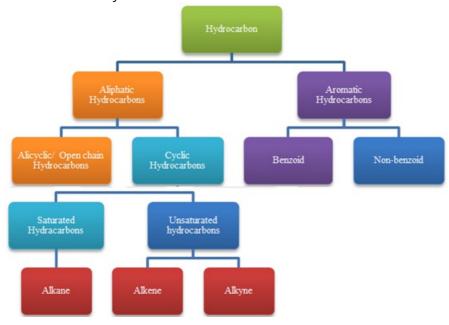
Hydrocarbons

- Compounds of carbon and hydrogen.
- Classification of Hydrocarbons:



Alkane

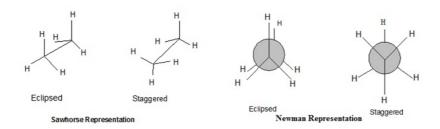
- Open chain saturated hydrocarbon with general formula (C_nH_{2n+2}).
- All the C atoms are single bonded i.e. sp³ hybridised.

Conformations of Alkane

- Conformations are the different arrangement of atoms that can be converted into one another by rotation about single bonds.
- Eclipsed Conformation: H atoms on two adjacent carbon atoms are closest to each other i.e. dehydral angle is 0.

dihedral angle
$$= \begin{array}{c} H \\ H \\ H \end{array}$$

• Staggered Conformation: H atoms on two adjacent carbon atoms are farthest to each other i.e. dehydral angle is 60.



Preparation of Alkanes:

• Reduction of Alkyl Halides:

RX + Zn: + H⁺
$$\Box$$
 RH + Zn²⁺ + X⁻
4RX + LiAlH₄ \Box 4RH + LiX + AlX₃ (X \neq F)
RX + (n - C₄H₉)₃ SnH \Box R-H + (n - C₄H₉)₃ SnX

• Grignard Reagent:

$$RX + 2Li \xrightarrow{dry \text{ ether}} R^* Li^+ + LiX \text{ then } R^* Li^+ + H_2O \longrightarrow RH + LiOH$$

$$RX + Mg \xrightarrow{dry \text{ ether}} R^* (Mg^+X) \qquad \text{then, } RMgX + H_2O \longrightarrow RH + Mg$$

$$OH$$
?

• Hydrogenation of Alkenes:

$$\begin{array}{ccc} CH_3 & CH_3 \\ | & | \\ CH_3 \cdot C = CH_2 + H_2 & \longrightarrow CH_3 \cdot CH \cdot CH_3 \end{array}$$

• Wurtz Reaction:

• Corey House Reaction:

R MgX or RLi
$$\xrightarrow{\text{CuX}}$$
 R-R' (R = 1°, 2° or 3°; R' = 1°)

• Decarboxylation of a mixture of the sodium salt of a carboxylic acid:

• Kolbe's electrolytic method:

Chemical Properties of Alkane

• Direct Halogenation

Order of Reactivity of X_2 : $F_2 > Cl_2 > Br_2$; I_2 does not react

?a. Initiation Step

 $CI-CI \xrightarrow{uv} 2CI$

b. Propagation Step

$$H_3C-H+Cl$$
· \square H_3C • + $H-Cl$

$$H_3C^{\bullet} + Cl-Cl \square H_3C-Cl +Cl^{\bullet}$$

c. Termination Step

Cl· + Cl· □Cl-Cl

$$H_3C^{\bullet} + H_3C^{\bullet} \square H_3C-CH_3$$

Nitration

Nitration of alkane is made by heating vapours of alkanes and HNO3 at about 400oC to give nitroalkanes.

"This is also known as vapour phase nitration.

$$CH_{4(g)} + HNO_{3(g)} \xrightarrow{400^{\circ}C} CH_3NO_2 + H_2O$$

• Combustion:

?Alkanes burn readily with non luminous flame in presence of air or oxygen to give CO2 & water along with evolution of heat.

$$C_2H_6 + 7O_2 \square CO_2 + 6H_2O + heat$$

Aromatization

?"Alkanes having six to 10 carbon atoms are converted into benzene and its homologues at high pressure and temperature in presence of catalyst.

$$\begin{array}{ccc} C_6H_4 & \xrightarrow{V_2O_5/Cr_2O_3/Mo_2O_3} & C_6H_6 \\ & \xrightarrow{773K \& 20 \text{ atm}} & Benzene \end{array}$$

Oxidization of 3⁰ alkane:?

Tertiary alkanes are oxidized to tertiary alcoholsby KMnO4

Alkene (olefins)

- Open chain, Unsaturated hydrocarbons with general formula (CnH2n).
- At least one >c=c< (double bond) group i.e. sp2 hybridisation, is present throughout the chain.
- Allene: alkene molecule in which at least one C has double bonds with each of the adjacent carbon i.e. -c=c=c- group.
- Isomeric with saturated cycloalkanes.

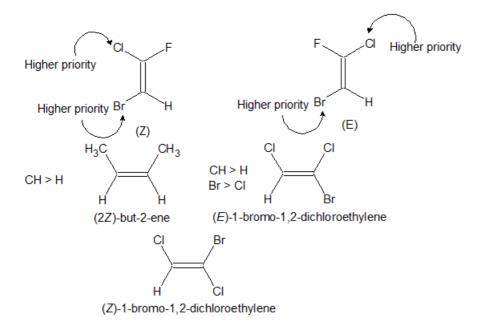
$$CH_3CH = CH_2$$
 $H_2C \longrightarrow CH_2$ CH_2

Geometric Isomers:

$$H_3C$$
 CH_3 H CH_3
 $C = CH_3$
 CH_3 's on same side called *cis*-

 CH_3 's on opposite sides: called trans-

Z is used if the higher - priority substituents on each C are on the same side of the double bond.letter E is used if they are on opposite sides



Heats of Hydrogenation: Heat of hydrogenation increases with increase in stability of alkene.

CH₃CH₂CH =CH₂ + H₂
$$\stackrel{\text{Pt}}{----}$$
 CH₃CH₂CH₂CH₃ Δ H° = -30.3 Kcal mol⁻¹ _{1 - Butene}

CH₃ CH₃

$$C = C + H_2 \xrightarrow{Pt} CH_3CH_2CH_2CH_3 \quad \Delta H^\circ = -28.6 \text{ Kcal mol}^{-1}$$

$$H \quad H$$

$$cis - 2 - B \text{ utene}$$

$$H_3C$$
 H $C = C$ $+ H_2$ \xrightarrow{Pt} $CH_3CH_2CH_2CH_3$ $\Delta H^\circ = -27.6$ Kcal mol⁻¹ $trans -2$ - Butene

Order of heat of hydrogenation: 1-Butene > cis-2-Butene > trans-2-Butene

Order of stability: 1-Butene> cis-2-Butene > trans-2-Butene

Preparation of Alkenes:

- 1. Cracking of petroleum: $R-CH_2-CH_3 \xrightarrow{Pt \text{ or } Pd} R-CH=CH_2+H_2$
- 2. Dehydrohalogenation of alkyl halides: RCH₂CH₂X + alc.KOH | RCH = CH₂

3. Dehydration of Alcohols:

Saytzeff Rule: In dehydration and dehydrohalogenation the preferential order for removal of an H is $3^{\circ} > 2^{\circ} > 1^{\circ}$

$$H_3C$$
 $\xrightarrow{conc. H_2SO_4}$ H_2C $\xrightarrow{CH_2 + H_2O}$ OH

$$\begin{array}{c}
OH \\
\hline
 & 85\% \text{ H}_{9}\text{PO}_{4} \\
\hline
 & 165-170^{\circ}\text{ C}
\end{array}$$
+ H₂O

$$H_3C$$
 CH_3
 OH
 H_3C
 CH_2
 CH_2
 CH_3
 CH_3
 CH_3
 CH_3

Order of reactivity of alcohols: 1°>2°> 3°

4. Reduction of alkynes:

Chemical Properties:

1. Electrophilic Polar Addition Reactions

Reagent		Product	
Name	Structure	Name	Structure
Halogens (Cl ₂ , Br ₂ only)	X:X	Ethylene dihalide	CH ₂ XCH ₂ X
Hydrohalic acids	H:X	Ethyl halide	CH ₃ CH ₂ X
Hypohalous acids	X:OH	Ethylene halohydrin	CH ₂ XCH ₂ OH
Sulfuric acid (cold)	H:OSO ₂ OH	Ethyl bisulfate	CH ₃ CH ₂ OSO ₃ H
Water (dil. H ₃ O ⁺)	н:ОН	Ethyl alcohol	СН ₃ СН ₂ ОН
Borane	H ₂ B:H	Ethyl borane	$(CH_3CH_2BH_2) \rightarrow (CH_3CH_2)_3B$
Peroxyformic acid	H:O-OCH=O (HCO ₃ H)	Ethylene glycol	СН ₂ ОНСН ₂ ОН

2. Addition of Hydrogen Halides to Alkenes: Markovnikov's Addition:

$$R - CH = CH_2 + HBr \square R - CHBr - CH_3$$

Mechanism:

$$R - CH = CH_2 + HBr \square R - CH^+ - CH_3 + Br^-$$

$$R - CH^+ - CH_3 + Br^- \square R - CHBr - CH_3$$

Anit- Markovnikov's Addition (Peroxide Effect):

$$R - CH = CH_2 + HBr + (C_6H_5CO)_2O_2 \square R - CHBr - CH_3$$

Mechanism

Initiation:

Propagation

$$CH_3CH = CH_2 + Br^{\bullet} \square CH_3 \cdot CH - CH_2Br$$

Termination:

3. Addition of Water to Alkenes: Acid Catalyzed Hydration:

$$H_3C$$
 CH_2
 $+$
 HOH
 H^+
 $25^{\circ}C$
 H_3C
 CH_3
 H_3C
 CH_3

4. Oxymercuration-Demercuration:

Oxymercuration Demercuration
$$C = C + H_2O + Hg(OAc)_2 \rightarrow C - C - OH + HgOAc OH H$$

Examples:

$$H_3C$$
 CH_2
 H_3C
 CH_3
 CH_3

5. Hydroboration-Oxidation:

Examples:

$$H_3C$$
 CH_3
 H_3C
 CH_3
 CH_3

6. Halogen Addition in Non-polar Solvent:

Mechanism:

$$Br$$
 C
 Br
 Br
 Br
 Br

7. Halogen Addition in Aqueous Medium:

$$C = C + X_2 + H_2O \longrightarrow -C - C - + -C - C - + HX$$

$$X = Cl_2 \text{ or } Br_2$$

Mechanism:

8. Syn – Hydroxylation: Formation of di-oles.

9. Ozonolysis of Alkenes:

Alkyne

- Saturated open chain hydrocarbon with general formula (C_nH_{2n-2}).
- At least one -c≡c- (triple bond) group i.e. sp hybridisation, is present throughout the chain.
- Physical properties of alkynes are similar to those of the corresponding alkenes

Preparation

1. Dehydrohalogenation of vic-Dihalides or gem-Dihalides

2. Dehalogenation of vic-Tetrahalogen Compounds

$$\begin{array}{c} \text{CH}_3-\text{CBr}_2-\text{CBr}_2-\text{CH}_3 + 2\text{Zn} \xrightarrow{\quad \text{EtOH} \quad} \text{CH}_3-\text{C}_{\equiv}\text{C}-\text{CH}_3 + 2\text{ZnBr}_2 \\ 2.2,3,3-\text{Tetrabromobutane} \end{array}$$

3. Alkyl Substitution in Acetylene; Acidity of ° C-H

4. From Calcium Carbide:

$$CaC_2 + 2H_2O \square Ca(OH)_2 + C_2H_2$$

5. Kolbe's Electrolysis:

$$\begin{array}{c} \text{CHCO}_2 \text{Na} \\ || \\ \text{CHCO}_2 \text{Na} \end{array} \xrightarrow{+2\text{H}_2 \text{O}, \text{ourrent}} \begin{array}{c} \text{CH} \\ ||| \\ \text{CH} \end{array} + 2\text{CO}_2 + 2\text{NaOH} + \text{H}_2 \end{array}$$

Chemical Properties

1. Hydrogenation: RC \equiv CCH₂CH₃ + 2H₂ \rightarrow CH₃CH₂CH₂CH₂CH₃

2. Hydro-halogenation:

Markovnikov addition: $RC \equiv CH + HBr \rightarrow RCBr = CH_2 + HBr \rightarrow RCBr_2 - CH_3$

Anti-markovnikov addition: RC=CH +HBr +peroxide

RCH=CHBr

3. Hydration:

$$CH = CH + H_2O \xrightarrow{H_2SO_4} [CH_2 = CHOH] \longrightarrow CH_3CHO$$

4. Addition of boron hydride:

$$R'-C = C-H + R_2BH \xrightarrow{R'} C = C \xrightarrow{H} \xrightarrow{BR_2} \xrightarrow{H_2O_2, NaOH} \xrightarrow{R'CH_2CHO} R'CH_2CHO$$

5. Dimerization:

2 H—C ≡ C — H
$$\xrightarrow{\text{Cu(NH_3)}_2^+\text{Cl}^-}$$
 H₂C=CH—C≡CH
Vinylacetylene

6. Oxidation:

$$\begin{array}{c} CH_3CH_2C\equiv\!C\text{-}CH_3+2KMnO_4\to CH_3CH_2COOK+CH_3COOK+2MnO_2+2H_2O\\ \xrightarrow{CH_3}: & CH_3\\ CH_3\text{-}CH\text{-}C\equiv\!C\ CH_2\ CH_2CH_3 \xrightarrow{ox\ dn.} & CH_3\\ \hline (Two\ isomeric\ acids\ each\ having\ M.F.\ C_4H_8O_2) \end{array}$$

7. Ozonolysis Hydrolysis:

$$\begin{array}{c} \text{CH}_3\text{C} \equiv \text{CCH}_2\text{CH}_3 & \xrightarrow{\hspace*{1cm} 1.\hspace*{0.5cm} 03} \\ \text{2-Pentyne} & \xrightarrow{\hspace*{1cm} 2.\hspace*{0.5cm} \text{hydrolysis}} & \text{CH}_3\text{COOH} + \text{HOOCCH}_2\text{CH}_3 \\ \text{Acetic acid} & \text{Propanoic acid} \end{array}$$

8. Cyclic polymerization:

Aromatic Hydrocarbons:

For being aromatic a hydrocarbon should

- be a cyclic compounds.
- have planarity in geometry.
- have complete delocalization of electrons over ring.
- follow Huckel Rule i.e. number of ?? electrons in ring = (4n+2).

Benzene (C₆H₆)

1. Structure:

2. Chemical Reactions of Benzene:

Anti-aromatic Hydrocarbons:

Highly unstable compounds.

Number of π electrons in ring = 4n.

Example:

