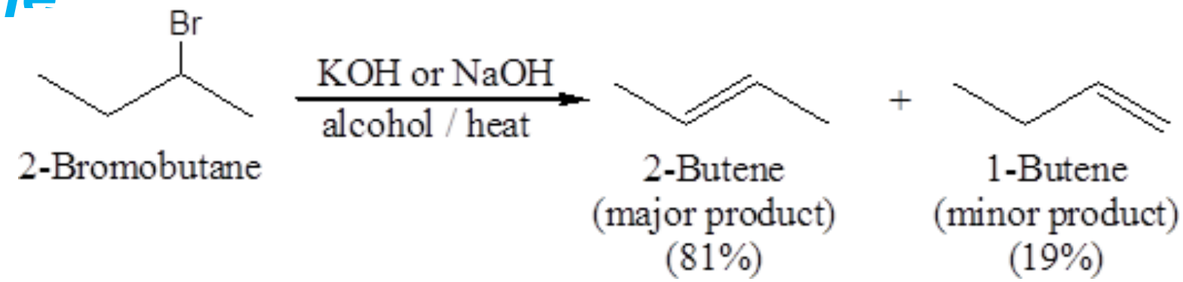
- **Generall**

1. The dehydration of alcohols requires an **acid catalyst**.
2. The predominant alkene formed follows **Saytzeffs rule**.
3. The reaction proceeds *via* a **carbocation intermediate**.
4. The stabilities of carbocations and the ease of dehydration of alcohols follows the order **3° > 2° > 1°**.

2) Dehydrohalogenation of Alkyl Halides

- **Alkenes can also be prepared under alkaline conditions.**

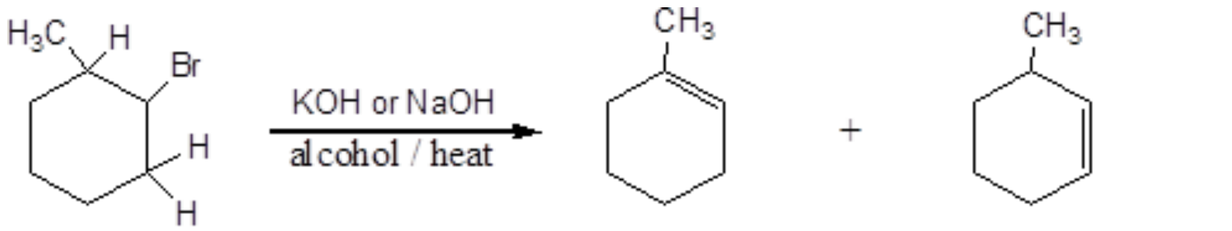
heating an alkyl halide with a solution of KOH or NaOH in alcohol, yields an alkene



2-Bromobutane

2-Butene (major product) (81%)

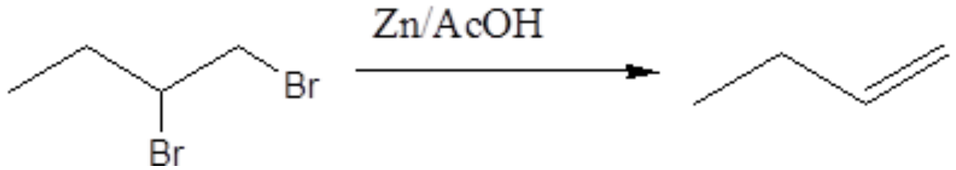
1-Butene (minor product) (19%)



1-Methylcyclohexene (major product)

3-Methylcyclohexene (minor product)

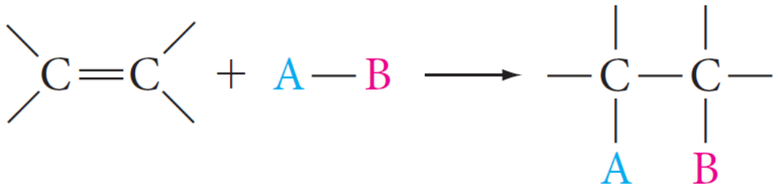
3) Dehalogenation of Vicinal Dibromides



Reactions of Alkenes

- The chemistry of alkenes can be divided into two general types of reactions:

(1) Electrophilic Addition Reactions



Addition of Symmetric and Unsymmetric Reagents to symmetric Alkenes.

1. Addition of Hydrogen: Catalytic Hydrogenation
2. Addition of Halogens: Halogenation

Addition of Unsymmetric Reagents to Unsymmetric Alkenes; Markovnikov's Rule

1. Addition of Hydrogen Halides
2. Addition of Sulfuric Acid
3. Addition of Water: Hydration
4. Addition of HOX: Halohydrin Formation

Reactions of Alkenes

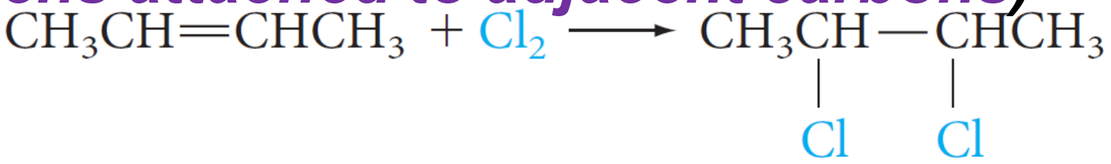
(2) Oxidation Reactions

1. Ozonolysis
2. Oxidation Using $KMnO_4$

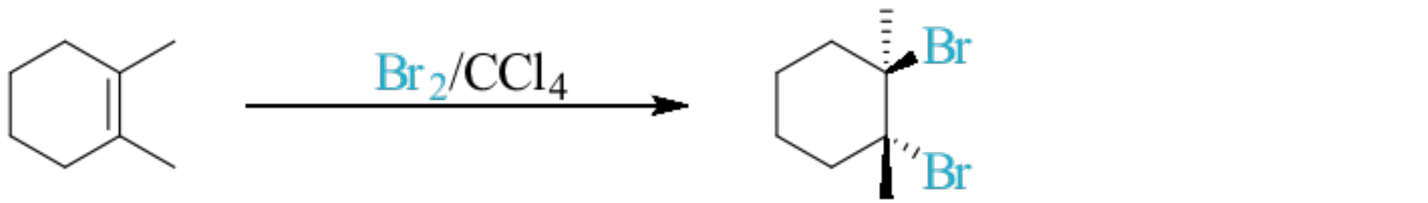
Electrophilic Addition Reactions

2. Addition of Halogen: Halogenation

When an alkene is treated at room temperature with a solution of bromine or chlorine in carbon tetrachloride to give the corresponding vicinal dihalide (two halogens attached to adjacent carbons)



2-butene — 2,3-dichlorobutane



1,2-Dimethyl-cyclohexene — *trans*-1,2-Dibromo-1,2-dimethyl-cyclohexane

- Iodine is too unreactive and will not add to the double bond.

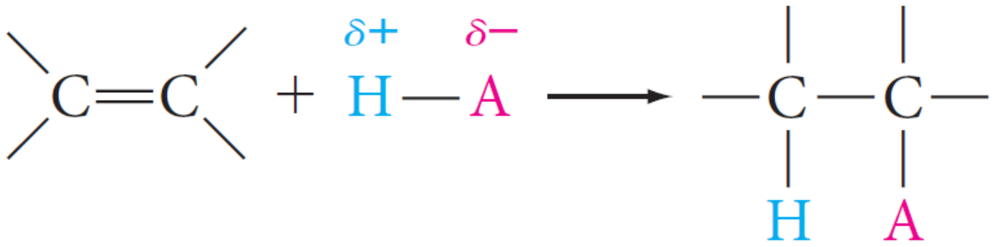
- Fluorine is too reactive and reacts explosively with an alkene.

Electrophilic Addition Reactions

3. Addition of Acids

- A variety of acids add to the double bond of alkenes.

The hydrogen ion (or proton) adds to one carbon of the double bond, and the remainder of the acid becomes connected to the other carbon.



- Acids that add in this way are the hydrogen halides (H-F, H-Cl, H-Br, H-I), and water (H-OH).

Note that

- Any electron-deficient species is called an electrophile.
- Any electron-rich species is called a nucleophile.

Electrophilic Addition Reactions

Examples of Electrophile:

i) Positive reagents: protons (H^+), alkyl group R^+ , nitronium ion (NO_2^+), etc….

ii) Neutral reagents having positively polarized centers: HCl, bromine (because it can be polarized so that one end is positive).

iii) Lewis acids: molecules or ions that can accept an electron pair ⇒ BF_3 and $AlCl_3$.

iv) Metal ions that contain vacant orbitals: the silver ion (Ag^+), the mercuric ion (Hg^{2+}), and the platinum ion (Pt^{2+}).

Examples of Nucleophile:

a)Negative ions

e.g. $H\ddot{O}:^-$ Hydroxide ion, $H\ddot{S}:^-$ Hydrosulphide ion, $R\ddot{O}:^-$ Alkoxide ions,

$:N\equiv C:^-$ Cyanide ion, $:\ddot{X}:^-$ Halide ions, ...etc.

b) Neutral molecules

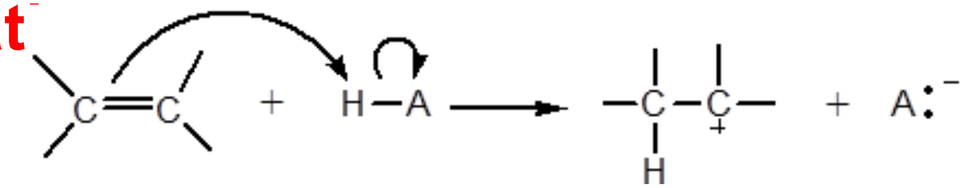
e.g. $H_2\ddot{O}$, $R—\ddot{O}—H$, $R—\ddot{O}—R$, $H_3\ddot{N}$, $R_3\ddot{N}$, ...etc.

Electrophilic Addition Reactions

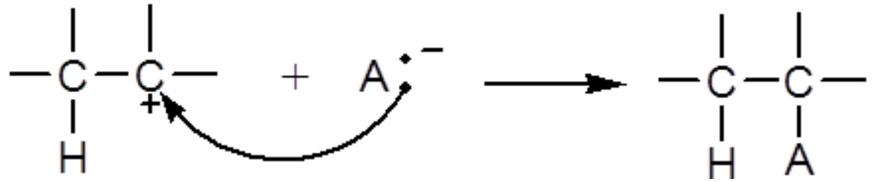
3. Addition of Acids

- The addition of H—A to an alkene is believed to be a **two-step process**.

Step 1. The hydrogen ion **(the electrophile)** attacks the ∏-electrons of the alkene, forming a C—H bond and a **carbocat**$^{-}$



Step 2. The negatively charged species A: - **(a nucleophile)** attacks the carbocation and forms a new C—A bond.



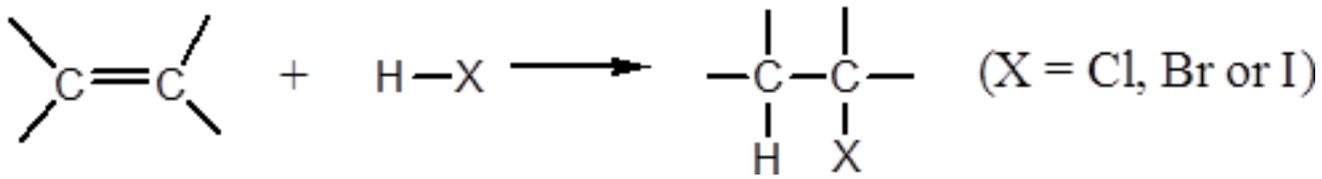
- The attack by an electrophilic reagent on the ∏-electrons, falls in a general category called **electrophilic addition reactions**.

Electrophilic Addition Reactions

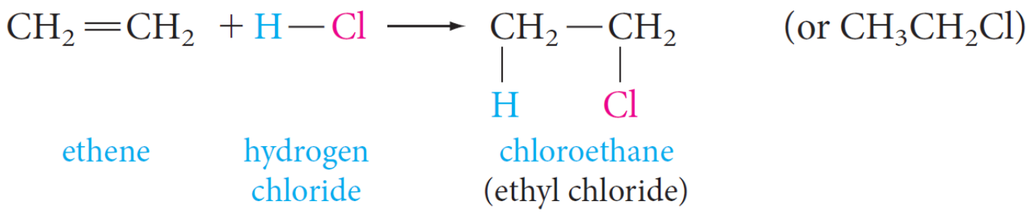
3.1. Addition of Hydrogen Halide

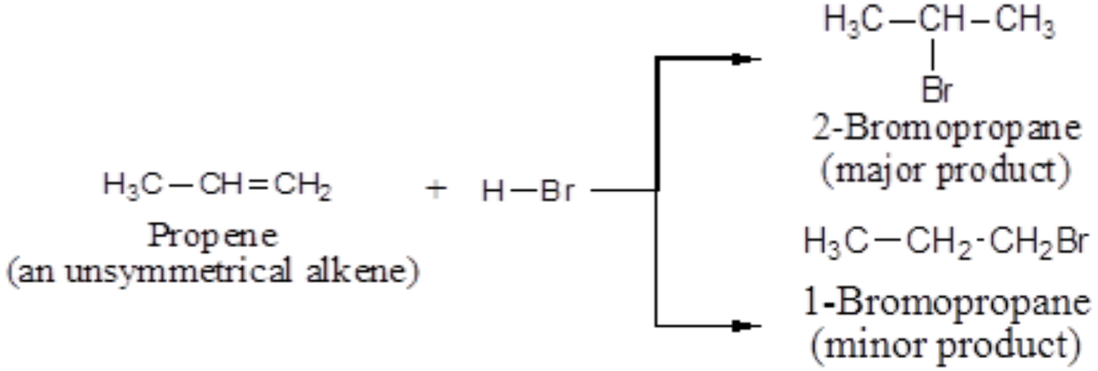
Alkenes react with hydrogen chloride, HC1, hydrogen bromide, HBr and hydrogen iodide, Hl, to form alkyl halides, RX.

General equation



Examples;





Electrophilic Addition Reactions

- **Reagents and alkenes can be classified as either symmetric or unsymmetric** with respect to addition reactions.
  - If a reagent and/or an alkene is symmetric, only one addition product is possible.
  - But if *both* the reagent *and* the alkene are *unsymmetric,* two products are, in principle, possible.

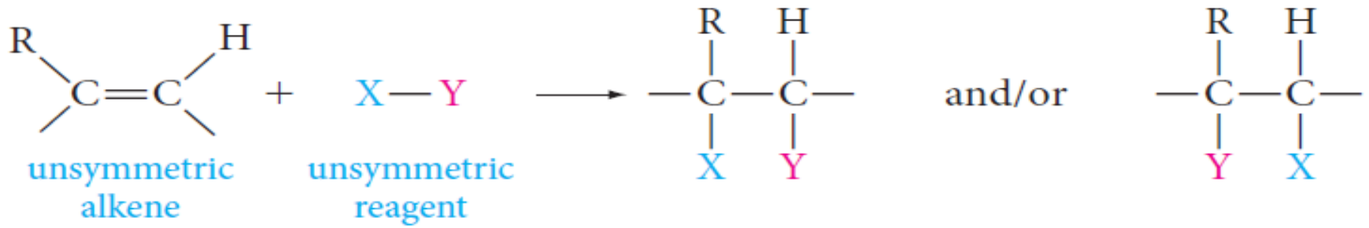


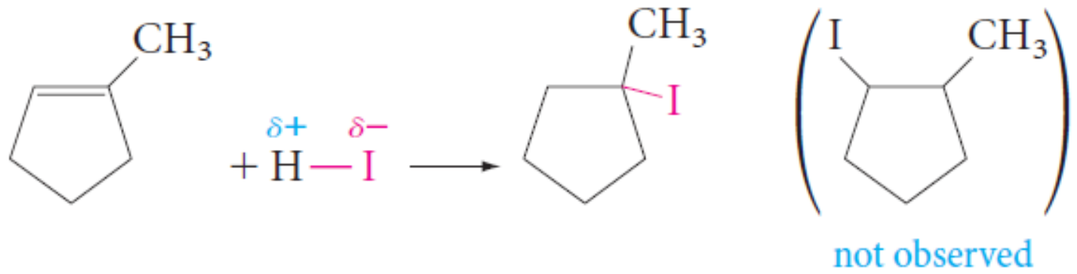
Table 3.2 Classification of Reagents and Alkenes by Symmetry with Regard to Addition Reactions

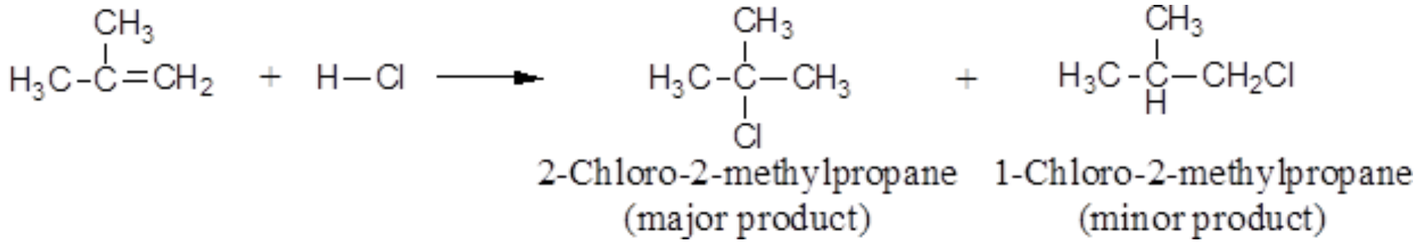
	Symmetric	Unsymmetric
Reagents	Br—Br Cl—Cl H—H	H—Br H—OH H—OSO_3H
Alkenes	$CH_2=CH_2$	$CH_3CH=CH_2$
	mirror plane	not a mirror plane

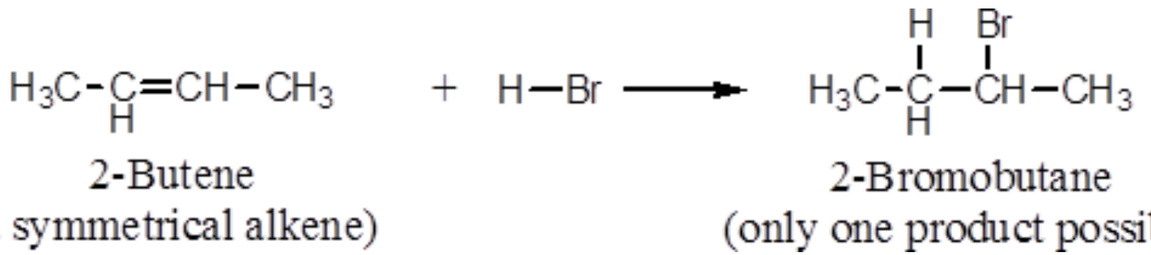
Electrophilic Addition Reactions

Markovnikov's Rule

In electrophilic addition of* H—X *to Unsymmetrical Alkenes the hydrogen of the hydrogen halide adds to the double-bonded carbon that bears the greater number of hydrogen atoms and the negative halide ion adds to the other double-bonded carbon.



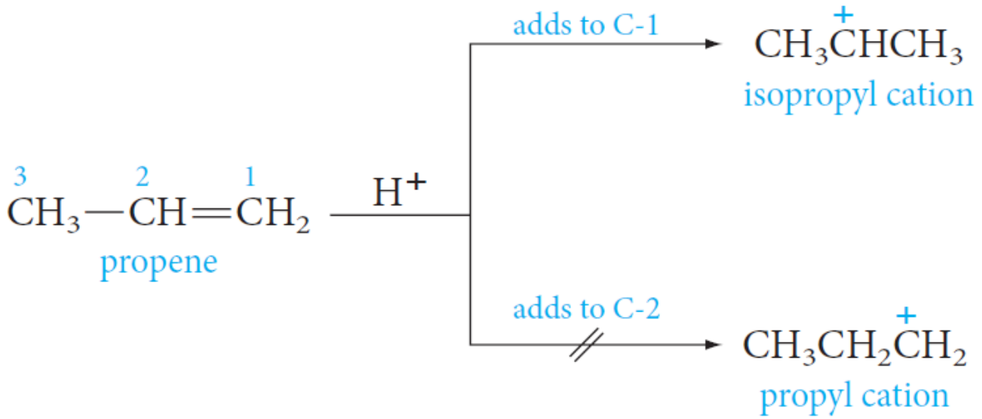




Electrophilic Addition Reactions

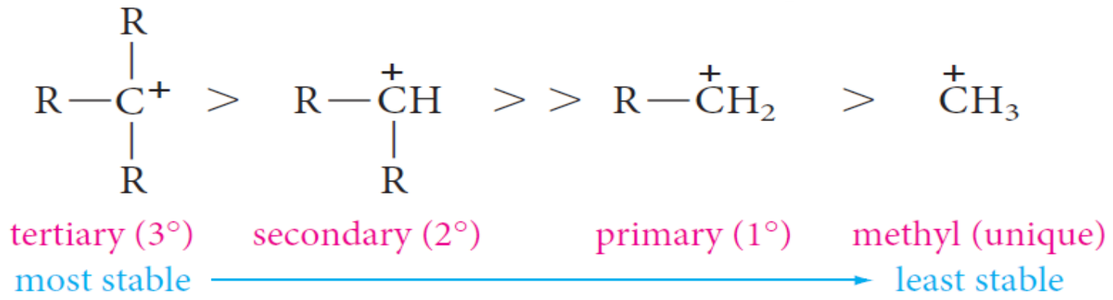
Explanation for Markovnikov's Rule

Example; Addition of HBr to propene



- **In modern terms Markovnikov's rule can be restated:**

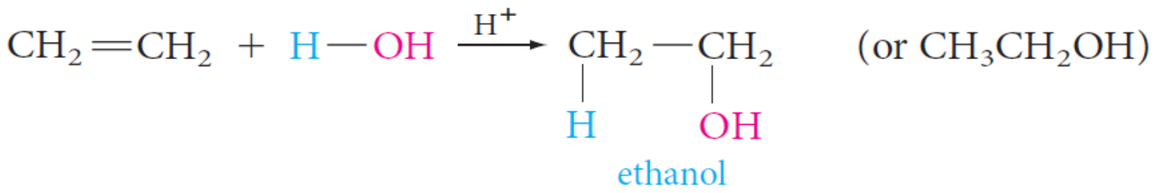
  The addition of an unsymmetrical reagent* HX *to an unsymmetrical alkene proceeds in such a direction as to produce the more stable carbocation.

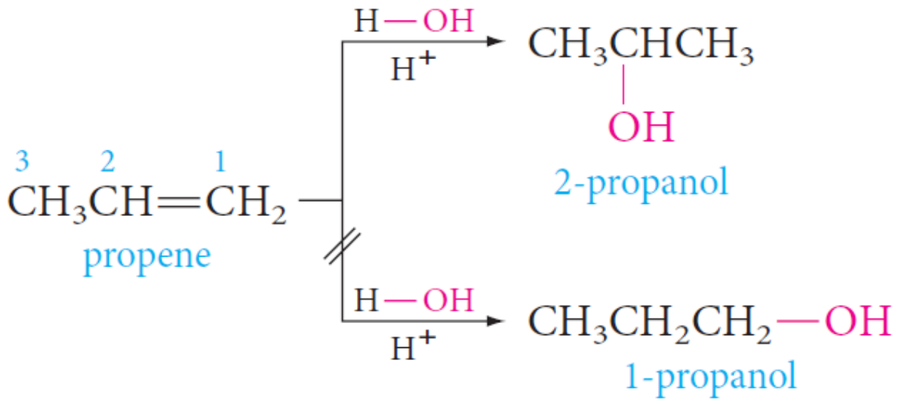


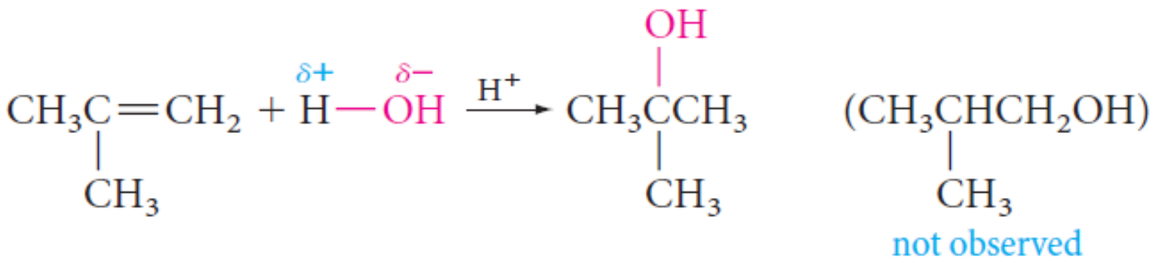
Electrophilic Addition Reactions

3.2. Addition of Water: Hydration

If an acid catalyst is present, water (as H-OH) adds to alkenes and the product is alcohol.

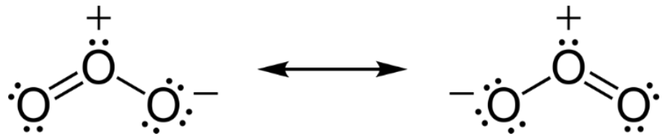




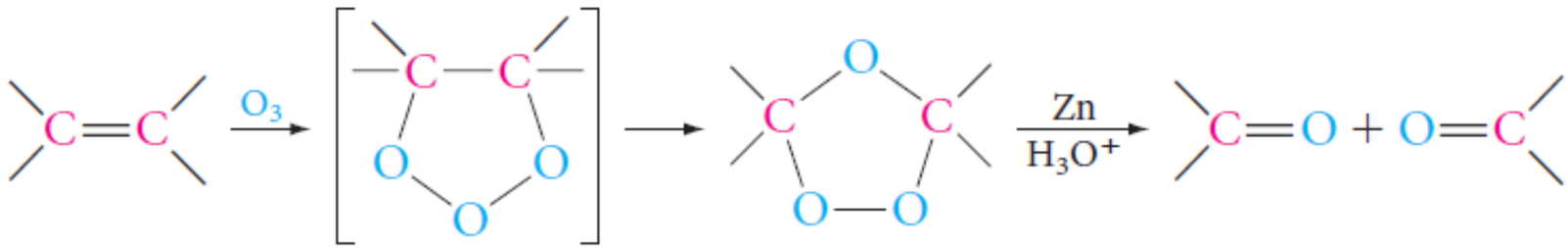


Oxidation Reactions

1. Ozonolysis



- The first product, a molozonide, is formed by cycloaddition of the oxygen at each end of the ozone molecule to the carbon–carbon double bond.
- This product then rearranges rapidly to an ozonide (explosive if isolated).
- They are usually treated directly with a reducing agent, commonly zinc and aqueous acid, to give carbonyl compounds as the isolated products.

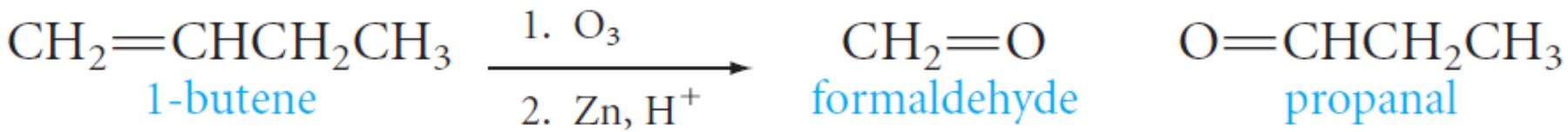


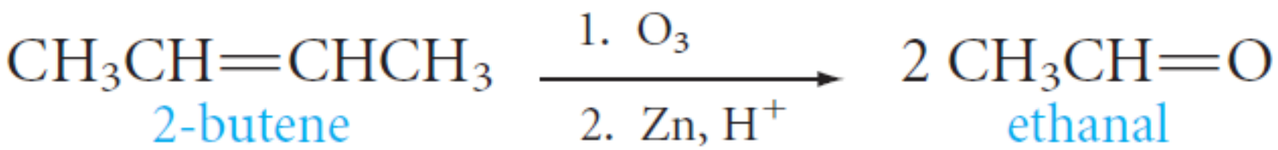
Oxidation Reactions

1. Ozonolysis

- Ozonolysis can be used to locate the position of a double bond.
- **Example;**

  Ozonolysis of 1-butene gives two different aldehydes, whereas 2-butene gives a single aldehyde.

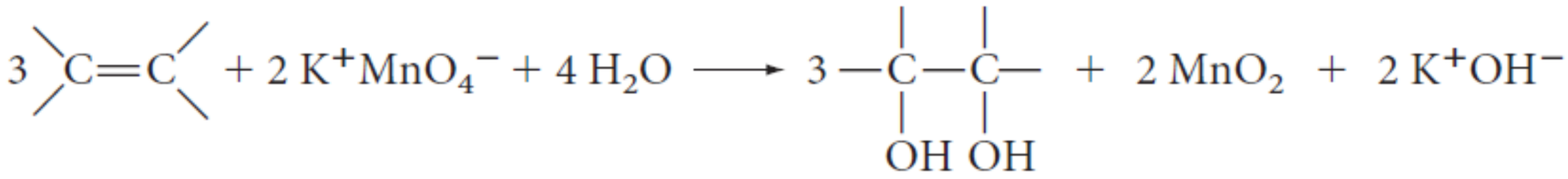




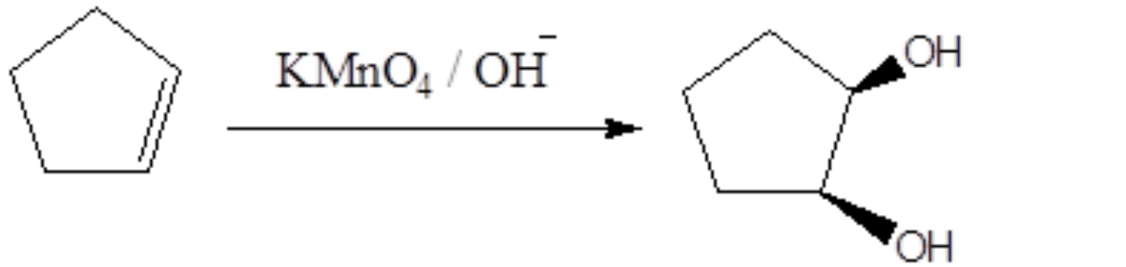
Oxidation Reactions

2. Oxidation Using $KMnO_4$

Alkenes react with alkaline potassium permanganate to form glycols (compounds with two adjacent hydroxyl groups).



alkene — potassium permanganate (purple) — a glycol — manganese dioxide (brown-black)



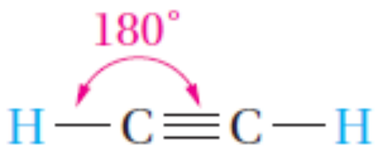
Cyclopentene — *cis*-Cyclopentane-1,2-diol

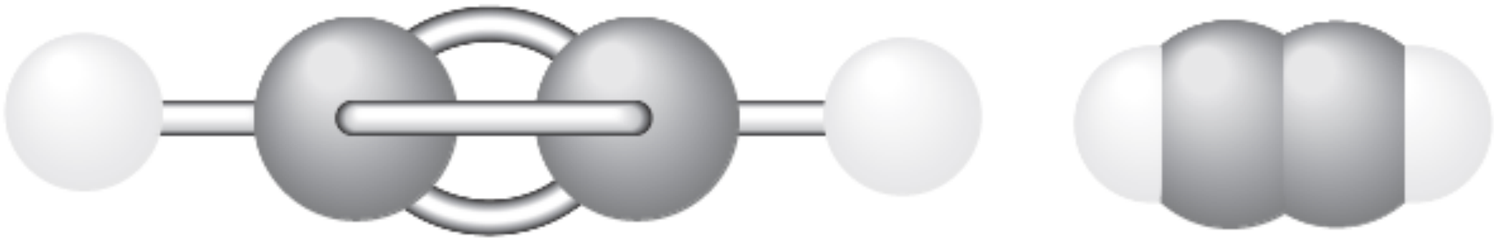
Hexane does not react with purple $KMnO_4$ (left); cyclohexene (right) reacts, producing a brown-black precipitate of MnO_2.

3. ALKYNES

The Structure of Alkynes

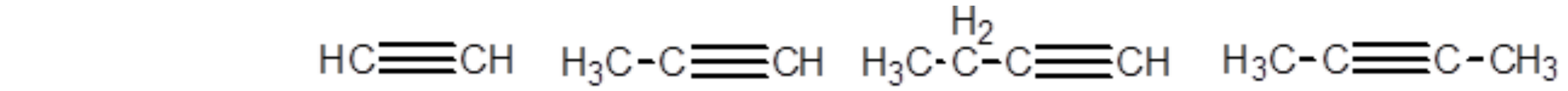
- **Alkynes** are hydrocarbons that contain a ***carbon–carbon triple bond*.**
- **Alkynes** are also known as *Acetylenes*.
- General formula is C_nH_{2n-2}
- Hybridization; ***sp*-hybridized orbitals**
- The angle between them is **180°** and the bond length **1.20 A°**
- The geometry is **Linear.**





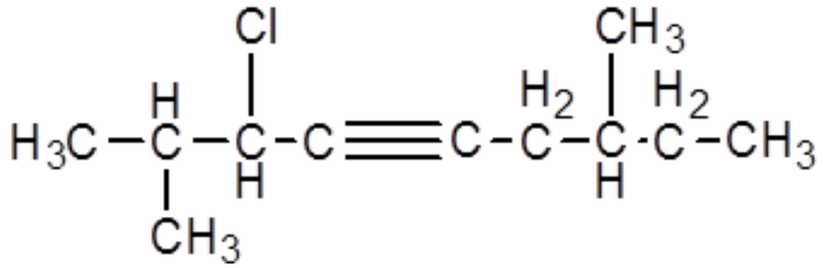
Nomenclature of Alkynes

- The simplest members of the **Alkynes** series are C_2 & C_3
- The IUPAC names are derived from the corresponding alkanes by replacing the **–ane** ending by **–yne**.
- IUPAC rules as discussed for Alkenes .



	$HC\equiv CH$	$H_3C-C\equiv CH$	$H_3C-\overset{H_2}{C}-C\equiv CH$	$H_3C-C\equiv C-CH_3$
IUPAC name:	Ethyne	Propyne	1-Butyne	2-Butyne
Common name:	Acetylene			

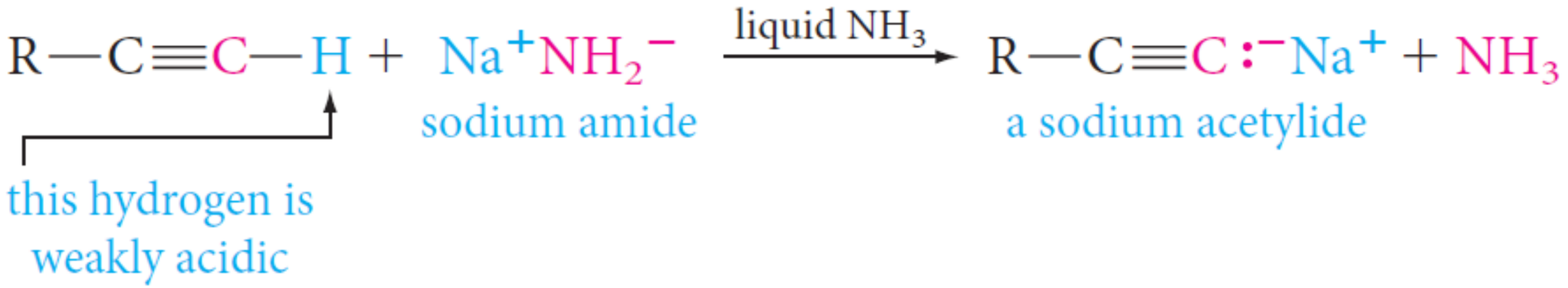
- **Example:**



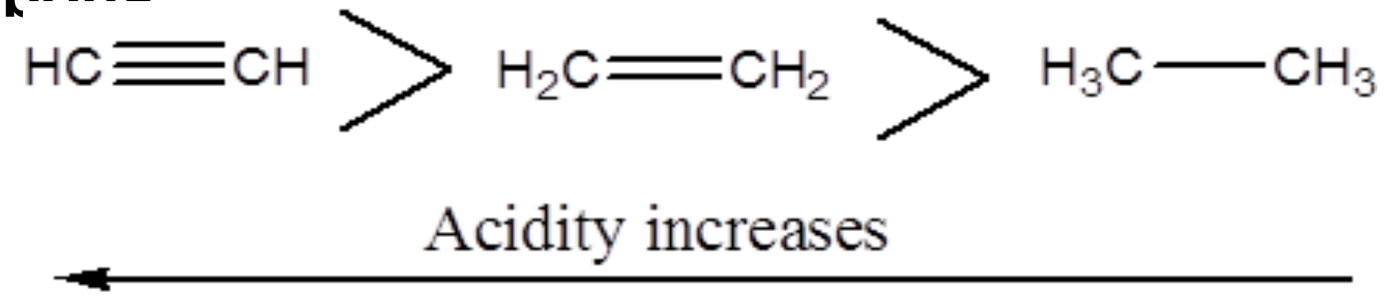
3-Chloro-2,7-dimethyl-4-nonyne

Acidity of Alkynes

- **A hydrogen atom on a triply bonded carbon (Terminal Alkyne) is weakly acidic and can be removed by a very strong base (as Sodium amide).**

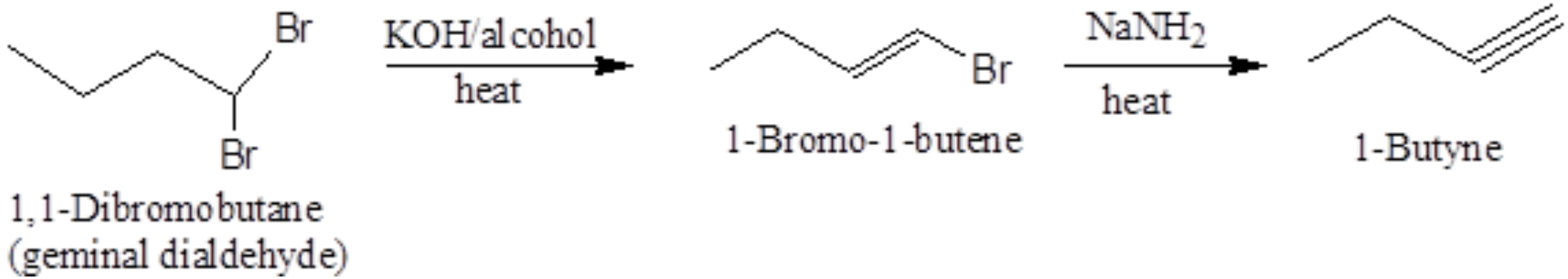


- **Internal alkynes (Non-Terminal Alkyne) have no exceptionally acidic hydrogens.**
  - **Relative Acidity of the Hydrocarbon.**
    Terminal alkynes, are more acidic than other hydrocarbons



Preparation of Alkynes

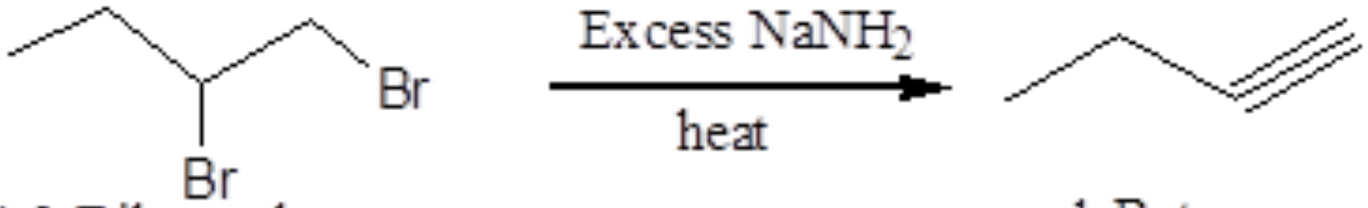
1) Dehydrohalogenation of Alkyl dihalides



1,1-Dibromobutane
(geminal dialdehyde)

1-Bromo-1-butene

1-Butyne



1,2-Dibromobutane
(vicinal dialdehyde)

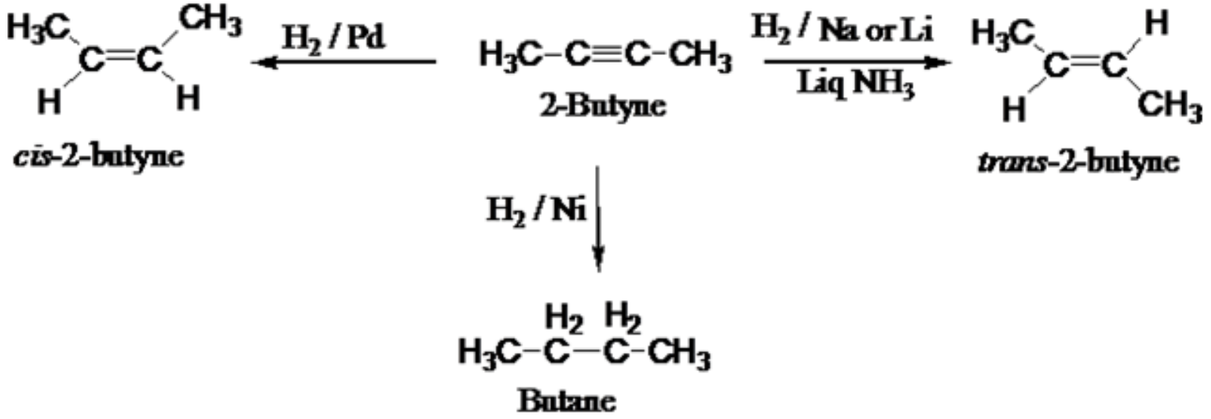
1-Butyne

Reaction of Alkynes

Electrophilic Addition Reactions

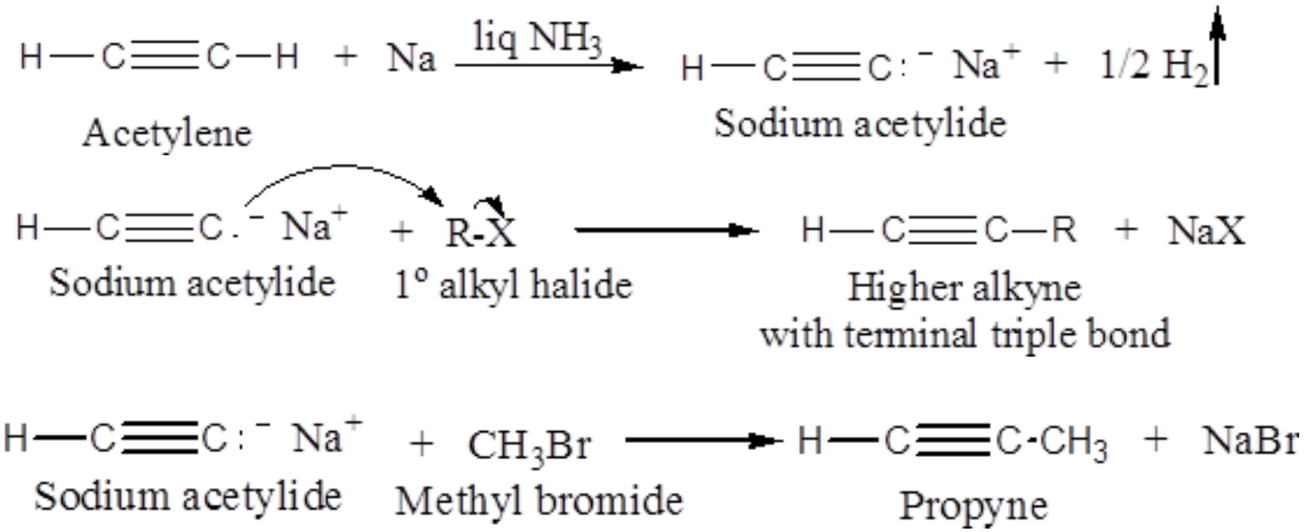
1. Addition of Hydrogen: Hydrogenation

- With an ordinary nickel or platinum catalyst, alkynes are hydrogenated all the way to alkanes.
- However, a special palladium catalyst (called Lindlar's catalyst) can control hydrogen addition so that only one mole of hydrogen adds. In this case, the product is a *cis* alkene.
- On the other hand, reduction using metals such a s sodium or lithium in liquid ammonia results i

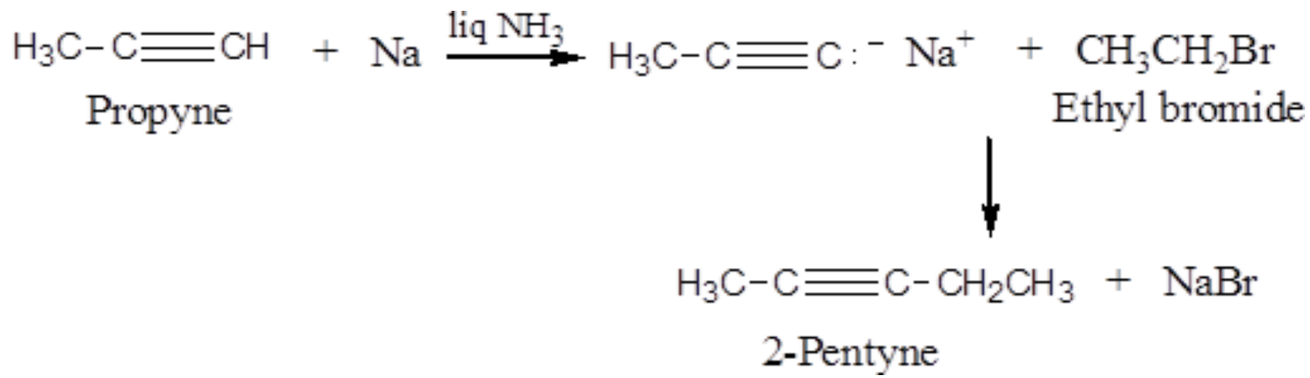


2) Reaction of Sodium Acetylide with Primary Alkyl Halides

- **Acetylene**



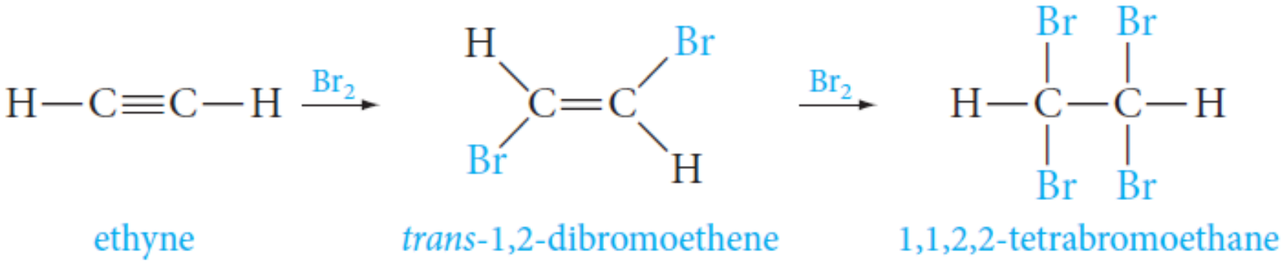
- **Monosubstituted Acetylenes**



Electrophilic Addition Reactions

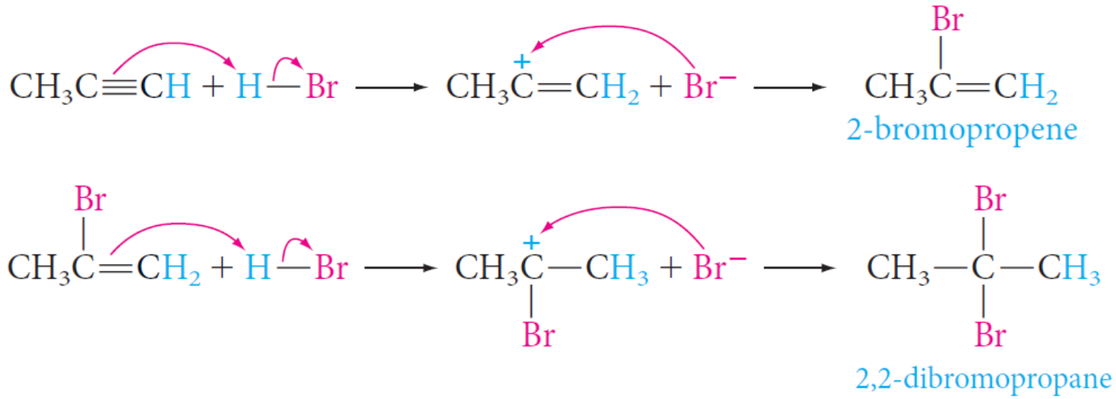
2. Addition of Halogen: Halogenation

Bromine adds as follows; In the first step, the addition occurs mainly *trans.*



3. Addition of Hydrogen Halide

With unsymmetrical triple bonds and unsymmetrical reagents, Markovnikov's Rule is followed in each step, as shown in the following example:



Electrophilic Addition Reactions

4. Addition of Water: Hydration

- **Addition of water to alkynes requires not only an acid catalyst but mercuric ion as well.**
- **Although the reaction is similar to that of alkenes, the initial product - a vinyl alcohol or enol - rearranges to a carbonyl compound (keto form).**
- **The keto form of aldehydes and ketones are in equilibrium with the enol form.**
- **The keto from predominates at equilibrium for most simple aldehydes and ketones.**
- **The inter conv**