Organic Chemistry

Assoc. Prof. Mohamed Frahat Foda

Email: m.frahat@fagr.bu.edu.eg

Webpage: https://bu.edu.eg/staff/mfrahat6-courses/18453

Coures Contents

- Introduction to Organic chemistry:

  Classification of organic Chemistry

(Alkanes, Alkenes , Alkynes, Alcohols, Aldehydes, Ethers, Ketones, Organic acids and its derivatives

1- What you need to know first about Organic Chemistry?

- **In all Organic Compounds:**
  - All **Carbon** atoms must make **four bonds**.
  - All **Oxygen** atoms must make **two bonds**.
  - All **Nitrogen** atoms must make **three bonds**.
  - All **hydrogen and halogens** atoms must make **one bond**.

. Organic Chemistry is defined as the Chemistry of Carbon and its compounds.

Hybridization:

The 4 bonds carbon forms is explained by Linus Pauling's theory of hybridization. Carbon atoms have an electron configuration of $1s^2 2s^2 2p^2$ This configuration corresponds to the following energy level diagram.

Alkanes

Alkenes

Alcohols

Esters

Organic Compounds

Ethers

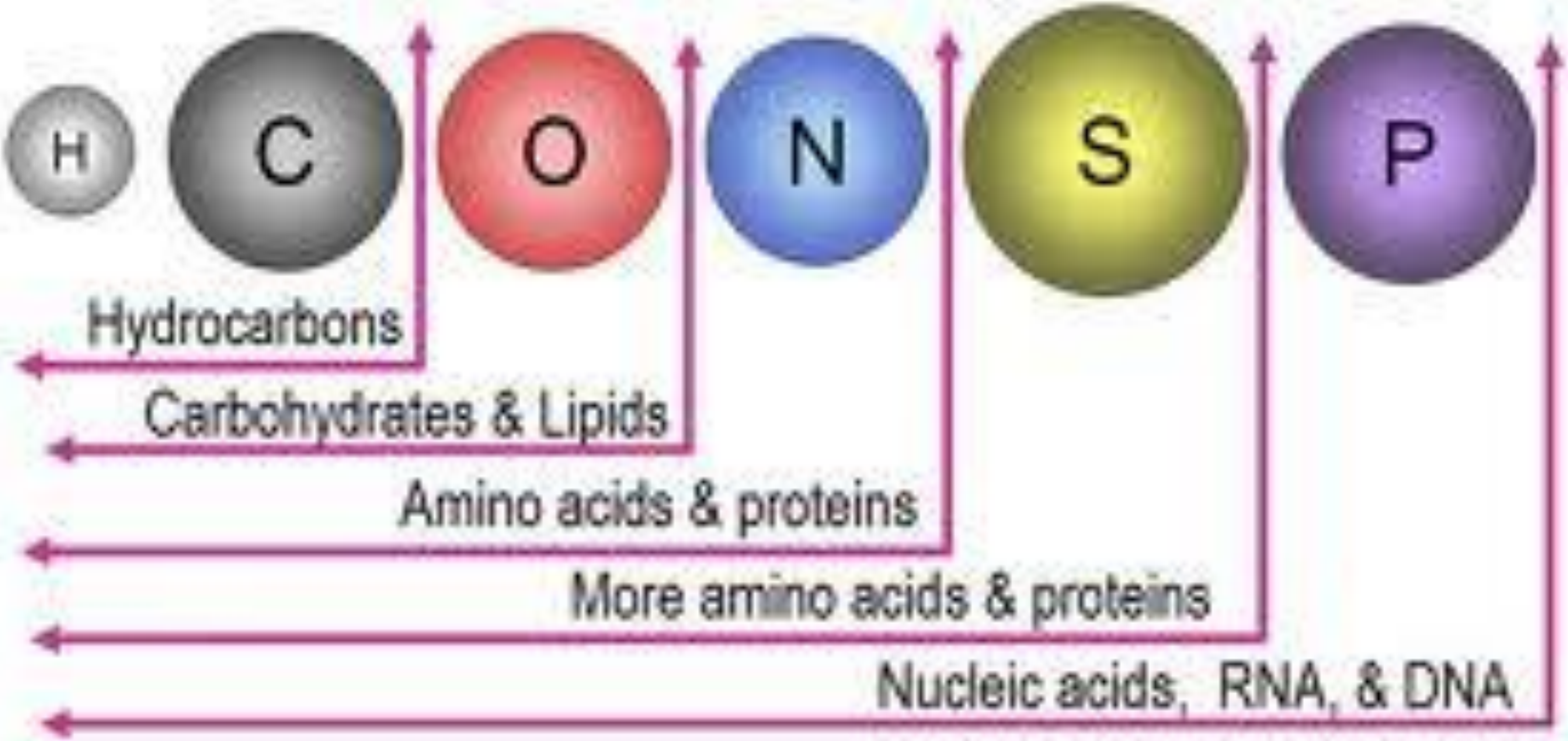
Acids

Aldehydes

Keytones

Amines

Organic Building Blocks



Hydrocarbons

Carbohydrates & Lipids

Amino acids & proteins

More amino acids & proteins

Nucleic acids, RNA, & DNA

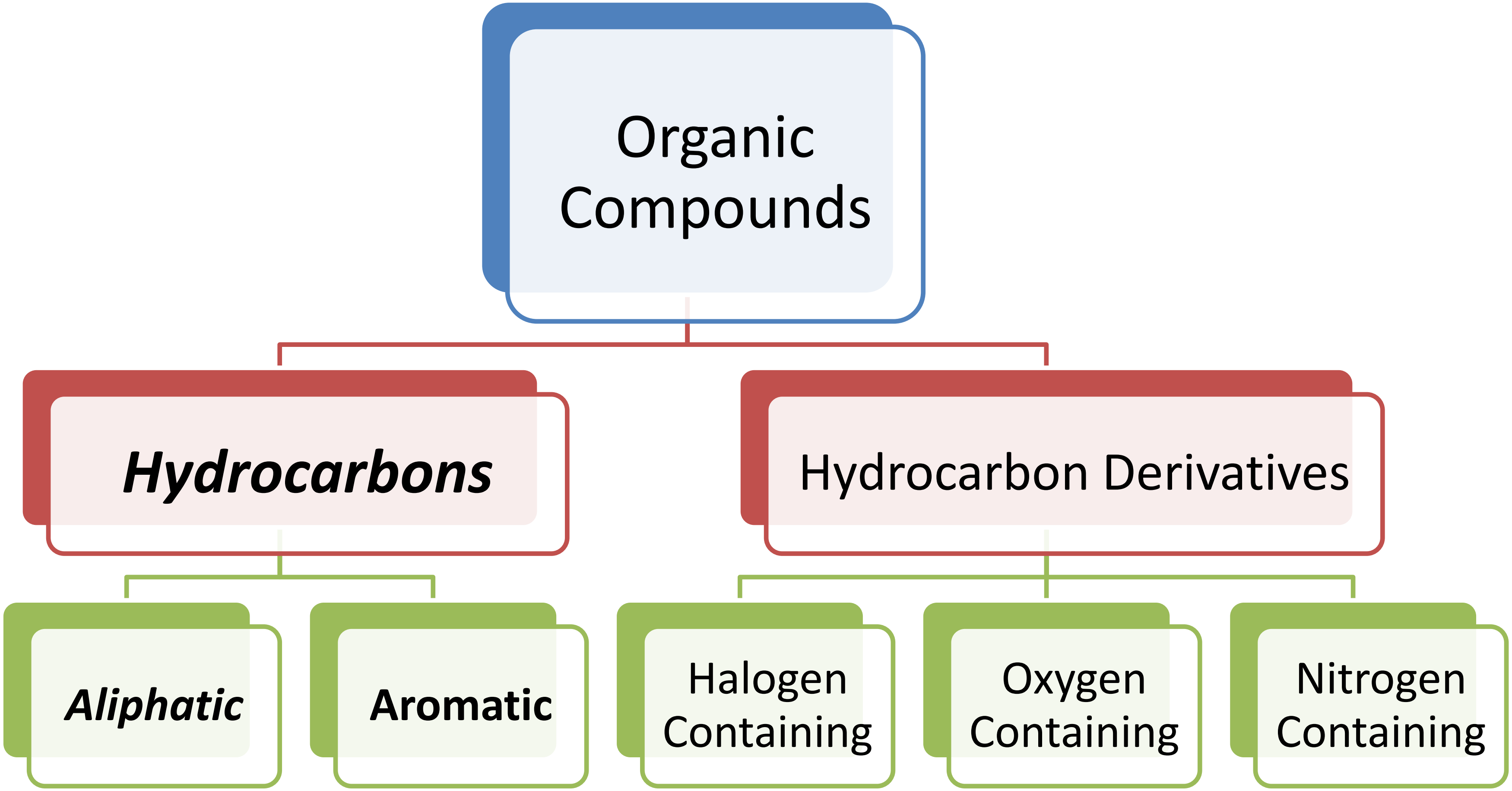
Single atoms of iron, copper, magnesium for some proteins

General Properties of Organic Molecules:

1. Flammable
2. High Vapor Pressure
3. Odorous
4. Covalently Bonded
5. Non-Polar – functional groups can change these from non-polar to polar or cause the molecule to be bi-polar.

6. Low Solubility in Water – due to being non-polar as water is polar
7. Rate of Chemical Reaction is Normally Slow
8. Normally Found as Gases and Liquids at Room Temp
9. Non-Conductive of Electrical Current

2- Classification of Organic Compounds



Organic Compounds

Hydrocarbons

Hydrocarbon Derivatives

Aliphatic

Aromatic

Halogen Containing

Oxygen Containing

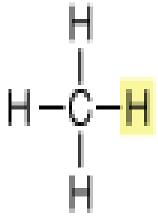
Nitrogen Containing

Organic Compounds and Functional Groups

Functional group	Class
$\mathrm{C - C}$ Single bond	Alkane
$\mathrm{C = C}$ Double bond	Alkene
$\mathrm{C \equiv C}$ Triple bond	Alkynes
$\mathrm{- C - OH}$ Hydroxyl group	Alcohols
$\mathrm{- COOH}$ Carboxyl group	Acids
$\mathrm{- COO -}$ Esters group	Esters

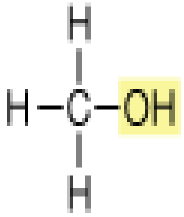
The leading families of organic compounds

Hydrocarbon



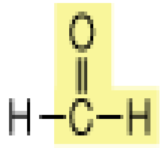
methane
(CH_4)

Alcohol



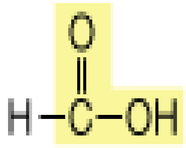
methyl alcohol
(CH_3OH)

Aldehyde



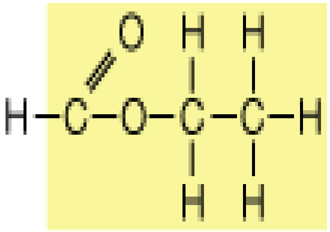
formaldehyde
($HCHO$)

Acid



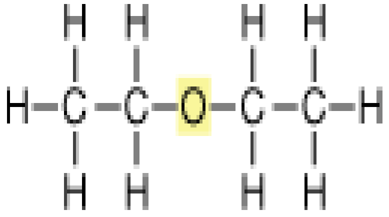
formic acid
($HCOOH$)

Ester



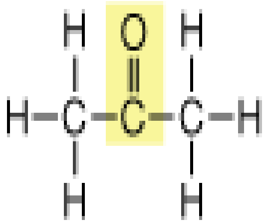
ethyl formate
(C_2H_5COOH)

Ether



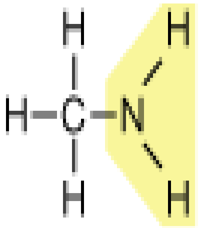
diethyl ether
($C_2H_5OC_2H_5$)

Ketone



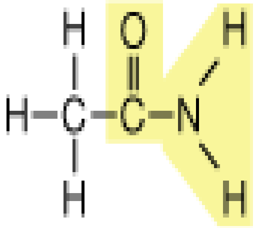
acetone
(CH_3COCH_3)

Amine



methyl amine
(CH_3NH_2)

Amide



acetamide
(CH_3CONH_2)

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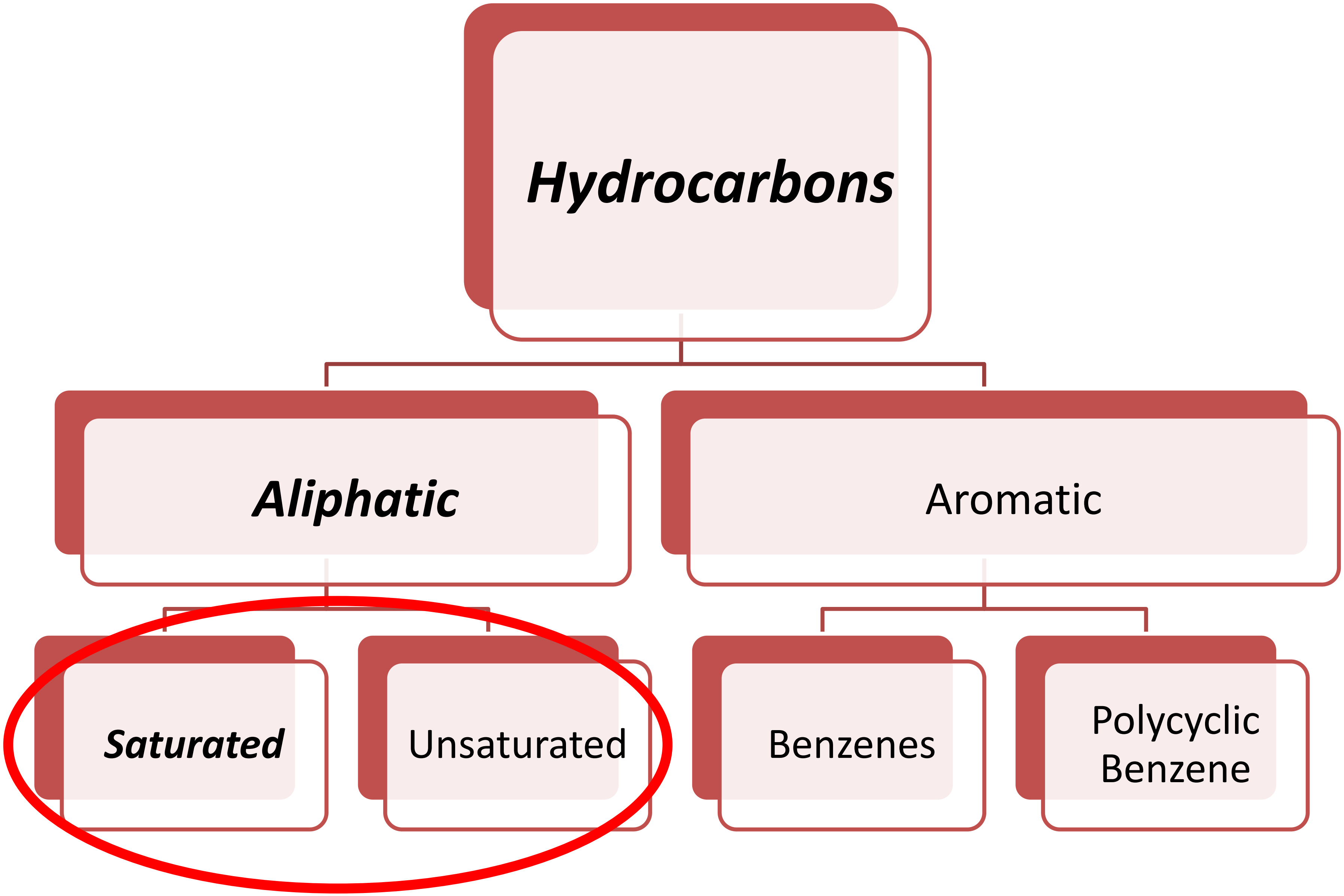


Hydrocarbons

Aliphatic

Aromatic

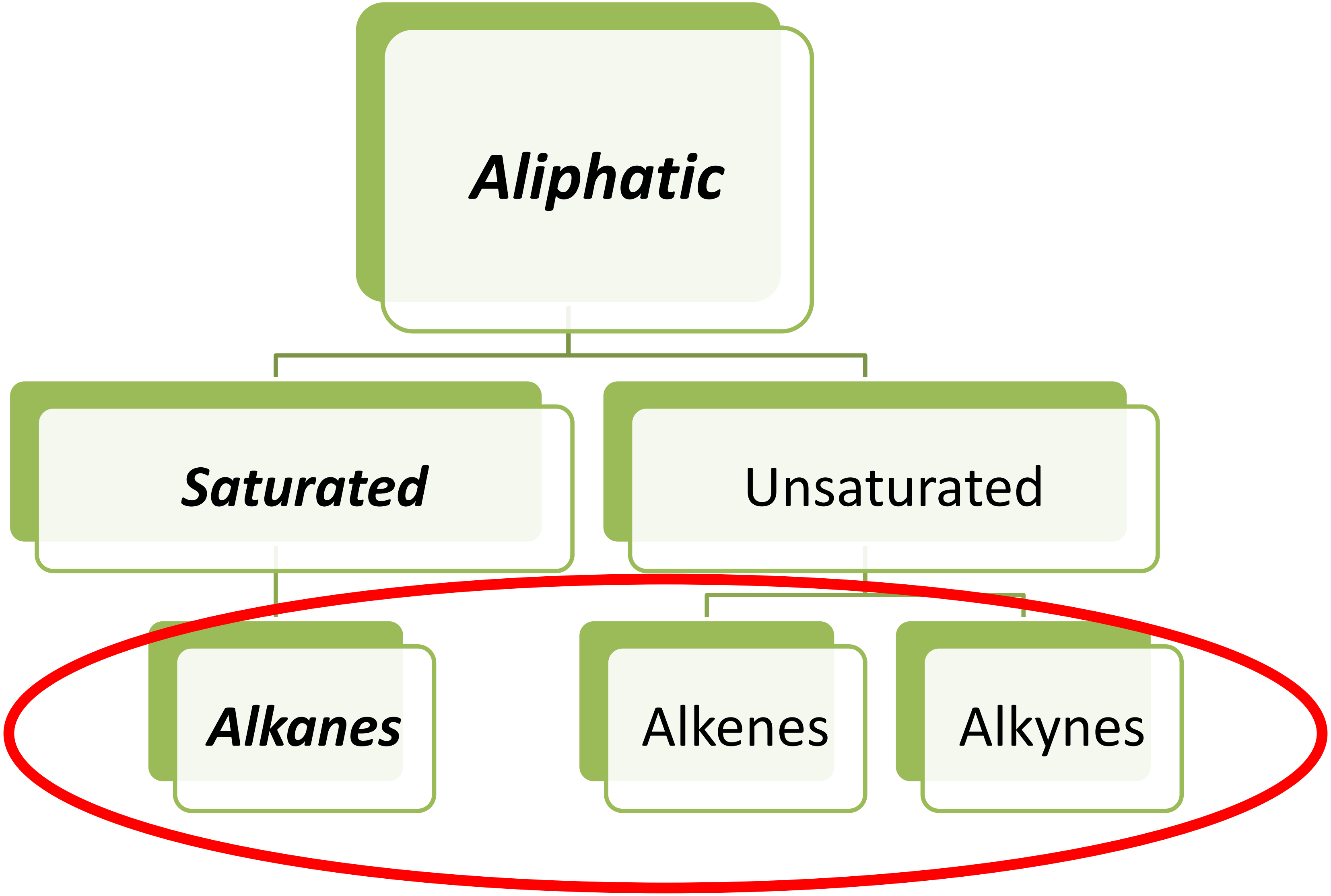
Saturated

Unsaturated

Benzenes

Polycyclic Benzene

Classification of Organic Compounds



Aliphatic

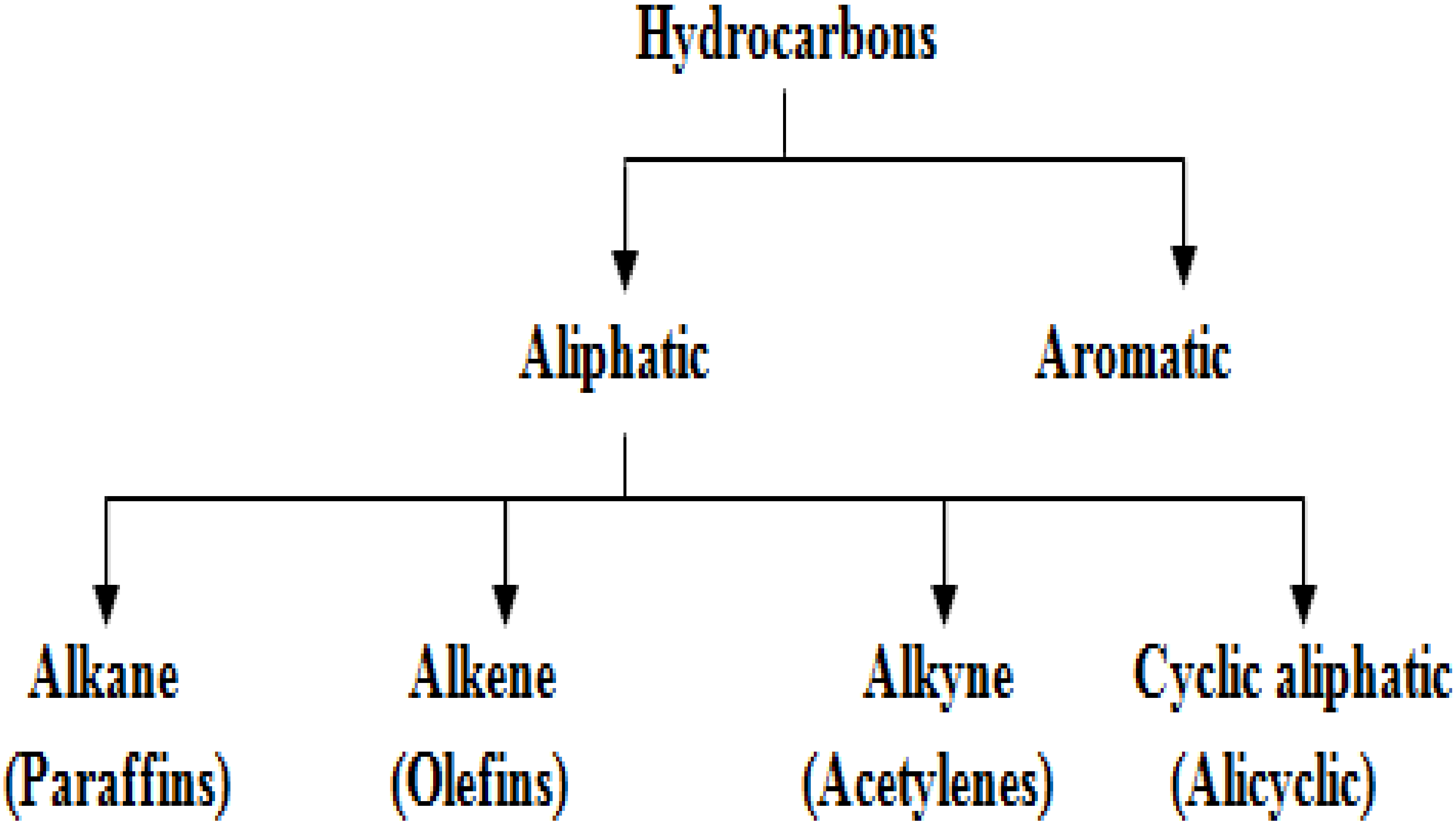
Saturated

Unsaturated

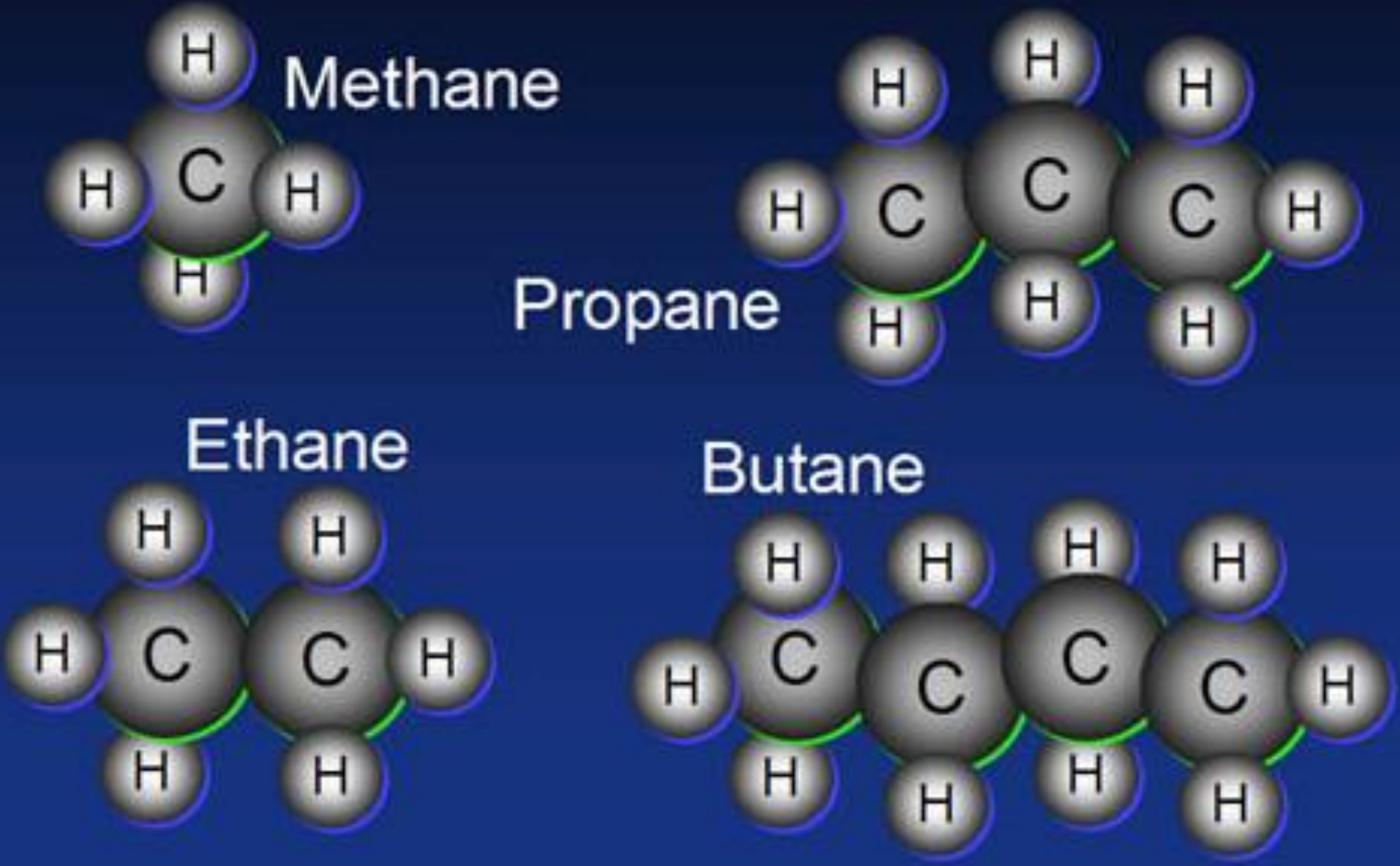
Alkanes

Alkenes

Alkynes


Hydrocarbons
Aliphatic
Aromatic
Alkane
(Paraffins)
Alkene
(Olefins)
Alkyne
(Acetylenes)
Cyclic aliphatic
(Alicyclic)

Hydrocarbons



3- Introduction to Naming of Organic Molecules

1- Alkanes

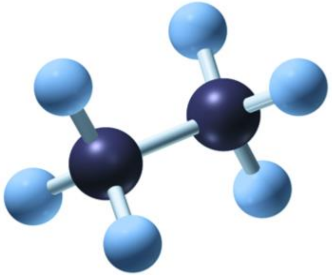
2- Alkenes

3- Alkynes

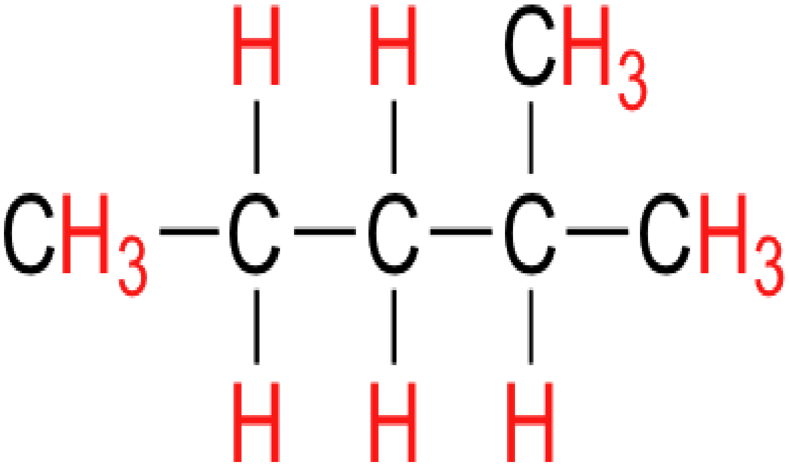
4- Cyclic Structures

3-1- Alkanes

- Alkanes are the simplest organic molecules, they only contain **C** and **H**, and only contain single bonds named as **hydrocarbons.**
- General Formula: C_nH_{2n+2}



- Alkanes are the most **saturated compounds** as they have the maximum number of bonded hydrogen's.

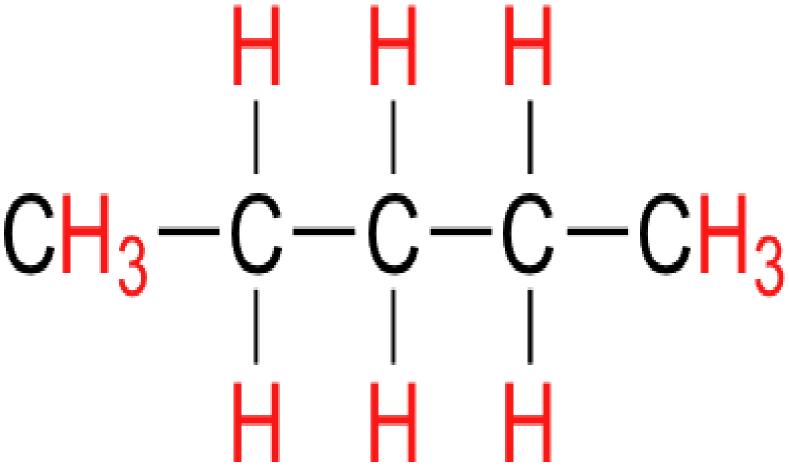


$$CH_3-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{CH_3}{C}}-CH_3$$

C_6H_{14}

$n = 6$

$2n+2 = 14$



$$CH_3-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-CH_3$$

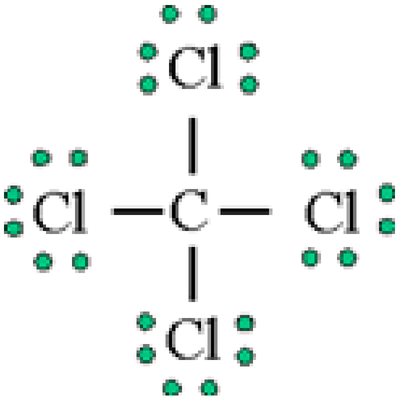
C_5H_{12}

$n = 5$

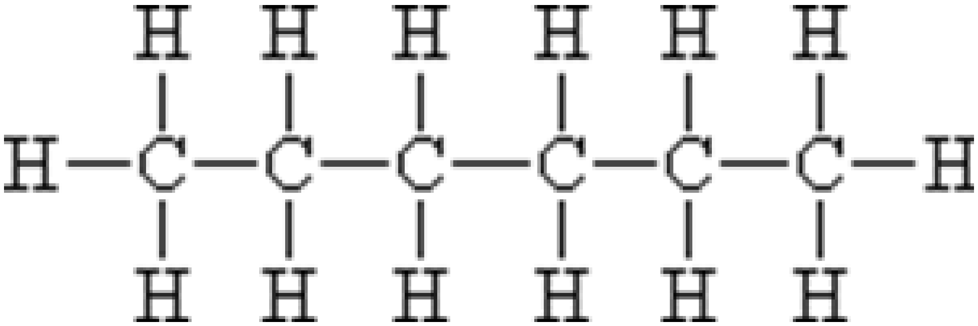
$2n+2 = 12$

Names of Structures

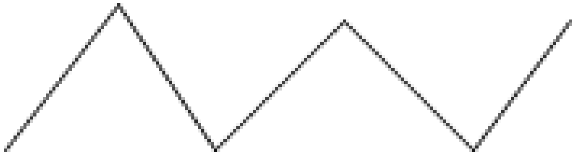
- Lewis Structures
- Structural Formulas
- Condensed Formulas & Structures
- Line Structures



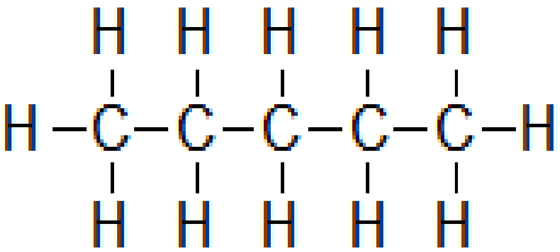
C_6H_{14} or $CH_3(CH_2)_4CH_3$



$$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H}$$

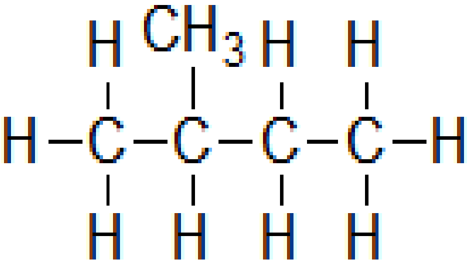


- Any series that differs only by an increasing number of $–CH_2$- groups is known as a **homologous series**. The individual members are said to be **homologs** of each other.
  - The series must contain the same functional group.



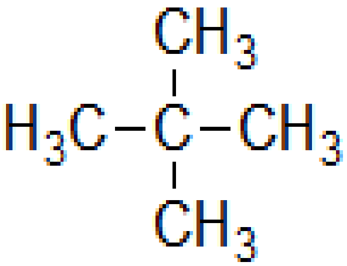
$$\begin{array}{ccccccccccccc} & & H & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & \end{array}$$

pentane
C_5H_{12}



$$\begin{array}{ccccccccccc} & & H & & CH_3 & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

isopentane
C_5H_{12}



$$\begin{array}{ccccc} & & CH_3 & & \\ & & | & & \\ H_3C & - & C & - & CH_3 \\ & & | & & \\ & & CH_3 & & \end{array}$$

neopentane
C_5H_{12}

Nomenclature for compounds

- The root name of the compound is based upon the number of carbon atoms in the **longest continuous chain.**

No. of C atom	General Name
1	Meth-
2	Eth-
3	Prop-
4	But-
5	Pent-
6	Hex-
7	Hep-
8	Oct-
9	Non-
10	Dec-

- methane (CH_4)
- ethane (C_2H_6)
- propane (C_3H_8)
- butane (C_4H_{10})
- pentane (C_5H_{12})

Alkane Nomenclature

Unbranched/ Normal Alkanes

# C	Name	#C	Name
1	Methane	11	Undecane
2	Ethane	12	Dodecane
3	Propane	13	Tridecane
4	Butane	14	Tetradecane
5	Pentane	15	Pentadecane
6	Hexane	16	Hexadecane
7	Heptane	17	Heptadecane
8	Octane	18	Octadecane
9	Nonane	19	Nonadecane
10	Decane	20	Eicosane

Alkane Nomenclature

To name alkanes, we use the system that’s approved by the International Union of Pure and Applied Chemistry **(IUPAC)** for just this purpose.

IUPAC Naming System: Alkanes

1) Find the longest continuous chain of carbon atoms. This is the base name of the compound.

2) Number the longest chain beginning with the end nearest a substituent.

3) Name the substituent groups attached to the longest chain as alkyl groups. Also state the location of each alkyl group according to its numbered carbon on the main chain.

4) When two or more substituents are present, list them in alphabetical order. If two or more of the same alkyl groups are present, use the prefixes di-, tri- etc. to avoid repetition.

IUPAC System

1. The longest chain of carbon atoms is taken as the **parent chain**.
2. Each substituent is given a name and a number. The number shows the carbon atom of the parent chain to which the substituent is bonded.
3. If there is one substituent, number the parent chain from the end that gives it the lower number.
4. If there are two or more different substituents, list them in alphabetical order.

Notes on Structures

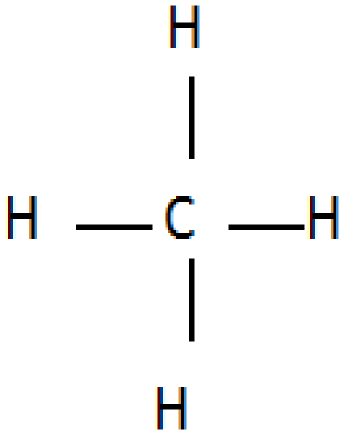
- Structural Formula: shows all bonds including hydrogen
- Condensed Formula: These are generally written without lines indicating bonds, or showing lone pairs, and parentheses are used for identical groups.
- Line Formula: Bonds are represented by lines, carbon atoms are assumed to be present at the start and finish of a line.
  - Nitrogen, oxygen and halogens are labeled, but hydrogens are only shown when bonded to a drawn atom.
  - Each atom is assumed to have sufficient hydrogen atoms around it to make it neutral.

Structural Formulas

Alkanes are written with structural formulas that are

- expanded to show each bond (Lewis Structure).
- condensed to show each carbon atom and hydrogen atoms attached to that carbon.

Expanded (Lewis)

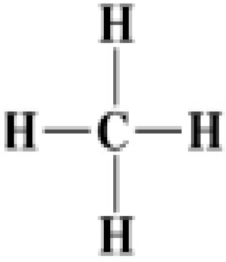
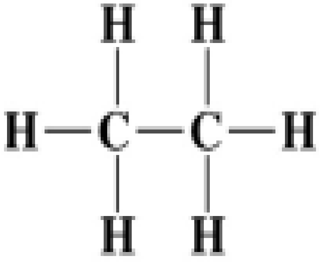
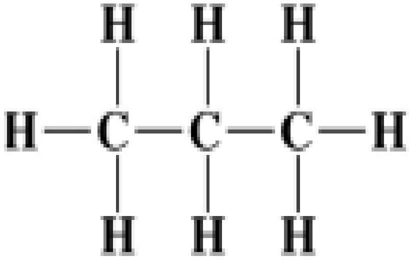
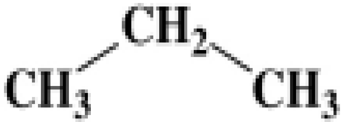


$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

Condensed

CH_4, methane

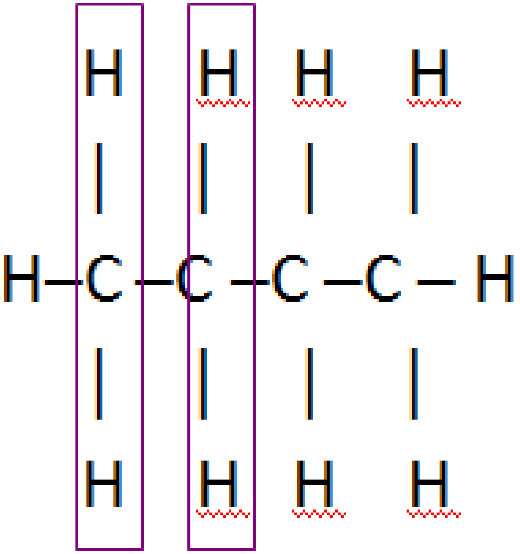
Expanded and Condensed Structures

Alkane	**Methane**	**Ethane**	**Propane**
Molecular formula	CH_4	C_2H_6	C_3H_8
Structural formulas			
Expanded			
Condensed	CH_4	$CH_3—CH_3$	$CH_3—CH_2—CH_3$ or 

Structural Formulas

Condensed formulas are written for expanded structural formula by showing each carbon and the attached hydrogen atoms.

Expanded

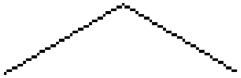


$$\begin{array}{ccccccccc} & & H & & H & & H & & H \\ & & | & & | & & | & & | \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | \\ & & H & & H & & H & & H \end{array}$$

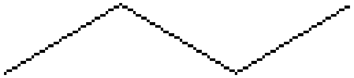
Condensed

$CH_3-CH_2-CH_2-CH_3$

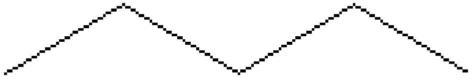
Alkane Nomenclature



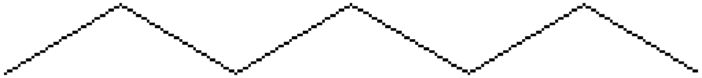
Propane



Butane



Pentane

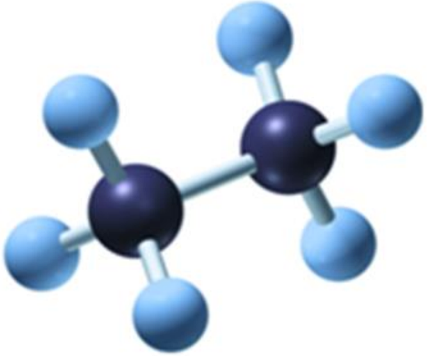


Heptane

- Condensed Structural Formula
- Actually Zig-Zag Structures
- All Carbons sp^3 Hybridized

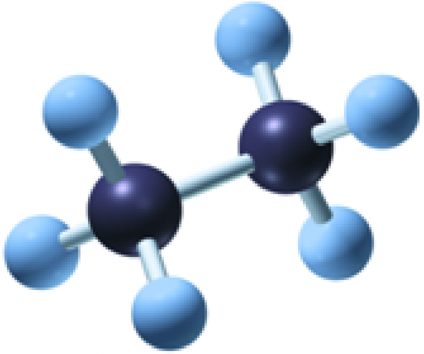
Alkane Nomenclature

- the names of ***all*** organic compounds stem from the names of the alkanes



Alkane Nomenclature

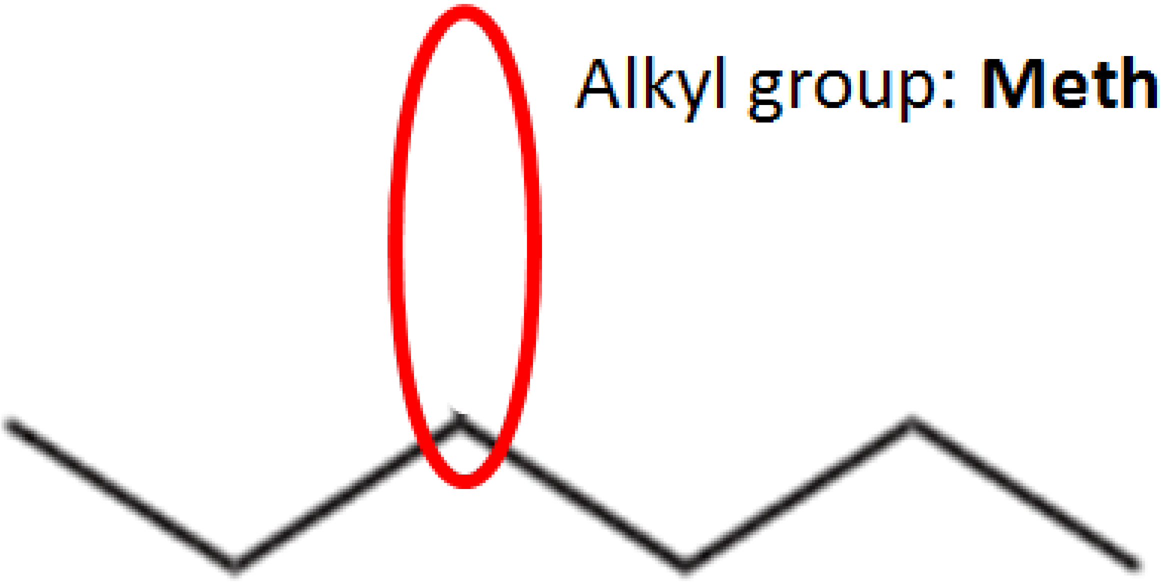
- Straight chain alkanes are alkanes in which all the carbon atoms line up in a row.
- Called unbranched or ***normal***



Alkane Nomenclature

Name the smaller rows that branch off of the larger rows as if they were little independent alkanes of their own, better known as ***alkyl groups***.

Alkane Nomenclature



Alkyl group: **Methyl**

Hexane or n-hexane

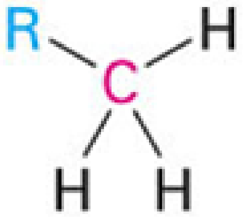
Alkyl Group Nomenclature

Unbranched Alkyl Groups

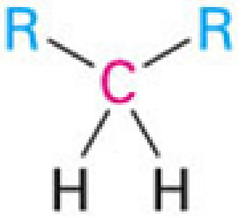
# C	Name	#C	Name
1	Methyl	11	Undecyl
2	Ethyl	12	Dodecyl
3	Propyl	13	Tridecyl
4	Butyl	14	Tetradecyl
5	Pentyl	15	Pentadecyl
6	Hexyl	16	Hexadecyl
7	Heptyl	17	Heptadecyl
8	Octyl	18	Octadecyl
9	Nonyl	19	Nonadecyl
10	Decyl	20	Eicosyl

Alkane Nomenclature

- Classified by the connection site
  - – a carbon at the end of a chain (primary alkyl group)
  - – a carbon in the middle of a chain (secondary alkyl group)



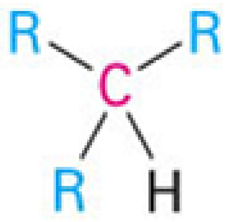
Primary **carbon (1°) is bonded to one other carbon.**



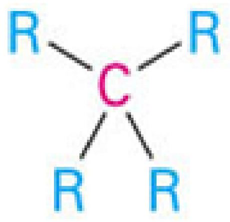
Secondary **carbon (2°) is bonded to two other carbons.**

Alkane Nomenclature

- Classified by the connection site
  - a carbon with three carbons attached to it (tertiary alkyl group)
  - a quaternary (4°) carbon atom has four other carbon atoms bonded to it.



***Tertiary* carbon (3°) is bonded to three other carbons.**



***Quaternary* carbon (4°) is bonded to four other carbons.**

Example for naming HYDROCARBONS

- The name of a hydrocarbon has three portions:

PREFIX + ROOT + SUFFIX

Identifies a group attached to the main chain and **the number of the carbon to which it is attached**

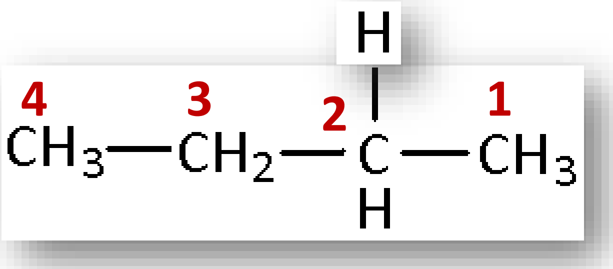
- have ***–yl*** as their **ending**

Tells the number of C atoms in the molecule (the longest and continuous)

Tells **the type of organic compound** the molecule represents **(functional group)**

Example for naming non-branched HYDROCARBONS

- Example:



$$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{\underset{H}{\overset{H}{|}{C}}}-\overset{1}{CH_3}$$

But ane

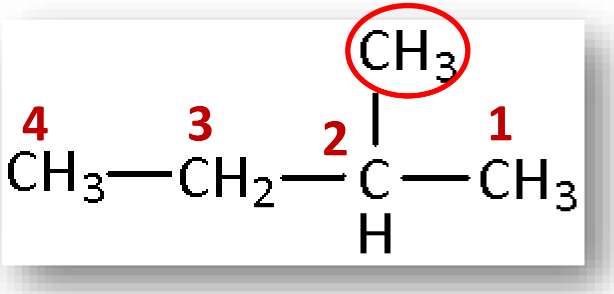
Is the ROOT
❖ The main chain has **4 C** atoms

Is the SUFFIX
❖ The compound is an **alkane**

Roots	No. of C atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

Example for naming branched HYDROCARBONS

- Example:



$$CH_3-CH_2-\underset{H}{\overset{CH_3}{C}}-CH_3$$

2-methyl but ane

Is the PREFIX
- ❖ A 1 C branch is attached to C – 2 of the main chain

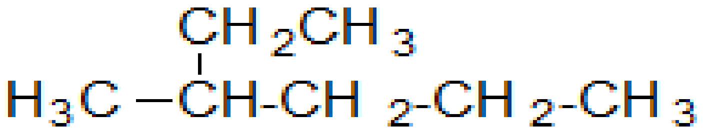
Is the ROOT
- ❖ The main chain has **4 C** atoms

Is the SUFFIX
- ❖ The compound is an **alkane**

Roots	No. of C atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

Alkane Nomenclature Examples

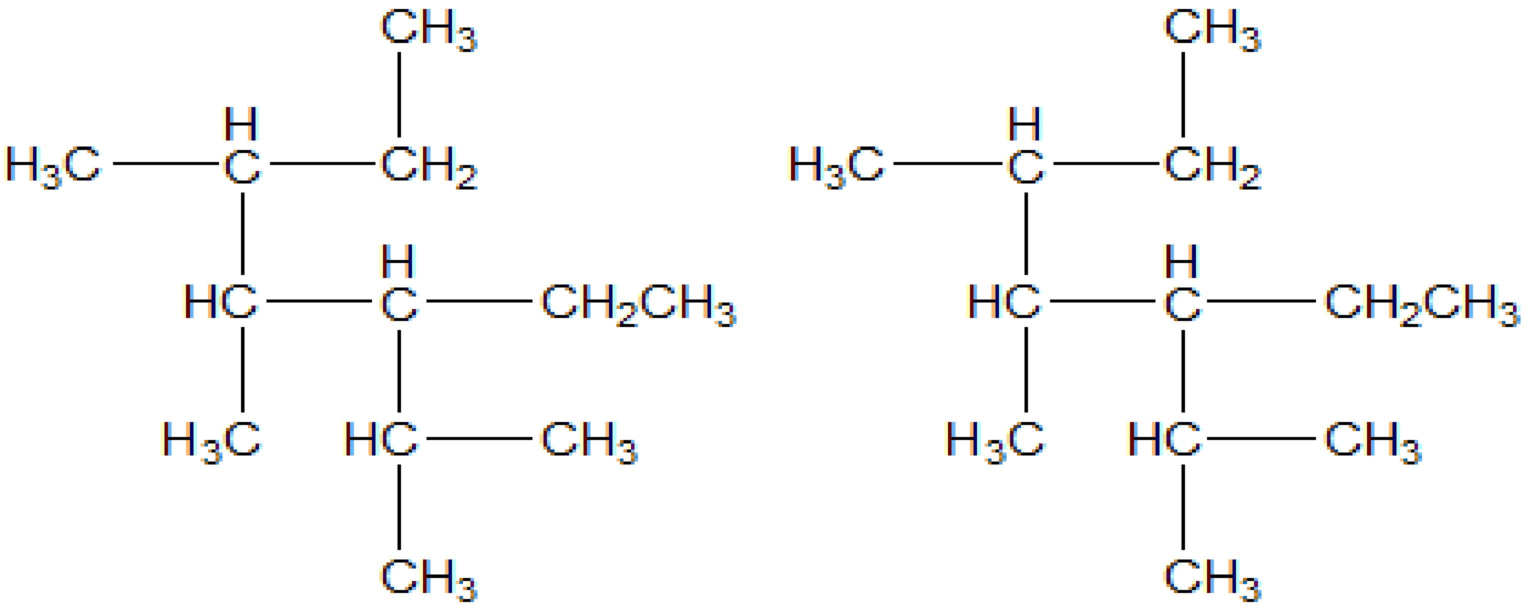
1)



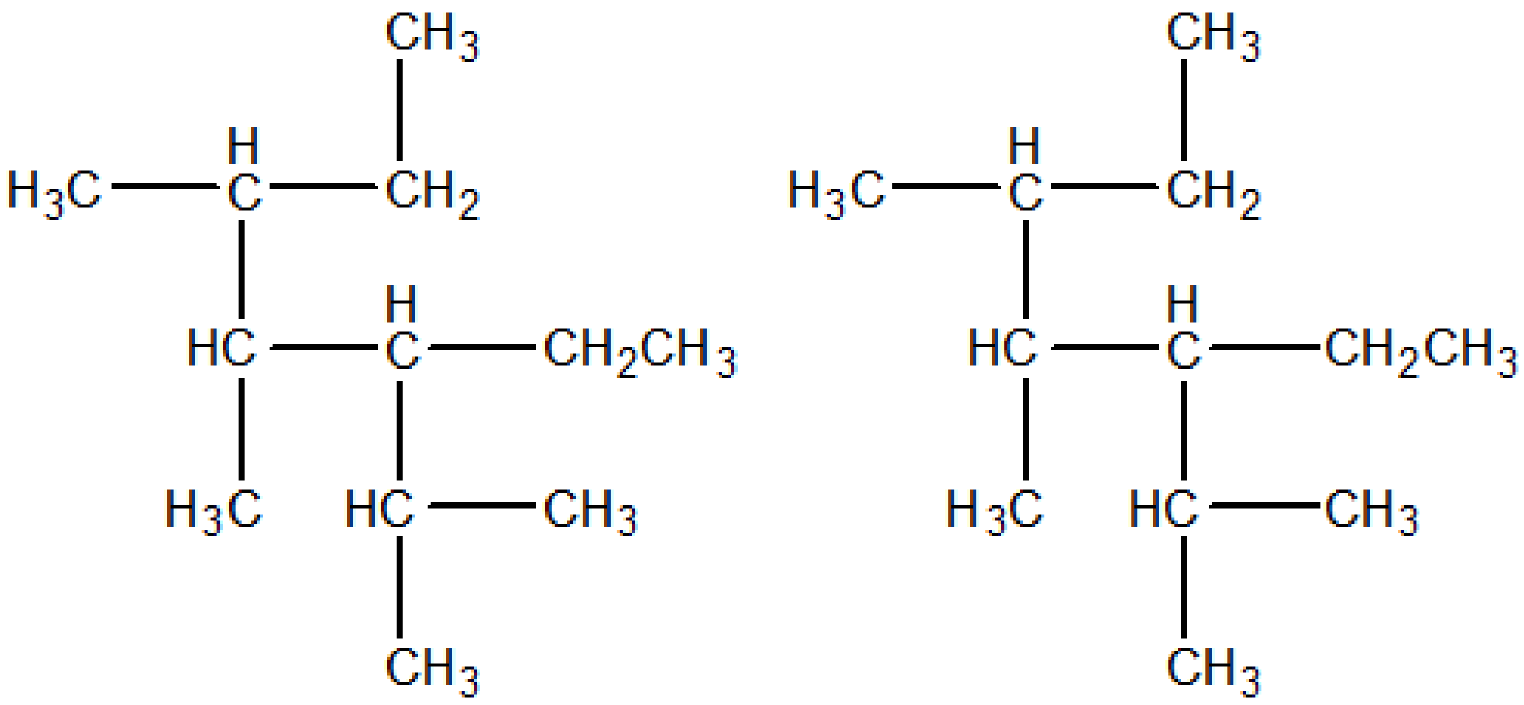
$$H_3C-\overset{\overset{\textstyle CH_2CH_3}{|}}{C}H-CH_2-CH_2-CH_3$$

3-methyl hexane

- If there are two chains of equal length, choose the chain that has the highest number of substituents.



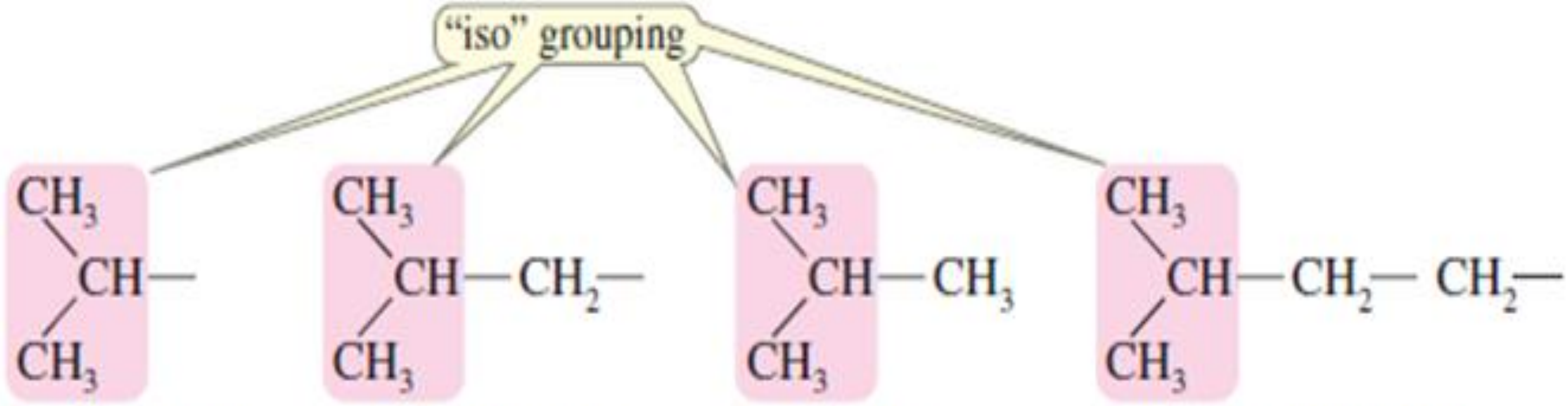
- Numbering starts at the end nearest a substituent so that the alkyl substituents have as low numbers as possible.



Alkyl groups are named by replacing the –ane suffix of the alkane name with –yl.

E.g.	CH_3CH_3	Ethane	CH_3CH_2-	Ethyl group
	$CH_3CH_2CH_3$	Propane	$CH_3CH_2CH_2$-	Propyl group

Alkane Nomenclature



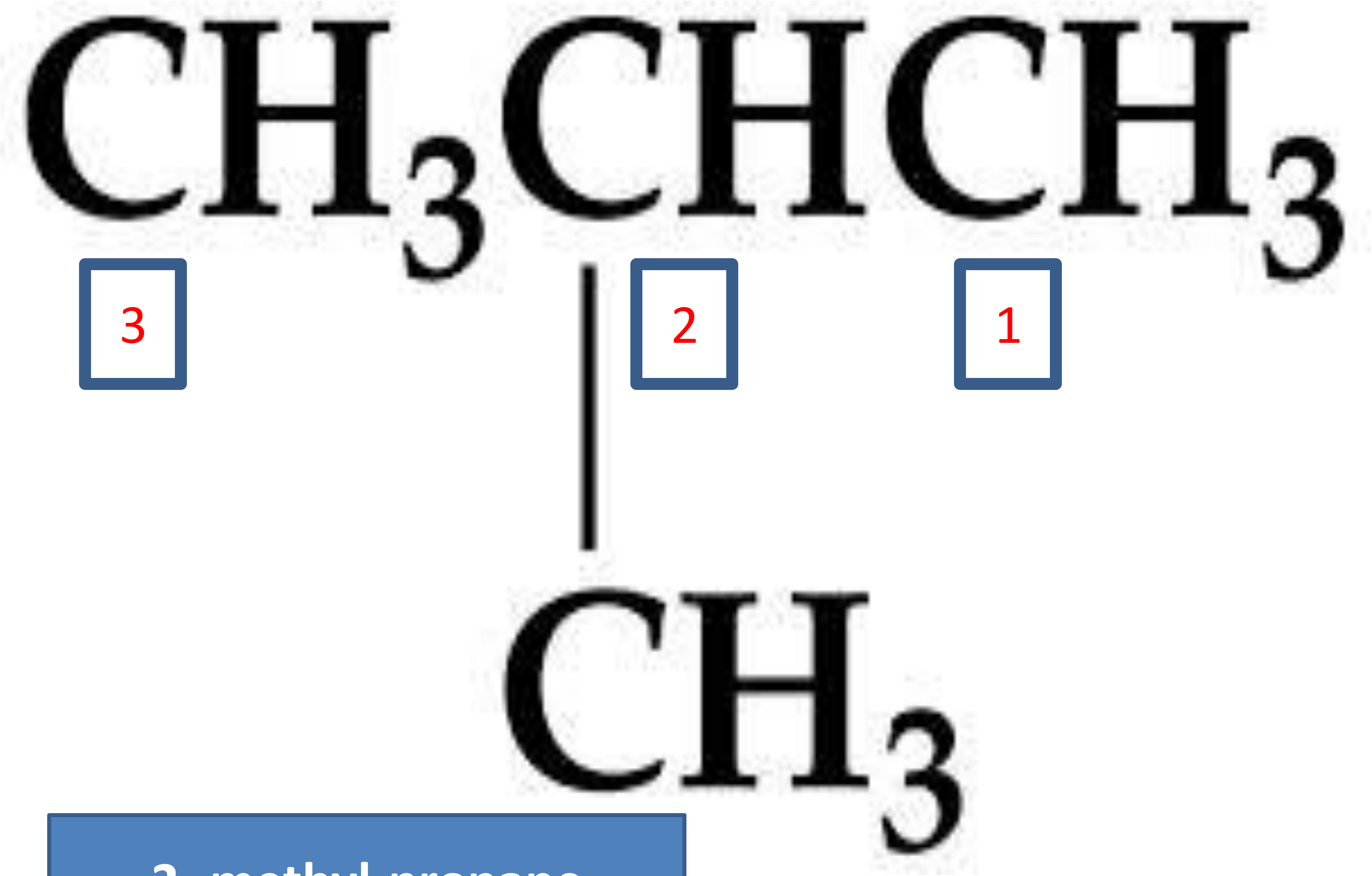
isopropyl group

isobutyl group

isobutane

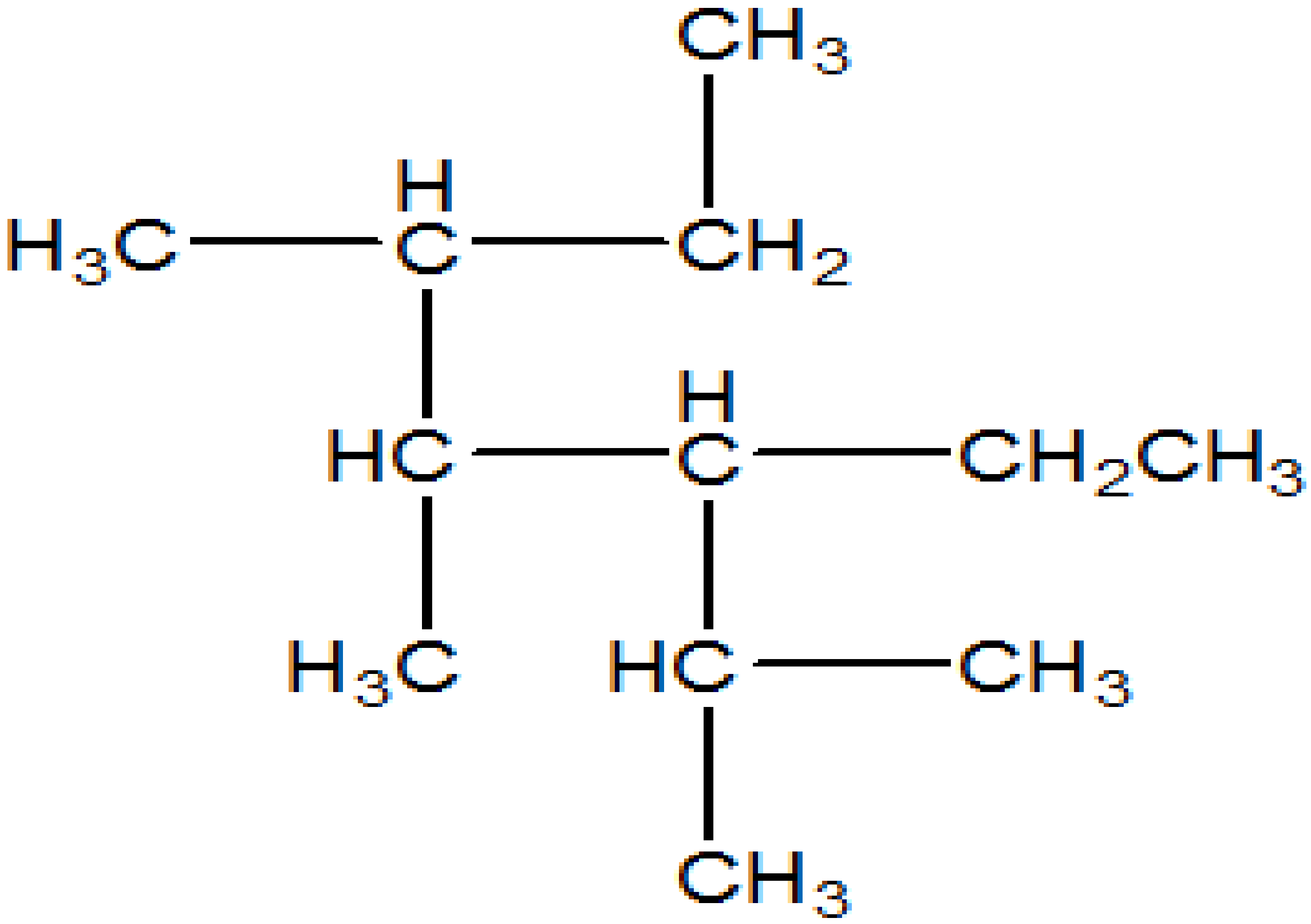
isopentyl group
(isoamyl group)

- Prefixes are used when there are more than one type of alkyl substituent.
  - Di = 2
  - Tri = 3
  - Tetra = 4
  - Penta = 5
- The prefixes do not count when alphabetizing.



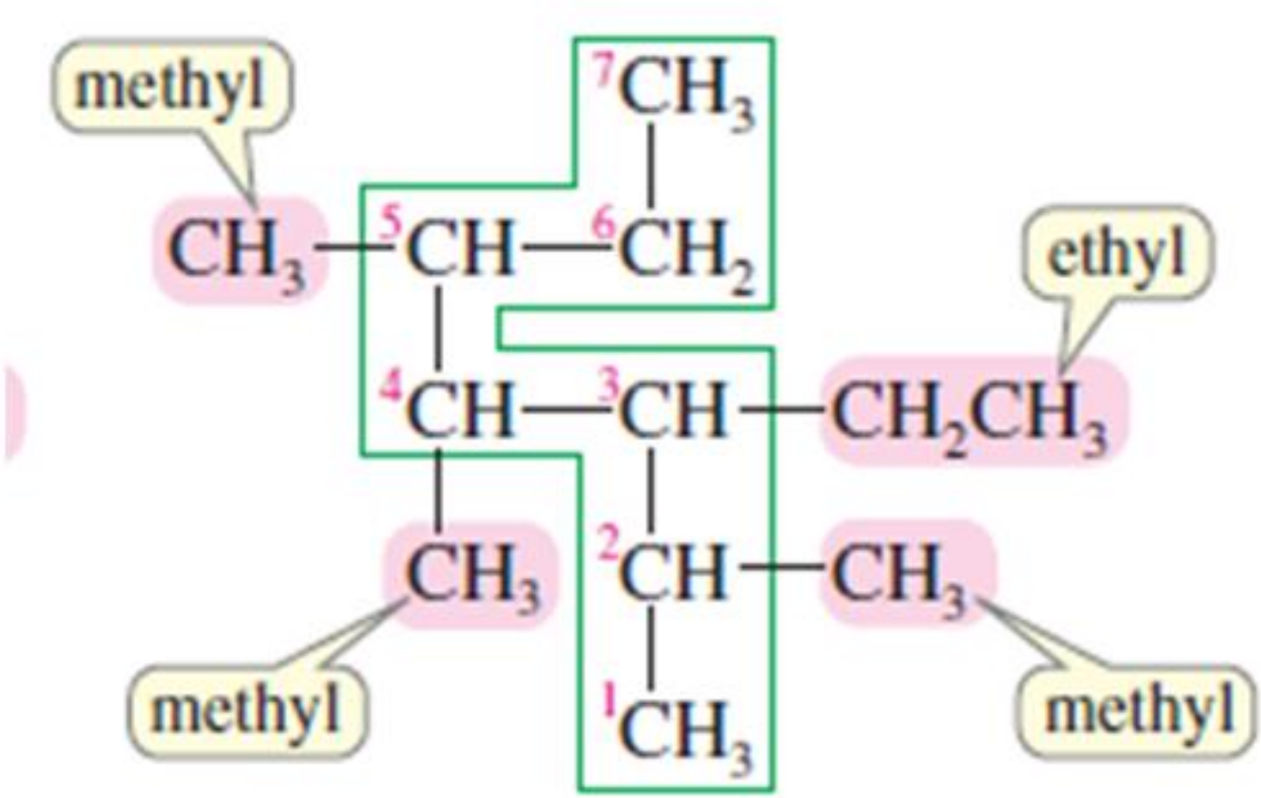
$$\mathrm{CH_3\underset{\underset{CH_3}{|}}{C}HCH_3}$$

2- methyl-propane



3-ethyl-2,4,5-trimethylheptane

3-ethyl-2,4,5-trimethylheptane



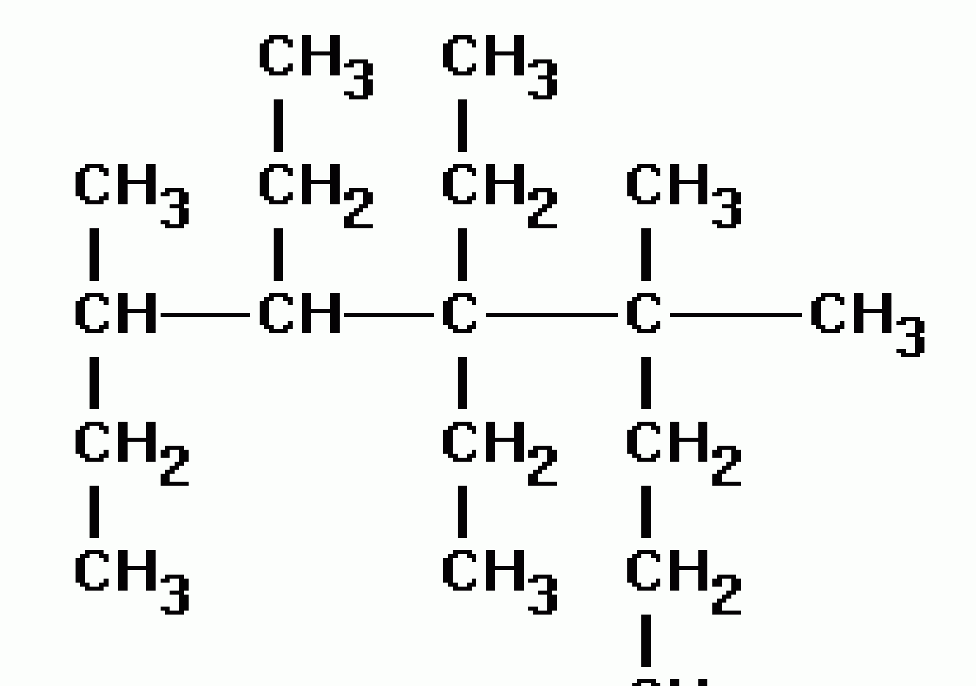
More Problems

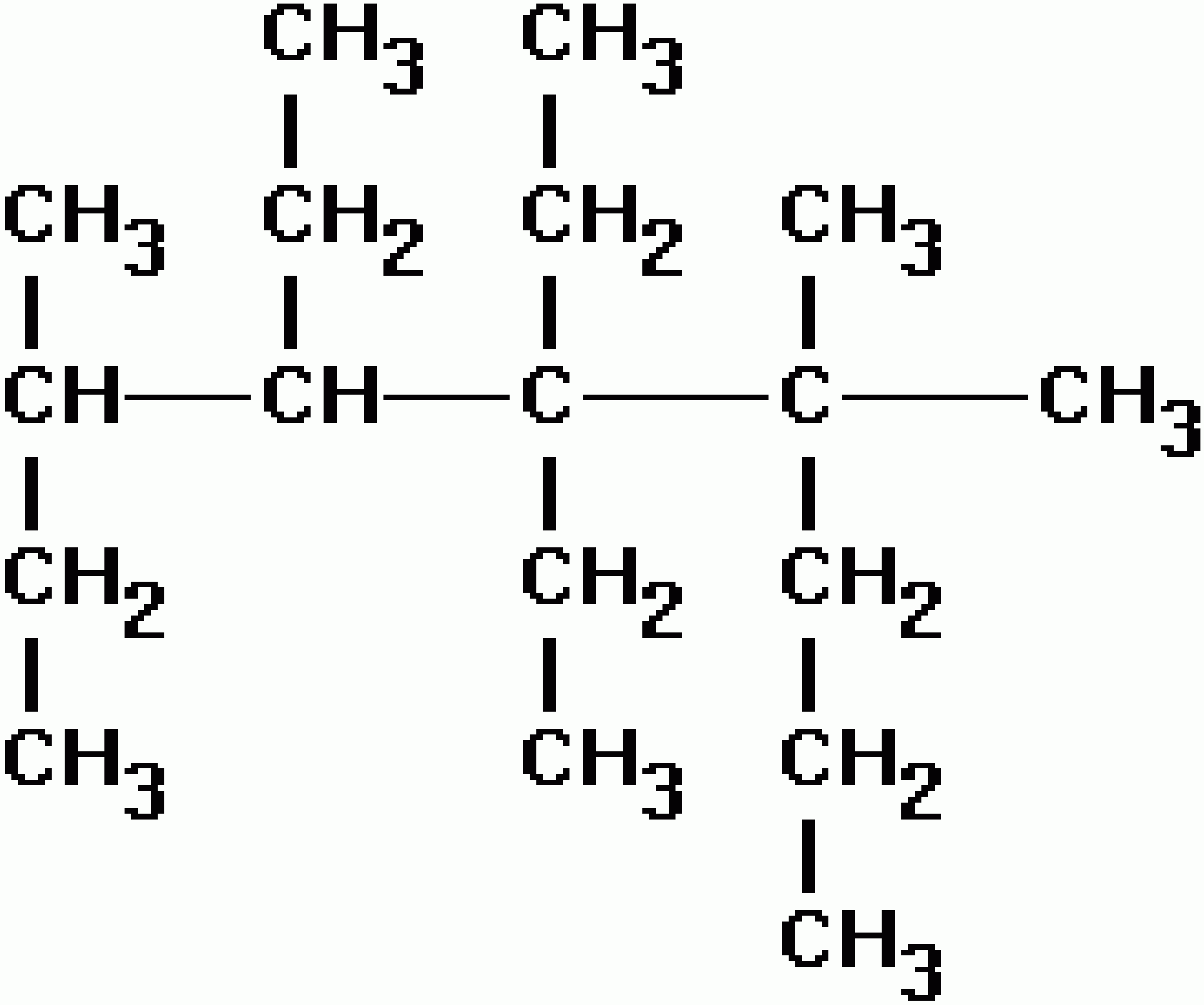
- Give the structures:

a. 4-isopropyloctane

b. 5-*tert-butyldecane.*

c.

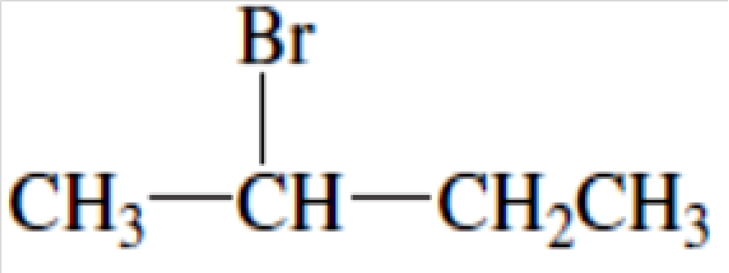




Haloalkanes

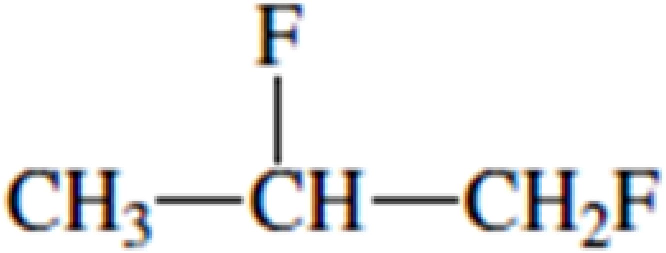
- Haloalkanes can be named just like alkanes, with the halogen atom treated as a substituent. Halogen substituents are named ***fluoro-, chloro-, bromo-,*** and ***iodo-.***
- When more than one halogen is present in the parent chain, they must be named ***alphabetically.***

Haloalkanes



$$\mathrm{CH_3{-}\overset{\overset{Br}{|}}{C}H{-}CH_2CH_3}$$

2-bromobutane



$$\mathrm{CH_3{-}\overset{\overset{F}{|}}{C}H{-}CH_2F}$$

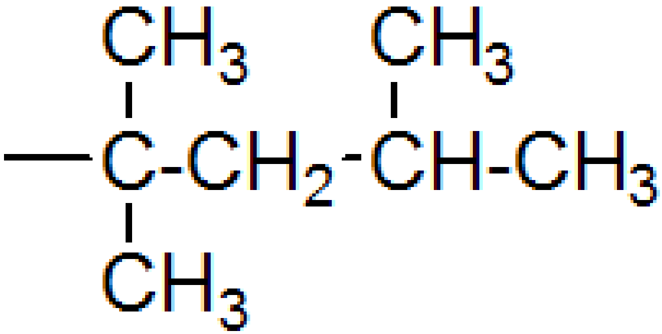
1,2-difluoropropane

Complex Substituents

These are named as follows:

(a) The base alkyl group is numbered staring with the carbon bonded to the main chain.

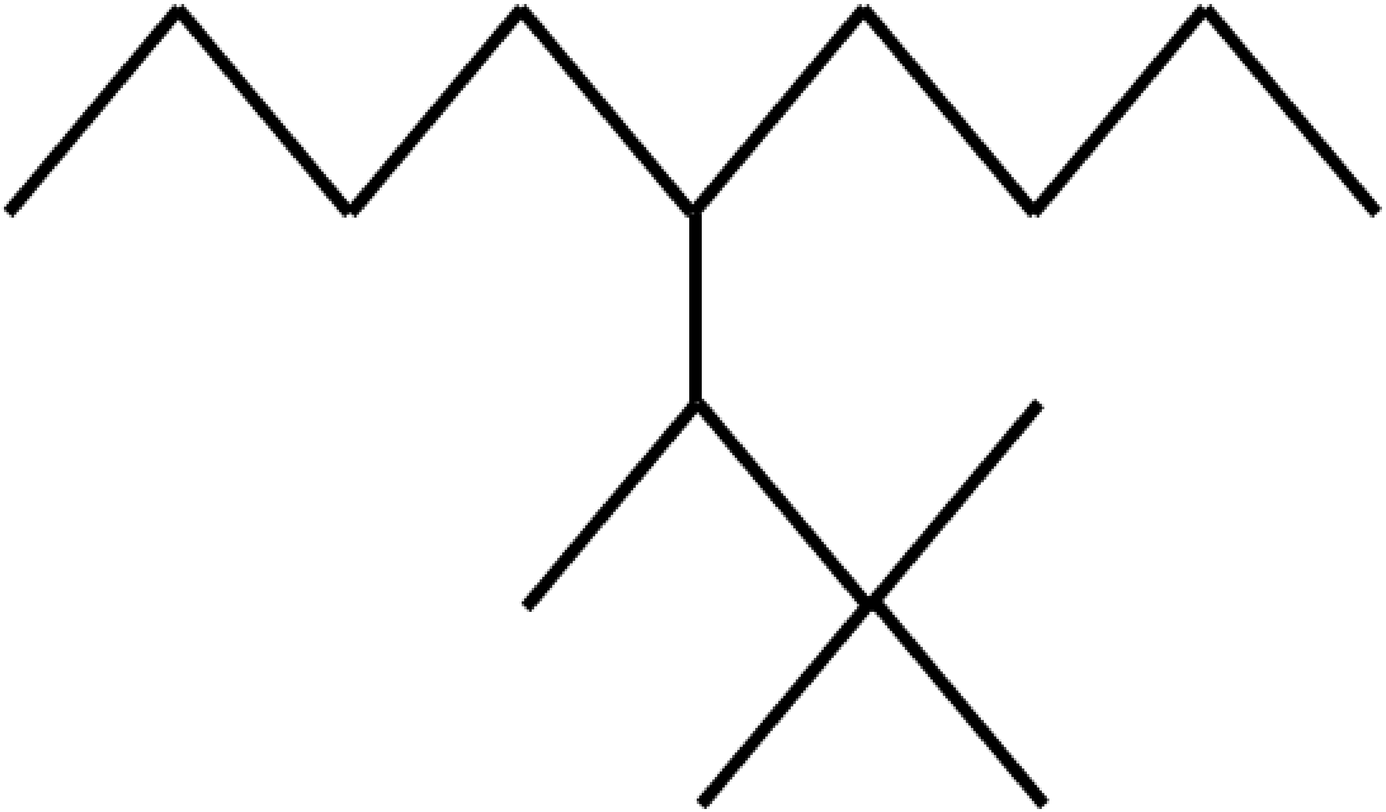
(b)The substituents are listed with the appropriate numbers, and parentheses are used to separate the substituent name.



$$-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_3$$

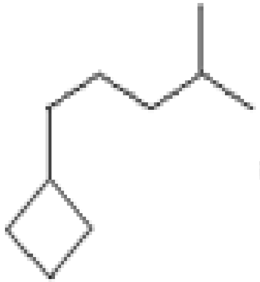
a (1,1,3-trimethylbutyl) group

5-(1,2,2-trimethylpropyl)nonane



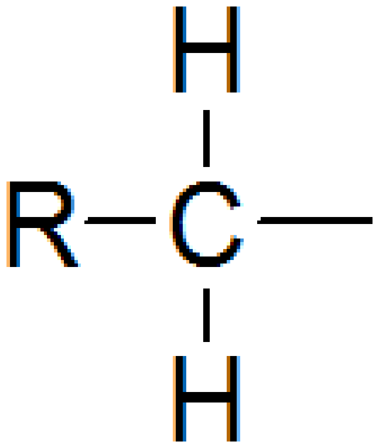
Examples

- Draw structures for the following compounds:
  1.) 3-ethyl-3-methylpentane
  2.) 3-methyl-5-propylnonane
  3.) 2,2,4,4-tetramethylhexane
  4.) pentylcyclohexane
  5.) 2,3-dimethyl-4-propylnonane
- Give the IUPAC names of the following alkanes:
  1.) **$(CH_3)_2CHCH_2CH(C_2H_5)C(CH_3)_3$**
  2.)



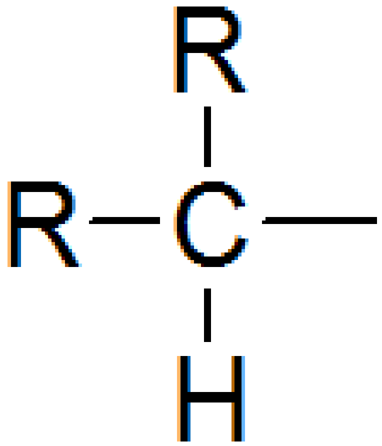
  3.) $(CH_3CH_2)_3CH$
  4.) $(CH_3)_2CH(CH_2)_3CH_3$

Recognizing Types of Substitution



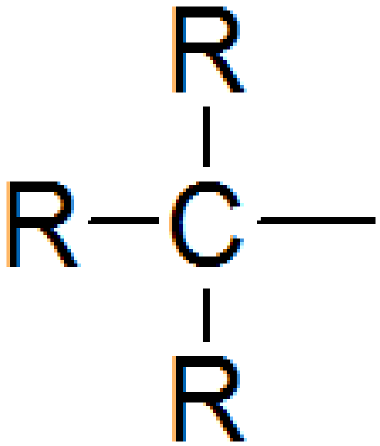
$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{R}-\mathrm{C}- \\ | \\ \mathrm{H} \end{array}$$

Primary
1° carbon



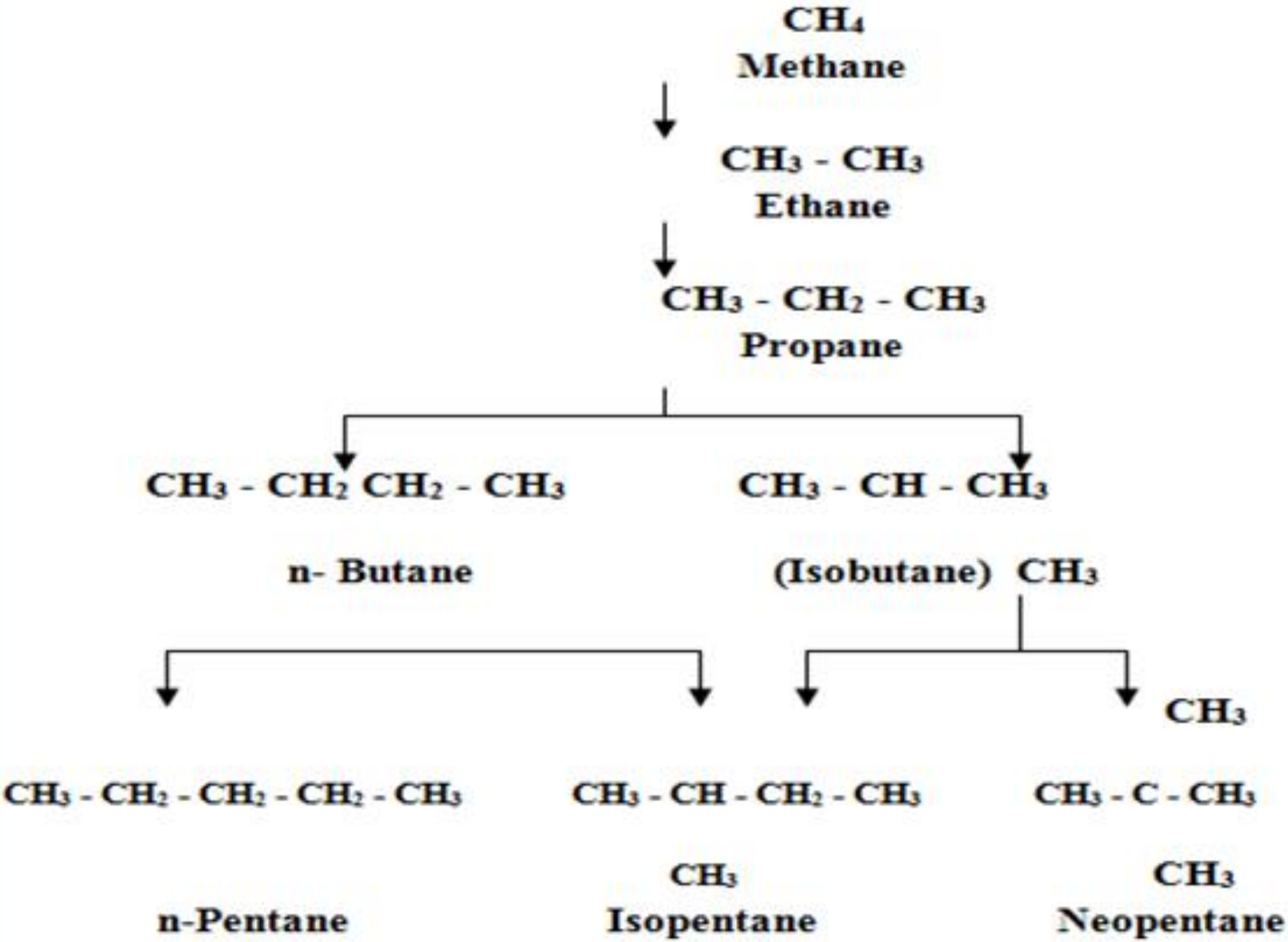
$$\begin{array}{c} \mathrm{R} \\ | \\ \mathrm{R}-\mathrm{C}- \\ | \\ \mathrm{H} \end{array}$$

Secondary
2° carbon



$$\begin{array}{c} \mathrm{R} \\ | \\ \mathrm{R}-\mathrm{C}- \\ | \\ \mathrm{R} \end{array}$$

Tertiary
3° carbon



CH_4

Methane

$CH_3 - CH_3$

Ethane

$CH_3 - CH_2 - CH_3$

Propane

$CH_3 - CH_2 CH_2 - CH_3$

n- Butane

$CH_3 - \underset{CH_3}{CH} - CH_3$

(Isobutane)

$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$

n-Pentane

$CH_3 - \underset{CH_3}{CH} - CH_2 - CH_3$

Isopentane

$CH_3 - \overset{CH_3}{\underset{CH_3}{C}} - CH_3$

Neopentane

Preparation of Alkanes

Hydrogenation of Alkenes

$$\underset{\text{Alkene}}{C_nH_{2n}} \xrightarrow{H_2 + \text{Pt, Pd or Ni}} \underset{\text{Alkane}}{C_nH_{2n+2}}$$

$$\underset{\text{Ethene}}{CH_2 = CH_2} + H_2 \xrightarrow{\text{Pt}} \underset{\text{Ethane}}{CH_3 - CH_3}$$

Reduction of alkyl halides bymetal and acid

$$RX + Zn + H^+ \longrightarrow RH + Zn^{++} + X$$

Alkyl halides Alkane

$$CH_3Cl \xrightarrow{Zn + H^+} CH_4$$

Methyl chloride Methane

$$CH_3\text{-}CH_2\text{-}CHBr\text{-}CH_3 \xrightarrow{Zn + H} CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

sec. Butyl bromide n-Butane

Hydrolysis of Grignard reagents

$$\mathrm{Rx + Mg \xrightarrow{ether} RMgx \xrightarrow{H_2O} RH + Mg(OH)X}$$

Alkyl halide

Grignard reagent

(Alkyl Magnesium halide)

$$\mathrm{CH_3I + Mg \xrightarrow{ether} CH_3MgI + H_2O \longrightarrow Mg\,(OH)I + CH_4}$$

Methyl magnesium iodide.

Methane

Coupling of alkyle halides with Grignard reagents

$$RX \xrightarrow{Mg} RMgX + RX \longrightarrow R.R' + MgX_2$$

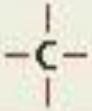
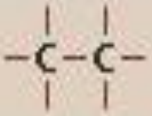
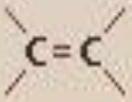
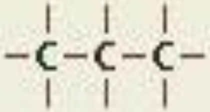
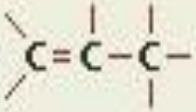
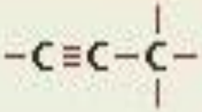
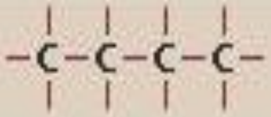
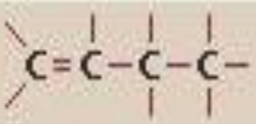
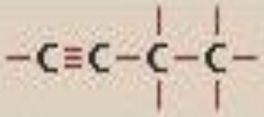
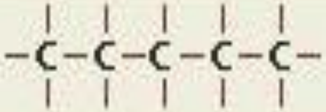
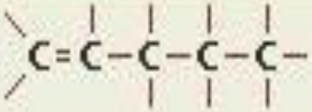
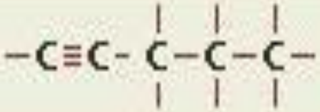
$$CH_3I \xrightarrow{Mg} CH_3MgI + CH_3CH_2Br$$

Methyl iodide

$$\downarrow$$

$$CH_3\text{-}CH_2CH_3 + MgBrI$$

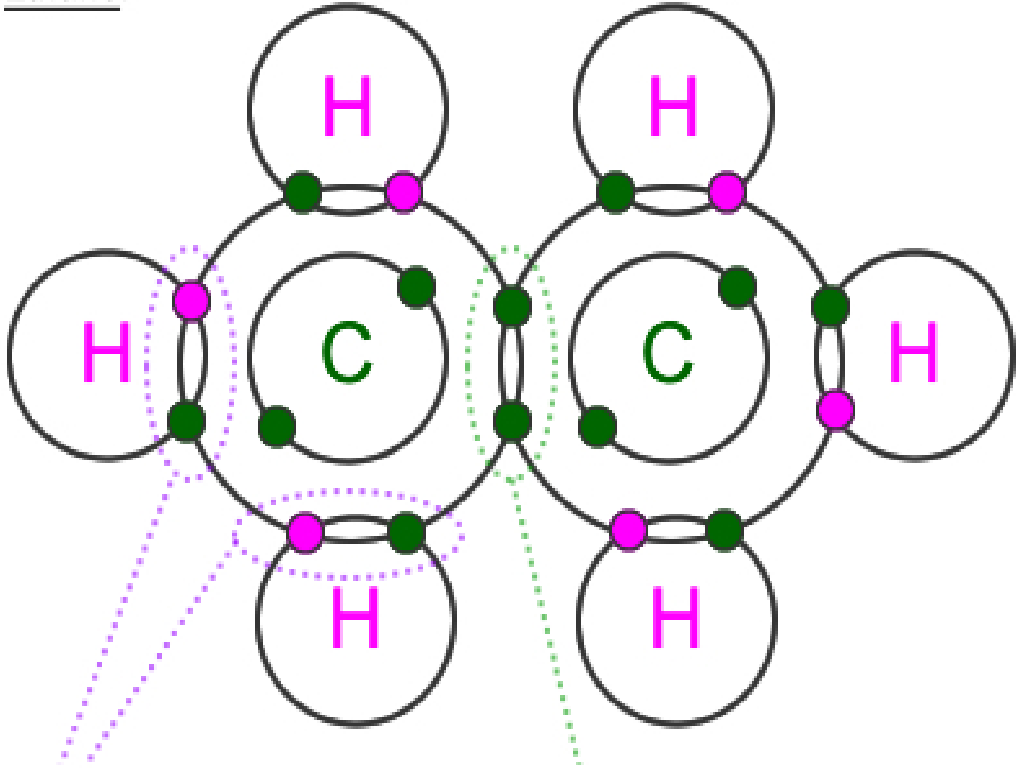
Propane

GROUP	ALKANE (C_nH_{2n+2})		ALKENE (C_nH_{2n})		ALKYNE (C_nH_{2n-2})	
Methyl-	Methane	 $-C-$	—		—	
Ethyl-	Ethane	 $-C-C-$	Ethene		Ethyne (acetylene)	$-C\equiv C-$
Propyl-	Propane	 $-C-C-C-$	Propene		Propyne	 $-C\equiv C-C-$
Butyl-	Butane	 $-C-C-C-C-$	Butene		Butyne	 $-C\equiv C-C-C-$
Pentyl-	Pentane	 $-C-C-C-C-C-$	Pentene		Pentyne	 $-C\equiv C- C-C-C-$

The lines between carbon atoms represent carbon-carbon bonds;
all other lines represent carbon-hydrogen bonds.

Greek prefixes are used from five-carbon atoms on: pent-, hex-, hept-,
oct-, non-, dec-, etc.

Ethane:



Hydrogen-Carbon Bonds

You can see that these are bonds between a hydrogen atom and a carbon atom because the hydrogen (shared) electron is indicated by a pink colour in the centre and the carbon (shared) electron is indicated by a green colour in the centre.

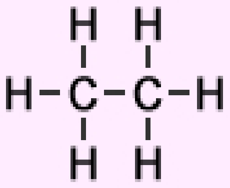
There are 6 hydrogen-carbon single covalent bonds in each molecule of ethane.

Carbon-Carbon Bond

You can see that this bond is between two carbon atoms because carbon (shared) electrons are indicated by a green colour in the centre.

There is only 1 carbon-carbon single covalent bond in each molecule of ethane.

This is a simpler representation of the molecular structure of ethane. This simpler form is also shown on other pages on this website:



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

In this (simpler) type of diagram of molecular structures covalent bonds are represented by short straight lines.

Some hydrocarbons include double covalent bonds represented by two parallel short straight lines, such as: =

Some hydrocarbons include triple covalent bonds represented by three parallel short straight lines, such as: ≡

Remember that double and triple covalent bonds may be thought of as multiple pairs of electrons "shared" by the same two atoms (in the case of hydrocarbons, double and triple bonds are only between **carbon atoms**).

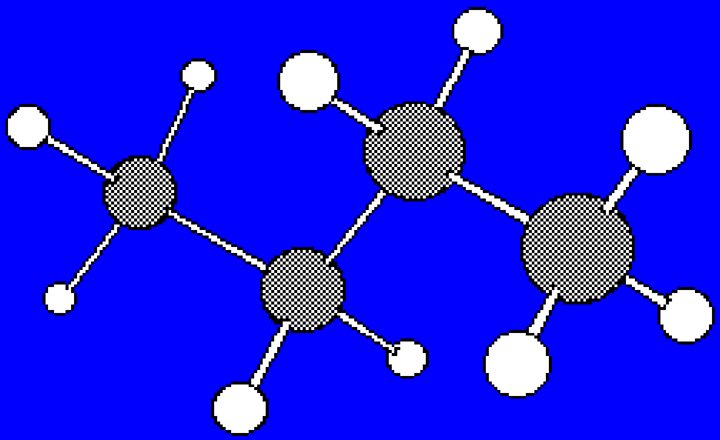
Obviously that would be very difficult to draw in two-dimensions using the type of diagram shown on the left. Both of these types of representation of organic molecules are imperfect ways of describing 3-dimensional structures in 2-dimensional space.

Physical properties

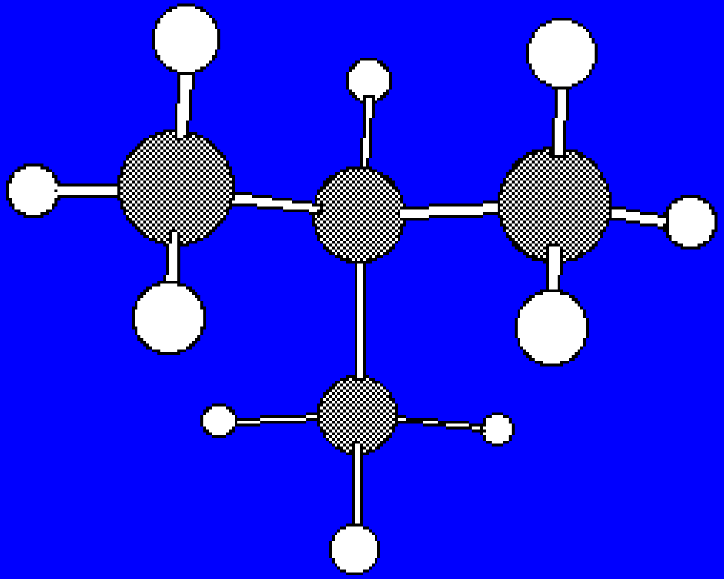
- The boiling point (b.p.) of straight chain alkanes increase steadily with relative molecular mass. The increase in b.p is due to the increasing forces of attraction between molecules of increasing size.
- Effect of branching on b.p
  - A branched chain alkane boils at lower temperature than the straight chain alkane with the same number of carbon atoms.
  - This is because the branched chain alkanes are more compact and have smaller surface area, smaller van der Waals forces = low b.p
- Comparing the b.p of alkanes and cycloalkanes.
  - The b.p of cycloalkanes are 10 - 15°C higher than the corresponding straight chain.

2.7 Isomeric Alkanes: The Butanes

n-Butane	$CH_3CH_2CH_2CH_3$
Isobutane	$(CH_3)_3CH$



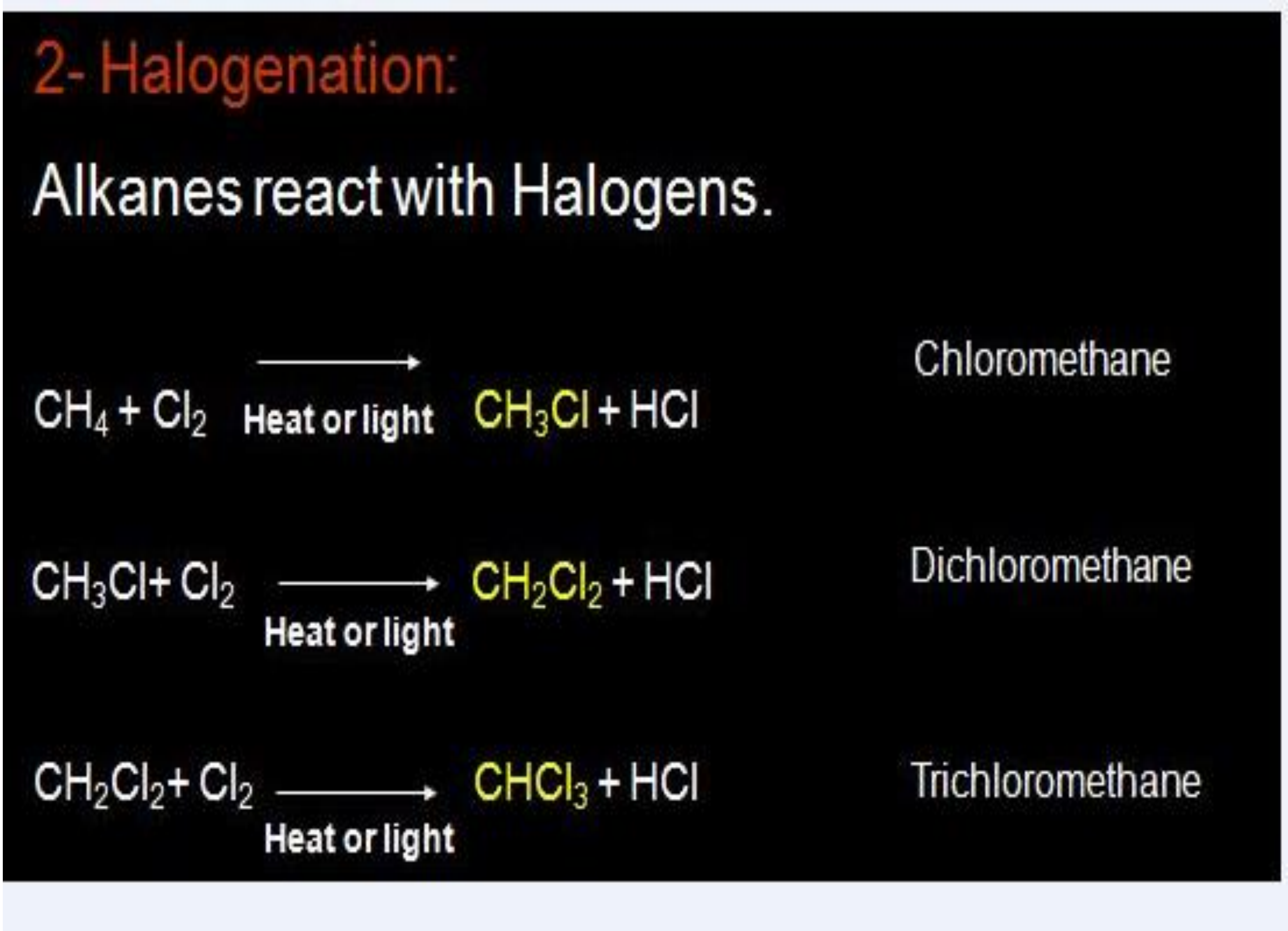
bp -0.4°C



bp -10.2°C

Physical properties of some hydrocarbons

Alkane	Formula	Boiling point [°C]	Melting point [°C]	Density [$g\cdot cm^3$] (at 20°C)
Methane	CH_4	-162	-183	gas
Ethane	C_2H_6	-89	-172	gas
Propane	C_3H_8	-42	-188	gas
Butane	C_4H_{10}	0	-138	gas
Pentane	C_5H_{12}	36	-130	0.626(liquid)
Hexane	C_6H_{14}	69	-95	0.659(liquid)
Heptane	C_7H_{16}	98	-91	0.684(liquid)
Octane	C_8H_{18}	126	-57	0.703(liquid)
Nonane	C_9H_{20}	151	-54	0.718(liquid)
Decane	$C_{10}H_{22}$	174	-30	0.730(liquid)



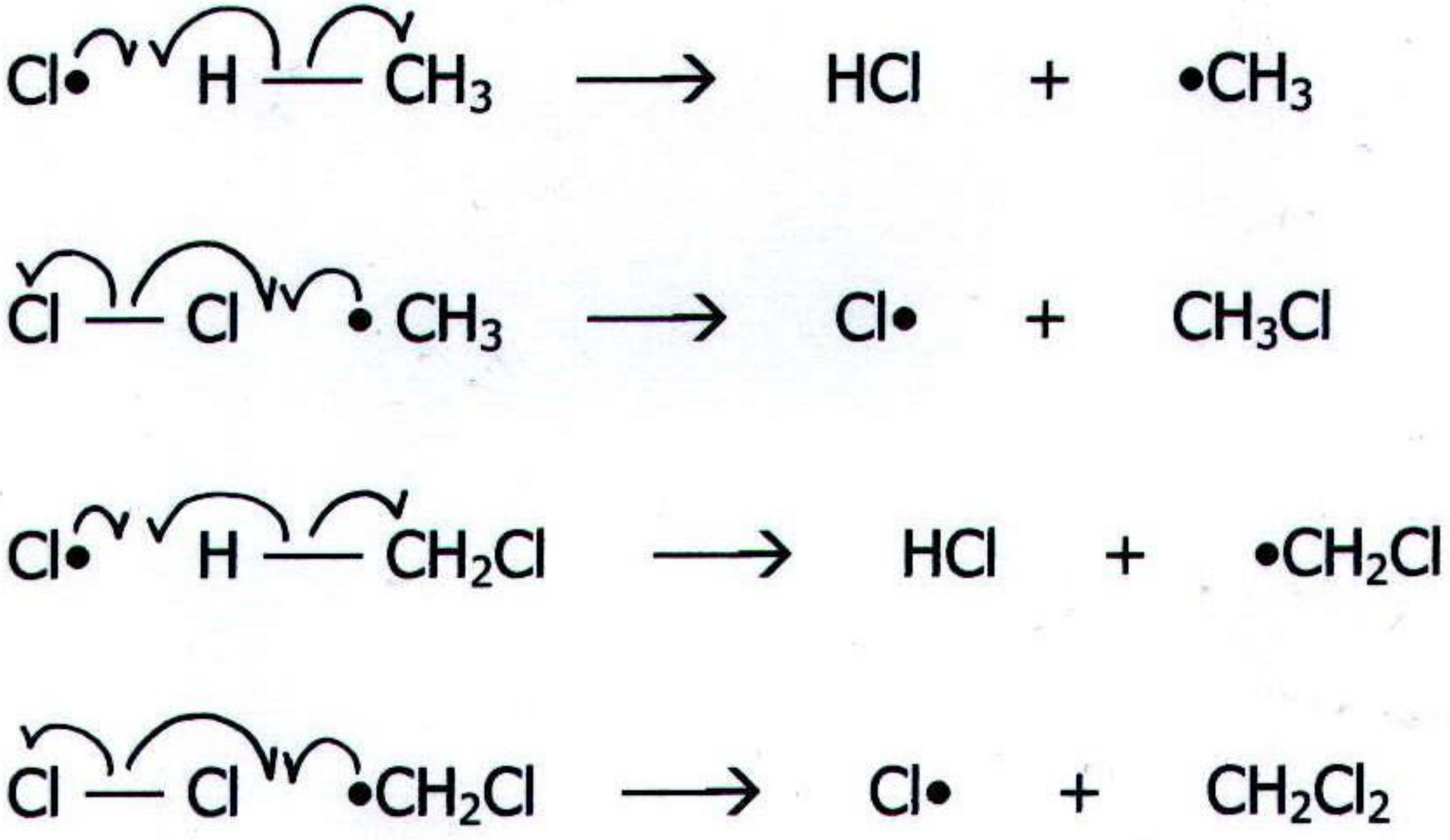
2- Halogenation:

Alkanes react with Halogens.

$$CH_4 + Cl_2 \xrightarrow[\text{Heat or light}]{} CH_3Cl + HCl$$ Chloromethane

$$CH_3Cl + Cl_2 \xrightarrow[\text{Heat or light}]{} CH_2Cl_2 + HCl$$ Dichloromethane

$$CH_2Cl_2 + Cl_2 \xrightarrow[\text{Heat or light}]{} CHCl_3 + HCl$$ Trichloromethane



$$Cl\bullet + H-CH_3 \longrightarrow HCl + \bullet CH_3$$

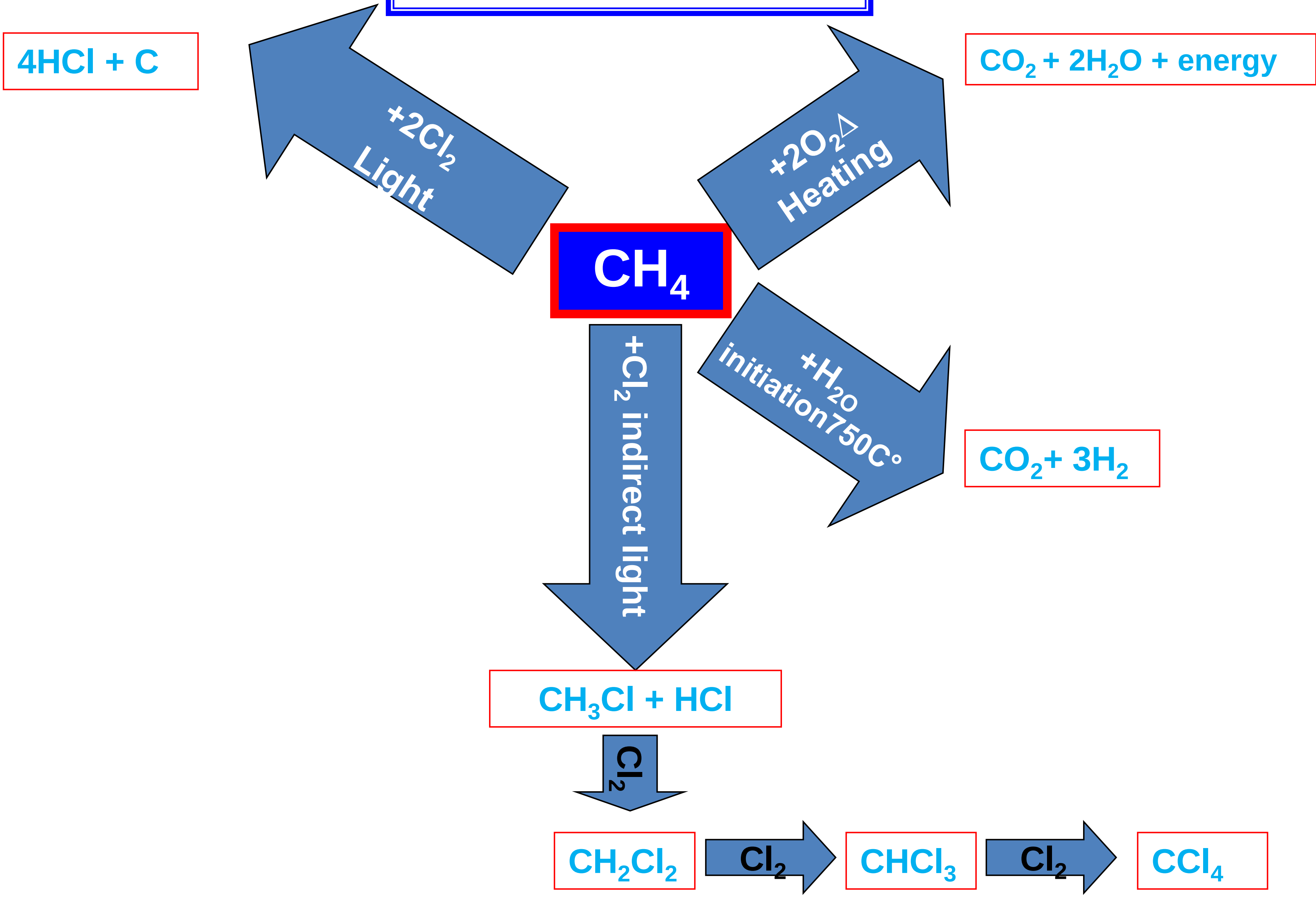
$$Cl-Cl + \bullet CH_3 \longrightarrow Cl\bullet + CH_3Cl$$

$$Cl\bullet + H-CH_2Cl \longrightarrow HCl + \bullet CH_2Cl$$

$$Cl-Cl + \bullet CH_2Cl \longrightarrow Cl\bullet + CH_2Cl_2$$

etc. - - - - → CCl_4

Methane Reactions



CH_4

$+2Cl_2$ Light

$4HCl + C$

$+2O_2 \Delta$ Heating

$CO_2 + 2H_2O$ + energy

$+H_{2O}$ initiation750C°

$CO_2 + 3H_2$

$+Cl_2$ indirect light

$CH_3Cl + HCl$

Cl_2

CH_2Cl_2

Cl_2

$CHCl_3$

Cl_2

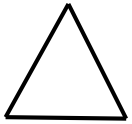
CCl_4

Commercial Uses of Alkanes

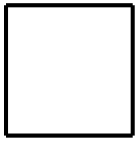
- Used mostly in the production of polymers.
- Serve as intermediates in the synthesis of drugs, pesticides and other valuable chemicals including ethanol, acetic acid, ethylene glycol and vinyl chloride.
- Ethylene is uses as a plant hormone, accelerating the ripening of fruit.

Cycloalkanes

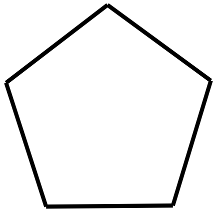
- Alkanes when carbon atoms are **joined in rings**
- General formula for cycloalkanes - C_nH_{2n} , $n \geq 3$
- Eg: cyclopropane, cyclobutane, cyclopentane, cyclohexane



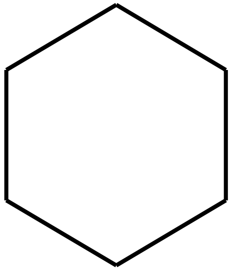
Cyclopropane



Cyclobutane



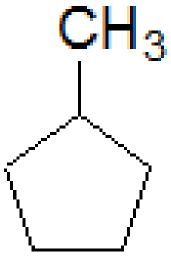
Cyclopentane



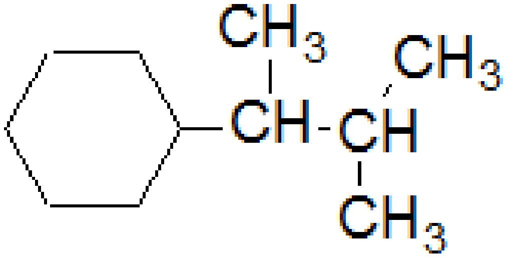
Cyclohexane

Two simple rules of cycloalkanes

- Rule A: Decide whether the cyclic or acyclic (non-cyclic) portion contains more carbons. This determines the base name. (Alkyl substituted cycloalkane or cycloalkane substituted alkane).
- Rule B: Carbons are numbered to give the lowest numbers for substituted carbons.



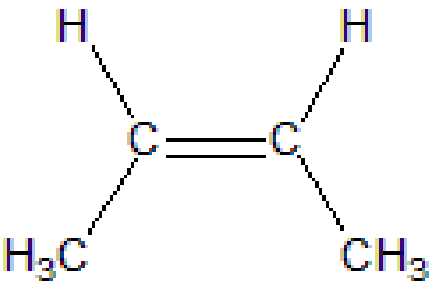
methylcyclopentane



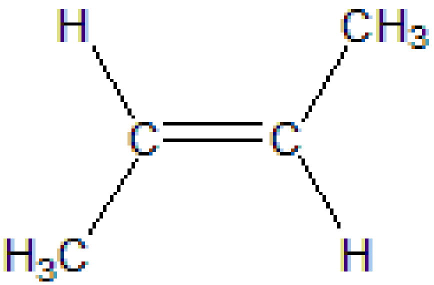
(1,2-dimethylpropyl)cyclohexane

3-2- Alkenes

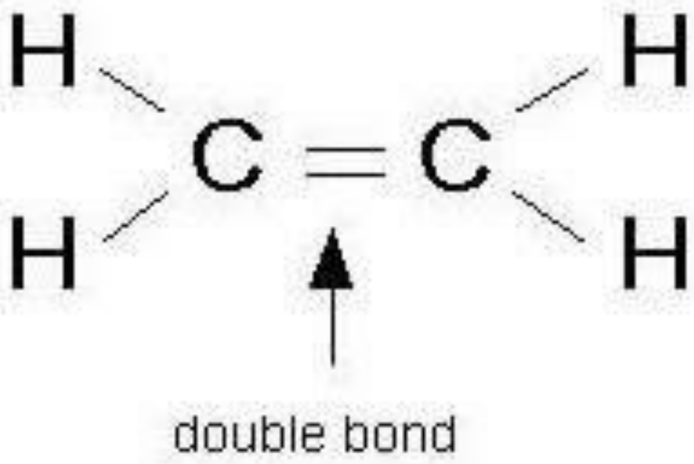
- Contain at least one carbon-carbon double bond.
- General formula for alkenes – **C_nH_{2n} , n ≥ 2**
  - Eg: $CH_2{=}CH_2$
- The **cis-**, **trans-** system



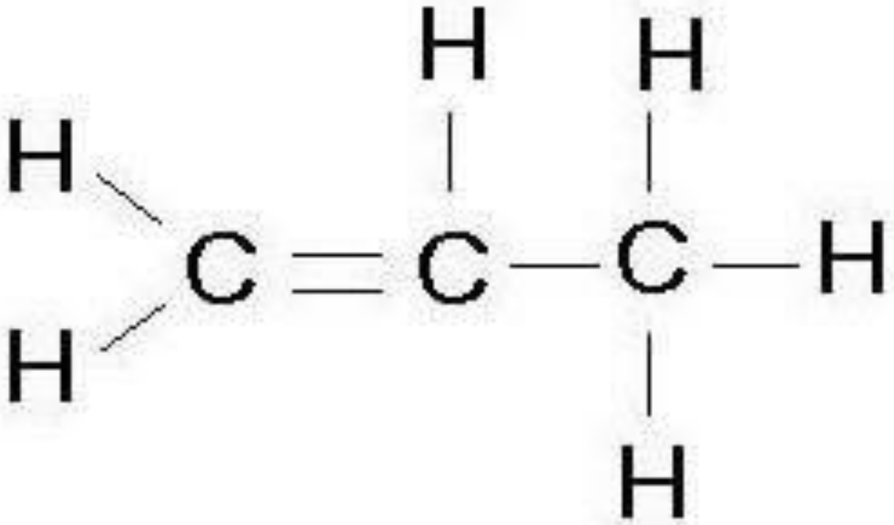
cis-2-butene



trans-2-butene



ethene



propene

Alkenes

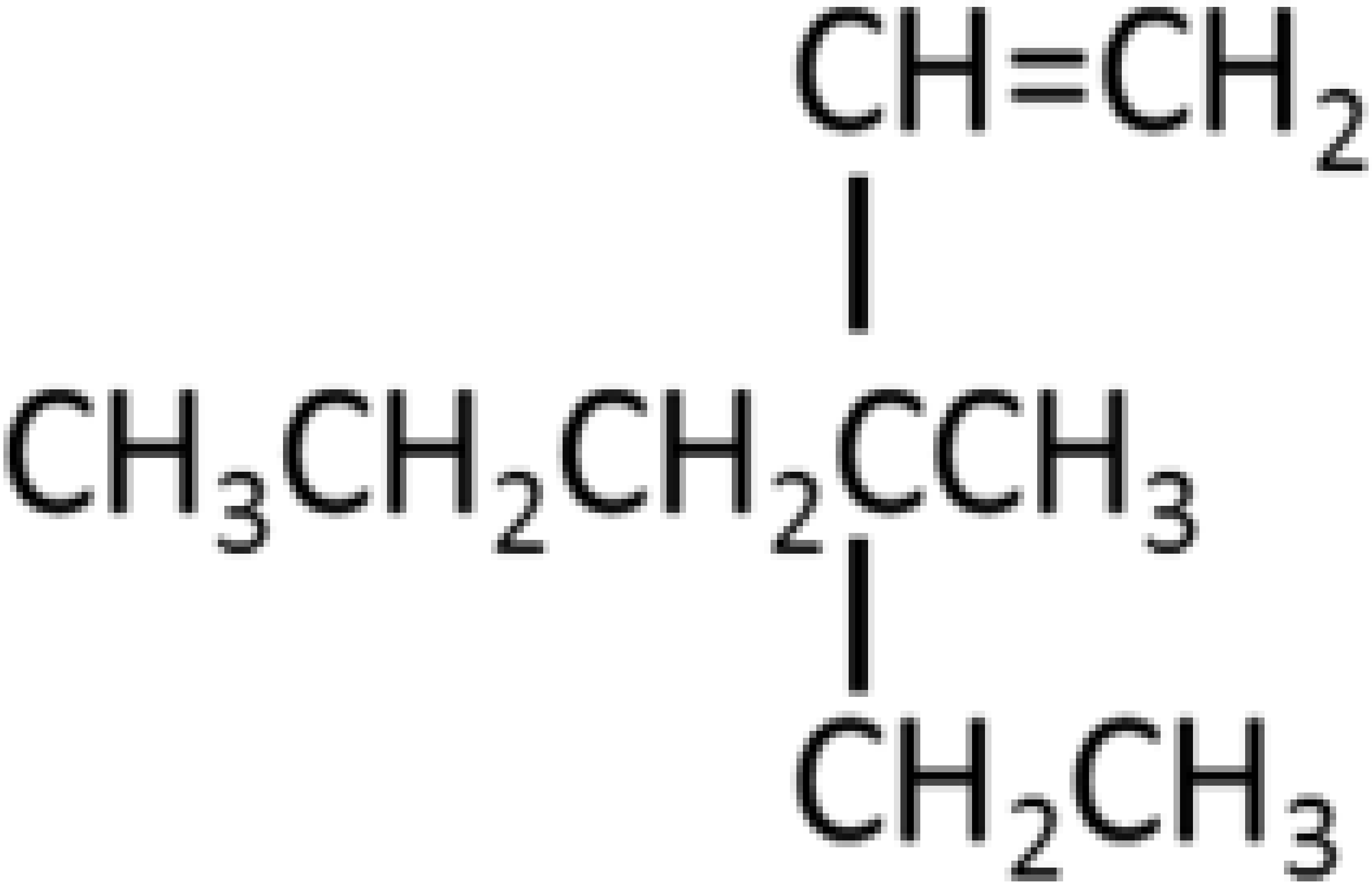
Alkene Nomenclature

- Parent is longest chain containing the double bond.
- -ane changes to -ene. (or -diene, -triene)
- Number the chain so that the double bond has the lowest possible number.
- In a ring, the double bond is assumed to be between carbon 1 and carbon 2.

Nomenclature

- Identify the name of parent hydrocarbon
- Number the carbon atoms in the main chain
- When the carbon chain contains more than 3 carbon atoms, a number is used to indicate the position of **‘=‘**
- Indicate the positions of the double bond and the substituent.

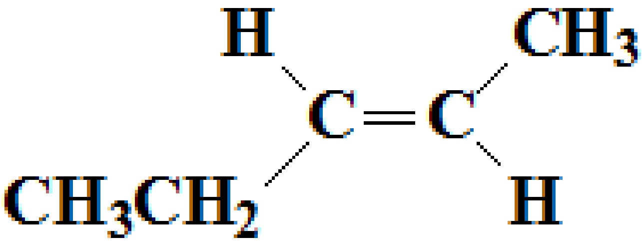
Name the following structure:



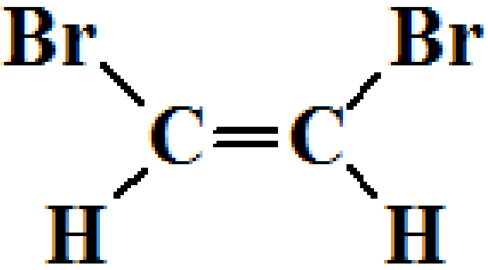
$$CH_3CH_2CH_2\overset{\displaystyle CH{=}CH_2}{\underset{\displaystyle CH_2CH_3}{C}}CH_3$$

Geometric Isomerism

- Similar groups on same side of double bond, alkene is cis.
- Similar groups on opposite sides of double bond, alkene is trans.



trans-2-pentene



cis-1,2-dibromoethene

alkenes: preparation and reactions

Alkenes: Preparation and reactions

Two ways of making alkenes:

- 1. Heat a concentrated solution of potasium /sodium hydroxide in alcohol (alcoholic KOH) with a haloalkane (halogenoalkane)

This is dehydrohalogenation (removal of hydrogen and halogen)

2. Heat concentrated sulphuric acid with the alcohol- dehydration. THE ACID IS A DEHYDRATING AGENT

PREPARATION OF ALKENES

- Alkenes can be prepared in the following ways:

i) Dehydration of alcohols

$$R\text{-}CH_2\text{-}CH_2\text{-}OH \xrightarrow[\Delta]{\text{conc. } H_2SO_4} R\text{-}CH{=}CH_2 + H_2O$$

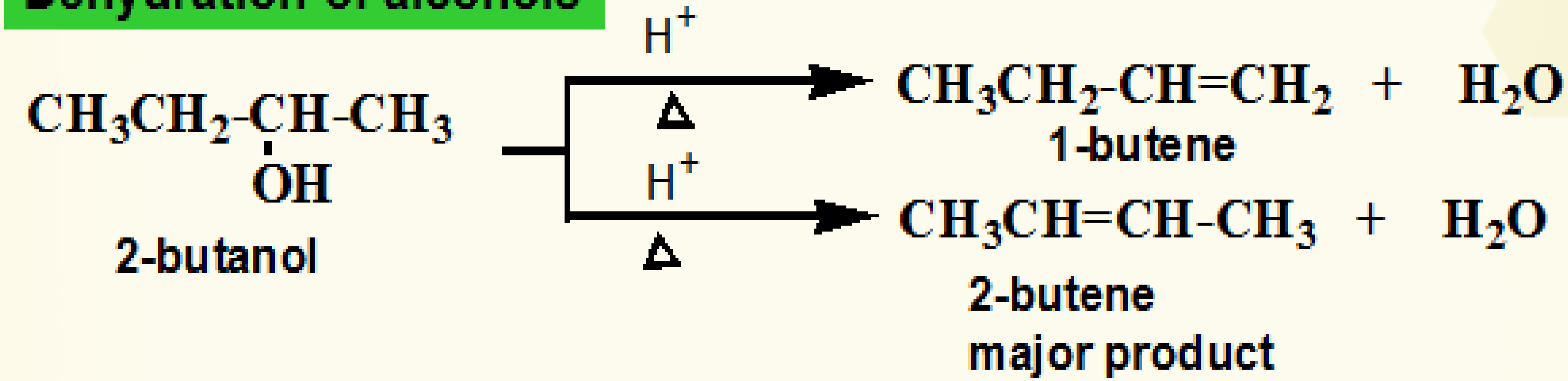
ii) Dehydrohalogenation of haloalkanes

$$R\text{-}CH_2\text{-}CH_2\text{-}X \xrightarrow[\text{reflux}]{\text{NaOH/ethanol}} R\text{-}CH{=}CH_2 + HX$$

NaOH can be replaced by KOH

- A reaction that produces an alkene would favour the formation of an alkene that has the greatest number of substituents attached to the C=C group.

Dehydration of alcohols



$$\underset{\text{OH}}{\mathrm{CH_3CH_2\text{-}\underset{|}{C}H\text{-}CH_3}} \begin{cases} \xrightarrow[\Delta]{H^+} \mathrm{CH_3CH_2\text{-}CH{=}CH_2} + \mathrm{H_2O} \\ \xrightarrow[\Delta]{H^+} \mathrm{CH_3CH{=}CH\text{-}CH_3} + \mathrm{H_2O} \end{cases}$$

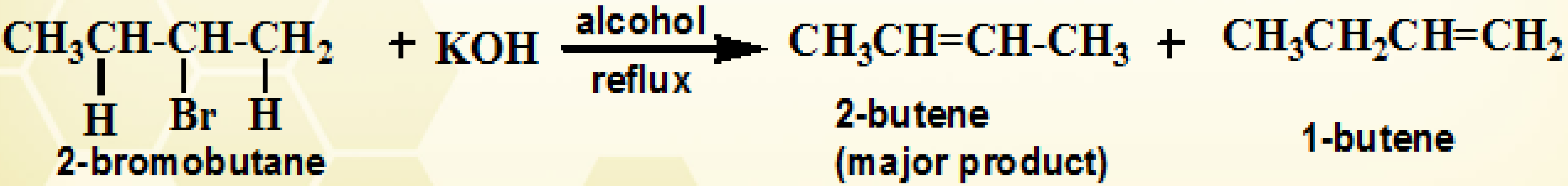
2-butanol

1-butene

2-butene

major product

Dehydrohalogenation of haloalkanes



$$\mathrm{CH_3\underset{\underset{H}{|}}{C}H\text{-}\underset{\underset{Br}{|}}{C}H\text{-}\underset{\underset{H}{|}}{C}H_2} + \mathrm{KOH} \xrightarrow[\text{reflux}]{\text{alcohol}} \mathrm{CH_3CH{=}CH\text{-}CH_3} + \mathrm{CH_3CH_2CH{=}CH_2}$$

2-bromobutane

2-butene

(major product)

1-butene

REACTIVITY OF ALKENES

More reactive than alkanes because:

i) A carbon-carbon double bond consists of a σ and a π bond. It is easy to break the π bond while the σ bond remains intact.

ii) The π electrons in the double bond act as a source of electrons (Lewis base). Alkenes are reactive towards electrophiles which are attracted to the negative charge of the π electrons.

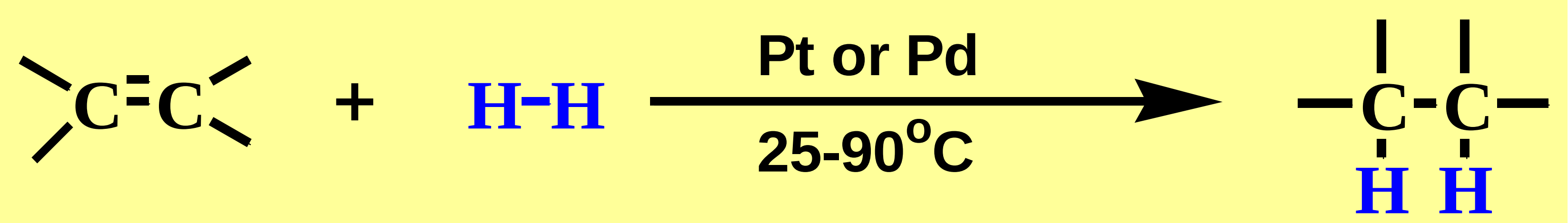
iii) π bond will broken, each carbon atom becomes an active site which can form a new covalent bond with another atom. One π bond is converted into 2 σ bonds.

REACTIONS OF ALKENES

Catalytic hydrogenation:

- hydrogenation: addition of hydrogen to a double bond and triple bond to yield saturated product.

- alkenes will combine with hydrogen in the present to catalyst to form alkanes.



Plantinum (Pt) and palladium (Pd) – Catalysts -

Pt and Pd: temperature 25-90°C -

Nickel can also used as a catalyst, but a higher temperature -
of 140°C – 200°C is needed.

EXAMPLES:

$$H_2C{=}CH_2 \quad + \quad H_2 \xrightarrow[\text{low pressure}]{\text{Pt}} H_3C{-}CH_3$$

ethylene

ethane

$$CH_3CH_2CH_2CH_2CH{=}CH_2 \quad + \quad H_2 \xrightarrow[\text{low pressure}]{\text{Pt}} CH_3CH_2CH_2CH_2CH_2CH_3$$

hexene

hexane

Addition of halogens:

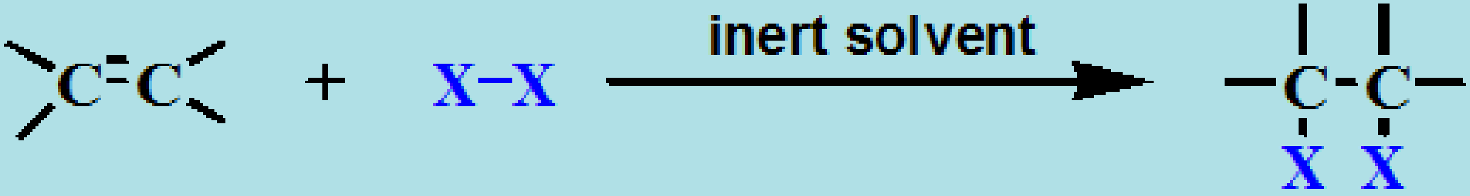
i) In inert solvent:

- alkenes react with halogens at room temperature and in dark.

- the halogens is usually dissolved in an inert solvent such as dichloromethane (CH_2Cl_2) and tetrachloromethane (CCl_4).

- Iodine will not react with alkenes because it is less reactive than chlorine and bromine.

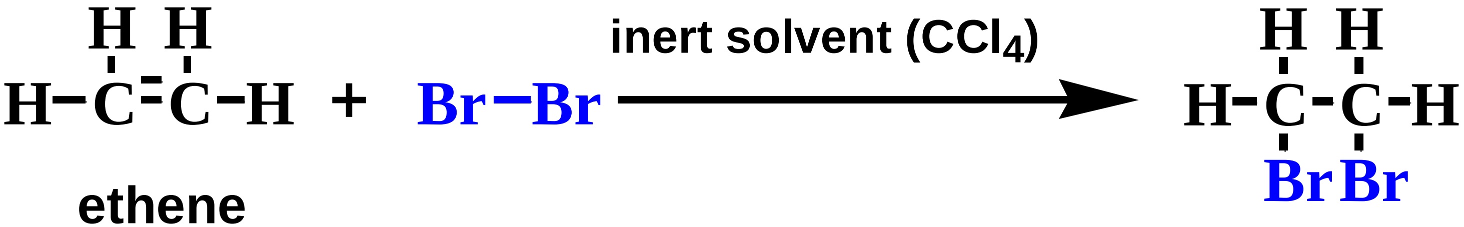
- Fluorine is very reactive. The reaction will produced explosion.



X−X = halogen such as Br_2 or Cl_2

Inert solvent = CCl_4 or CH_2Cl_2

EXAMPLES:

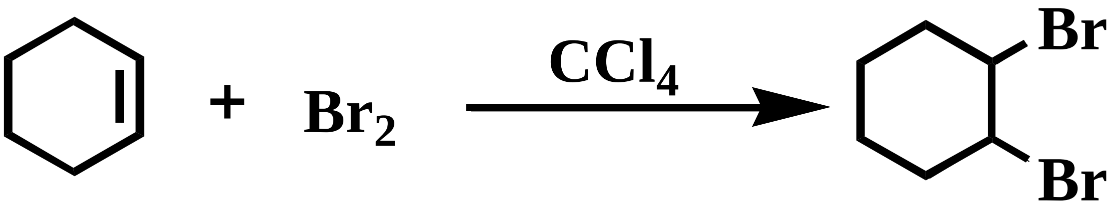


$$\mathrm{H{-}\overset{H}{\overset{|}{C}}{=}\overset{H}{\overset{|}{C}}{-}H} + \mathrm{Br{-}Br} \xrightarrow{\text{inert solvent } (CCl_4)} \mathrm{H{-}\underset{Br}{\underset{|}{\overset{H}{\overset{|}{C}}}}{-}\underset{Br}{\underset{|}{\overset{H}{\overset{|}{C}}}}{-}H}$$

ethene

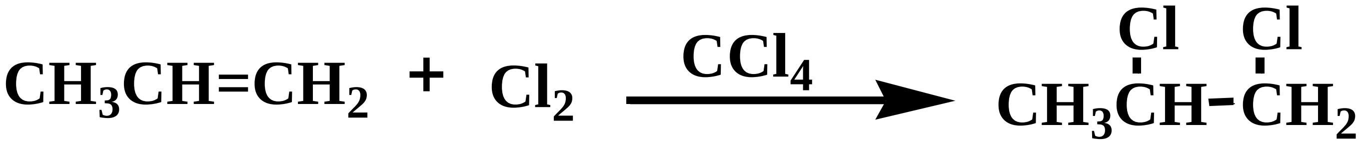
1,2-dibromoethane

*** the red-brown colour of the bromine solution will fade and the solution becomes colourless.**



cyclohexene

1,2-dibromocyclohexane



$$CH_3CH{=}CH_2 + Cl_2 \xrightarrow{CCl_4} CH_3\overset{Cl}{\overset{|}{C}}H{-}\overset{Cl}{\overset{|}{C}}H_2$$

propene

1,2-dichloropropane

Addition of halogens:

ii) In water / aqueous medium:

- chlorine dissolves in water to form HCl and chloric (I) acid (HOCl).

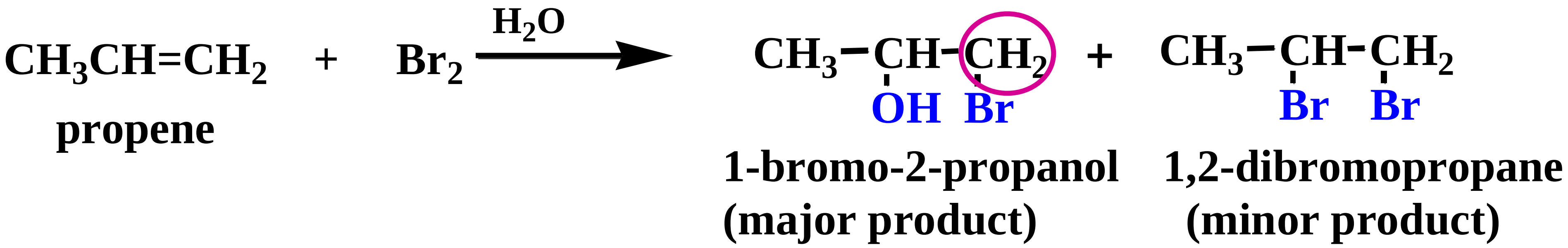
$$Cl_2\,(aq) + H_2O(l) \rightleftharpoons HCl(aq) + HOCl\,(aq)$$

- same as bromine

$$Br_2\,(aq) + H_2O(l) \rightleftharpoons HBr(aq) + HOBr(aq)$$

* **Reaction of alkenes** with **halogens in water** (eg. chlorine water and bromine water) produced **halohydrins** (an alcohol with a halogen on the adjacent carbon atom).

EXAMPLES:



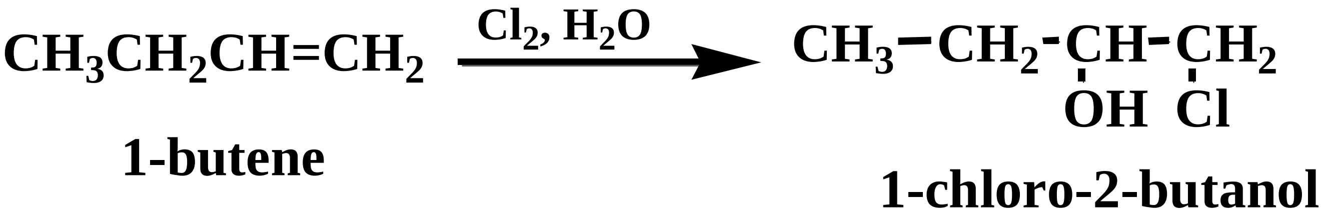
$$CH_3CH{=}CH_2 + Br_2 \xrightarrow{H_2O} CH_3-\underset{OH}{CH}-\underset{Br}{CH_2} + CH_3-\underset{Br}{CH}-\underset{Br}{CH_2}$$

propene

1-bromo-2-propanol
(major product)

1,2-dibromopropane
(minor product)

* Br atom attached to the carbon atom of the double bond which has the greater number of hydrogen atoms.



$$CH_3CH_2CH{=}CH_2 \xrightarrow{Cl_2,\ H_2O} CH_3-CH_2-\underset{OH}{CH}-\underset{Cl}{CH_2}$$

1-butene

1-chloro-2-butanol

Addition of hydrogen halides:

- **Addition reaction with electrophilic reagents.**
- **Alkenes react with hydrogen halides (in gaseous state or in aqueous solution) to form addition products.**
- **The hydrogen and halogen atoms add across the double bond to form haloalkanes (alkyl halides).**
- **General equation:**

alkene **haloalkane**

Reactivity of hydrogen halides : HF < HCl < HBr < HI -

* Reaction with HCl needs a catalyst such as $AlCl_3$

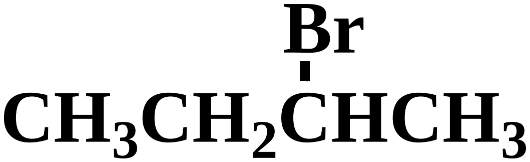
$$H_2C{=}CH_2 + HCl \xrightarrow{AlCl_3} CH_3CH_2Cl$$

EXAMPLES:

cyclopentene

iodocyclopentane

$$CH_3CH{=}CHCH_3 + H\text{-}Br \longrightarrow$$



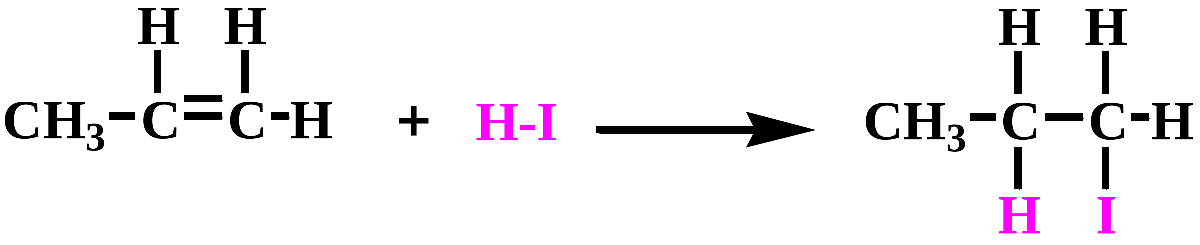
$$CH_3CH_2\overset{\overset{\displaystyle Br}{|}}{C}HCH_3$$

2-butene

2-bromobutane

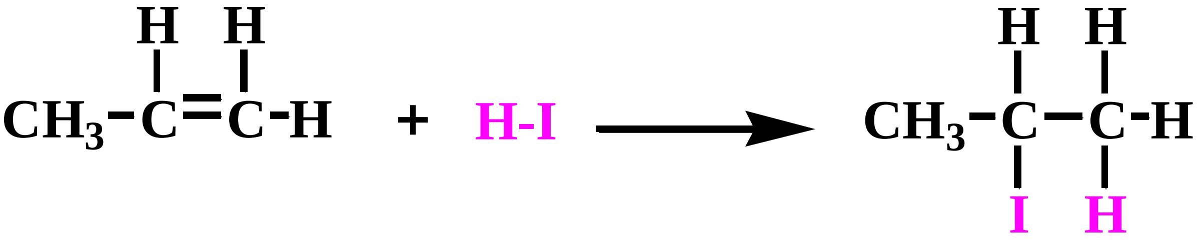
MARKOVNIKOV'S RULE

- **There are 2 possible products when hydrogen halides react with an unsymmetrical alkene.**
- **It is because hydrogen halide molecule can add to the C=C bond in two different ways.**



$$CH_3-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H + H\text{-}I \longrightarrow CH_3-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{I}{\underset{|}{\overset{H}{\overset{|}{C}}}}-H$$

1-iodopropane



$$CH_3-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H + H\text{-}I \longrightarrow CH_3-\underset{I}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-H$$

2-iodopropane
(major product)

Markovnikov’s rules:

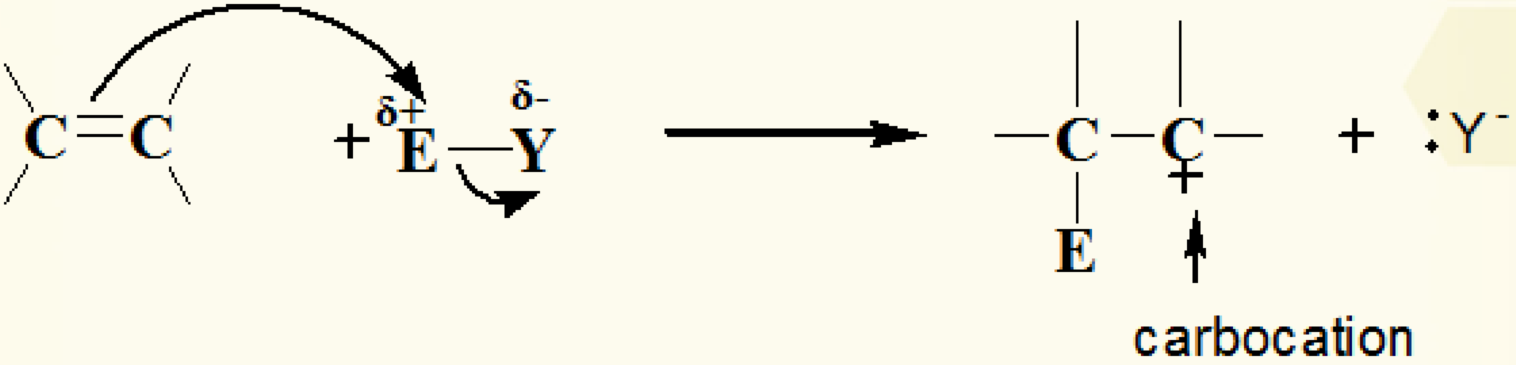
- the addition of HX to an unsymmetrical alkene, the hydrogen atom attaches itself to the carbon atom (of the double bond) with the larger number of hydrogen atoms.

Mechanism of electrophilic addition reactions:

- C=C : electron rich part of the alkene molecule
- Electrophiles: electron-seeking

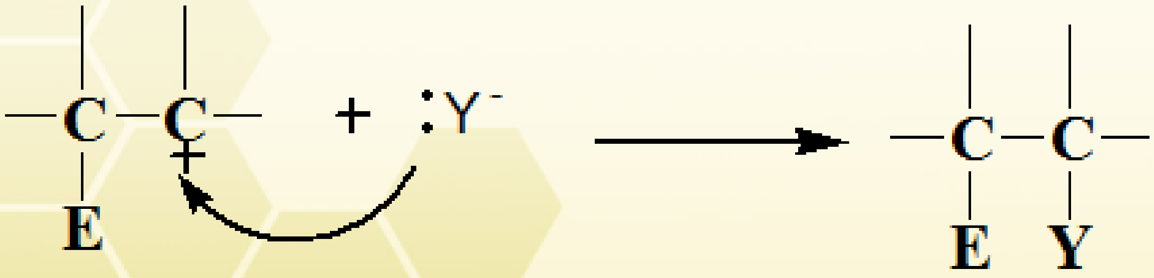
Step 1: Formation of carbocation.

Attack of the pi bond on the electrophile to form carbocation.

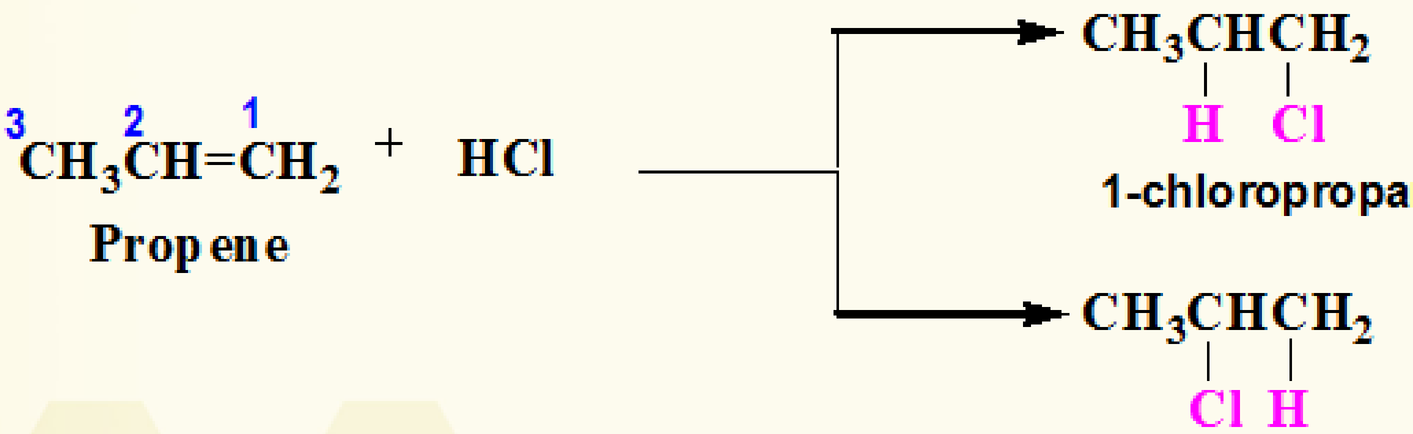


Step 2: Rapid reaction with a negative ion.

The negative ion (Y^-) acts as nucleophile and attacks the positively charged carbon atom to give product of the addition reaction.



ADDITION OF HYDROGEN HALIDES TO UNSYMMETRICAL ALKENES AND MARKOVNIKOV'S RULE



$$\overset{3}{C}H_3\overset{2}{C}H=\overset{1}{C}H_2 \; + \; HCl$$

Propene

$$CH_3\underset{|\atop H}{CH}\underset{|\atop Cl}{CH_2}$$

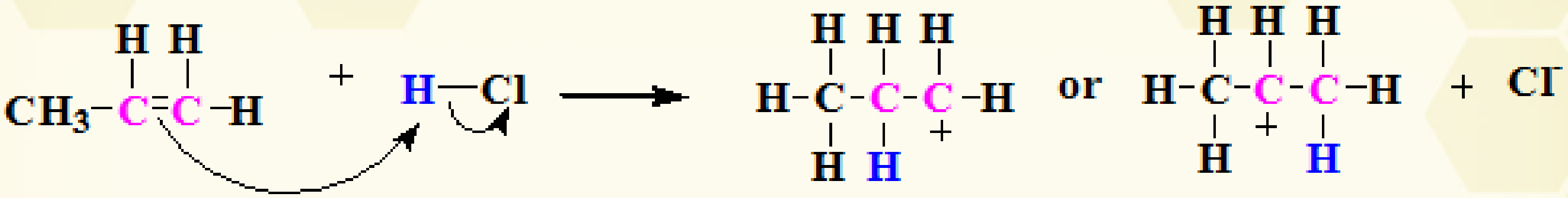
1-chloropropane

$$CH_3\underset{|\atop Cl}{CH}\underset{|\atop H}{CH_2}$$

2-chloropropane
(major product)
according to Markovnikov's rules

MECHANISM:

Step 1: Formation of carbocation

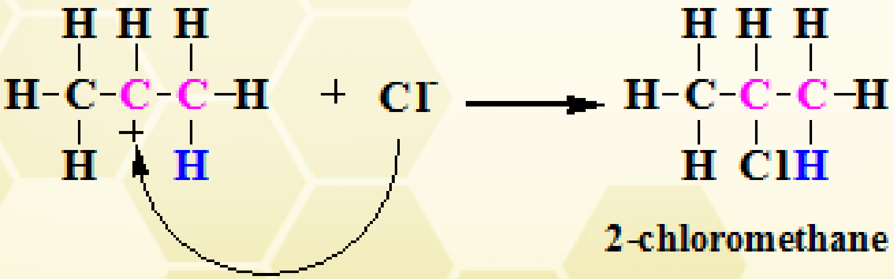


less stable carbocation (1° carbocation)

more stable carbocation (2° carbocation)

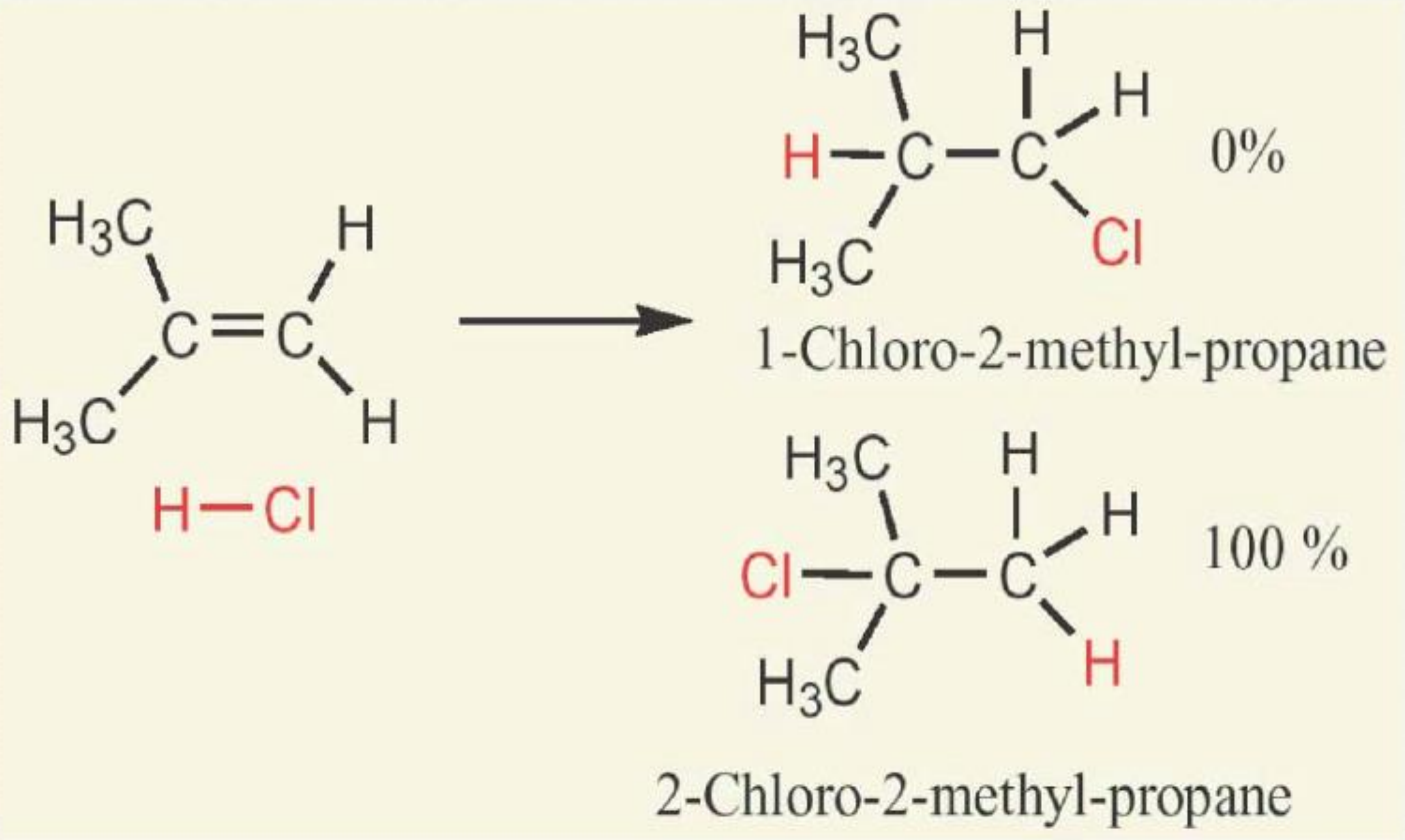
- 2° carbocation is more stable than 1° carbocation.
- 2° carbocation tends to persist longer, making it more likely to combine with Cl^- ion to form 2-chloromethane (basis of Markovnikov's rule).

Step 2: Rapid reaction with a negative ion



2-chloromethane (major product)

- Addition of HCl to 2-methylpropene
- Regiospecific
- If both ends have similar substitution, then not regiospecific

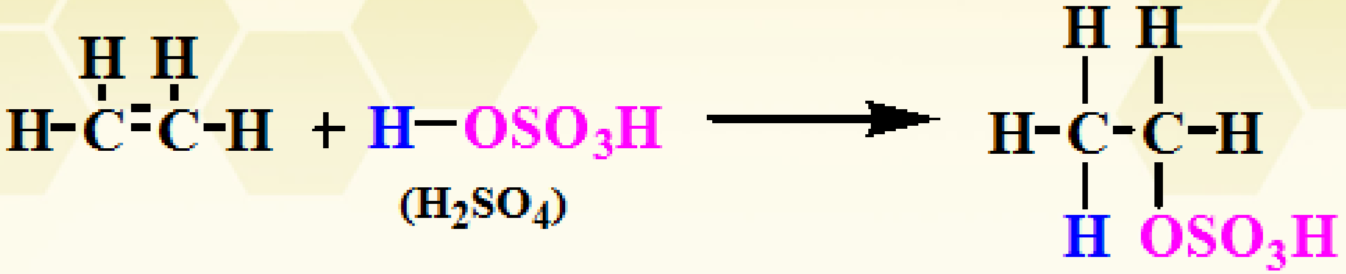


Addition reaction with concentrated sulfuric acid: hydration of alkenes

- the alkene is absorbed slowly when it passed through concentrated sulfuric acid in the cold (0-15°C).

- involves the addition of H atom and HSO_4 group across the carbon-carbon double bond.

- follows Markovnikov's rule.



$$\mathrm{H{-}\overset{H}{C}{=}\overset{H}{C}{-}H} + \underset{(H_2SO_4)}{\mathrm{H{-}OSO_3H}} \longrightarrow \mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{OSO_3H}{C}}{-}H}$$

ethyl hydrogensulphate
($CH_3CH_2HSO_4$)

When the reaction mixture is added to water and warmed, ethyl hydrogensulphate is readily hydrolysed to ethanol

$$CH_3CH_2OSO_3H + \underset{(H_2O)}{H\text{-}OH} \longrightarrow CH_3CH_2OH + H_2SO_4$$

ethene reacts with concentrated H_2SO_4 to form ethanol

or

alkene reacts with concentrated H_2SO_4 to form alcohol

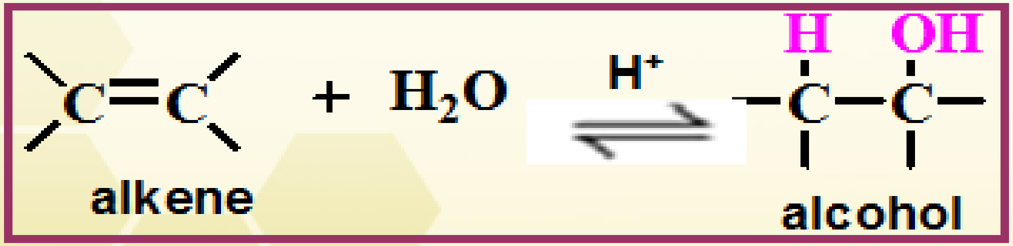
Addition reaction with acidified water (H_3O^+): hydration of alkenes

- **Hydration**: The addition of H atoms and –OH groups from water molecules to a multiple bond.
- Reverse of the dehydration reaction.
- Direct hydration of ethene:

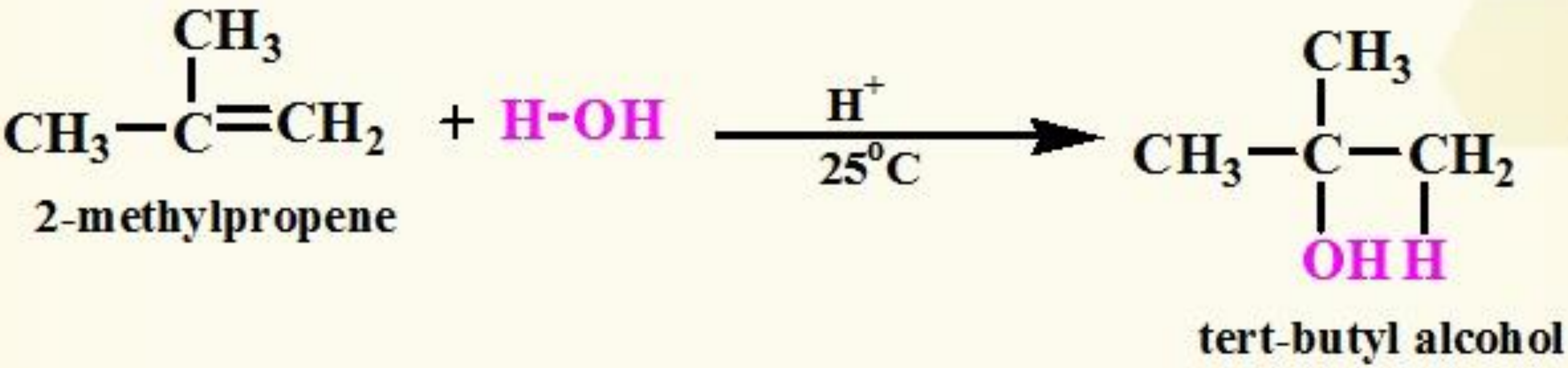
  - passing a mixture of ethene and steam over phosphoric (v) acid (H_3PO_4) absorbed on silica pellets at 300°C and a pressure of 60 atmospheres.

  - H_3PO_4 is a catalyst.

$$\underset{\text{ethene}}{CH_2{=}CH_2\,(g)} + H_2O(g) \xrightarrow[300\ ^{o}C,\ 60\ atm]{H_3PO_4} \underset{\text{ethanol}}{CH_3CH_2OH\,(g)}$$



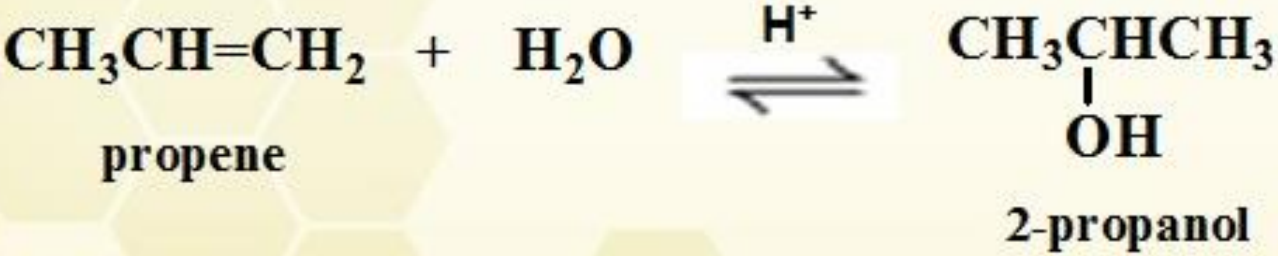
- **Markovnikov's rule is apply to the addition of a water molecule across the double bond of an unsymmetrical alkene.**
- **For examples:**



$$\mathrm{CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2} + \mathrm{H{-}OH} \xrightarrow[25^{0}\mathrm{C}]{\mathrm{H^+}} \mathrm{CH_3{-}\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}\underset{\underset{\displaystyle H}{|}}{CH_2}}$$

2-methylpropene

tert-butyl alcohol



$$\mathrm{CH_3CH{=}CH_2} + \mathrm{H_2O} \overset{\mathrm{H^+}}{\rightleftharpoons} \mathrm{CH_3\underset{\underset{\displaystyle OH}{|}}{C}HCH_3}$$

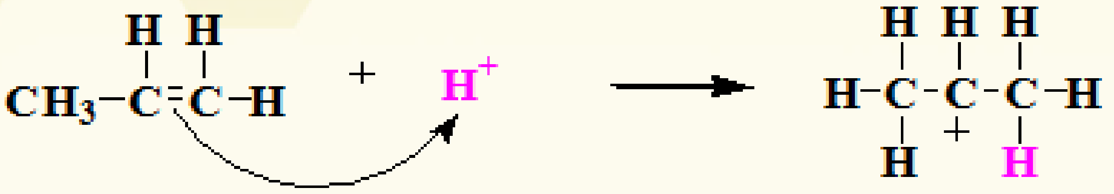
propene

2-propanol

H^+ = catalyst

MECHANISM OF ACID CATALYSED HYDRATION OF ALKENES

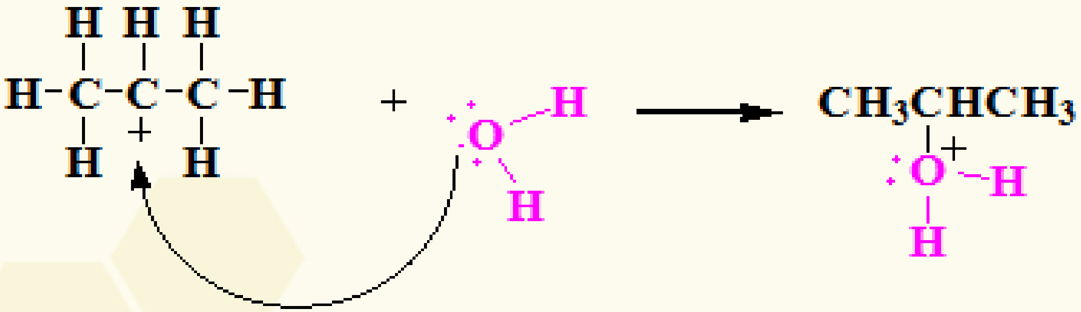
Step 1: Protonation to form carbocation



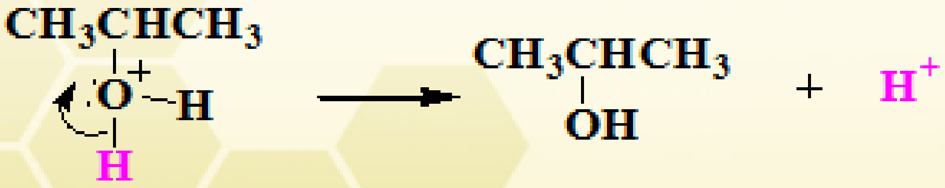
more stable carbocation

(2° carbocation)

Step 2: Addition of H_2O to form a protonated alcohol



Step 3: Loss of a proton (deprotonated) to form alcohol



H⁺ = catalyst

ANTI-MARKOVNIKOV’S RULE: FREE RADICAL ADDITION OF HYDROGEN BROMIDE

- When HBr is added to an alkene in the absence of peroxides it obey Markovnikov’s rule.
- When HBr (not HCl or HI) reacts with unsymmetrical alkene in the presence of peroxides (compounds containing the O-O group) or oxygen, HBr adds in the opposite direction to that predicted by Markovnikov’s rule.
- The product between propene and HBr under these conditions is 1-bromopropane and not 2-bromopropane.

$$CH_3CH{=}CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3CH_2CH_2Br$$

1-bromopropane
(major product)
anti-Markovnikov's orientation

- ***Anti-Markovnikov's addition:***

  - peroxide-catalysed addition of HBr occurs through a free radical addition rather than a polar electrophilic addition.

  - also observed for the reaction between HBr and many different alkenes.

  - not observed with HF, HCl or HI.

Combustion of alkenes:

- The alkenes are highly flammable and burn readily in air, forming carbon dioxide and water.
- For example, ethene burns as follows :

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

OXIDATION

- *Oxidation*: reactions that form carbon-oxygen bonds.

- Oxidation reaction of alkenes:

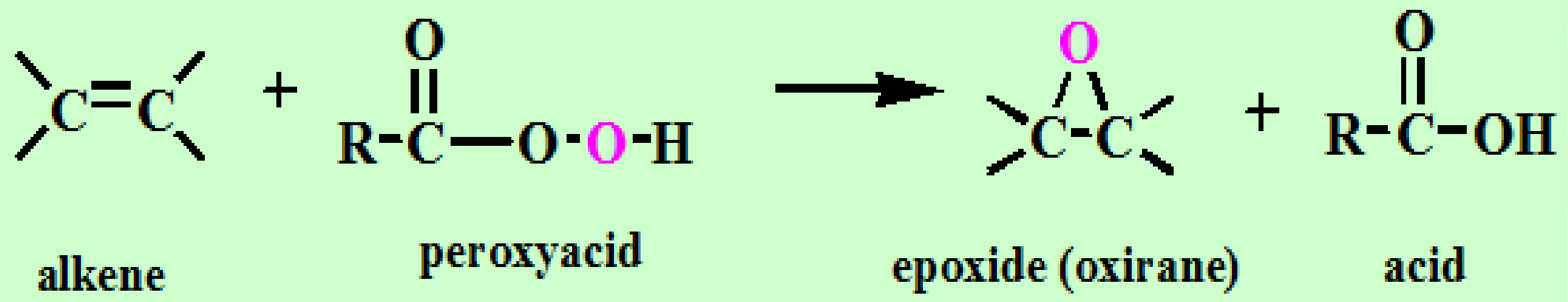
  i) epoxidation

  ii)hydroxylation

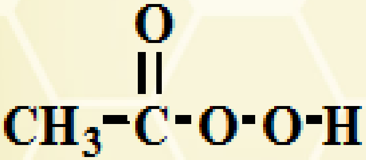
  iii)Ozonolysis

EPOXIDATION OF ALKENES

- Epoxide / oxirane: a three-membered cyclic ether.

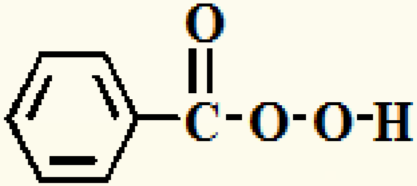


- Examples of epoxidizing reagent:

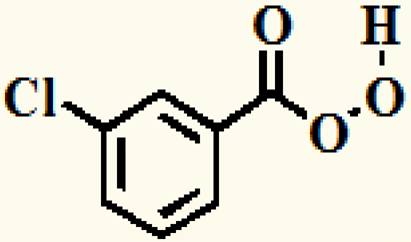


$$CH_3-\overset{O}{\overset{\|}{C}}-O-O-H$$

peroxyacetic acid

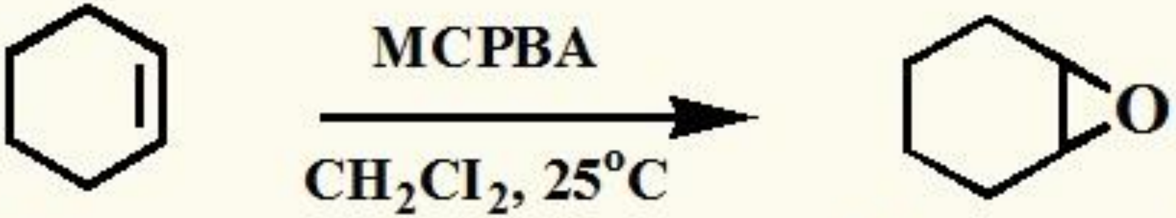


peroxybenzoic acid
($PhCO_3H$)



m-chloroperoxybenzoic acid
(MCPBA)

Examples:

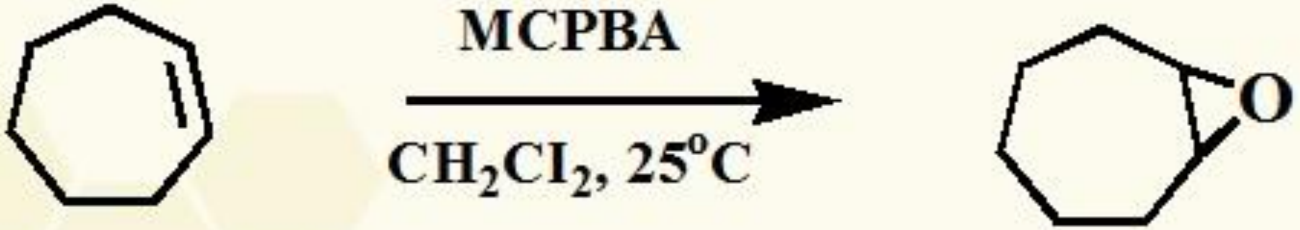


cyclohexene

MCPBA

CH_2CI_2, 25°C

1,2-epoxycyclohexane



cycloheptene

MCPBA

CH_2CI_2, 25°C

1,2-epoxycycloheptane

HYDROXYLATION OF ALKENES

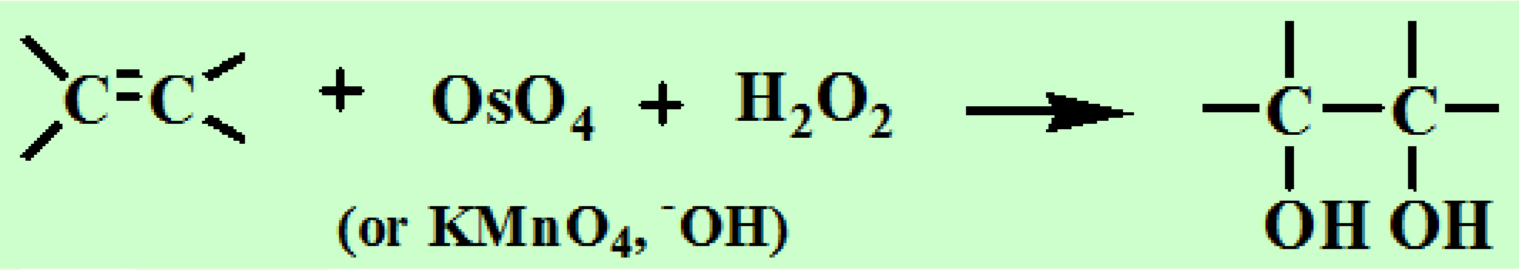
- ***Hydroxylation:***

  - Converting an alkene to a glycol requires adding a hydroxyl group to each end of the double bond.

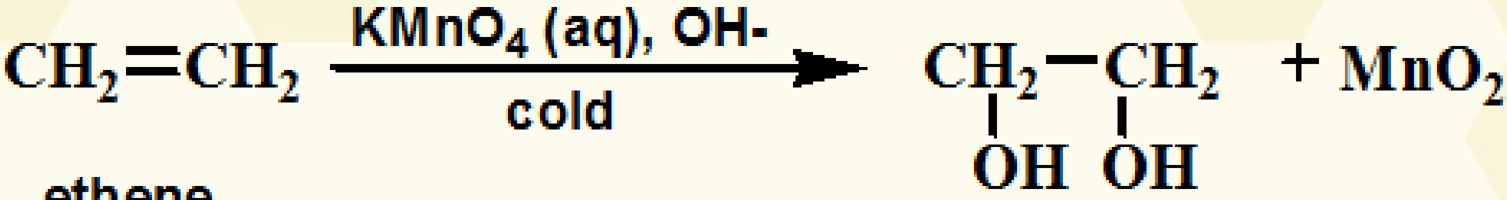
- Hydroxylation reagents:

  i) Osmium tetroxide (OsO_4)

  ii)Potassium permanganate ($KMnO_4$)



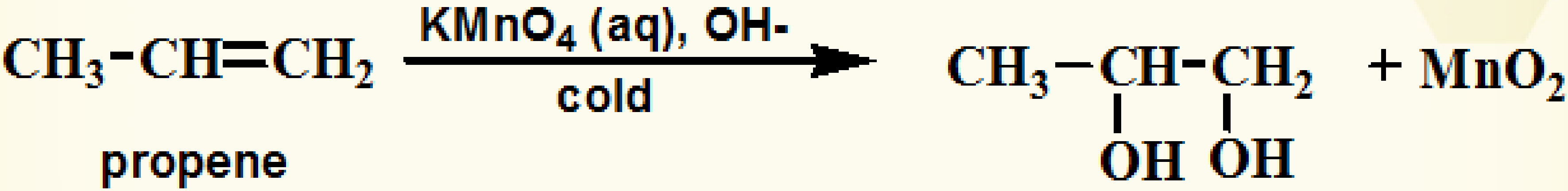
glycol



$$CH_2{=}CH_2 \xrightarrow[\text{cold}]{\text{KMnO}_4\text{ (aq), OH-}} \underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH_2}} + MnO_2$$

ethene

1,2-ethanediol



$$CH_3{-}CH{=}CH_2 \xrightarrow[\text{cold}]{\text{KMnO}_4\text{ (aq), OH-}} CH_3-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}} + MnO_2$$

propene

1,2-propanediol

* Also known as Baeyer’s test

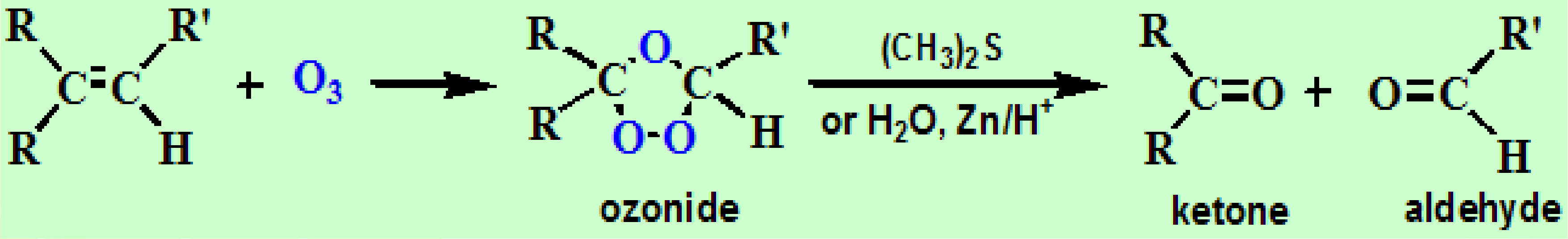
OZONOLYSIS OF ALKENES

- ***Ozonolysis:***

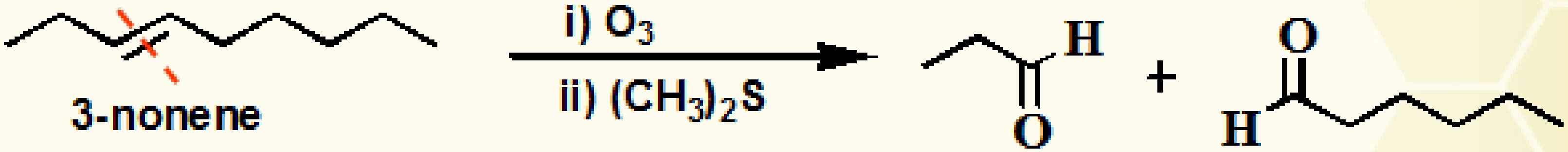
  - The reaction of alkenes with ozone (O_3) to form an ozonide, followed by hydrolysis of the ozonide to produce aldehydes and /or ketone.

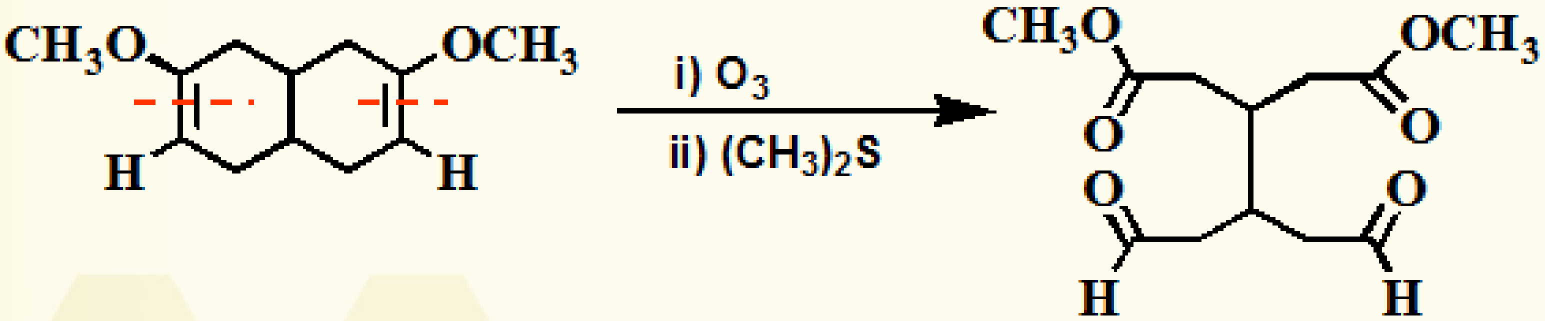
  - Widely used to determine the position of the carbon-carbon double bond.

  - Ozonolysis is milder and both ketone and aldehydes can be recovered without further oxidation.

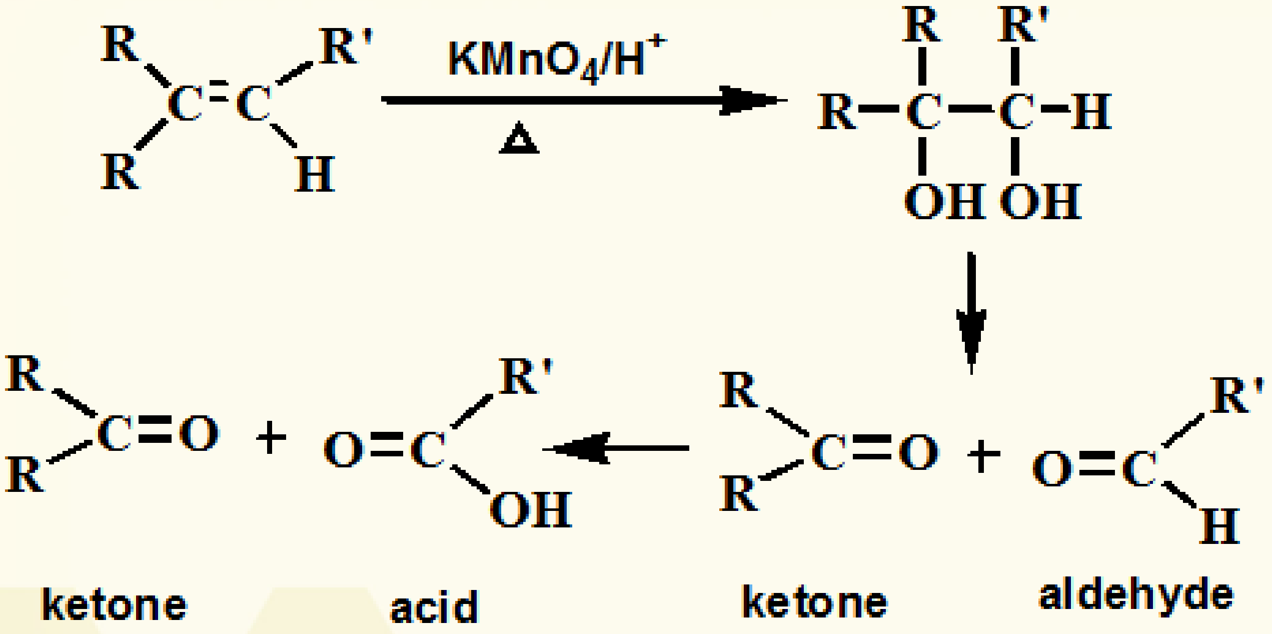


EXAMPLES:

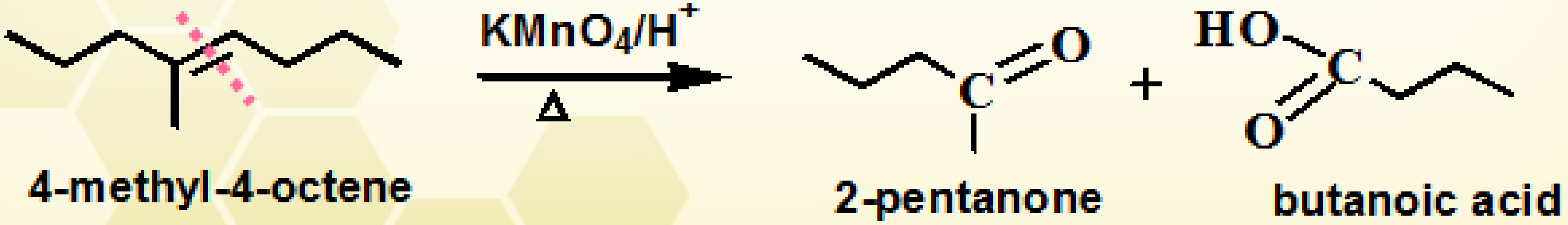

3-nonene
i) O3
ii) (CH3)2S
H
O
+
O
H


CH3O
OCH3
H
H
i) O3
ii) (CH3)2S
CH3O
OCH3
O
O
O
O
H
H

REACTIONS OF ALKENES WITH HOT, ACIDIFIED $KMnO_4$



Example:



POLYMERIZATION OF ALKENES

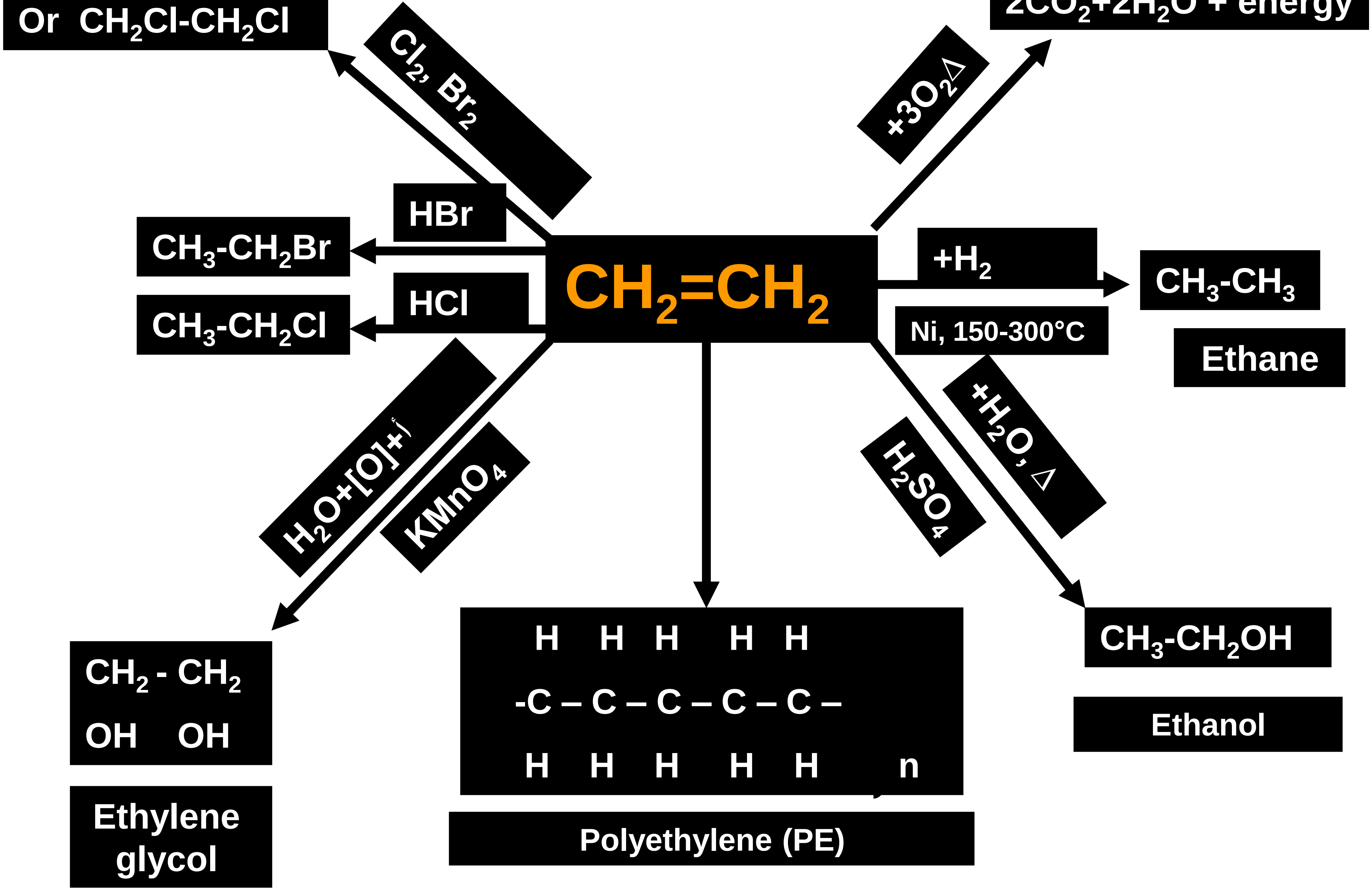
- **Polymer**: A large molecule composed of many smaller repeating units (the monomers) bonded together.

- Alkenes serves as monomers for some of the most common polymers such as polyethylene (polyethene), polypropylene, polystyrene, poly(vinyl chloride) and etc.

- Undergo addition polymerization /chain-growth polymer:

  - a polymer that results from the rapid addition of one molecule at a time to a growing polymer chain, usually with a reactive intermediate (cation, radical or anion) at the growing end of the chain.

Ethylene Reactions



$CH_2=CH_2$

Cl_2, Br_2

CH_2Br-CH_2Br

Or CH_2Cl-CH_2Cl

HBr

CH_3-CH_2Br

HCl

CH_3-CH_2Cl

$H_2O+[O]+$أ

$KMnO_4$

CH_2-CH_2

OH OH

Ethylene glycol

H H H H H

-C – C – C – C – C –

H H H H H n

Polyethylene (PE)

$+3O_2 \Delta$

$2CO_2+2H_2O$ + energy

$+H_2$

Ni, 150-300°C

CH_3-CH_3

Ethane

$+H_2O, \Delta$

H_2SO_4

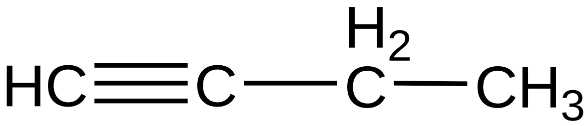
CH_3-CH_2OH

Ethanol

Alkynes

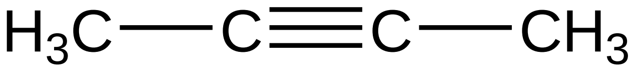
3-3- Alkynes

- Contain at least one carbon-carbon triple bond.
- General formula for alkynes – C_nH_{2n-2} , $n \geq 2$
- Eg: 1-butyne, 2-butyne



$HC\equiv C-\overset{H_2}{C}-CH_3$

But-1-yne



$H_3C-C\equiv C-CH_3$

But-2-yne

Alkynes

- Alkynes contain a triple bond.
- General formula is C_nH_{2n-2}
- Two elements of unsaturation for each triple bond.

Alkyne Nomenclature

- Find the longest chain containing the triple bond.
- Change ***-ane*** ending to ***-yne***.
- Number the chain, starting at the end closest to the triple bond.
- Give branches or other substituents a number to locate their position.

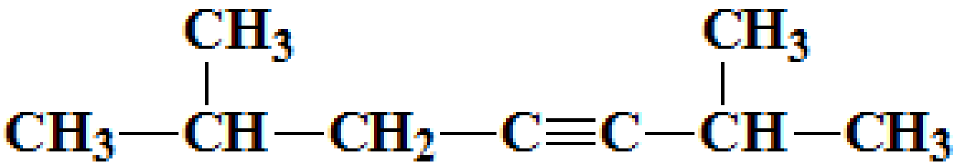
Try these

$CH_3-C\equiv CH$

propyne

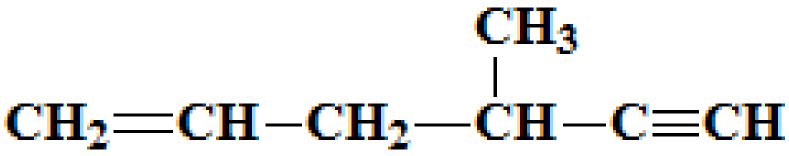
$CH_3-C\equiv C-CH_2-CH_2-Br$

5-bromo-2-pentyne



$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-C\equiv C-\overset{\overset{CH_3}{|}}{CH}-CH_3$

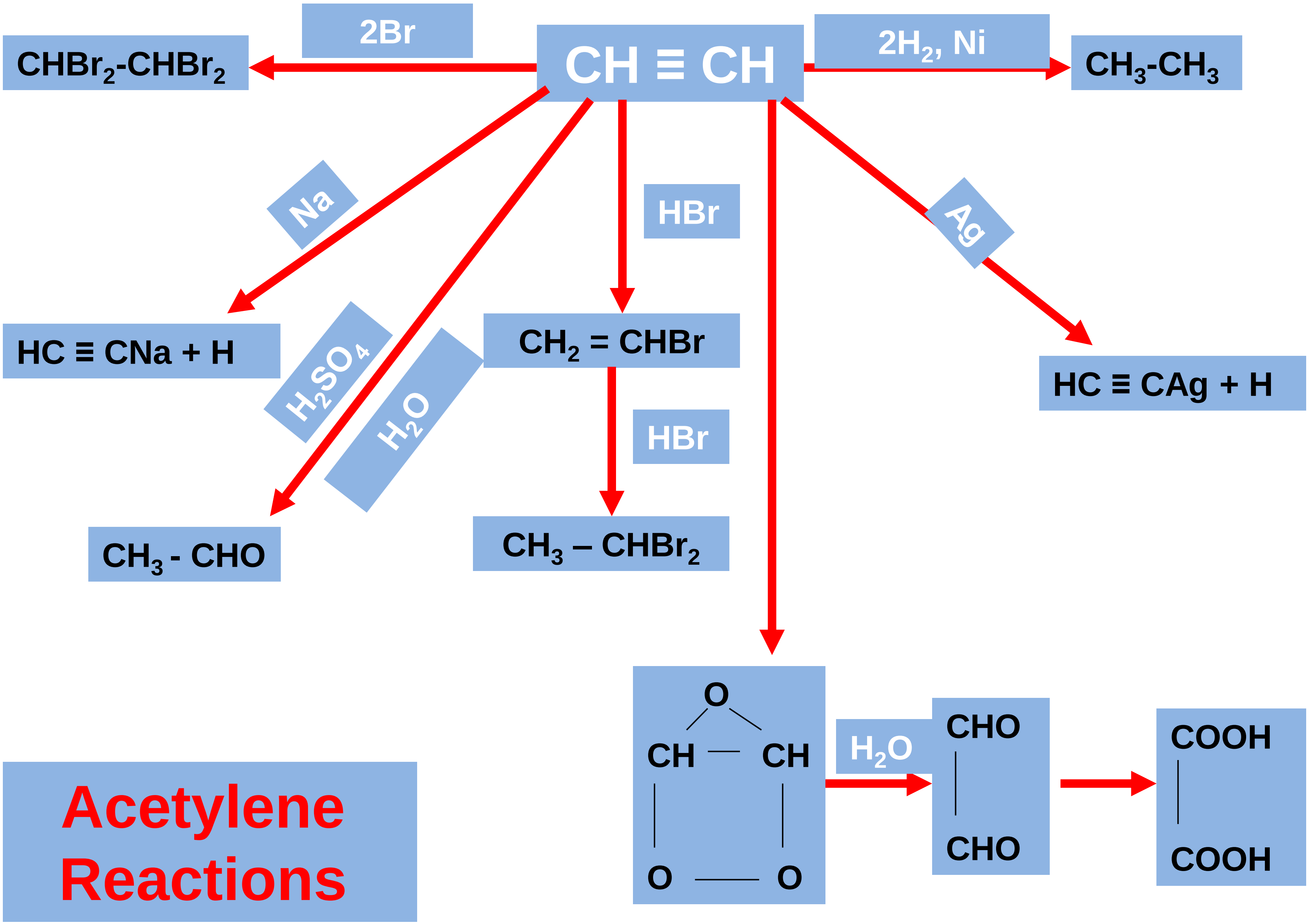
2,6-dimethyl-3-heptyne



$CH_2=CH-CH_2-\overset{\overset{CH_3}{|}}{CH}-C\equiv CH$

3-methyl-1-hexyn-5-ene

Acetylene Reactions



$CH \equiv CH \xrightarrow{2Br} CHBr_2\text{-}CHBr_2$

$CH \equiv CH \xrightarrow{2H_2,\ Ni} CH_3\text{-}CH_3$

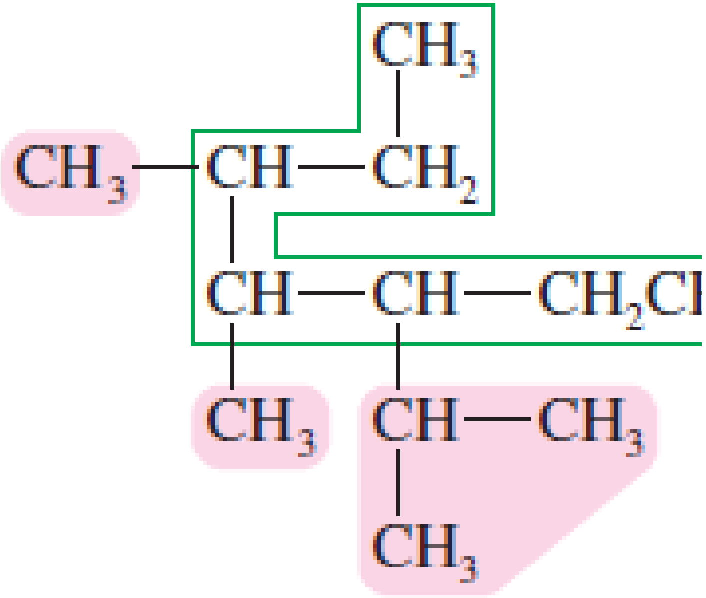
$CH \equiv CH \xrightarrow{Na} HC \equiv CNa + H$

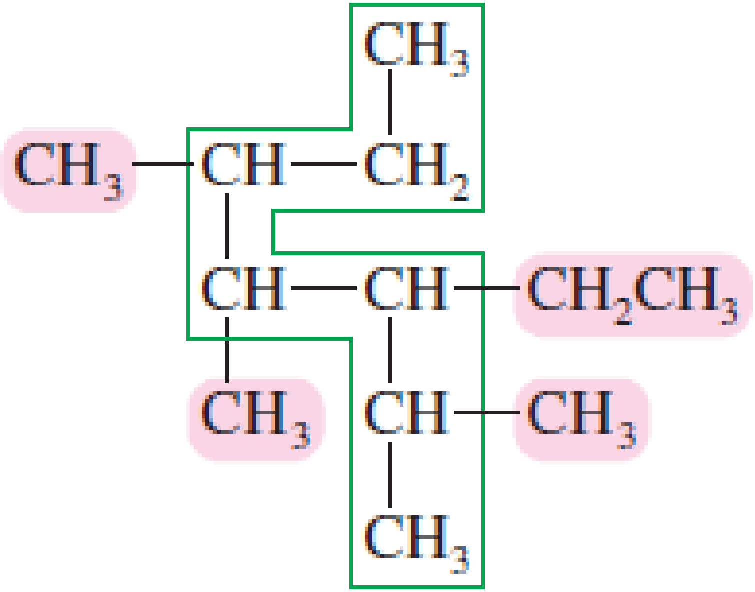
$CH \equiv CH \xrightarrow{H_2SO_4,\ H_2O} CH_3 - CHO$

$CH \equiv CH \xrightarrow{HBr} CH_2 = CHBr \xrightarrow{HBr} CH_3 – CHBr_2$

$CH \equiv CH \xrightarrow{Ag} HC \equiv CAg + H$

Which is correct?





Please do all the Assignments in the two lectures

Thank you