# **Organic Reaction Mechanisms-II** (Chemical properties of Benzene, Alkanes, Alkenes & Alkynes)

## Introduction :

All organic compounds classify into two broad classes, aliphatic compounds and aromatic compounds. Aromatic compounds are those that resemble with benzene in chemical behaviour.

## Proposed structure of benzene :





[Prism like structure proposed

by Albert Ladenberg]

\* Benzene mostly represents by Kekule structure.

# Huckel's (4n + 2) rule for aromaticity :

An aromatic compound must have cyclic clouds of delocalised (4n+2)  $\pi$  electrons above and below the plane of the molecule.

### Comparison between Aromatic, Anti-aromatic and Non-aromatic compounds :

Characteristics	Aromatic	Anti-aromatic	Non-aromatic
1. Structure	Cyclic	Cyclic	Cyclic or acyclic
<b>2</b> . Shape	Planar	Planar	Planar or non planar
3. Conjugation	Close cyclic	Close cyclic	Any kind of conjugation
4. Hybridization	All atoms of the ring are sp <sup>2</sup> or sp	All atoms of the ring are sp <sup>2</sup>	Any kind of hybridization
5. Number of delocalised electrons	2,6,10,14 (4n+2) e <sup>-</sup>	4,8, (4n) e <sup>-</sup>	Any number of electrons
6. Resonance energy	High	Zero	Normal

### Stability : aromatic > nonaromatic > antiaromatic

### Some noteworthy points :

(1) Some other aromatic species are Pyridine, Furan, Pyrrole, Thiophene, Ferrocene (sandwich compound)

Dipotassium cyclooctatetraenide anion, Buckminster fullerene.

(2) Antiaromatic compounds are paramagnetic in character.

(3) [10] Annulene is not aromatic, although 1,6-Methano [10] annulene (C<sub>11</sub>H<sub>12</sub>) is aromatic.

(4) Aromatic compound has the ability to sustain an induced ring current.

(5) Azulene is coloured and highly polar although its isomer naphthalene does not have significant zwitter ionic character.

(6) Fullerrene has been called the most symmetrical possible molecule, its buck side salt becomes a super conductor when cooled below 18 K.

(7) In pyrrole the sp<sup>2</sup> hybridized nitrogen must contribute two electrons to give an aromatic sextet.

(8) Aromatic hydrocarbons contain higher percentage carbon content so burn with sooty flame.

### **Carcinogenicity and Toxicity**

Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together are toxic and said to possess cancer producing (carcinogenic) property. Such polynuclear hydrocarbons are formed

on incomplete combustion of organic materials like tobacco, coal and petroleum. They enter into human body and undergo various biochemical reactions and finally damage DNA and cause cancer. Some of the carcinogenic hydrocarbons are given below.



# Section (A) : Preparation and chemical properties of benzene

### (a) **Preparation of Benzene**



(4) By reduction of Benzene diazonium chloride :



(5) By reduction of Phenol :



(6) By Grignard reagent :



**Preparation of Toluene :** (b)

(1) By Friedel-craft's reaction :





(C) **Preparation of Xylene :** 



Toluene  $\xrightarrow{CH_3X, AlCl_3} 0-X$  ylene +p-Xylene

### (d) Comparison of Aromatic compounds with alkenes :

Benzene is not as reactive as alkenes. Alkene gives addition reaction while benzene gives substitution reaction.

H  
H + Br<sub>2</sub> 
$$\rightarrow$$
 H  
H  $\Delta H^{\circ} = -29 \text{ kcal } (-121 \text{ kJ})$ 

The analogous addition of bromine to benzene is endothermic because it requires the loss of aromatic stability. The addition is not seen under normal circumstances. The substitution of bromine in place of hydrogen atom gives an aromatic product. The substitution requires a Lewis acid catalyst to convert bromine into a stronger electrophile.



### (e) Aromatic electrophilic substitution (ArS<sub>E</sub>2) reactions of benzene

It is a two step reaction, In Ist step sigma complex is formed in slow step. Formation of the sigma complex is rate determining and the transition state leading to it occupies the highest-energy point on the energy diagram.

Step-1 : Attack of an electrophile on benzene ring forms the sigma complex



Step-2 : Loss of a proton gives the substitution product.



Energy diagram : For bromination reaction, electrophile is bromonium ion (Br+)



Reaction coordinate ------

Electrophilic aromatic substitution reaction to overcome the high activation energy that charaterizes the first step, the electrophile must be a fairly reactive one. Many of the electrophilic reagents that react rapidly with alkenes do not react at all with benzene. For example peroxy acids and diborane, fall into this category, others such as bromine react with benzene only in presence of catalysts that increases their electrophilicity.

**Note :** (1) Aromatic rings have stable pi electrons still they are available to attack on a strong electrophile to give a carbocation.

(2) This resonance-stabilized carbocation is called a **sigma complex** because the electrophile is joined to the benzene ring by a new sigma bond.

(3) The sigma complex (also called an arenium ion) is not aromatic because the sp<sup>3</sup> hybrid carbon atom interrupts the ring of p orbitals.

(4) This loss of aromaticity contributes to the highly endothermic nature of this first step. The sigma complex regains aromaticity either by a reversal of the first step (returning to the reactants) or by loss of the proton on the tetrahedral carbon atom, leading to the substitution product.

(5) The overall reaction is the substitution of an electrophile  $(\stackrel{\overset{\oplus}{E})}{(E)}$  in place of a proton  $(\stackrel{\overset{\oplus}{H})}{(H)}$  on the aromatic ring. (i.e. electrophilic aromatic substitution)

(6) Electrophilic substitution occurs preferentially in the 5-membered ring of azulene.

### Effect of substituent groups in monosubstituted benzene :

(1) Ortho-para directing and activating groups : All electron releasing groups (+m, +I) are ortho-para directing groups and activating towards electrophilic reactions.

(2) Ortho para directing but deactivating groups : Halogens are deactivating but ortho-para directing groups.

Reactivity of benzene decreases by –I effect of halogens and ortho-para directing nature decided by +m effect of halogens.

(3) Meta directing and deactivating groups : Mostly electron withdrawing groups (-m, -l) are meta directing groups and deactivating towards electrophilic reactions.

	Substituent groups	Reactivity (effect on rate)	Directing nature (effect on orientation)
1.	$-O^{-} > -NH_2 > -NHR$ > $-NR_2 > -OH$	Very strongly activating	Ortho-para directing
2.	0 0 ∥ ∥ −OR > − NH−C−R > −O−C−R	Strongly activating	Ortho-para directing
3.	$-R$ , $-Ar$ , $-CH=CH_2$	Activating	Ortho-para directing
4.	–X(F, Cl,Br,I), –N=O, –CH <sub>2</sub> X, –CHX <sub>2</sub>	Deactivating	Ortho-para directing
5.	O ∥ –CHO, –C–R, –COOH, –COOR, –COCI, –C≡N,–SO₃H	Strongly deactivating	Meta directing
6.	-NO <sub>2</sub> , -NR <sub>3</sub> , -SR <sub>2</sub> , -CF <sub>3</sub>	Very strongly deactivating	Meta directing

## Effect of substituent groups in disubstituted benzene :

(1) If activating and deactivating both groups are present in a system then position of electrophile will be determined by activating group.

(2) If both groups present in a system are deactivator then position of electrophile will be determined by stronger deactivator.

(3) If both the groups are activating group then position of electrophile will be determined by stronger activator.

(4) There is often little substitution between two groups that are meta to each other.



e.g. Nitration product of

(% nitro product)

# (i) Halogenation

(1) Bromine or chlorine itself is not sufficiently electrophilic to react with benzene so a strong Lewis acid such as FeBr<sub>3</sub> or AlCl<sub>3</sub> catalyzes the reaction.

(2) Iodination takes place in presence of oxidising agents like HNO<sub>3</sub> or HIO<sub>3</sub>. Kinetic isotope effect is also observed in iodination reaction of benzene.

(3) Order of effectiveness :  $CI_2 > BrCI > Br_2 > ICI > I_2$ 

(4) Other halogenating agents are ICI, HOCI etc.

**Step-1**: Formation of a stronger electrophile.

$$: \overset{\overset{\overset{}}{\text{B}}\text{r}}{=} - \overset{\overset{\overset{}}{\text{B}}\text{r}}{=} + \text{FeBr}_{3} \rightleftharpoons \left[: \overset{\overset{}}{\text{B}}\text{r} - \overset{\overset{\overset{}}{\text{B}}\text{r}}{=} - \overset{\overset{\overset{}}{\text{FeBr}}\text{r}_{3}\right]$$

Step-2 : Electrophilic attack and formation of the sigma complex.



Step-3 : Loss of a proton gives the products.



# (ii) Nitration

 $\cdot$  HNO<sub>3</sub> alone is a weak nitrating agent where as the mixture of concentrated HNO<sub>3</sub> and concentrated H<sub>2</sub>SO<sub>4</sub> is strong nitrating mixture. In this mixture HNO<sub>3</sub> is act as base.

### Mechanism



## (iii) Sulphonation

Sulphur trioxide in sulphuric acid is used as the sulphonation agent.



Sulphonation, is reversible and takes place in concentrated sulphuric acid. (K-1K2)

### **Energy Diagram**



Some  $A\vec{r} \leq S_{0_3}$  or  $A\vec{r} \leq S_{0_3}$  go on to product, some revert to the starting material and decrease the rate of reaction. This effect is known as isotope effect.

### (iv) IPSO Substitution



attack at the position bearing the substituent is called IPSO position. Examples of IPSO



**Note :** If ortho position or para position of phenol or aniline has presence of –COOH or –SO<sub>3</sub>H group. When it reacts with Br<sub>2</sub>/water IPSO takes place.



### **Organic Reaction Mechanisms - II**





(v) **Friedel Craft reaction** 

## (a) Alkylation :

- (1) Electrophile is carbocation.
- (2) Alkylating agents are : RX + AIX<sub>3</sub> (lewis acid), Alkene in acidic medium and alcohol in acidic medium.
- (3) The order of effectiveness of Lewis acid catalyst has been shown to be

AICI₃ **FeCl**<sub>3</sub> BF₃ TiCl<sub>3</sub> > ZnCl<sub>2</sub> > > > > SnCl<sub>4</sub>

Mechanism :

(i) 
$$R - \dot{C}I: + \dot{A}ICI_3 \longrightarrow \overset{\delta^+}{R} - --- CI - --- \overset{\delta^-}{AICI_3}$$

(

· Rate law  $\rightarrow$  rate = k. [Ar - H]. [R - X]. [MX<sub>3</sub>]

· Me<sub>3</sub>CCH<sub>2</sub>Cl/FeCl<sub>3</sub> on benzene gives wholly the unrearranged product PhCH<sub>2</sub>CMe<sub>3</sub>

· On heating p-xylene or o-xylene with AICl<sub>3</sub>/HCl results in the conversion of the majority of it into the more stable meta-xylene.

## (b) Acylation :

(1) Electrophile is acylium ion.

(2) Acylation of benzene may be brought about with acid, acid chlorides or anhydrides in presence of Lewis acids.

sigma complex

Mechanism :

R

Step-1 : Formation of an acylium ion.

sigma complex



Acylbenzene

· Friedel-Crafts acylations are generally free from rearrangements and multiple substitution. (but decarbonylation can take place)



One significant difference of acytation from alkylation is that in former rather more than one mole of lewis acid is required.

## (vi) Limitations of Friedel Craft reaction :

(1) Re-arrangement : In Friedel craft alkylation carbonium ion can rearrange but in Friedel craft acylation acylium ion can not rearrange.

(2) Polyalkylation takes place because alylated benzene is more activited than benzene but polyacylation does not take place because acyl benzene is more deactivated.

### (3) Friedel craft reaction is not possible in presence of following functional groups:-

- (a) If -m groups are attahced to benzene ring.
- (b) If strong +m groups are attahced to benzene ring.



Ex.

In presence of OH/NH<sub>2</sub> groups Friedel craft reaction is not possible because these groups make coordinate bond with Lewis acid (AIX<sub>3</sub>) and the aromatic ring becomes deactivated.

### (4) Friedel craft reaction is Possible in following compounds :



 $\cdot$  In acylation rearrangement of R does not takes place, but decarbonylation can take place so the end result is then alkylation.

Que. How will you get propylbenzene from benzene ?





# Section (B) : Alkanes

### Physical properties of alkanes :

Alkane molecules are held together by weak Vander waal force which depends upon surface area. On increasing molecular mass surface area increases hence Vander waal forces also increased and thus physical properties are increased.

**Note :** (1) On increasing branching surface area tends to be spherical i.e.Vander waal interaction reduced and hence boiling point decreased.

(2) Melting point of alkane having even number of carbon atoms is higher than neighbouring alkanes having odd number of carbon atom. Because in even number of alkanes two ends are facing towards opposite side hence there will be minimum intermolecular repulsion as a result they fit better into crystal lattice.

(3) Density of alkane increases with molecular mass and then acquires a constant value  $0.8 \text{ gm/cc}^3$ . Thus also it is clear that alkane is lighter than water.

### Comparative study of alkane, alkene & alkyne :

Hydrocarbon	H H     H—C—C—H   H H H (A)	H = C = C = H (B)	$H - C \equiv C - H$ (C)
•	Alkane	Alkene	Alkyne
(i) C—C Bond distance	1.54 A°	1.34 A°	1.20 A°
(ii) C—H Bond distance	1.09 A°	1.08 A°	1.05 A°
(iii) Hybridisation state	sp <sup>3</sup>	sp <sup>2</sup>	sp
(iv) Structure	Tetrahedral	Planner	Linear
(v) Electronegativity $sp^3 < sp^2 < sp$	less than sp <sup>2</sup> /sp	less than sp more than sp <sup>3</sup>	more than sp <sup>2</sup> /sp <sup>3</sup>
(vi) C—C bond energy	415 kJ	615 kJ	835 kJ
(vii) density	0.5 g/cm <sup>3</sup>	0.52 g/cm <sup>3</sup>	0.67 g/cm <sup>3</sup>

# **Organic Reaction Mechanisms - II**

(viii) % s-charactor	25%	33.33 %	50 %
Lab Test :			
Hydrocarbon	Alkane	Alkene	Alkyne (Terminal)
(i) Br <sub>2</sub> /H <sub>2</sub> O solution	No effect	Decolorise	Decolorise
(ii) Cold dil. alkaline	No effect	Brown colour	Brown colour
+ KMnO <sub>4</sub> Solution			
(iii) Tollen's Reagent	No effect	No effect	White ppt. of silver acetenilied
(iv) Ammonical cuprous	No effect	No effect	Red ppt. of cuprous
acetenilied			
chloride solution			

# Chemical reaction of alkanes (free radical substitution)

## (a) Halogenation :

Reagents : UV light / hv/ high temp ( 250°-400°C) / Peroxide + X2 (Cl2 + Br2)

**General reaction :-**

 $R-H + X_2 \xrightarrow{UV \text{ light or } 250^\circ - 400^\circ} R-X + HX$ 

**Mechanism :** Free radical substitution this reaction is chain reaction which is completed in following three steps.

(i) Chain initiation step : It is homolytic clevage of chlorine molecule to give chlorine free radical. It is an endothermic step .

$$\xrightarrow{\text{UV or temp.}}_{X_2} \xrightarrow{250^\circ - 400^\circ\text{C}} 2\dot{X}$$

(ii) Chain propagation step : The step in which reactant and product, both are having free radical. It is longest step.

 $\dot{X} + R - H \longrightarrow \dot{R} + HX$ ; [rds] First propagation step  $\dot{R} + X - X \longrightarrow R - X + \dot{X}$  Secod propagation step

(iii) Chain Termination step : It is the step in which any two free radicals combine to give a product without free radical. It is always exothermic step.

$$\dot{X}_{+} \dot{X} \longrightarrow X_{2} \dot{R}_{+} \dot{R} \longrightarrow R - R \dot{R}_{+} \dot{X} \longrightarrow R - X$$

## Remarks :

### (1) Other halogenating reagent are

(a) Chlorination : SO<sub>2</sub>Cl<sub>2</sub>/ Peroxide ; (b) Bromination : SO<sub>2</sub> Br<sub>2</sub>/ Peroxide Mechanism for (a)

$$RO \longrightarrow OR \longrightarrow 2 OR$$
$$OR + SO_2Cl_2 \longrightarrow ROCI + SO_2CI$$
$$SO_2CI \longrightarrow CI + SO_2$$
$$RH + CI \longrightarrow R + HCI$$

## (2) Methane reacts with excess of chlorine in diffused sunlight to give the final product as

(3) Reactivity of H =  $3^{\circ}H > 2^{\circ}H > 1^{\circ}H$ 

### (4) Reactivity of X<sub>2</sub>

# Reactivity of $X_2 = F_2 > CI_2 > Br_2 > I_2$

	-	
1.Direct fluorination of alkane is not	Bromination	1. Iodination is reversible reaction since H-
possible because it is very explosive. So	is	I is formed as a by product, that is strong
F2 reacts with alkane in dark at room	similar to	reducing agent so reduces alkyl iodide back
temperature.	chlorination	to alkane. Hence iodination can be done
	but slower	only in presence of strong oxidizing agent
	in rate.	like HIO <sub>3</sub> , HNO <sub>3</sub> and HgO etc. which destroy
		HI into I <sub>2</sub> .
		$CH_4 + I_2 \longrightarrow CH_3I + HI$
		$HIO_3 + 5HI \longrightarrow 3I_2 + 3H_2O$
2. Halogen exchange reaction		2. Halogen exchange Reactions :
(Swart's Reaction)		(FinkIstein Reaction)
Reagents : AgF+H <sub>2</sub> O (Major) + C <sub>2</sub> H <sub>5</sub> OH		Reagents : Nal + Acetone
(Minor) Only AgF is soluble among all		Acetone
silver halides in water.		ې R–X + Nal <sup>S</sup> <sub>N</sub> <sup>2</sup> R–I + NaX
		(X = Cl,Br)
$R-X \xrightarrow{S_N^1} R^+ \xrightarrow{F^-} R-F + \xrightarrow{AgX} \downarrow$		In acetone, Nal is soluble/Ionised but
		NaCl/NaBr are insoluble. So NaCl/NaBr
$2C_2H_5Br + HgF_2 \rightarrow 2C_2H_5F + HgBr_2$		get precipitate out.

### (5) In a chain reaction following reagents are involved :

**Initiators** : They initiate the chain reaction, Initiators are peroxide  $(R_2O_2)$ , Perester's etc. **Inhibitors** : A substance that slows down or stops the reaction is known as inhibitors

For example  $O_2$  is a good inhibitor.

$$\dot{R} + O_2 \longrightarrow R - O - \dot{O} + \dot{R} \longrightarrow R - O - O - R$$

all reactive alkyl free radicals are consumed so reaction stops for a period of time.

### Examples :

$$(1) CH_{3}-CH_{2}-CH_{3} \xrightarrow{Cl_{2}} CH_{3} - CH_{2} - CH_{3} - CH_{2} - CH_{2} - CI$$

$$(1) CH_{3}-CH_{2}-CH_{3} \xrightarrow{Iight, 25^{\circ}C} CH_{3} - CH_{2} - CI \xrightarrow{CH_{3}} 45\%$$

$$(1) CH_{3} - CH_{2}-CH_{3} \xrightarrow{CH_{2}} CH_{3} - CH_{2} - CI \xrightarrow{CH_{3}} CH_{3} - CH_{2} - CI \xrightarrow{CH_{3}} \frac{1}{CH_{3}} \frac{1}{CH_{3}}$$

### Factors affecting the relative yields :

(1) Probability factor : This factor is based on the number of each kind of H atom in the molecule.

(2) Reactivity of hydrogen : The order of reactivity is  $3^{\circ} > 2^{\circ} > 1^{\circ}$  the relative rate per hydrogen atom is found to be :

Prim	ary	Secondar	гу	tertiary	
1	:	3.8	:	5	For chlorination at 25°C
1	:	82	:	1600	For bromination at 127°C

(3) Reactivity v/s selectivity principle : The more reactive substance is less selective.

Ex.  

$$\begin{array}{c}
6 \text{ equivalent } 1^{\circ}\text{H} \\
CH_{3} - CH_{2} - CH_{2} - CH_{3} \\
CH_{3} - CH_{2} - CH_{2} - CH_{3} \\
4 \text{ equivalent } 2^{\circ}\text{H} \\
6(1^{\circ}\text{H}) \times (\text{Reactivity } 1.0) \\
= 6.0 \\
\end{array}$$

$$\begin{array}{c}
CI \\
CH_{3} - CH_{2} - CH_{3} \\
CH_{3} \\
CH_{3} - CH_{3} \\
CH_$$

### (b) Nitration of alkane :

It takes place in vapour phase and gives a mixture of nitroderivatives due to cracking.

$$RH + HNO_{3} \xrightarrow{400^{\circ}C} RNO_{2} + H_{2}O$$

$$CH_{4} + HNO_{3} \xrightarrow{\Delta} CH_{3}NO_{2} + H_{2}O$$

$$CH_{3}-CH_{2}-CH_{3} + HNO_{3} \xrightarrow{\Delta} CH_{3}-CH_{2}-CH_{2}-NO_{2} + NO_{2} + CH_{3}-CH_{2}-NO_{2} + CH_{3}-NO_{2} + CH_{3}$$

**Note :** Nitration of propane gives a mixture of four nitroderivatives as it as two types of replaceable H-atom (1° and 2°) and also it undergoes cracking at high temperature.

## (c) Sulphonation of alkane :

Lower alkanes do not undergo sulphonation easily but higher members (from hexane onward) are sulphonated slowly when treated with fuming acid (oleum) at around 400°C

$$RH + H_2SO_4 \xrightarrow{SO_3} R-SO_3H + H_2O$$

- **Note :** 1. Lower members like propane, butane and pentane etc. react with SO<sub>3</sub> in vapour phase to give corresponding sulphonic acid.
  - 2. Decreasing order of sulphonation of alkane

 $3^{\circ} > 2^{\circ} > 1^{\circ} H$ -atom

3. It s follows free radical mechanism as

 $\begin{array}{l} H_2SO_4 & \stackrel{\Delta}{\longrightarrow} & HO + SO_3H \\ RH + & OH & \longrightarrow R + H_2O \\ R + & HOSO_3H & \longrightarrow R - SO_3H + OH \end{array}$ 

#### (d) Isomerization of alkane :

n-Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas isomerise to branched chain alkanes.

 $\begin{array}{ccc} CH_{3}-CH-(CH_{2})_{2}-CH_{3} & CH_{3}-CH_{2}-CH-CH_{2}-CH_{3} \\ I \\ CH_{3} & CH_{3} \\ 2-methyl pentane \\ \end{array}$  $CH_3(CH_2)_4CH_3$ Anhy. AICl<sub>3</sub> / HCl n-Hexane → 2-methyl pentane 3-methyl pentane

#### (e) **Reaction with steam :**

Methane reacts with steam at 1273 K in the presence of nickel catalyst to form carbon monoxide and dihydrogen.

$$CH_4 + H_2O \xrightarrow{NI} CO + 3H_2$$

(f) Cracking of alkane :

$$C_{6}H_{14} \xrightarrow{773} K \xrightarrow{C_{6}H_{12} + H_{2}} C_{4}H_{8} + C_{2}H_{6} \xrightarrow{C_{6}H_{14} + C_{14}} C_{3}H_{6} + C_{2}H_{4} + CH$$

HBr/

# Section (C) : Free radical addition and substitution in alkenes / alkynes

Free Radical Addition of HBr (Kharash Effect or Peroxide Effect) : (a) Reagents : HBr, Peroxide or sunlight

CH<sub>3</sub>—CH=CH<sub>2</sub><sup>-</sup>

$$\begin{array}{ccc} CH_{3} - CH_{-} CH_{3} \\ I \\ Br \\ R_{2}O_{2}/hv} \\ \end{array} CH_{3} - CH_{2} - CH_{2} - Br \\ \hline R_{2}O_{2}/hv} \\ \end{array}$$
(minor) (major)

Remarks : Anti Markovnikov's Addition; Free radical chain reaction ;

Among all the HX peroxide effect observed with only HBr, not with HF, HCl, HI.

Because HF and HCI are held together by strong electrostatic force. So they can never be broken into free radical. HI will give I' but being larger in size I' (inspite of going to C=C) will combined with another I' to give I<sub>2</sub> molecule. Just because of comparable size.

**Mechanism :** Mechanism of this reaction is completed in following three steps.

(i) Chain initiation step : This reaction is free radical addition reaction in this reaction peroxide undergoes homolytic cleavage to give a free radical from HBr to give Br.

- $(1) R O O R \longrightarrow 2RO^{\bullet}$
- (2)  $RO^{\bullet} + HBr \longrightarrow ROH + Br^{\bullet}$

(ii) Chain propagating step : This Br. will go to either carbon of carbon-carbon double bond of propene to give two type of free radicals.

(i) 1° free radical (ii) 2° free radical Since 2º free radical is more stable then 1º free radical, hence major product is 1-bromopropane. (3) CH<sub>3</sub> - CH = CH<sub>2</sub> + Br → CH<sub>3</sub> - CH - CH<sub>2</sub> - Br + CH<sub>3</sub> - CH - CH<sub>2</sub>1° free radical 2° free radical l Br (minor) (major) (4)  $CH_3 - CH_2 - CH_2 - Br + HBr \longrightarrow CH_3 - CH_2 - CH_2 - Br + Br$ Br repeats step (3).

(iii) Chain termination step :

 $R-O+O-R \longrightarrow R-O-O-R$ 

**Que.** Predict the product for the followings.



# Section (D) : Alkene

### (a) Structure and Bonding :

(1) Alkenes (C<sub>n</sub>H<sub>2n</sub>) are unsaturated hydrocarbons having at least one double bond. Alkenes are also known as olefins.

(2) The  $\pi$  e<sup>-</sup> cloud is present above and below the plane of  $\sigma$ -bonded skeleton.

(3) These are also known as olefins since ethene, the first member of the homologous series forms oily liquid substance when treated with halogens.



**Note** : Bond angle a > b since repulsion due to  $\pi$  electrons (double bond - single bond repulsion > single bond - single bond repulsion according to VSEPR theory).

### (b) Physical Properites of Alkene

(i) From  $C_2$ - $C_4$  they are colourless, odourless gases, from  $C_5$ - $C_{17}$  they are colourless liquids,  $C_{18}$  onwards alkenes are solids.

(ii) Alkenes are practically insoluble in water because they can not form hydrogen bonds with H<sub>2</sub>O molecules. They dissolve freely in organic solvents like benzene, chloroform, CCl<sub>4</sub> petroleum ether., etc. (iii) The boiling and melting points of alkenes are slightly higher than the corresponding alkanes because the intermolecular forces of attraction are stronger due to the presence of easily polarizable  $\pi$  bond. alkenes are therefore, lesser volatile than the corresponding alkanes.

Their boiling points, melting points and specific gravities rise with the increase of molecular weight. The increase in branching in carbon chain decreases the boiling point among isomeric alkenes.

**MP.** and **BP.**  $\propto$  mol. wt.

B.P  $\alpha$  branching in alkenes

# (c) Chemical reactions (Electrophilic addition) of alkene



(3) Addition of H<sub>2</sub>SO<sub>4</sub>.

- (3) Oxymercuration-demercuration
  - (4) Addition of NOCI

**Markovnikoff rule :** The rule states that negative part of the addendum (adding molecule) or acid reagent gets attached to that carbon atom of unsymmetrical alkene (C=C) which possesses lesser number of hydrogen atom.

### Reactivity of an Alkene:

- (1) Presence of electron releasing groups (+M, +I) at C=C increases electrophilicity and reactivity.
- (2) Presence of ERG stabilises the intermediate carbocation.
- (3) More stable  $C^{\oplus}$ , more is reactivity.



Que. Predict the product for the following : -

(i) 
$$\begin{array}{c} & & & \\ & & \\ \hline \\ (ii) \\ (iii) \\ (iii) \\ (iii) \\ CH_3 - CH = CH_2 \xrightarrow{ICl} \\ H_3C \\ H_3C \\ H_3C \\ C = C \\ H \\ C \\ H_4 \\ C \\ H_5 \\ H_6 \\ H_7 \\ H_7$$

Ans.

(v)

(ii) Addition of HOX : "Mechanism-II"

CH<sub>2</sub>CH<sub>3</sub>

 $\label{eq:Reagents} \textbf{Reagents}: \qquad (i) \ X_2 + H_2O \rightarrow HOX + HX \quad or \ (ii) \ HOX \ , \ H^+$ 

CH<sub>2</sub>CH<sub>2</sub>

**Electrophile :** X<sup>+</sup>, Halonium ion :

Remarks : Anti addition ; No rearrangement ;

Threo enantiomers

$$\begin{array}{c} OH \\ | & | \\ -C = C - + HOX \longrightarrow X \end{array}$$

Markovnikoff's addition

### Evidence to support of formation non classical cation :

When addition of Br<sub>2</sub> was carried out in the presence of aq. NaCl, we get 3-products.

(i) 1,2-dibromoethane (ii) 1-Bromo-2-chloroethane (iii) 2-Bromoethanol



Formation of these three products clearly indicates about intermideate (A) thus addition of bromine water over alkene is electrophilic addition reaction.

**Note :** This addition always takes place in trans manner because of bulky nature of bromine atom in bromonium, which is a cyclic bridge intermediate. Cyclic bridge intermediate is non-classical cation.



### (iii) Addition of NOCI :

Reagents : NOCI

Electrophile : NO<sup>+</sup>

Remarks : Anti addition ; No rearrangement ;

Markovnikoff's addition



 $CH_3 - CH = CH_2 \xrightarrow{NOCI}$ 

# (iv) Addition of Hydrogen Halides (HX) : "Mechanism-I"

Reagents : HX (HI > HBr > HCI)

### Electrophile : H+

Remarks : Markovnikoff additon ; Intermediate carbocation ; Rearrangement may take place





Ex.

Above reaction is electrophilic addition reaction hence electrophile will go to that carbon atom of C=C which has more no. of H-atoms.

Since 2º carbocation is more stable, hence major product is 2-bromopropane.

Que. Predict the product for the followings :



(1) Acid-Catalyzed Hydration of Alkenes : "Mechanism-I"

Reagents : Dilute  $H_2SO_4$  or  $H_3O^+$ 

Electrophile : H<sup>+</sup>

**Remarks :** Markovnikoff additon ; Intermediate carbocation ; Rearrangement may take place

$$C = C + H_2O \xrightarrow{H^{\oplus}} H OH$$

(a)  

$$CH_{3} \xrightarrow{C} CH_{3} CH_{2} CH_{3} \xrightarrow{C} CH_{3} CH_{3} CH_{3} \xrightarrow{C} CH_{3} CH_{3} \xrightarrow{C}$$

Ex.

### (2) Oxymercuration-Demercuration : "Mechanism-II"

Reagents : (i) Hg(OAc)<sub>2</sub>, H<sub>2</sub>O (ii) NaBH<sub>4</sub>

Electrophile : HgOAc

Remarks : No rearrangement ; Markovnikoff's addition

Mechanism :

Step-1 : Oxymercuration

$$C = C + H_2O + Hg(CH_3COO)_2 \xrightarrow{\text{THF}} Hg - OCCH_3 + CH_3COH$$

Step-2 : Demercuration



~ . .



Ex.

### (3) Alkoxymercuration - demercuration : "Mechanism-II"



### (4) Hydroboration-oxidation : (Syn addition)

Reagents : (i) BH<sub>3</sub>,THF (ii) H<sub>2</sub>O<sub>2</sub>,-OH

### **Electrophile : Boron**

**Remarks :** Anti Markovnikov's addition, Stereo specific Syn addition.

Less hindered alkene is more reactive.

Reaction proceeds through 4-membered transition state.

### Mechanism :



Ex.

# Section (E) : Alkyne

## (a) Introduction

(1) Alkynes ( $C_nH_{2n-2}$ ) are hydrocarbons that contain carbon-carbon triple bond.

(2) Two  $\pi$  bonds result from overlap of the two remaining unhybridized p orbitals on each carbon atom. These orbitals overlap at **right angles** (90°) to each other, forming one  $\pi$  bond with electron density above and below the C–C sigma bond, and the other with electron density in front and in back of the sigma bond. This result in a cylindrical  $\pi$  electron cloud around  $\sigma$  bonded structure



(3) Any type of stereoisomerism does not arise in acetylenic bond due to linearity of  $C \equiv C$  bond.

(4) Acidic nature of alkynes.



All these reactions are possible with 1-alkyne or acetylene.

# (b) Physical Properties of Alkyne :

(i) Alkynes are colourless, odourless and tasteless.

(ii) Lower alkynes are partially soluble in H<sub>2</sub>O. (It is due to its polarizability)

(iii) Higher alkynes are insoluble in water due to more % of covalent character.

(iv) Completely soluble in organic solvents.

(v) Melting point and boiling point are directly proportional to molecular mass and inversely proportional to number of branches.

(vi) Alkynes upto C<sub>4</sub> are gaseous,  $C_5$ - $C_{11}$  are liquid,  $C_{12}$  & above are solids.

(vii) Order of Solubility, density, B.P., M.P. and Acidic nature : Alkyne > Alkene > Alkane

\* All terminal alkynes are acidic in nature.

# (c) Chemical properties of alkyne :

Mechanism : Electrophilic addition to alkynes

$$\begin{array}{cccc} & & & & & & & & \\ & & & & & \\ \textbf{General Reaction}: & & -\textbf{C} \equiv \textbf{C} - & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & &$$

## (i) Halogenation :

$$\begin{array}{c} Br & Br & Br & Br & Br \\ R-C \equiv C-R & \stackrel{R-C \equiv C-R}{\xrightarrow{r_1}} (Trans-dihalide) & \stackrel{r_2}{\xrightarrow{r_2}} (1eq.) \end{array}$$

Remarks: (1) Reaction is Anti in both step

(2) In above reaction  $r_2 > r_1$ 

(3) Alkyl carbocation is more stable than vinyl carbocation



[a-Haloketone]

 $[\alpha, \alpha$ -Dihaloketone]

90% (major)

 $\xrightarrow{Cl_2/H_2O}_{\text{or}} \xrightarrow{CH_3} - \underset{OH}{C} = CH - CI \xrightarrow{HOCI}_{HOCI} CH_3 - \underset{I}{C} - CHCI_2 \xrightarrow{-H_2O}_{H_2O} CH_3 - \underset{I}{C} - CHCI_2$ Ex. CH<sub>3</sub>–C≡CH

**Remarks:** 

(1) Two molecules of HOX can be added, the end product is  $\alpha$ ,  $\alpha$ -Dihaloketone.

(2) The intermediate product is an enol which gives a minor product  $\alpha$ -haloketone.

#### Addition of Hydrogen Halides (HX) : (iii)





### **Remarks :**

- (1) Markovnikov's Addition in both steps.
- (2) If two moles of HX are added the final product is Gemdihalide.
- (3) Electrophilic addition to terminal alkyne is regioselective.

## (iv) Addition of H<sub>2</sub>O (Hydration Reaction) :

### (1) Mercuric ion catalyzed hydration :



**Note:** By above reaction it is clear that carbonyl carbon is formed from that carbon of ' $C \equiv C$ ' over which nucleophile water attacks.

Ex. (i)  $CH_2 - C \equiv CH$   $CH_2 - CH_2 - CH_0$ (ii) CI  $Hg^{++}/H_2SO_4$  CI  $CH_2 - CH_0$ (iii)  $CH_2 - CH_0$   $Hg^{++}/H_2SO_4$   $CH_2 - CH_0$   $Hg^{++}/H_2SO_4$   $CH_3 - CH_3$ (iii)  $CH_3 - CH_3$   $CH_3 - CH_3$ (iii)  $CH_3 - CH_3$   $CH_3 - CH_3$ 

### Remarks :

(1) Alkynes add one molecule of water.

- (2) The product enol tautomerises to a carbonyl compound (aldehyde or ketone) and further addition does not take place.
- (3) The reaction is catalysed by  $Hg^{+2}$  ions.
- (4) The product is Markownikoff Addition of water.
- (5) If hydroboration method is used, then Anti Markownikoff addition of water takes place.

**Important :** The product does not appears to be addition product.

### (2) Hydroboration Oxidation of Alkynes :

It is used to get aldehyde from terminal alkyne.

$$R - C = C - H \xrightarrow{Hg^{+2}/H_2SO_4} R - C - CH_3$$

$$Hydroboration R - CH_2 - CH = O$$

$$3 R - C = C - H + BH_3 \xrightarrow{(R - CH = CH)_3} B. \xrightarrow{CH_3 - COOD} R - CH = CH - D$$

$$(trialkenyl borane)$$

$$CH_3 - COOH / J 3H_2O_2, \overline{OH}$$

$$R - CH = CH_2 \quad 3R - CH = CH - OH$$

$$(i) \qquad R - CH_2 - CH = O$$

(ii) 
$$H-C\equiv C-H \xrightarrow{HCI+Hg^{+2}} CH_2 = CH-CI \xrightarrow{HCI} CH_3 - CHCI_2$$
  
(Vinyl chloride) (ethylidene chloride)  
 $CH_3 - CHO \xleftarrow{-H_2O} CH_3 - CH \xleftarrow{OH}_{OH} H_2O$ 

## (v) Other reactions of Alkynes :

Que.1 Convert acetylene into Neoprene, Polybutadiene, Buna-S and Buna-N.

$$CH=CH \xrightarrow{\text{aq. NH}_{4}Cl}_{Cu_{2}Cl_{2}} \xrightarrow{CH_{2}=CH-C=CH} \xrightarrow{1eq. HCl}_{CH_{2}=CH-C=CH_{2}} \xrightarrow{Polymerises} \text{Neoprene}$$

$$vinyl acetylene \qquad Cl \\ chloroprene \\ Lindlar's catalyst \\ CH_{2}=CH-CH=CH_{2} \xrightarrow{Ph-CH=CH_{2}}_{Polymerisation} \text{Buna-S-rubber}$$

$$CH_{2}=CH-CH=CH_{2} \xrightarrow{Ph-CH=CH_{2}}_{Polymerisation} \text{Buna-S-rubber}$$

$$CH=CH \xrightarrow{HCN}_{Ba(CN)_{2}} \xrightarrow{CH_{2}=C-C=N}_{Acrylonitrile} \xrightarrow{Polymer}_{Acrylonitrile} \text{Polymerisation}$$

Ans.

War gas is musturd gas which is obtained from ethylene as :





Ans.

Que.3 Write apropriate interconversion reaction of the following  $H-C\equiv C-H \rightarrow (i)$  meso-2,3-dibromobutane (ii) dl-butane-2, 3- diol  $HC \equiv CH$ 

Excess of NaNH,



Ans.

### **Organic Reaction Mechanisms - II**



Que.4

Ans.

# Section (F) : Conjugate addition in Alkadienes

$$\begin{array}{c} HCI \\ HCI \\ CH_2=CH-CH=CH_2 \\ HCI \\$$

Que. Give the equation for the reaction of one equivalent of HBr with Pent -1-en-4-yne

$$H_{2}C=CHCH_{2}C\equiv CH \xrightarrow{H^{+}} H_{3}C \xrightarrow{\oplus} H_{2}C \equiv CH \xrightarrow{Br^{-}} H_{3}CCHBrCH_{2}C \equiv CH$$
$$\xrightarrow{H^{+}} H_{2}C=CHCH_{2}C=CH_{2} \text{ (no reaction)}$$

This reaction proceeds through a carbocation. Since the alkyl carbocation from the alkene group is more stable than the vinyl carbocation from the alkyne group.