3RD SEM COMPLEMENTARY CHEMISTRY

CALICUT UNIVERSITY

ORGANIC CHEMISTRY

2017 ADMISSION

Prepared by

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Chemistry

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SEMESTER III
Course Code: CHE3C03
Complementary Course III: ORGANIC CHEMISTRY

Total Hours: 48; Credits: 2; Hours/Week: 3; Total Marks 75 (Internal 15 & External 60)

Objective:

- To provide the students a thorough knowledge about basic theory and concepts of organic chemistry.

Syllabus:

Module I: Organic Chemistry – Some Basic Concepts (10 hrs)

Introduction: Homolysis and heterolysis of bonds – Electrophiles and nucleophiles.
Reaction Intermediates: Carbocations, carbanions and free radicals (types, hybridization and stability).
Types of organic reactions: Addition,elimination,substitution and rearrangement reactions(definition and one example each)
Electron Displacement Effects: Inductive effect: Definition – Characteristics - +I and –I groups.
Applications: Explanation of substituent effect on the acidity of aliphatic carboxylic acids.
Mesomeric effect: Definition – Characteristics - +M and –M groups. Applications: Comparison of electron density in benzene, nitrobenzene and aniline. Hyperconjugation: Definition – Characteristics. Example: Propene.
Applications: Comparison of stability of 1-butene & 2-butene. Electromeric effect: Definition – Characteristics - +E effect (addition of H^+ to 86isulp) and –E effect (addition of CN^- to acetaldehyde). Steric effect (causes and simple examples).

References

1. Peter Sykes, *A Guide book to Mechanism in Organic Chemistry*, 6th Edn., Pearson Education.
2. P. S. Kalsi, *Organic Reactions and their Mechanisms*, New Age International Publishers.
3. K. S. Tewari, N. K. Vishnoi, *Organic Chemistry*, 3rd Edn., Vikas Publishing House.
4. M. K. Jain, S.C. Sharma, *Modern Organic Chemistry*, 3rd Edn., Vishal Publishing Company Co.
5. R. T. Morrison, R. N. Boyd, *Organic Chemistry*, 6th Edn., Prentice Hall of India.
6. I. L. Finar, *Organic Chemistry*, 6th Edn., Vol.- I, Pearson.

Module II: Stereochemistry (6 hrs)

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Conformations: Conformations of ethane, cyclohexane and methylcyclohexane – Explanation of stability.
Geometrical Isomerism: Definition – Condition – Geometrical isomerism in but-2-ene and but-2-ene-1,4-dioic acid – Methods of distinguishing geometrical isomers using melting point and dipole moment.
Optical Isomerism: Optical activity – Chirality – Enantiomers – Meso compounds – Diastereoisomers – Optical isomerism in lactic acid and tartaric acid.

References

1. R. T. Morrison, R. N. Boyd, *Organic Chemistry*, 6th Edn., Prentice Hall of India.
2. I. L. Finar, *Organic Chemistry* – Vol. 1, 6th Edn., Pearson Education.
3. M. K. Jain, S. C. Sharma, *Modern Organic Chemistry*, 3rd Edn., Vishal Publishing Company Co.
4. K. S. Tewari, N. K. Vishnoi, *Organic Chemistry*, 3rd Edn., Vikas Publishing House.

Module III: Aromatic Hydrocarbons (5 hrs)

Nomenclature and isomerism in substituted benzene. Structure and stability of benzene:

Kekule, resonance and molecular orbital description.
Mechanism of aromatic electrophilic substitution: Halogenation, nitration, sulphonation and Friedel- Craft's reactions – Orientation effect of substituents.
Aromaticity and Huckel's rule: Application to benzenoid (benzene, naphthalene and anthracene) and nonbenzenoid (pyrrole, pyridine and indol) aromatic compounds.

References

1. R. T. Morrison, R. N Boyd, *Organic Chemistry*, 6th Edn., Prentice Hall of India.
2. I. L. Finar, *Organic Chemistry* – Vol.1, 6th Edn., Pearson Education.
3. M. K. Jain, S. C. Sharma, *Modern Organic Chemistry*, 3rd Edn., Vishal Publishing Company Co.
4. K. S. Tewari, N. K. Vishnoi, *Organic Chemistry*, 3rd Edn., Vikas Publishing House.

Module IV: Chemistry of Functional Groups – I (8 hrs)

Halogen Compounds: Preparation of alkyl halides from alkanes and alkenes – Wurtz reaction and Fittig's reaction – Mechanism of S_N1 and S_N2 reactions of alkyl halides – Effect of substrate and stereochemistry.
Alcohols: Preparation from Grignard reagent – Preparation of ethanol from molasses – Wash, rectified spirit, absolute alcohol, denatured spirit, proof spirit and power alcohol (mention only) – Comparison of acidity of ethanol, isopropyl alcohol and *tert*-butyl alcohol – Haloform reaction and iodoform test – Luca's test – Chemistry of methanol poisoning – Harmful effects of ethanol in the human body.
Phenols: Preparation from chlorobenzene – Comparison of acidity of phenol, *p*-nitrophenol and *p*-methoxyphenol – Preparation and uses of phenolphthalein.

Module V: Chemistry of Functional Groups – II (8 hrs)

88
Aldehydes & Ketones: Preparation from alcohols – Nucleophilic addition reactions (HCN and 88isulphate) – Comparison of nucleophilic addition rate of aliphatic aldehydes and ketones.
Carboxylic Acids: Preparation from Grignard reagent – Decarboxylation – Kolbe electrolysis.
Amines: Preparation from nitro compounds – Hofmann's bromamide reaction – Hofmann's carbylamines reaction. Basicity: Comparison of basicity of ammonia, methyl amine and aniline
Diazonium Salts: Preparation and synthetic applications of benzene diazonium chloride – Preparation and uses of methyl orange.

References

1. R. T. Morrison, R. N Boyd, *Organic Chemistry*, 6th Edn., Prentice Hall of India.
2. I. L. Finar, *Organic Chemistry* – Vol.1, 6th Edn., Pearson Education.
3. M. K. Jain, S. C. Sharma, *Modern Organic Chemistry*, 3rd Edn., Vishal Publishing Company Co.
4. K. S. Tewari, N. K. Vishnoi, *Organic Chemistry*, 3rd Edn., Vikas Publishing House.

Module VI: Biomolecules (8 hrs)

*Carbohydrates: C*lassification with examples-cyclic structures of glucose and fructose-Applications of carbohydrates
Proteins: Amino acids – Classification – Zwitter ion formation – Peptide linkage – Polypeptides and proteins – Primary, secondary and tertiary structure of proteins – Globular and fibrous proteins – Denaturation of proteins.
Enzymes: Characteristics and examples.
Nucleic acids: Structure of pentose sugar, nitrogenous base, nucleoside and nucleotide – Double-helical structure of DNA – Difference between DNA and RNA – DNA fingerprinting and its applications.

References

1. R. T. Morrison, R. N Boyd, *Organic Chemistry*, 6th Edn., Prentice Hall of India.

2. I. L. Finar, *Organic Chemistry* – Vol.1, 6th Edn., Pearson Education.
3. M. K. Jain, S. C. Sharma, *Modern Organic Chemistry*, 3rd Edn., Vishal Publishing Company Co.
4. K. S. Tewari, N. K. Vishnoi, *Organic Chemistry*, 3rd Edn., Vikas Publishing House.

Moldule VII: Alkaloids and Terpenes (3 hrs)

Alkaloids: Classification – Source, structure and physiological functions of nicotine, coniine and piperine.

Terpenes: Classification with examples – Isoprene rule – Isolation of essential oils by steam distillation – Uses of lemongrass oil, eucalyptus oil and sandalwood oil – Source, structure and uses of citral and menthol – Natural rubber – Vulcanization and its advantages.

Note: Structural elucidation not expected in any case.

References

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1. R. T. Morrison, R. N Boyd, *Organic Chemistry*, 6th Edn., Prentice Hall of India.
2. I. L. Finar, *Organic Chemistry* – Vol.1, 6th Edn., Pearson Education.
3. M. K. Jain, S. C. Sharma, *Modern Organic Chemistry*, 3rd Edn., Vishal Publishing Company Co.
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MODULE -1-ORGANIC CHEMISTRY- SOME BASIC CONCEPTS

INTRODUCTION

- Organic chemistry is the chemistry of carbon compounds.

- Carbon atom have a tendency to form bonds between its own atoms to form long chains. This property is called catenation.

- Carbon atoms can form strong covalent bonds with other elements such as H,O,N,S and halogens .

FUNDAMENTAL CONCEPTS OF ORGANIC REACTION MECHANISMS

- In an organic reaction, the organic molecule(substrate) reacts with an attacking reagent which leads to the formation of an intermediate and finally products.

- Curved arrow indicates the movement of electrons, not the movement of atoms.

- Full arrowhead indicates the movement of two electrons simultaneously and half -headed arrow represent the movement of single electron.

TYPES OF BOND FISSION

- Two types: Homolytic fission and heterolytic fission.

- When a covalent bond breaks in a symmetrical manner such that each fragment retains an unpaired electron, the process is called homolytic fission or homolysis

- When a covalent bond breaks in an unsymmetrical manner such that one of the fragments retains both the bonding electrons, the process is called heterolytic bond fission or heterolysis.

TYPES OF REAGENTS

- Three types- Electrophiles, Nucleophiles and free radicals

- ***Electrophiles***- They are electron deficient and can accept an electron pair in a reaction. They are lewis acids which are positively charged or neutral species.

  Eg: H^+, Cl^+, Br^+,NO_2^+,BF_3,$AlCl_3$ etc

  Electrophilic reactions are the reactions in which attacking reagent is electrophile.

- ***Nucleophiles***- They are electron rich having lone pair of electrons. They are lewis bases which may be negatively charged ions or neutral molecules having lone pairs.

  Eg: OH^- , H_2N^- ,R^-, NH_3, H_2O etc.

Nucleophilic reactions are the reactions in which attacking reagent is nucleophile.

- ***Free radicals***- They are neutral species with unpaired electrons. Highly reactive and is formed by homolytic fission.

  Eg: $Cl^{\bullet}$, $CH_3^{\bullet}$, $C_6H_5^{\bullet}$ Etc.

  Free radical reactions are the reactions in which attacking reagent is free radical.

ELECTRON DISPLACEMENT EFFECTS

- Refers to displacement of bonding electrons.
- Electron displacement effect may be permanent or temporary.
- Different electron displacement effects are:
  1. Inductive effect
  2. Electromeric effect
  3. Mesomeric effect
  4. Hyperconjugation
  5. Steric effect

INDUCTIVE EFFECT

- The polarization of a sigma bond due to electron withdrawing or electron donating effect of adjacent groups or atoms is called inductive effect or **I** effect.
- It is a permanent electron displacement effect.
- Two types- **+I** and **-I** effect
- **-I EFFECT-** The polarization of sigma bond due to the presence of electron withdrawing groups.

C—>—X

- Electron withdrawing group showing -I effect are

  NO2 > CN > COOH > F > Cl > Br > I > OCH3

- **+I EFFECT-** The polarization of sigma bond due to the presence of electron donating groups.

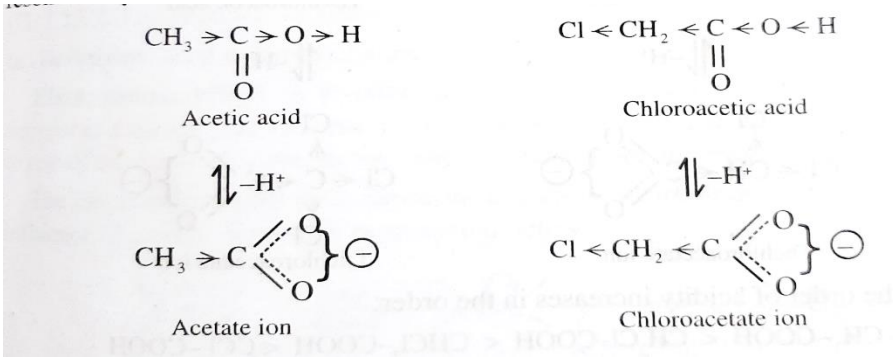
C—<— Y

- Electron donating groups showing +I effect are

  $(CH_3)_3C > (CH_3)_2CH > CH_3CH_2 > CH_3$

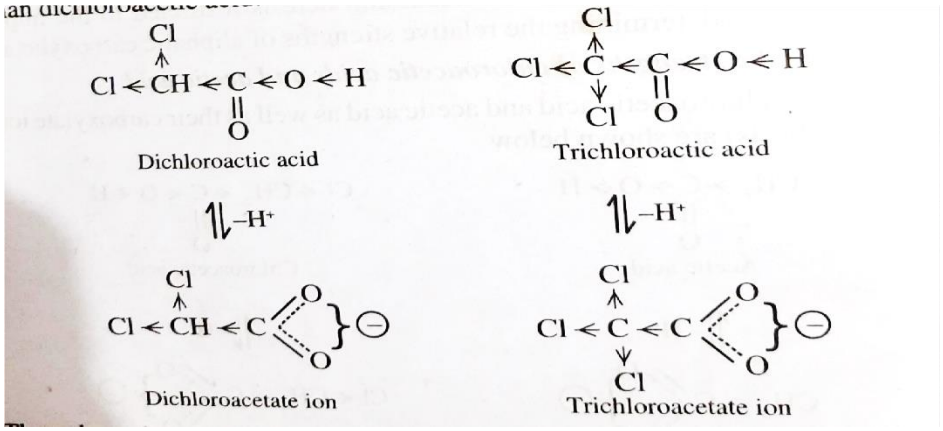
EFFECTS OF SUBSTITUENTS ON ACIDITY OF ALIPHATIC CARBOXYLIC ACIDS

1. Relative acid strengths of chloroacetic acids and acetic acid.



Chloroacetic acid is stronger than acetic acid. Because in chloroacetic acid **-I** effect of Cl group decreases electron density around carboxyl hydrogen. Also because of the dispersal of negative charge on the carboxylate ion, the ion is stabilized than acid. In acetic acid due to the +I effect of CH3 group acidity decreases.

- Comparison of acid strength of dichloroacetic acid and trichloroacetic acid.



Since there are three Cl groups in trichloroacetic acid, -I effect would be more than in dichloroacetic acid. So acid strength of trichloroacetic acid is greater.

- As Acid strength increases PKa value decreases.

2. Relative acid strength of formic acid, acetic acid and propanoic acid.

H-COOH > CH_3-COOH > CH_3-CH_2-COOH

Propanoic acid is least acidic due to the +I effect of CH2-CH3 group. Acetic acid is comparatively stronger and the strongest acid is formic acid.

3. Relative acid strength of fluoroacetic acid, chloroacetic acid, bromoacetic acid and iodoacetic acid.

$F\text{-}CH_2COOH > Cl\text{-}CH_2COOH > Br\text{-}CH_2COOH > I\text{-}CH_2COOH$

This is because the electronegativity order of halogens are

$F > Cl > Br > I$

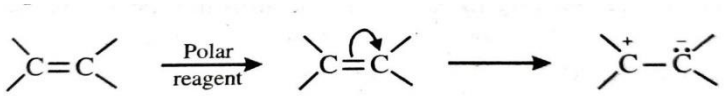
4. Relative acid strength of 2-chloropropanoic acid and 3- chloropropanoic acid

$CH_3\text{-}CHCl\text{-}COOH > ClCH_2\text{-}CH_2\text{-}COOH$

This is because the intensity of inductive effect decreases with increasing distance of electron withdrawing substituents.

ELECTROMERIC EFFECT:

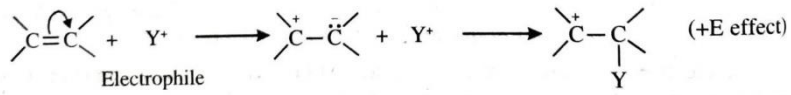
1. Temporary effect involving the complete transfer of a shared pair of pi- electrons of a multiple bond to one of the bonded atoms, in the presence of an attacking reagent.



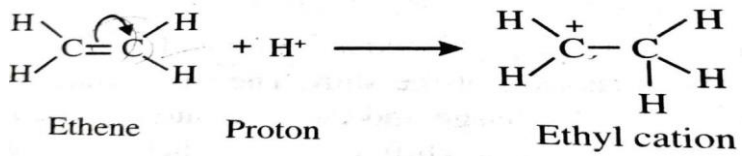
Types:

i. Positive Electromeric effect (+E effect)

- In +E effect, the Electromeric shift of pi- electrons of a multiple bond is towards that atom to which reagent gets attached.

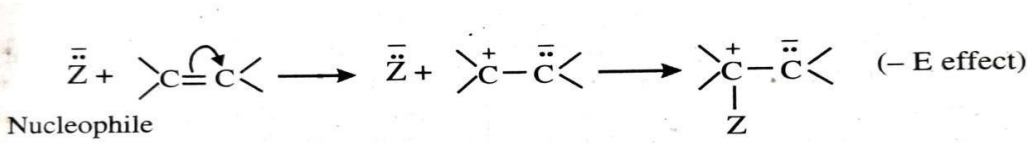


- Eg: Addition of H+ to ethene

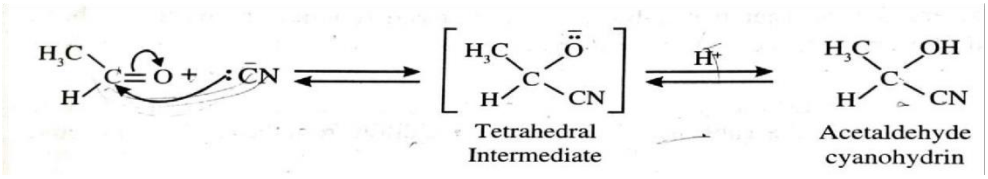


ii. Negative Electromeric effect (- E effect)

- In -E effect, the Electromeric shift of pi- electrons of a multiple bond is away from that atom to which the reagent gets attached.



Eg: Nucleophilic attack of CN- on acetaldehyde



Distinction between Inductive and Electromeric effect

Inductive effect	**Electrometric effect**
1. It refers to partial displacement of sigma electrons.	1. It refers to complete transfer of pi-electrons of a multiple bond
2. Permanent effect	2.Temporary effect
3. It requires the presence of polar bond in molecule.	3 . It requires the presence of an attacking reagent.
4. It involves partial charge separation.	4 . It involves complete charge separation.

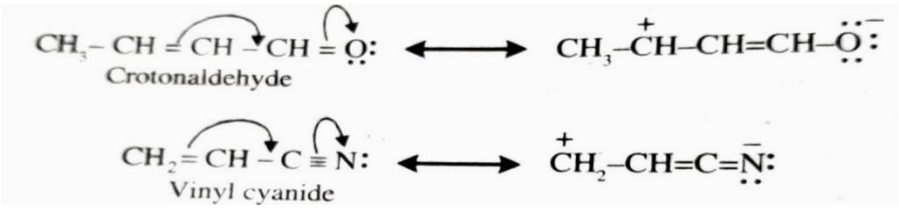
MESOMERIC / RESONANCE EFFECT

• The polarity induced in a molecule by the interaction of two pi- bonds or between a pi-bond and lone pair of electrons present

Types Of mesomeric effect

1. **-R or -M effect:**

Groups like C=O, NO2, COOH When present adjacent to conjugated multiple bonds ,bring resonance by withdrawing pi-electrons of multiple bond thereby causing electron displacement towards themselves . The effect produced is called -R/-M effect. Eg:

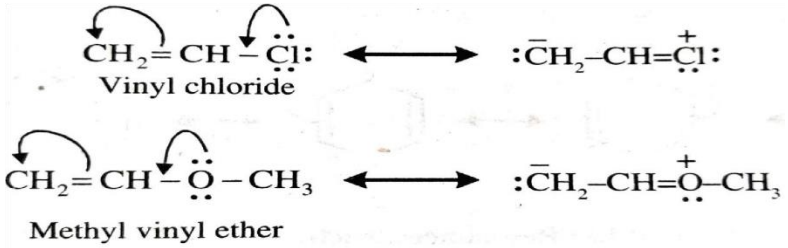


2. +R or +M effect:

Groups like OH, OR, SR etc with one or more lone pairs whenpresent adjacent to multiple bond, bring resonance by releasing electrons in the direction of multiple bond thereby causing electron displacement away from themselves.

The effect produced is called +R/+M effect.

Eg:

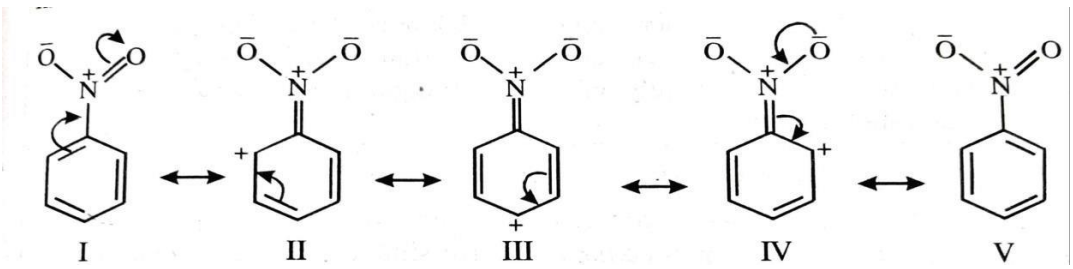


Applications

- **Comparison of electron density of benzene, nitrobenzene and aniline:**

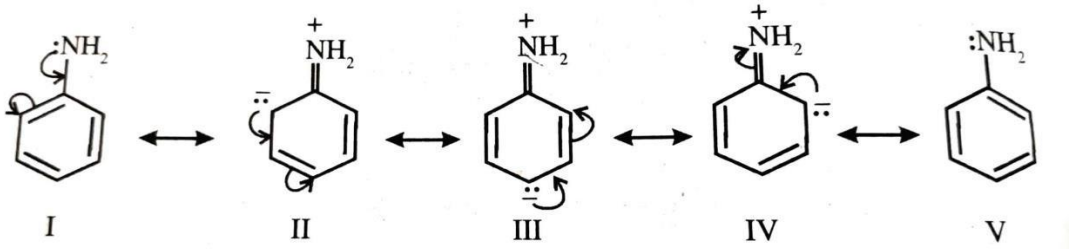
The pi electrons of benzene ring are uniformly delocalized. They are easily attacked by electrophiles. However, substituted benzene show +M or -M effect. The substituents can either donate or withdraw electron density from ring.

Nitrobenzene:



NO2 is a group which shows – M effect. They make the benzene ring less reactive towards electrophilic substitution reactions by withdrawing electrons from the ring by resonance. Such groups are called deactivating groups or substituents.

Aniline



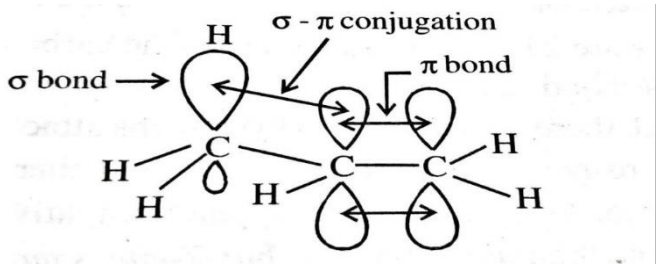
NH2 is a group which shows +M effect. They make the benzene ring more reactive towards electrophilic substitution reactions by donating electrons to the ring by resonance. Such groups are called activating groups or substituents.

HYPERCONJUGATION

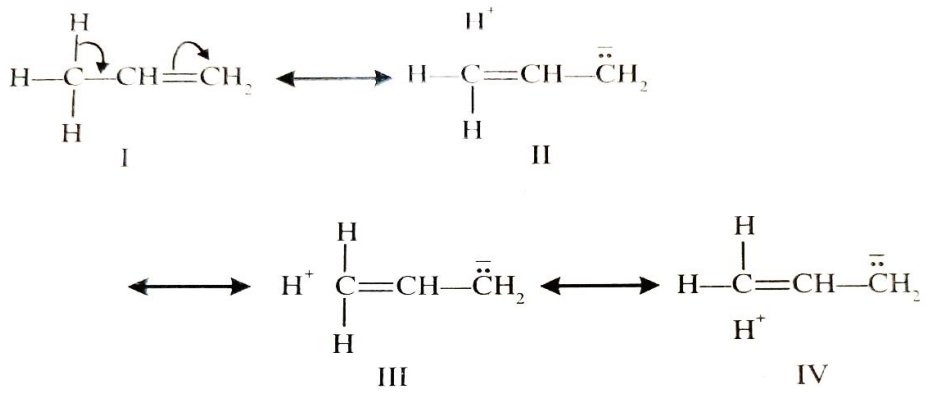
- Delocalization of electrons by the overlap of a sigma bond orbital with a pi- or p-orbital is called hyperconjugation.
- Hyperconjugation is a stabilizing interaction as it brings about lowering of energy.
- Eg: Hyperconjugation in propylene (propene).

CH3-CH=CH2

Propene



In propene,CH3 group is attached to C=C that has a pi- bond. The sigma orbital of C-H bonds of CH3 is in conjugation with pi orbital of double bond. Hyperconjugation in propene can be represented in terms of resonance as follows:



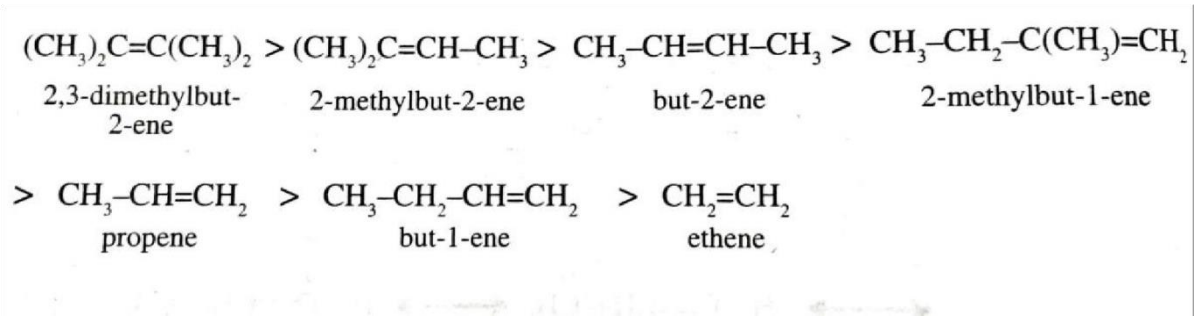
- Hyperconjugation is also called **no-bond resonance** since there is no real bond between Carbon and Hydrogen in hyperconjugative structures. But the H+ ion is bound firmly to pi bond and is not free to move.

- Comparison of stability of But-1-ene and But-2-ene.

In But-1-ene, there are two hydrogen atoms attached to alpha carbon atom.

Hence, two hyperconjugative interactions are possible. In But-2-ene, there are 6 hydrogens attached to alpha carbon atom and 6 hyperconjugative interactions are possible. As the number of hyperconjugative structures are greater for But-2-ene, it is more stable.

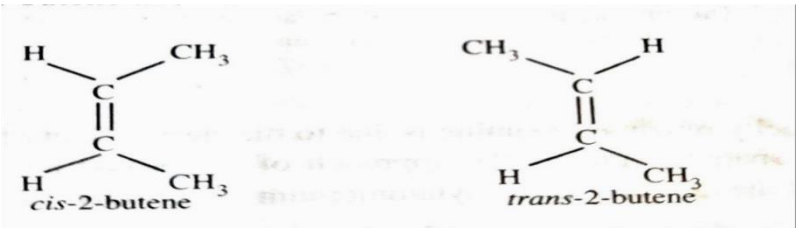
- The decreasing order of stability of alkenes in terms of Hyperconjugation.



STERIC EFFECT

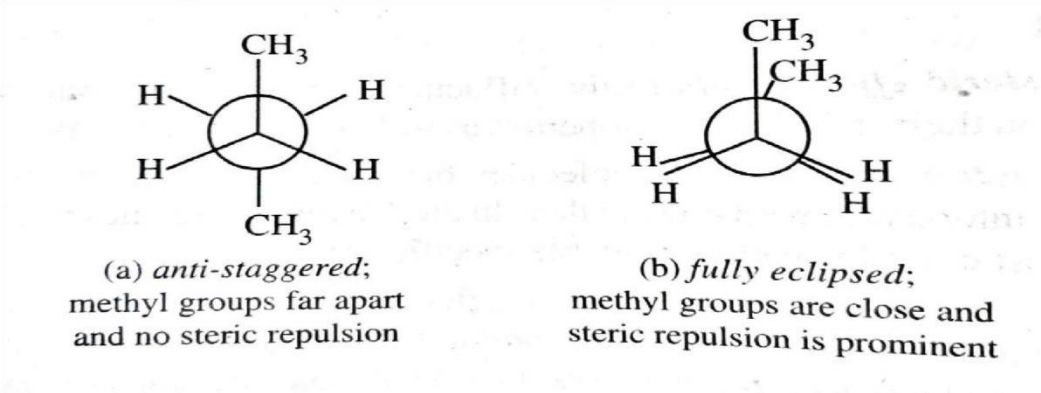
- Steric effect refers to the spatial interaction which arises due to the spatial crowding of bulky groups in a molecule.
- They affect the stability of the molecule as the groups do not get enough space for their accommodation and also there occurs repulsion between them.
- They also obstruct the approach of attacking reagents.

- Eg: a)stability of cis-2- butene and trans-2-butene



In cis-2-butene, the two bulky methyl groups are on the same side of double bond. They are close to each other and cause spatial crowding. In trans-2-butene,the two groups are on the opposite side of double bond and there is no crowding. So, cis-2-butene is less stable.

a) stability of conformations of butane



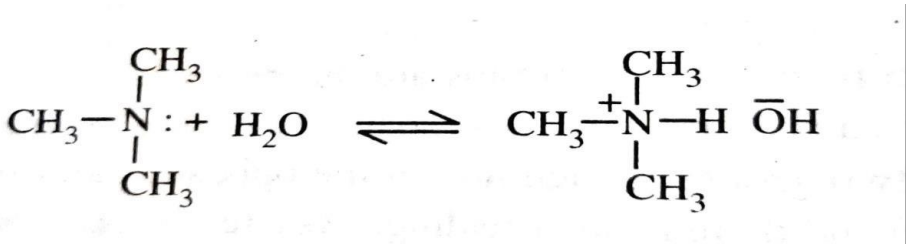
Anti- staggered conformation of butane is more stable since the two methyl groups are far away from each other. In fully eclipsed conformation, the two methyl groups are near to each other. Hence it is least stable.

C) The order of basicity of methyl amine (1º amine), dimethyl amine (2º amine) and trimethylamine (3ºamine).

$(CH_3)_2NH$	>	CH_3NH_2	>	$(CH_3)_3N$
Dimethylamine		Methylamine		Trimethylamine
(2º amine)		(1º amine)		(3º amine)
3.13		3.37		4.22

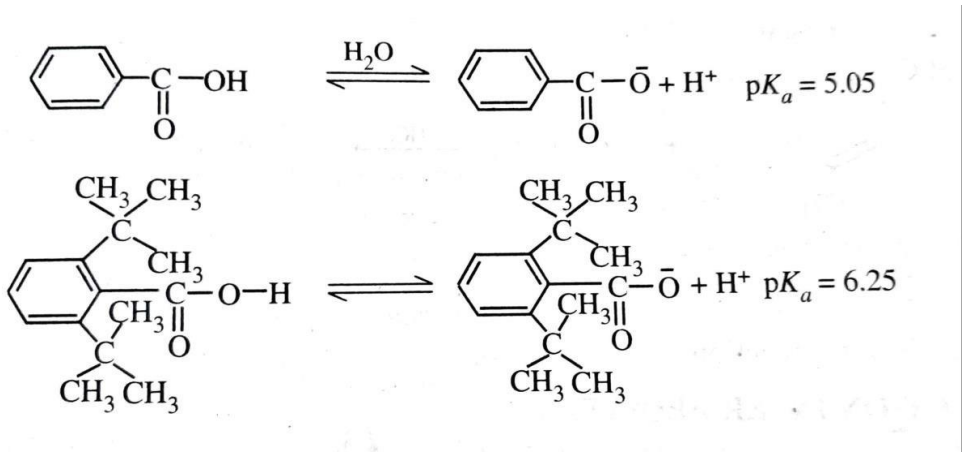
In terms of Inductive effect, we would expect trimethylamine is more basic than dimethylamine or methylamine because an increase in number of methyl groups increase the electron availability at Nitrogen atom. However, the order of basicity of the above amines in aqueous solution is as follows

The lower basicity of trimethylamine is due to steric effect of the three methyl groups which hinders the approach of the proton and also hinders the stabilization of resulting trimethylammonium ion through solvation.



d) Effect of bulky groups at the ortho- position of carboxylic acids.

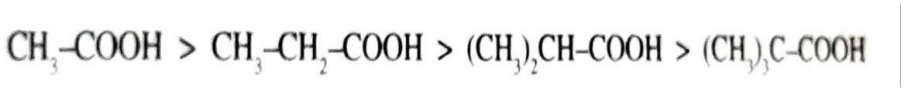
Acidity of carboxylic acid is decreased by the presence of bulky groups as they cause steric hindrance to the solvation of carboxylate ion through solvation.



e) Steric effect in esterification reactions:

Esterification reaction:

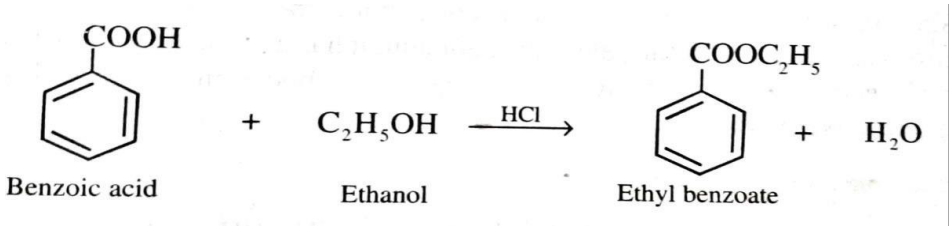
Acid + Alcohol----------→ Ester + water

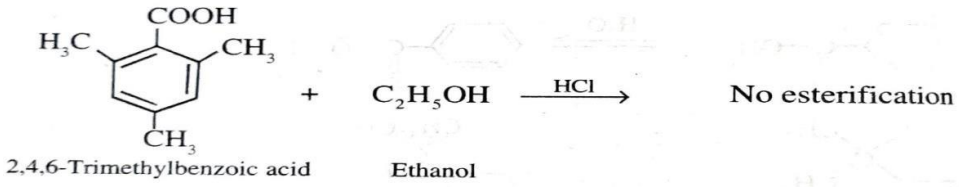


- The rate of esterification decreases in the order

The decrease in rate of esterification is due to steric effect on acids which hinders the approach of alcohol to reaction site on acids.

- Benzoic acid is esterified easily than 2,4,6-trimethylbenzoic acid. This is because the two methyl groups sterically hinder the approach of alcohol.





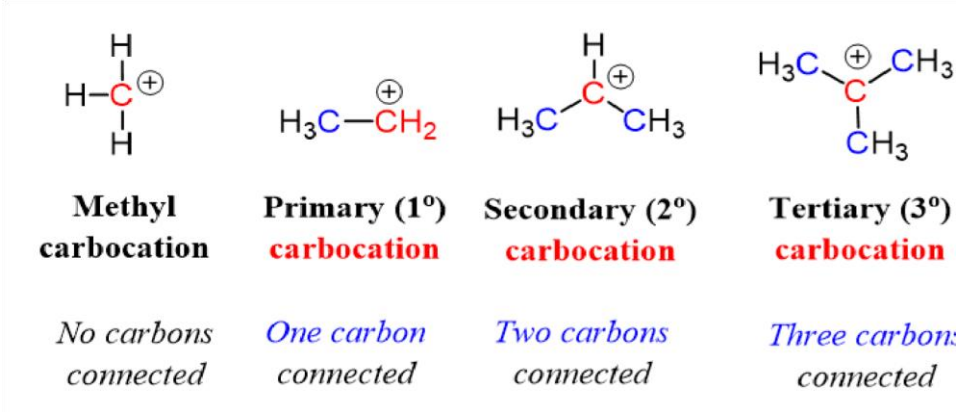
REACTION INTERMEDIATES

- The intermediate species formed during the stepwise progress of a reaction to reach its preferred products are called reaction intermediates.
- They are short-lived, high energy and highly reactive molecules.
- They may be cations, anions or neutral species with one or more unpaired electrons.
- Eg: carbocations, carbanions, free radicals etc

CARBOCATIONS

- Carbon bearing a positive charge is called carbocation.
- Carbocation has only six valence electrons.
- Electron deficient species.

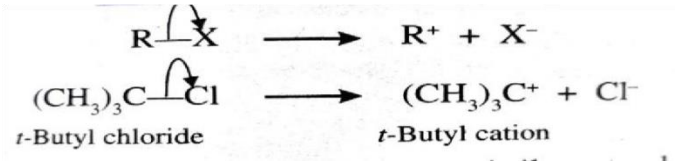
- Types :



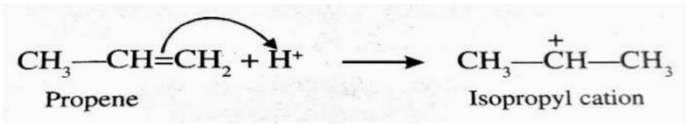
Formation of carbocations

- Formed by heterolytic cleavage of covalent bonds.

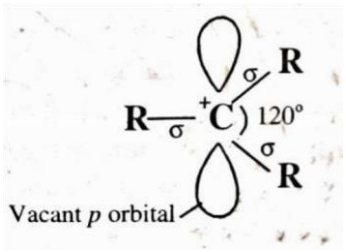
Eg: 1. Ionization of alkyl halide in polar solvents.



2. Protonation of alkenes.



Hybridisation and structure



- Cabon atom in a cabocation is sp^2 hybridized.
- The three sp^2 hybrid orbitals form σ-bonds with three groups or atoms.
- One vacant p-orbital remain unhybridised and lies perpendicular to the plane.
- Carbocation has trigonal planar shape with bond angle 120°.

Stability

- Any factor that disperse the positive charge on the carbon stabilize the carbocation whereas any factor that intensify the positive charge on the carbon destabilize the carbocation.
- Electron-donating groups attached to the carbocation decrease the positive charge on carbon thereby stabilizing them. Electron-withdrawing groups attached to carbocation intensify the positive charge on carbon thereby destabilizing them.

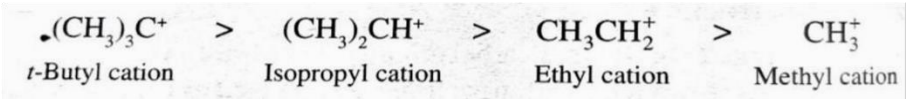
Examples:

(a)*Stability of alkyl cations.*

- The order of stability of alkyl cations is

  Tertiary > secondary > primary > methyl

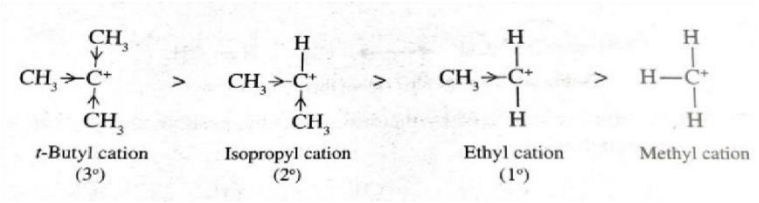
  Eg:



The order can be explained by inductive effect and hyperconjugation effect

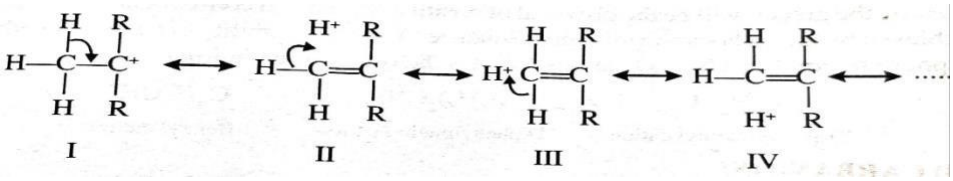
Inductive effect

- Alkyl groups show +I effect. They releases electrons in the direction of positive charge thereby dispersing the positive charge. Thus,the carbocation gets stabilized. Greater the number of alkyl groups attached to positive carbon, greater would be the charge dispersal and greater would be the stability of carbocation.



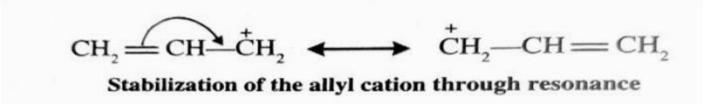
Hyperconjugation effect:

- Carbocation is sp^2 hybridized. It has a vacant unhybridized p-orbital. σ –p hyperconjugation is possible. Greater the number of α-hydrogens attached to positive carbon, greater will be the number of hyperconjugative structures and greater would be stability. Tertiary has greater number of σ hydrogens, then secondary,primary. Methyl carbocation has no α-hydrogens. Thus stability of carbocations are in the order 3°>2°>1°

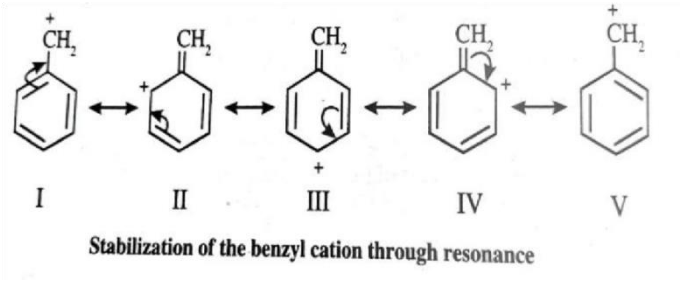


(b) Stability of unsaturated carbocations and carbocations with phenyl rings:

- Allyl carbocation disperses positive charge by resonance and thereby stabilizes it.



- Benzyl cation disperses positive charge by resonance and thereby stabilizes it.



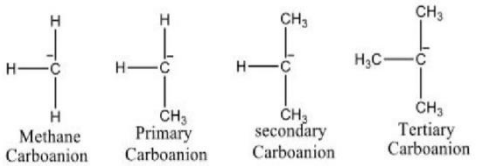
Stabilization of the benzyl cation through resonance

- Greater the number of phenyl groups attached to the positively charged carbon, greater will be the number of resonance structures,greater will the dispersal of positive charge and greater will be the stability.

CARBANIONS

- Carbon bearing a negative charge is called carbanion.
- They have 8 valence electrons around carbon atom.
- Electron rich species.
- They are nuleophiles and Lewis bases**.**

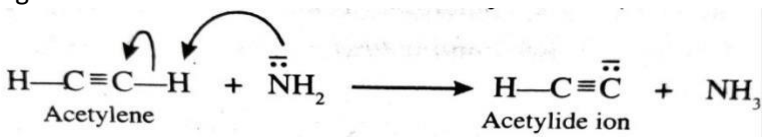
Classification



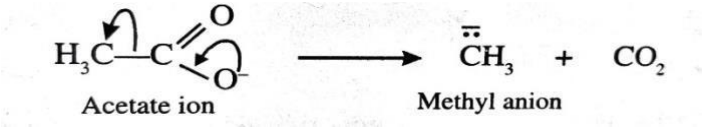
Formation of cabanions:

1. By heterolytic fission of a bond.

Eg:

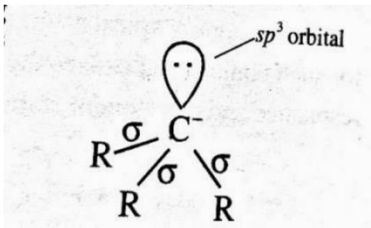


2. By the decomposition of carboxylate ion .



3. By the decomposition of organometallic compounds .

Hybridization and structure



- Carbon atom in a carbanion is sp^3 hybridized.
- Out of the four sp^3 hybrid orbitals, three of them form σ- bonds with three groups or atoms and remaining one contains unshared electron pair.
- Carbanion has pyramidal shape with bond angle between 97° and 100°.

Stability

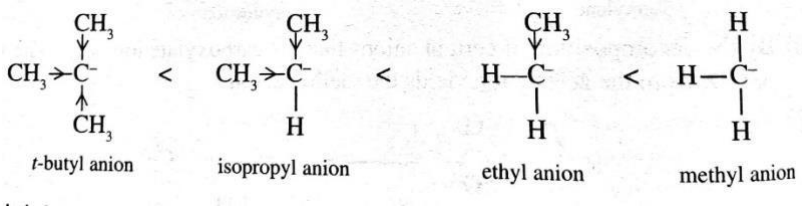
- Any factor that disperse the negative charge on the carbon stabilize the carbanion where as any factor that intensify the negative charge on the carbon destabilize the carbanion.
- Electron-donating groups attached to the carbanion increases the negative charge on carbon thereby destabilizing them. Electron-withdrawing groups attached to carbanion disperse the negative charge on the carbon thereby stabilizing them. Examples:

(a)Stability of alkyl carbanions

- The order of stability of alkyl carbanions is
  Methyl > primary > secondary > tertiary
  Eg:

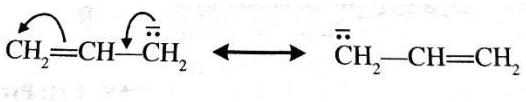
$$CH_3^- > CH_3CH_2^- > (CH_3)_2CH^- > (CH_3)_3C^-$$

The order can be explained on the basis of Inductive effect. Alkyl groups show +I effect. They releases electron in the direction of negative charge thereby intensifying the negative charge on carbon. Greater the number of alkyl groups attached to the negative carbon, greater the intensification of negative charge on carbon and lower is its stability.



b)Stability of unsaturated carbanions

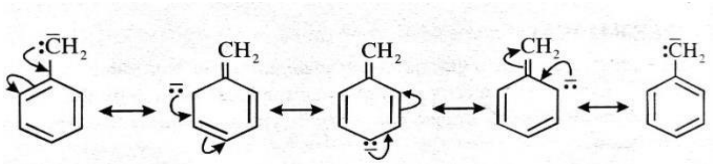
- Allyl carbanion disperses negative charge by resonance and thereby stabilize them.



Resonance stabilization of the allyl anion

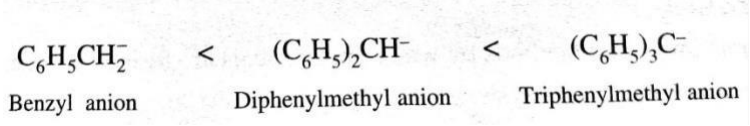
stability of benzyl carbanion

- The negative charge on benzyl carbanion can enter into conjugation with phenyl ring, causing delocalization of negative charge and greater stability.



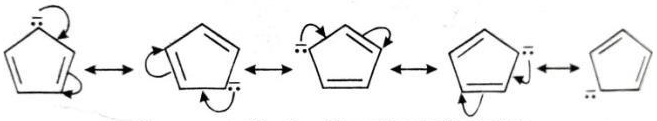
Resonance stabilization of the benzyl anion

- Greater the number of phenyl groups attatched to the negative carbon,greater will be the dispersal of negative charge and more stable would be the carbanion.



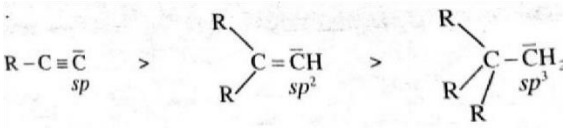
stability of cyclopentadienyl anion

- The cyclopentadienyl anion is a six π- electron system and is aromatic. The six π-electrons are completely delocalized over the pentagonal ring bringing stability to the anion through resonance.



Resonance stabilization of the cyclopentadienyl anion

- As the s-character of carbon increases, the electrons are more attracted to the nucleus thereby lowering energy . the order of stability is



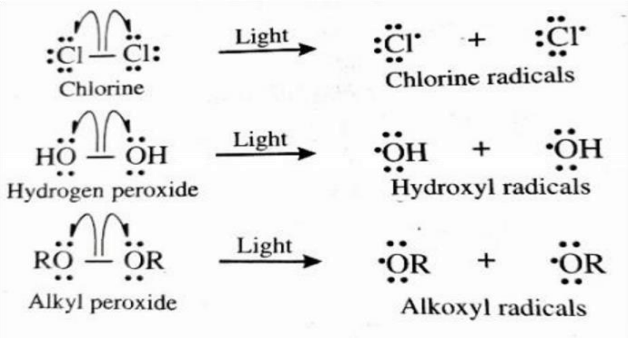
FREE RADICALS

- Free radicals are atoms or groups having an unpaired electron.
- They are neutral and highly reactive.
- Short lived species
- Paramagnetic due to the presence of unpaired electron.

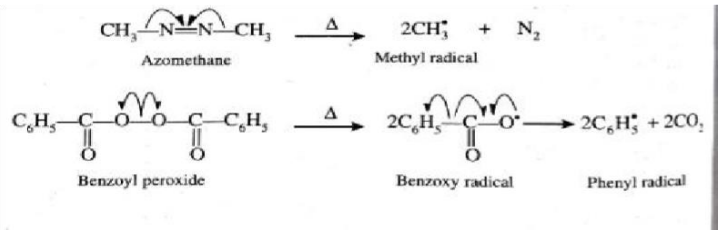
Formation:

(i) Photochemical homolysis

Eg:

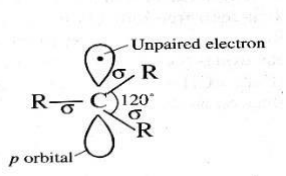


(ii) Thermal homolysis



(iii) Gain of electron by a carbocation or loss of electron by a carbanion.

Hybridization and structure



- Carbon atom is sp^2 hybridized in a free radical.
- The three sp^2 hybrid orbitals form σ bonds with three atoms or groups.
- Unpaired electron resides in an unhybridized p-orbital.
- Carbon free radicals have trigonal planar shape with bond angle 120°.

Stability

(a)Stability of alkyl free radicals:

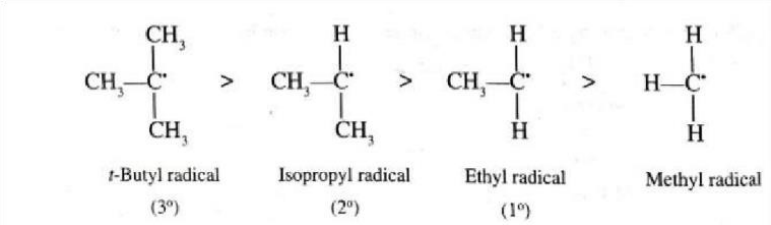
The order of stability is

Tertiary > secondary > primary >methyl

Eg:

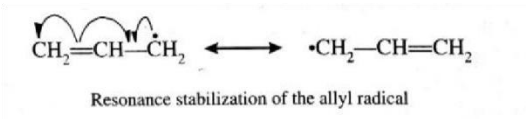
$(CH_3)_3C\bullet > (CH_3)_2CH\bullet > CH_3CH_2\bullet > CH_3\bullet$

The order can be explained on the basis of hyperconjugation. Greater the number of α-hydrogens, greater would be the number of hyperconjugative structures and greater would be the stability.



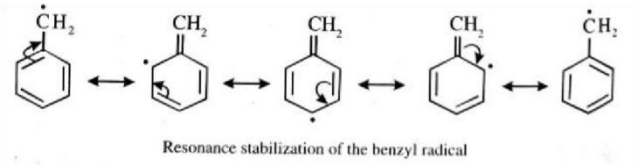
(b) *stability of unsaturated free radicals*

- If resonance stabilization of free radicals is possible, such free radicals are more stable. Resonance stabilization become possible when delocalization of unpaired electron is possible over aromatic system.



(c) *Stability of benzyl free radical.*

- Benzyl free radical is resonance stabilized through delocalization of unpaired electron.



- Larger the number of phenyl groups attached to the carbon having unpaired electron, greater will be the extend of delocalization, greater will be the number of resonance structures and more stable will be the free radical.

TYPES OF ORGANIC REACTIONS

- Five types of organic reactions-
    1. Substitution reactions
    2. Addition reactions
    3. Elimination reactions
    4. Rearrangement reactions.
    5. Redox reactions

1. **Substitution reactions**

- An atom or a group of the substrate molecule is replaced by an atom or group from reagent.
- Depending on the type of attacking reagents ,substitution reaction is of 3 types-

a) Nucleophilic substitution reactions

- Substitution reaction in which attacking reagent is nucleophile.
- Eg:

Ethyl bromide *Ethanol*

b)Electrophilic substitution reactions

- Substitution reaction in which attacking reagent is electrophile.
- Eg :

Benzene *Nitrobenzene*

c)Free radical substitution reaction

- Substitution reaction in which the attacking reagent is free radical.

Eg :

Methane *Methyl chloride*

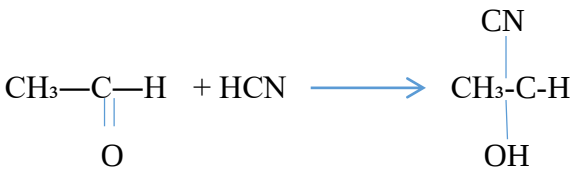
2.Addition reactions:

- Reaction in which reagent adds to the substrate to yield a single product.
- Depending upon the type of attacking reagent, addition reaction is of 3 types-

a)Nucleophilic addition reactions

- Attacking reagent is nucleophile.
- Initially Nucleophile attack on substrate.

Eg :



Acetaldehyde *acetaldehyde cyanohydrin*

b)Electrophilic addition reactions

- Attacking reagent is electrophile.
- Initially Electrophile attack on substrate.

propene *2- Bromo propane*

c)Free radical addition reactions

- Attacking reagent is free radical.
- Free radical attacks on substrate.
  - Eg :

Propene 1- bromo propane

This reaction takes place in the presence of peroxide.

2.Elimination reactions

- Reaction in which two atoms or groups of the substrate are removed together are called elimination reactions.
- Depending upon whether the two groups are removed from the same carbon or adjacent carbons, elimination reactions are of two types.

a) α- elimination reaction:

- Two atoms or groups are removed from same carbon of the substrate.
- ***Carbenes*** , having an unshared pair of electrons are formed in this reaction.
  - Eg :

$$CHCl_3 + OH^- \longrightarrow :CCl_2 + H_2O + Cl^-$$

Chloroform — Dichlorocarbene

b) β – elimination reaction:

- Two atoms or groups are removed from adjacent carbon atoms of the substrate.
- One σ- bond is from each carbon and a π-bond is created between the two carbon atoms.

Eg:

- Dehydrohalogenation of ethyl bromide using alcoholic. KOH

$$CH_3—CH_2Br \longrightarrow CH_2=CH_2 + HBr$$

Ethyl bromide — Ethylene

- Dehydration of ethanol using excess of Con.H_2SO_4 at 400 K.

. $CH_2=CH_2 + H_2O \longrightarrow CH_3—CH_2—OH$

Ethylene — Ethanol

c) **Rearrangement reactions:**

- A single reactant molecule undergoes reorganization of bonds and atoms through the migration of an atom or groups from one position to another.
- Eg:

  Isomerisation of 1- Bromobutane to 2-Bromobutane in the presence of anhydrous $AlCl_3$.

$$CH_3—CH_2—CH_2—CH_2Br \xrightarrow{\text{Anhy. } AlCl_3} CH_3—CH_2—CHBr—CH_3$$

1- Bromobutane — 2- Bromobutane

d) **Redox reactions:**

- Reaction in which both oxidation and reduction processes are involved.
- Either the substrate gets oxidised and products gets reduced or viceversa.

Eg: Oxidation of ethanol to acetaldehyde by potassium dichromate ($K_2Cr_2O_7$)

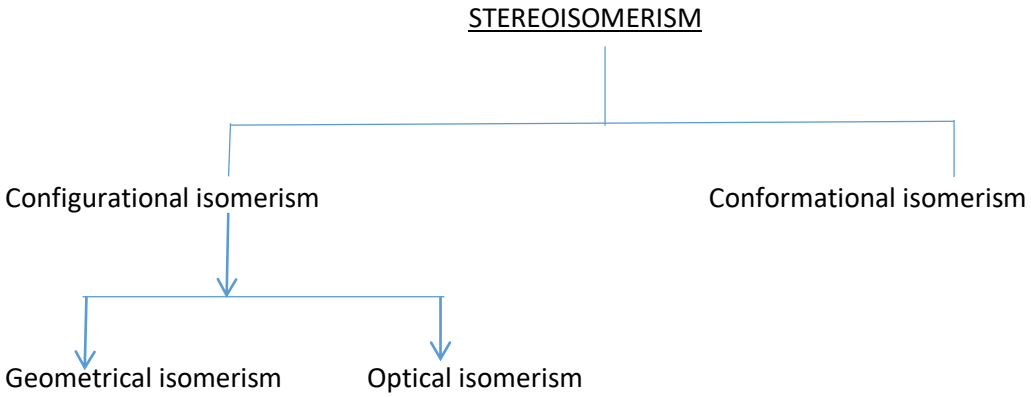
$$CH_3—CH_2—OH \longrightarrow CH_3—CHO + H_2O$$

Ethanol — Acetaldehyde

MODULE 2- STEREOCHEMISTRY

INTRODUCTION

- Stereochemistry is the branch of chemistry which deals with the spatial arrangement of atoms and groups in molecules.
- Isomers having same structure but different spatial arrangement of atoms or groups are called stereoisomers and the phenomenon is called stereoisomerism.
- Stereoisomerism is classified into two- configurational isomerism and conformational isomerism.



CONFORMATIONAL ISOMERISM

- The different spatial arrangements of atoms or groups in a molecule that arises from free rotation about a single bond is called conformations and the isomerism is called **conformational isomerism** or rotational isomerism. The isomers obtained are called conformational isomers or conformers or rotamers.
- There is no cleavage or formation of bonds during the rotation.
- The interconversion between conformations is fast.
- Rotational barrier is low.
- There exist a dynamic equilibrium between isomers.
- The isomers are non-seperable.

CONFORMATIONS OF ETHANE

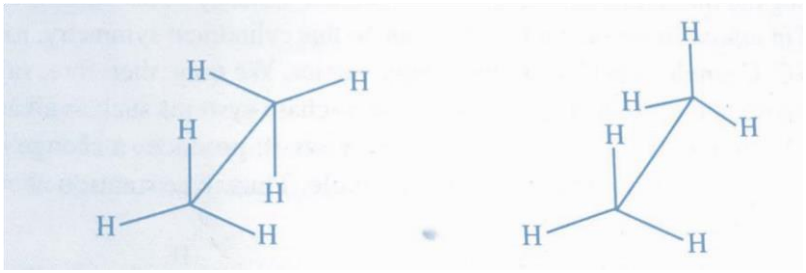
CH_3—CH_3

Ethane

- Out of the infinite conformations possible for ethane, two extreme cases are ***staggered*** and ***eclipsed*** conformation.
- In staggered conformation, the hydrogen atom on one carbon are far apart as possible from hydrogen atoms on other carbon.

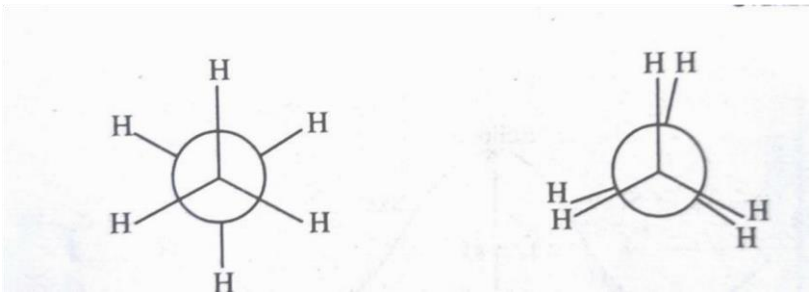
- In eclipsed conformation, the hydrogen atoms on one carbon are as close as possible to the hydrogen atoms on other carbon.
- The intermediate conformations between staggered and eclipsed are called ***skew conformations.***

Sawhorse projection of ethane



Staggered conformation **Eclipsed conformation**

Newman projection of ethane

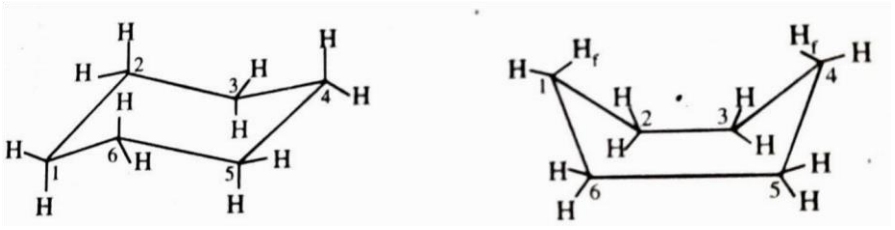


Staggered conformation **Eclipsed conformation**

Relative stabilities

- The staggered conformation of ethane is more stable than eclipsed conformation.
- In eclipsed conformation, since the hydrogen atoms on the two carbons are close to each other, there arises repulsive interaction forces between sigma electrons of C-H bonds and also between the non- bonded hydrogen atoms on the two carbons.
- In staggered conformation, the hydrogen atoms on the two carbons are far apart as possible. So there is less repulsive interaction.
- Skew conformations have intermediate stability between staggered and eclipsed.
- The energy difference between staggered and eclipsed conformations is called torsional barrier. Or it is the energy difference between lowest and highest energy conformations.
- For ethane torsional barrier is 12.6KJ/mol. Since this energy barrier is too low, free rotations about C-C bond is possible. So individual conformors cannot be isolated.

CONFORMATION OF CYCLOHEXANE



A

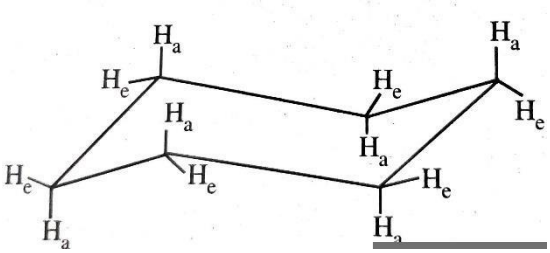
Chair conformation **Boat conformation**

- Cyclohexane has a non-polar or puckered (twisted) six membered ring structure.
- Bond angle is 109.5°
- Two conformations of cyclohexane which are free from angle strain are ***chair*** and ***boat*** conformation.

Relative stabilities

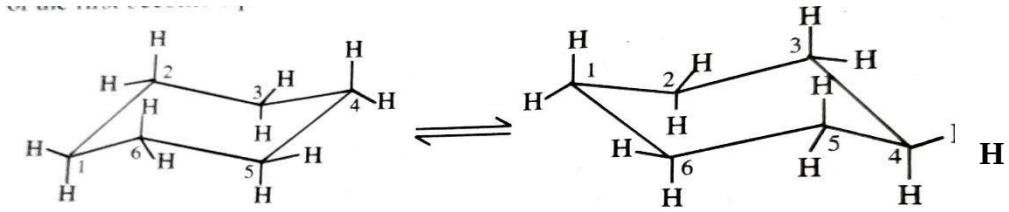
- chair conformation is more stable than boat conformations.
- Both chair and boat conformations are free from angle strain because the bond angle is not deviated from normal tetrahedral angle(109.5°).
- In the chair conformation all the hydrogen atoms are far apart, thus devoid of torsional strain as well as steric strain.
- In boat conformation, the hydrogens on C^2 and C^3 and on C^5 and C^6 are eclipsed. There occurs repulsive interactions between σ- electron clouds of C-H bonds. These repulsive interactions are called torsional strain. Also in boat conformation, the two hydrogens marked as H**f**, called flagpole hydrogens, on C^1 and C^4 are close causing steric strain in the molecule.
- Boat conformation has higher energy than chair conformation. The energy difference is 29 KJ/mol. This energy difference is large enough to prevent interconversions of the two forms. So, the two conformers cannot be separated.

Axial and equatorial bonds



- The six C-H bonds which are parallel to the symmetry axis of the ring are called axial bonds and the six hydrogens of these bonds are called axial hydrogens (H_a).
- The six C-H bonds which lie in a belt about the equator of the ring are called equatorial bonds and the six hydrogens of these bonds are called equatorial hydrogens (H_e).

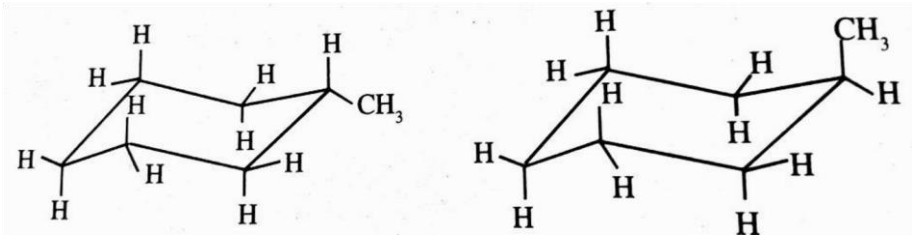
- Two chair conformations are possible for cyclohexane:



- The interconversion of one chair form into other is called ***ring flip***.

CONFORMATIONS OF METHYL CYCLOHEXANE

Two important conformations are equatorial methyl cyclohexane and axial methyl cyclohexane.



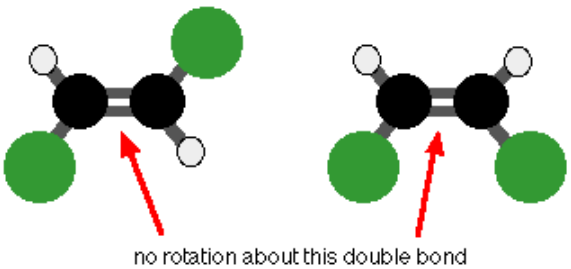
Equatorial methyl cyclohexane **Axial methyl cyclohexane**

Relative stabilities

- The chair conformation in which methyl group is in equatorial position is more stable than one in which methyl group is in axial position.
- In Axial methyl cyclohexane there occurs **1,3-diaxial interaction**. It is the repulsive interaction between CH_3 and two axial hydrogens. But in equatorial methyl cyclohexane the methyl group is away from axial hydrogens. It does not experience steric overcrowding.

GEOMETRICAL ISOMERISM

- Isomers having same structural formula but different spatial arrangement of atoms or groups around double bond is called geometrical isomers and the phenomenon is called geometrical isomerism.
- It arises due to restricted rotation about double bonds.



- There are two necessary conditions for a compound to possess geometrical isomerism:

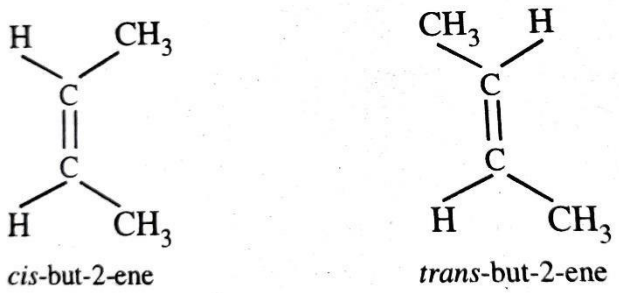
(i) It must contain a carbon-carbon double bond in the molecule.

(ii) Two unlike atoms or groups must be linked to each doubly bonded carbon atoms.

- The geometrical isomers with similar groups on the same side of double bond is called ***cis*** isomer. And the isomer with similar groups on the opposite sides of double bond is called ***trans*** isomer. The geometrical isomerism is called cis- trans isomerism.

Examples of Geometrical isomerism

But-2-ene (CH_3-CH=CH-CH_3)



cis-but-2-ene *trans*-but-2-ene

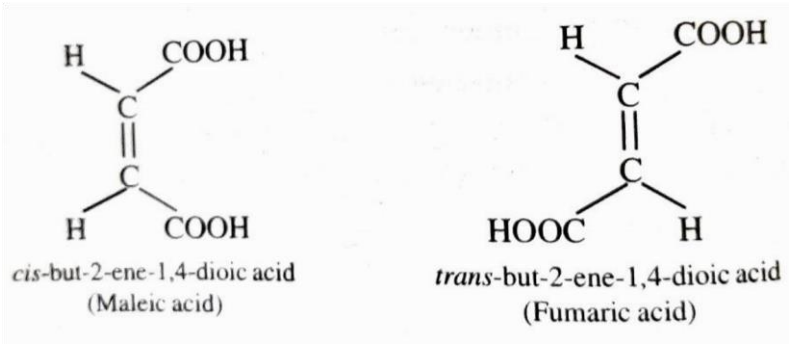
- But-2-ene exist as cis-but-2-ene and trans-but-2-ene.
- **Trans-2-butene is more stable than cis-2-butene**. In cis-2-butene the two methyl groups are on the same side of double bond where as in trans-2-butene they are on opposite side. Since the two methyl groups are close to each other in cis compound, there occurs overcrowding leading to steric effect. In trans compound, the two methyl groups are separated and there is no steric effect.
- **Boiling point of cis isomers are higher than trans isomers** because cis isomers are polar and hence they have strong intermolecular forces between the molecules. Because of this high polarity and high intermolecular force, a lot of energy will be required to break the bonds. Hence, cis isomers have higher boiling point.
- **Melting point of cis isomers are lower than trans isomers**. Trans isomers pack better than cis isomers. Cis isomers pack poorly, which means that the intermolecular forces aren't much effective and thus less amount of energy is required to melt the cis molecule. Hence, cis molecules have lower melting point.

GEOMETRICAL ISOMERISM IN BUT-2-ENE-1,4-DIOIC ACID

Structure of But-2-ene- 1,4- dioic acid

HOOC—CH=CH—COOH

- But -2- ene- 1,4- dioic acid exist in cis and tans forms. In Cis isomer two –COOH groups are on the same side of C=C double bond, it is commonly called maleic acid. In Trans isomer the two –COOH groups are on the opposite side of C=C., it is commonly called fumaric acid.



- Maleic acid has lower melting point and higher boiling point, refractive index, dipole moment than fumaric acid.

- On heating maleic acid above the melting point, it is readily converted to maleic anhydride. Fumaric acid, on strong heating is converted to maleic acid which is then converted to maleic anhydride. This method helps in determination of cis and trans forms.

- <u>*Stability*</u>- maleic acid is less stable than fumaric acid. In maleic acid the two –COOH groups are on the same side of double bond. This causes crowding. In fumaric acid the two- COOH groups are on the opposite side. The steric strain is thus greater in maleic acid.

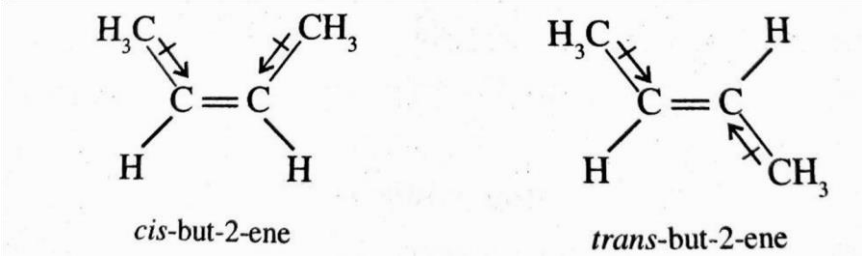
<u>Methods of distinguishing geometrical isomers:</u>

(a) *On the basis of melting points of isomers*-

Trans isomer is more symmetrical as the two symmetrical groups lie on opposite side of double bond. Cis isomer is less symmetrical and does not pack well into the crystal lattice. As a result intermolecular forces are stronger in the trans isomer and its melting point is higher.

(b) *On the basis of dipole moments*.-

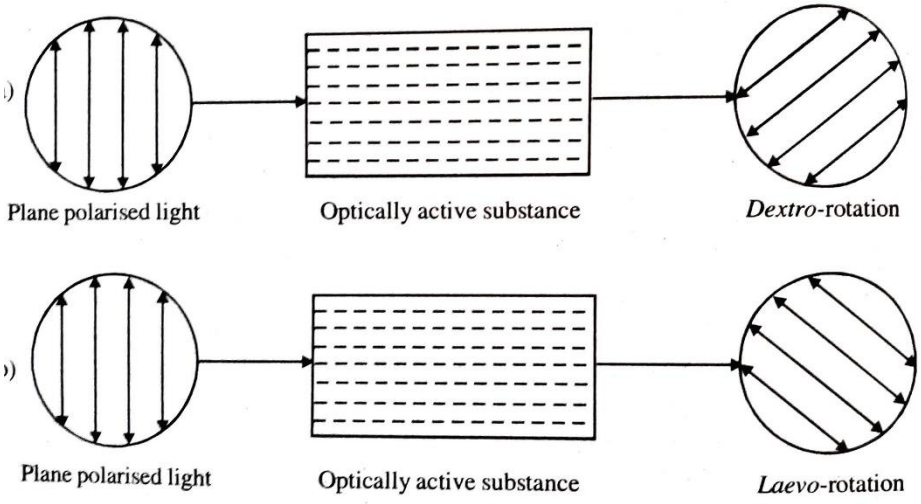
Trans isomer has lower dipole moment because as the similar groups lie on the opposite side of double bond, the bond moments get cancelled out. Cis isomer has a high value of dipole moment.



μ =0.33 D μ =0 D

OPTICAL ISOMERISM

- Light waves whose vibrations occur in only one plane is called **plane polarised light** and the phenomenon is known as polarisation. The plane in which plane polarised light vibrate is called plane of polarisation.
- When a plane polarised light is passed through certain substances, its plane of polarisation is rotated either towards right (clockwise) or towards left (anticlockwise). This phenomenon is called **optical activity**. Such substances are said to be optically active.
- Substances which rotate the plane of polarised light to the right are called **dextrorotatory(** d or (+)**)** and those which rotate it to left are called **laevorotatory (** l or (-)**)**



- **Specific rotation**-

  Specific rotation of an optically active compound, at specified temperature and specified wavelength, is the observed rotation in degrees when plane polarised light is passed through one decimetre (10 cm) of the solution having a concentration of one gram/ml.

$$\text{Specific rotation, } [\alpha]_{\lambda}^{T} = \frac{\alpha_{obs}}{l \times c}$$

  α obs = observed rotation

  l = length of the solution

  c= concentration (g/ ml)

  T= Kelvin temperature

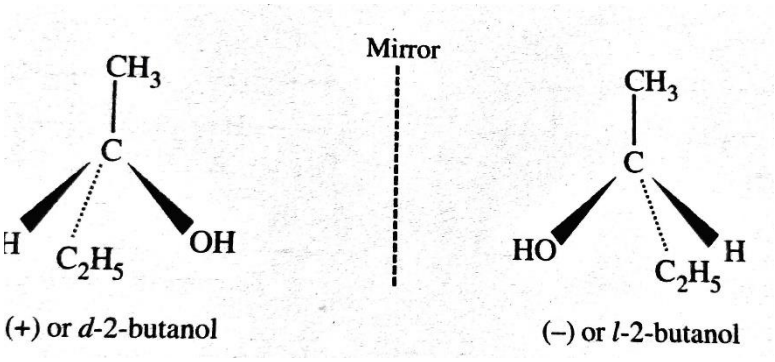
  λ = wavelength of incident light

- A molecule with no element of symmetry is called asymmetric molecule.

- A molecule non- superimposable on its mirror image is called dissymmetric molecule or chiral molecule. Such molecules will not have a plane of symmetry.
- All asymmetric molecules will be dissymmetric but all dissymmetric molecules need not be asymmetric.
- ***Optical isomerism***- Stereoisomerism in which the isomers resemble in most of their properties but differ in their behaviour towards plane polarised light.
- A necessary condition for optical isomerism is that the molecule should be chiral. Chirality or dissymmetry is the non superimposability of a structure on its mirror image.
- A chiral carbon atom is one whose four valencies are satisfied by four different groups or atoms.
- Chirality, in most of the organic compounds is caused by the presence of one or more chiral carbon atoms (asymmetric carbon atoms). In some molecules, there are more than one chiral centres, yet they are achiral. Thus, the presence or absence of chiral centre is not a criterion for chirality.
- The presence of chirality is a criterion for optical isomerism.

ENANTIOMERISM

- Stereoisomers which are related to each other as non-superimposable mirror images and rotate the plane polarised light to equal extends but in opposite direction are called enantiomers or enantiomorphs and the phenomenon is known as enantiomerism.
- Enantiomers are optically active.
- They have same chemical properties.
- Enantiomer which rotates the plane of plane polarised light to the right is called dextrorotatory (d or(+)) and that which rotates the plane of plane polarised light to the right is called laevorotatory (l or (-)).
- Eg:Enantiomers of butan-2-ol

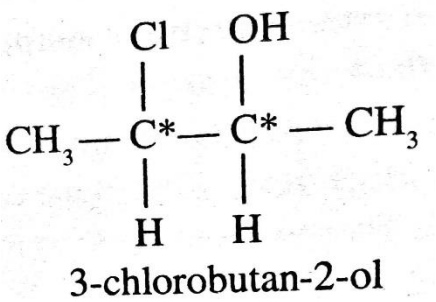


- An equimolecular mixture of the two enantiomers of a substance is known as ***racemic mixture*** (dl or ±). Racemic mixture is optically inactive because the optical rotation due to one enantiomer is exactly cancelled out by the equal and opposite rotation due to other. This is called external compensation. The separation of racemic mixture into d and l forms is called resolution of racemic mixture.

DIASTEREOISOMERISM

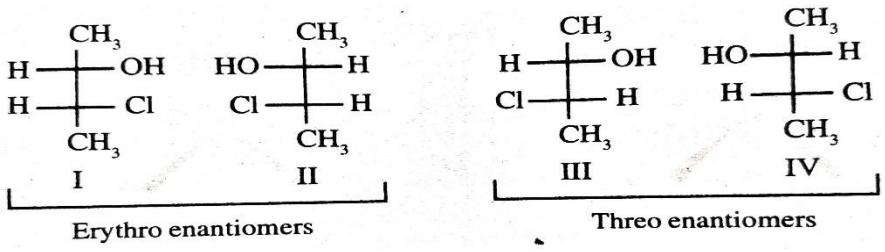
- Stereoisomers which are not mirror images of each other are called diastereoisomers.
- They may or maynot be optically active.
- They show different physical and chemical properties.
- They react at different rates with an achiral reagent.

Eg: 3- chlorobutan-2-ol



3-chlorobutan-2-ol

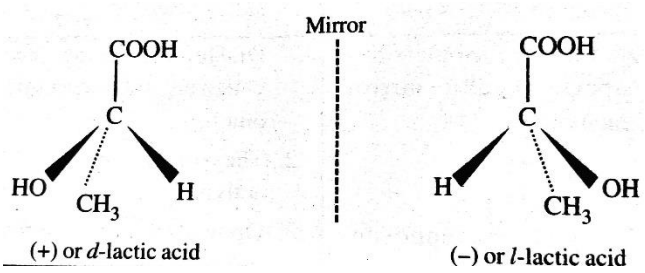
There are two asymmetric carbons. So they have 2^2=4 stereoisomers. (2^n, n= no. of asymmetric centres)



- Stereoisomers I and II are non- superimposable mirror images and thus they are enantiomers. They have similar groups (hydrogen) on the same side and are called erythro enantiomers. Similarly III and IV are enantiomers and they are called threo enantiomers as the similar groups (hydrogen) are on opposite side.
- Stereoisomers I and III, I and IV, II and III, II and IV are not mirror images of each other. They are called diastereoisomers.

OPTICAL ISOMERISM OF LACTIC ACID (2- Hydoxypropanoic acid)

- Lactic acid is CH_3-CHOH-COOH. It contains one asymmetric carbon atom. Therefore number of stereoisomers possible is 2^1=2. Two stereoisomers are thus possible for lactic acid which are related to each other as object to its non-superimposable mirror image. They rotate the plane of plane polarised light to equal extends but in opposite direction. Hence, are called enantiomers.
- The two enantiomers of lactic acid are d- lactic acid and l- lactic acid. d –lactic acid(dextro-lactic acid) rotates the plane of plane polarised light to the right. l-lactic acid(laevo-lactic acid) rotates the plane of plane polarised light to the left.



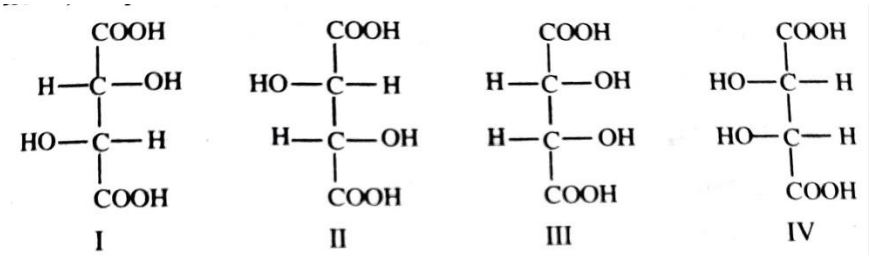
- An equimolecular mixture of d-lactic acid and l-lactic acid is optically inactive due to external compensation of optical rotations and is called racemic mixture.
- The separation of racemic lactic acid into d and l forms is called resolution.

OPTICAL ISOMERISM OF TARTARIC ACID

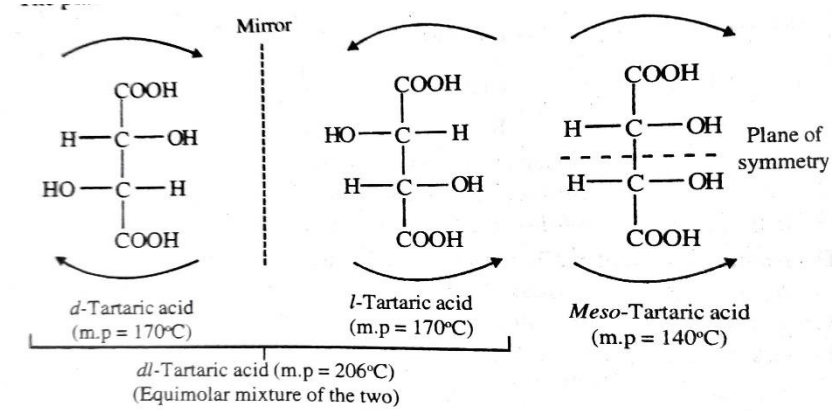
- The structural formula of tartaric acid is

  CH(OH)COOH
  |
  CH(OH)COOH

  It contains two asymmetric carbon atoms. Theoretically, $2^2=4$ stereo isomers are possible. They are



The structure IV when rotated through 180º becomes identical with structure III. Hence, tartaric acid has three different isomers I, II and III.



- Dextro- tartaric acid-

  d- tartaric acid rotates the plane of plane polarised light to the right. They have no plane of symmetry. The optical rotation due to lower half is strengthened by optical rotation due to upper half.

- Laevo-tartaric acid-

l- tartaric acid rotates the plane of plane polarised light to the left. They have no plane of symmetry. The optical rotation due to lower half is strengthened by optical rotation due to upper half.

- Meso- tartaric acid-

  Meso- tartaric acid contains a plane of symmetry. It is optically inactive. The optical rotation due to lower half of the molecule is exactly compensated by the optical rotation due to upper half. This is called internal compensation.

- Racemic-tartaric acid-

  Racemic or dl-tartaric acid is an equimolecular mixture of d and l forms. It is optically inactive. The optical rotation of one form is cancelled by optical rotation of other form. This is called external compensation.

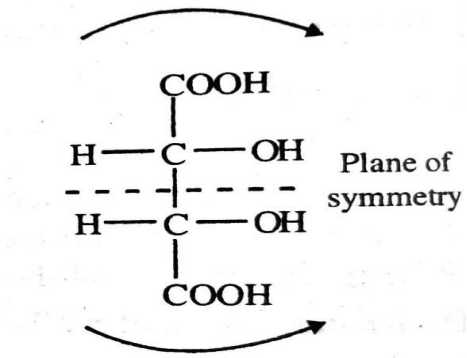
- d and l forms of tartaric acid are enantiomers. They are non- super imposable mirror images.

- The meso form is not a mirror image of either d or l forms. Hence they are diastereoisomers.

  MESO COMPOUNDS

  If a compound contains two or more chiral centers, still it is achiral due to the presence of a plane of symmetry and thereby optically inactive due to internal compensation, it is called a **meso compound**.

  Eg; In tartaric acid,one of the stereoisomer is meso- compound. It is optically inactive.



Meso-Tartaric acid

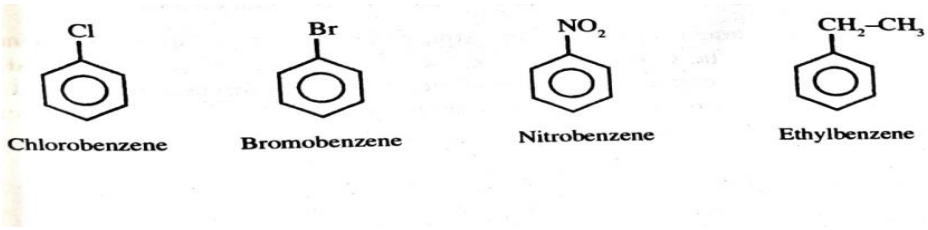
MODULE 3- AROMATIC HYDROCARBONS

NOMENCLATURE AND ISOMERISM IN SUBSTITUTED BENZENES

A) MONOSUBSTITUTED BENZENE

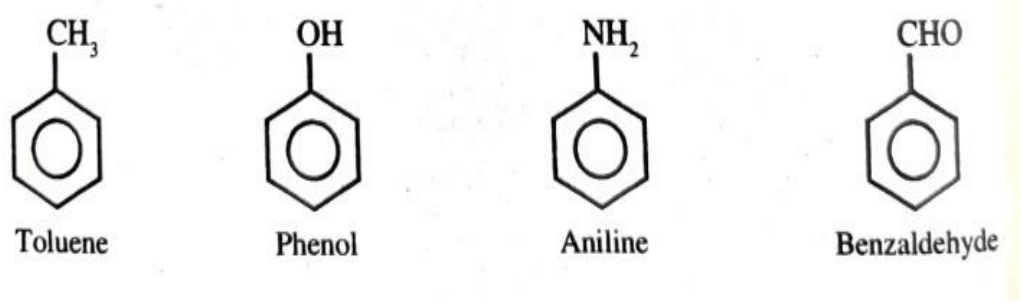
- In monosubstituted benzene, a single hydrogen of benzene is replaced by a group.
- The substituent is given as prefix to benzene.

  Eg:



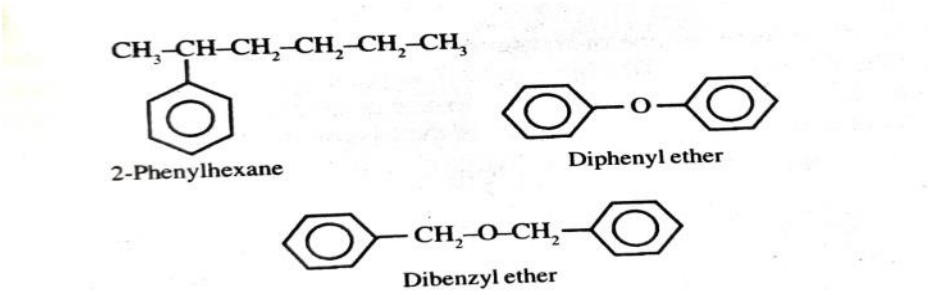
- Some mono substituted benzene have common names which are accepted by IUPAC.

  Eg:



- When the substituent on the benzene ring is a complex group, the C_6H_5 group (phenyl group) is treated as substituent.

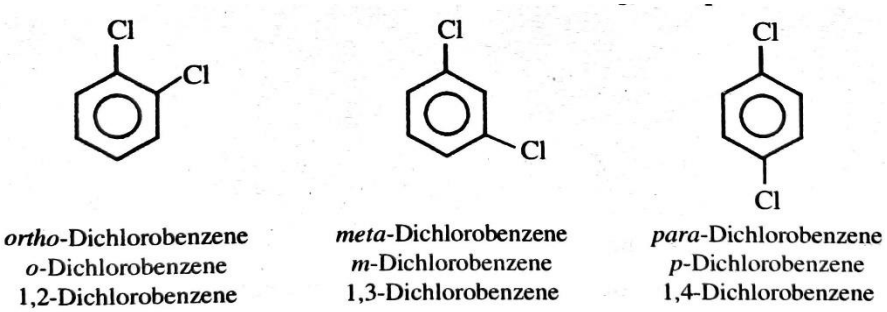
  Eg:



B) DISUBSTITUTED BENZENE

- In disubstituted benzene, two H atoms of benzene are replaced by two similar or dissimilar groups.
- Three Position isomers are possible for disubstituted benzene- ortho(o), meta(m) and para(p). Numbers are also used to indicate their relative positions.

Eg:



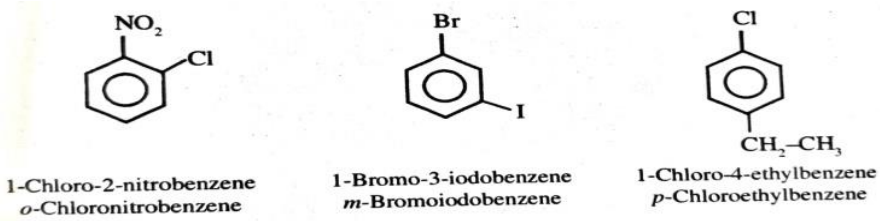
ortho-Dichlorobenzene
o-Dichlorobenzene
1,2-Dichlorobenzene

meta-Dichlorobenzene
m-Dichlorobenzene
1,3-Dichlorobenzene

para-Dichlorobenzene
p-Dichlorobenzene
1,4-Dichlorobenzene

- If two substituents are different, the first in the alphabetical order is assigned 1- position. The numbering is done in such a way that the second substituent gets the lowest number.

Eg:



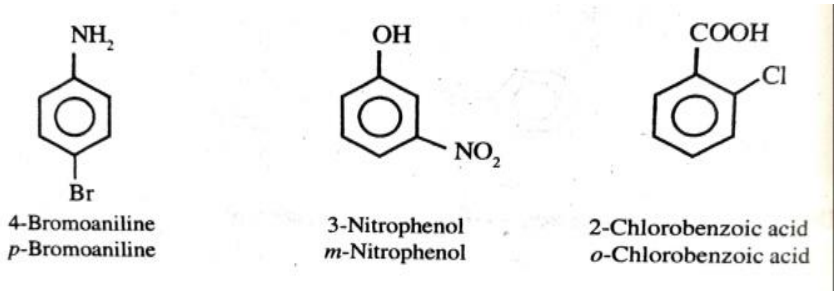
1-Chloro-2-nitrobenzene
o-Chloronitrobenzene

1-Bromo-3-iodobenzene
m-Bromoiodobenzene

1-Chloro-4-ethylbenzene
p-Chloroethylbenzene

- If the name of one substituent is already incorporated into the name of compound, then the incorporated substituent is given 1- position. The second substituent is given a number or o, m, p specifications on the basis of their position relative to first substituent.

Eg:



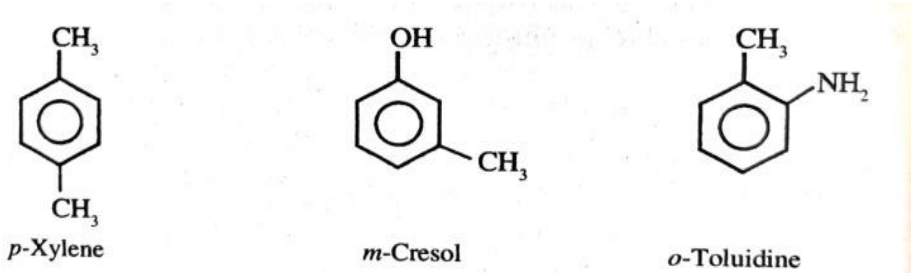
4-Bromoaniline
p-Bromoaniline

3-Nitrophenol
m-Nitrophenol

2-Chlorobenzoic acid
o-Chlorobenzoic acid

- A few disubstituted benzene have names that incorporate both the substituent.

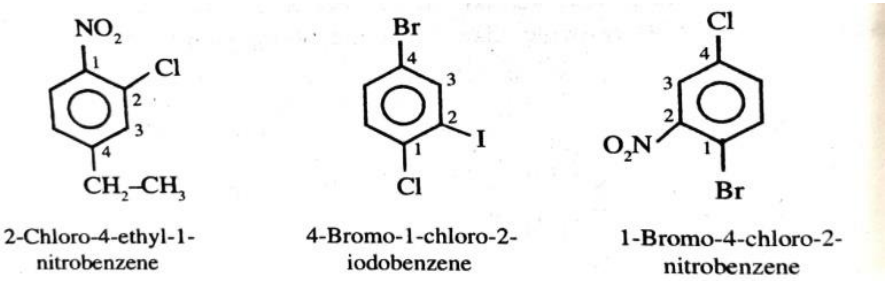
  Eg:



C) POLYSUBSTITUTED BENZENE

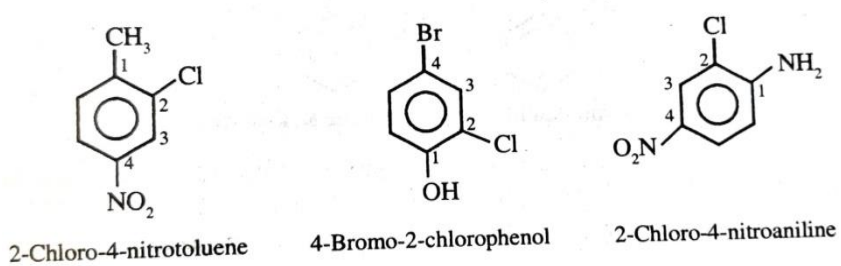
- Polysubstituted benzene have more than two carbon atoms attatched to the benzene ring.
- In polysubstituted benzene, numbering is done such that the substituents get the lowest numbers. First priority is given to a sustituent , that assign lowest numbers to the remaining substituents. Naming is then done by indicating the substituents in alphabetical order.

  Eg:



- If one of the substituent is already incorporated into the name, it is given first position and the numbering is done such that the remaining substituents gets the lowest number.

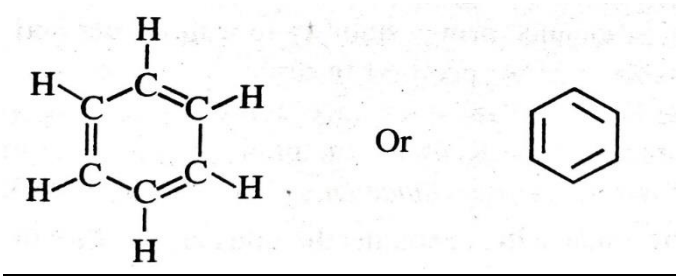
  Eg:



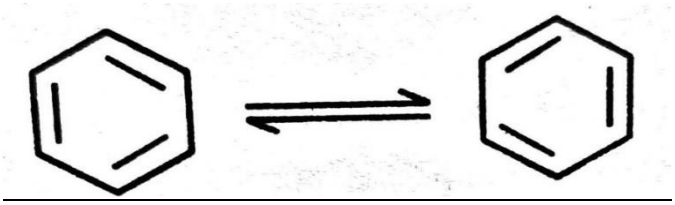
STRUCTURE AND STABILITY OF BENZENE

I. KEKULE′S STRUCTURE

- Kekule proposed a structure for benzene in which six carbon atoms of benzene have a hexagonal ring with alternate single and double bonds between them.



- The single and double bonds alternate in their positions between the carbons to yield two equivalent structures which exist in dynamic equilibrium.

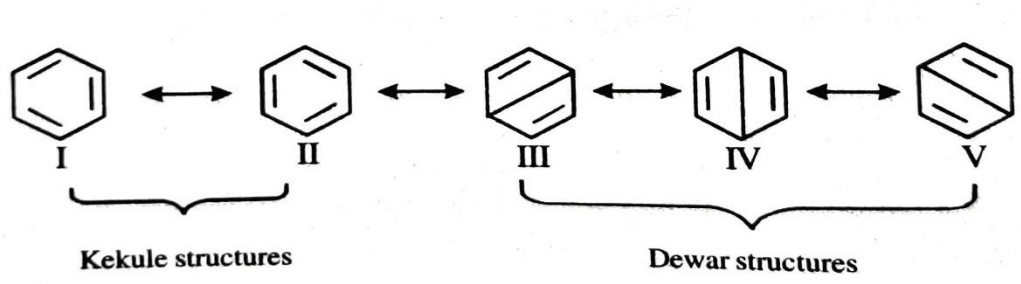


Limitations of Kekule structure

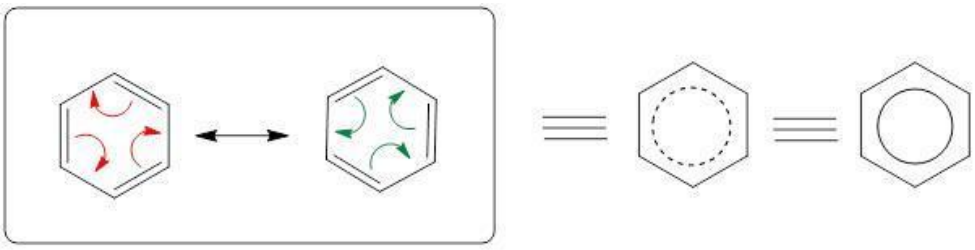
- It could not explain the stability of benzene towards strong oxidants like KMnO4.
- Kekule could not explain why benzene undergo substitution reactions rather than addition reactions.
- Kekule structure predicts two types of bond lengths in benzene, that is, for single bond 1.54 Å and for double bonds 1.34 Å. Actually all the bonds of benzene are of equal length 1.39Å.

II. RESONANCE CONCEPT

- According to resonance concept, benzene molecule is a resonance hybrid of the 5 structures.



- Actual molecule of benzene has an electronic structure intermediate between the two Kekule structures. This actual structure is called resonance hybrid.

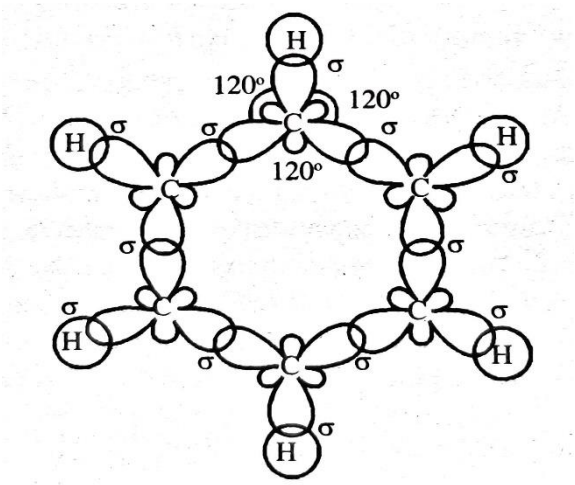


Benzene 2 Resonance forms Hybrid Forms

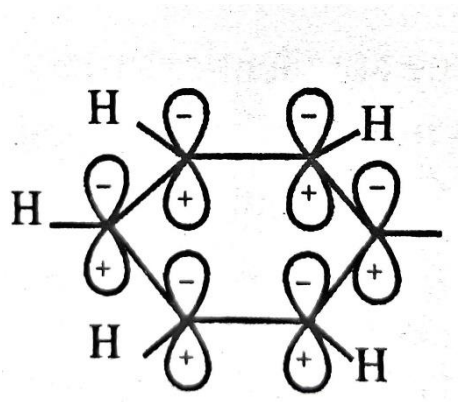
- The resonance hybrid has lower energy and hence greater stability than the contributing structures.
- Resonance energy of resonance hybrid is lower than the kekule structures.
- Resonance concept explains the unusual stability of benzene. It also explain the existence of a single bond length in benzene (1.39 Å).

III. MOLECULAR ORBITAL CONCEPT

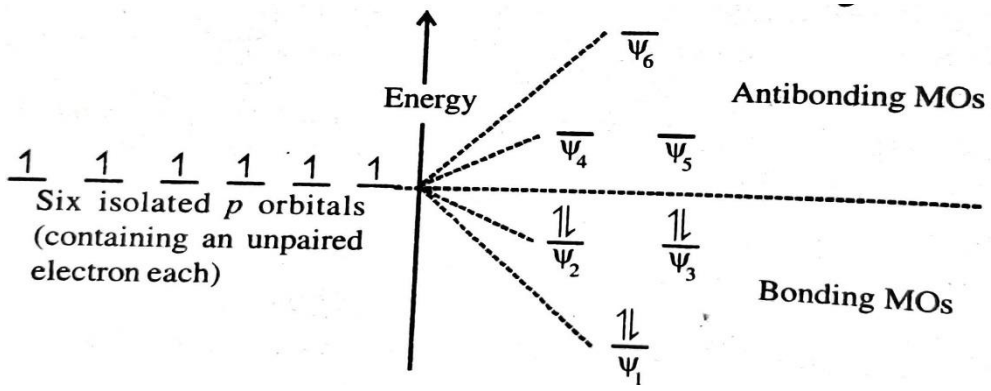
- Each C atom of benzene is sp^2 hybridized. Three sp^2 hybrid orbitals are arranged in a triagonal planar manner. Two of the sp^2 hybrid orbitals of each C atom form sigma bonds with adjacent C atoms. Remaining one sp^2 hybrid orbitals form sigma bond with 1s orbital of hydrogen. The six C-C σ bonds form a regular hexagon with C-C-C bond angles 120º. An unhybridised p-orbital lie perpendicular to the plane.



- The six perpendicular p- orbitals overlap sideways above and below the plane of hexagonal ring. This π electron delocalization causes lowering of energy of molecule and thereby stabilizes it.

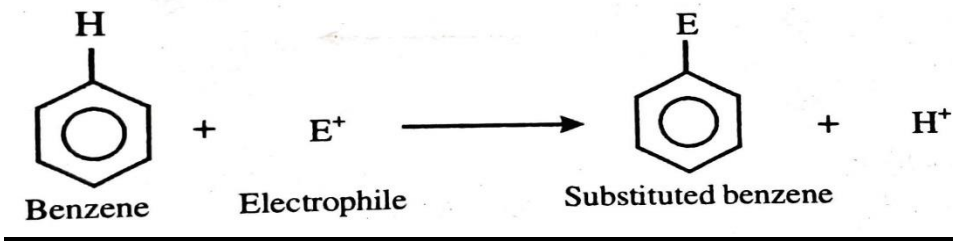


- Since, the π- electrons of benzene are delocalized, all the C-C bonds are of same length (1.39 Å).
- The delocalization energy of benzene is -150KJ/mol.
- According to molecular orbital theory, the six overlapping p- orbitals combine to form six molecular orbitals. Among these, three are of lower energy. These are called bonding molecular orbitals. The remaining three are of higher energy and are called antibonding molecular orbitals.
- In benzene, six π electrons occupy the bonding molecular orbitals. The antibonding molecular orbitals remain empty. Benzene, thus have a closed bonding shell of delocalized π electrons.



MECHANISM OF AROMATIC ELECTROPHILIC SUBSTITUTION

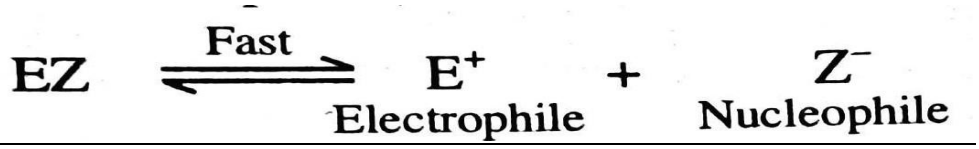
- Electrophilic aromatic substitution reaction is organic reaction in which an atom attached to an aromatic system (usually hydrogen) is replaced by an electrophile.



- The common electrophilic aromatic substitution reactions are halogenation, nitration, sulphonation , Friedel-crafts alkylation and Friedel- craft acylation.

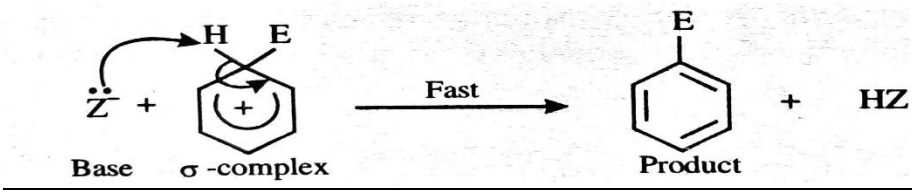
General Mechanism of an electrophilic aromatic substitution reaction

- Step 1 – The reagent is polarized and an electrophile is generated.



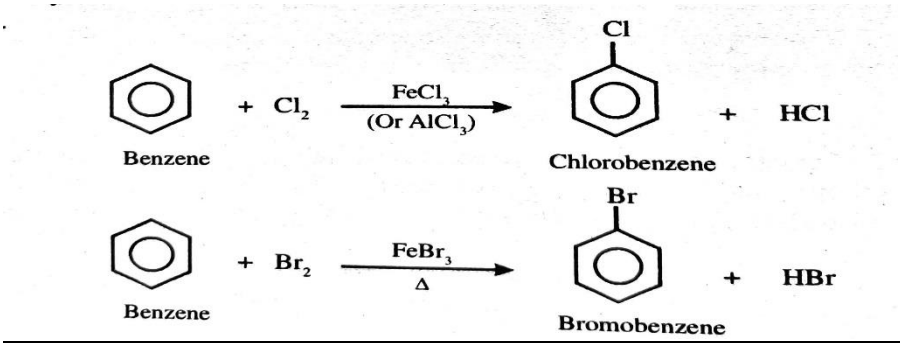
- Step 2- The generated electrophile is then attracted by π- electron cloud of benzene ring. This interaction results in the formation of a loose intermediate called a π-complex. This slowly changes to a nonaromatic carbocation intermediate known as σ complex. During this change, the electrophile takes two electrons from the pi- system and form a sigma bond. The σ bond is stabilized through resonance.

- Step 3- A base abstract a proton from the carbon that bears the electrophile of σ complex. The electrons are returned to the aromatic system and hence aromaticity is restored.

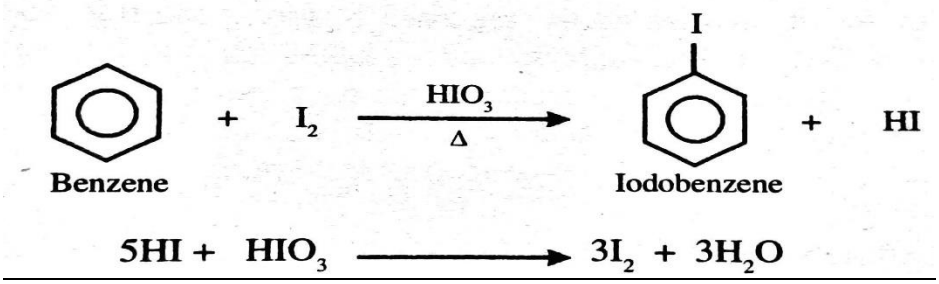


1.HALOGENATION

- Benzene reacts with chlorine and bromine in the presence of Lewis acid to yield corresponding halobenzene.



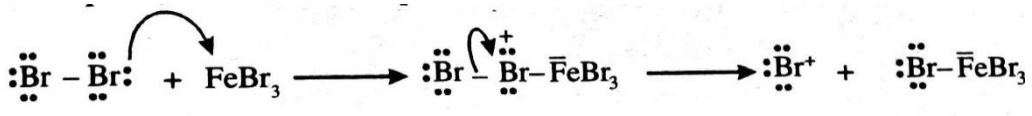
- Fluorination of benzene is a very fast reaction. It is not easily controllable.
- Iodination of benzene is a very slow reaction. It is usually carried out in the presence of a strong oxidizing agent like iodic acid or nitric acid to bring about oxidative destruction of HI.



***Mechanism of aromatic halogenation*.**

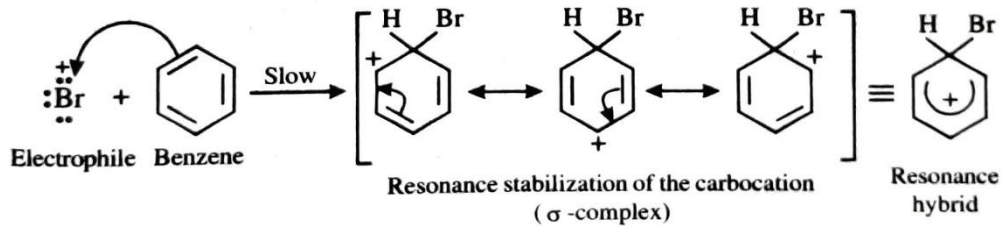
- Step 1- Generation of electrophile

Br_2 combines with $FeBr_3$ to form a complex that dissociates to give electrophile, Bromonium ion, Br^+.



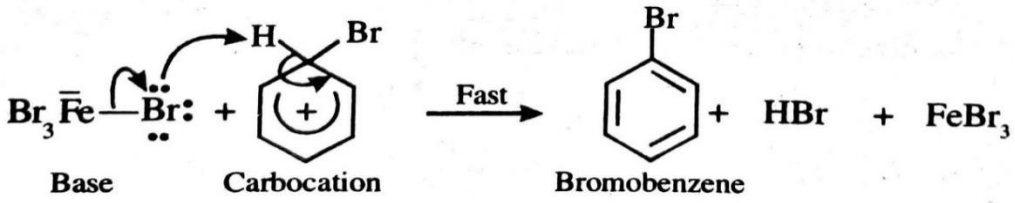
- Step 2- Formation of σ complex.

  Br^+ attack benzene to form a carbocation (arenium ion) called σ complex, which is stabilized by resonance. This is the rate determining process.



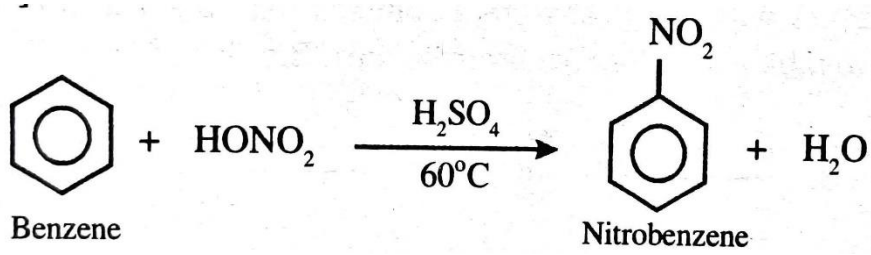
- Step 3- loss of a proton from σ complex.

  The base $FeBr_4^-$ present in the reaction mixture abstracts a proton from the carbocation and restores aromaticity to yield bromobenzene.



2. NITRATION

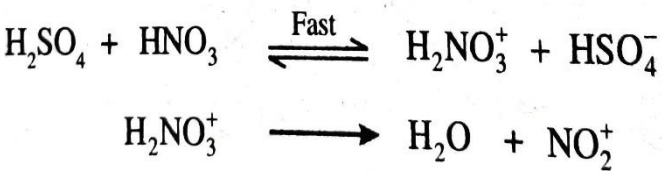
- When benzene is heated with a mixture of concentrated nitric acid and concentrated sulphuric acid (nitrating mixture) at about 333 K, nitrobenzene is obtained.



Mechanism of nitration

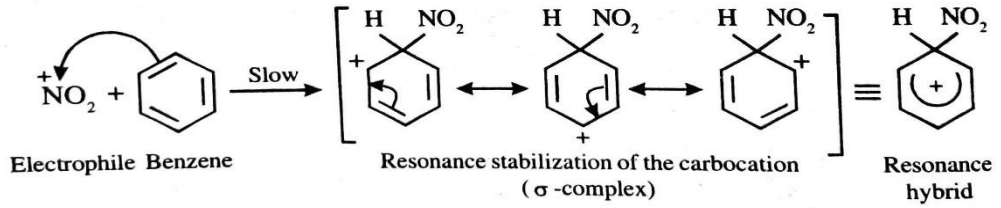
- Step 1 – Generation of electrophile

  HNO_3 accepts a proton from H_2SO_4 and the protonated form dissociates to yield the electrophile nitronium ion, NO_2^+.



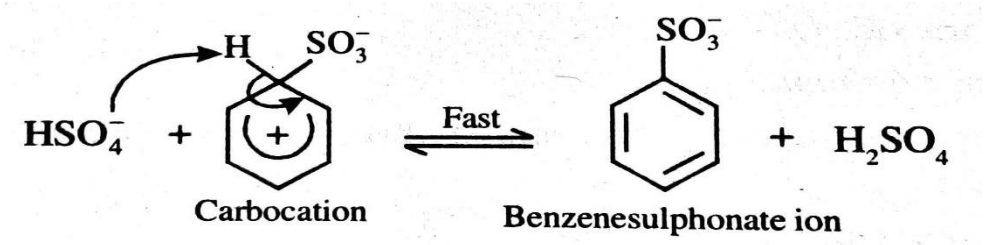
- Step 2 – Formation of σ complex

  NO_2^+ attacks benzene to form a carbocation, generally called σ complex. This carbocation is stabilized by resonance. This is the rate determining step.



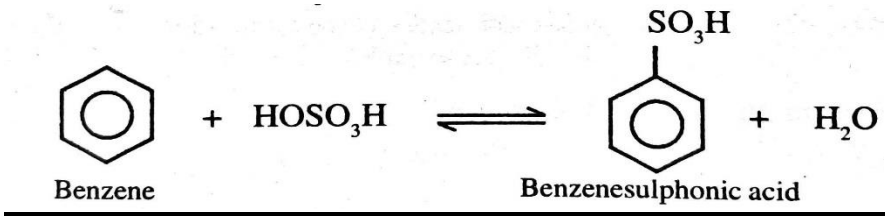
- Step 3 –loss of proton from a σ complex.

  HSO_4^- present in the reaction mixture abstracts a proton from the carbocation and restore aromaticity to yield nitrobenzene.



3. SULPHONATION

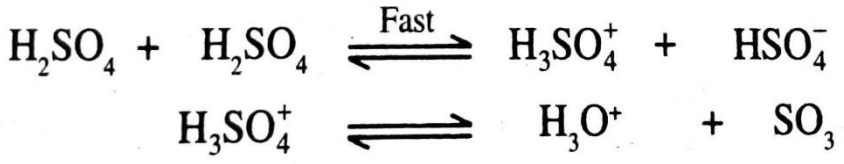
- Benzene when treated with fuming sulphuric acid at ordinary temperature yields benzene sulphonic acid.



Mechanism of sulphonation.

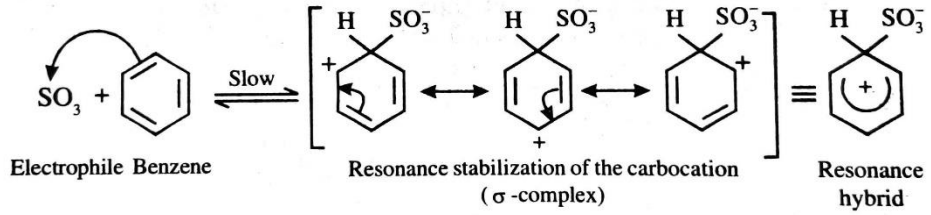
- Step 1- Generation of electrophile

  The electrophile SO_3 is produced by the autoionization of H_2SO_4.



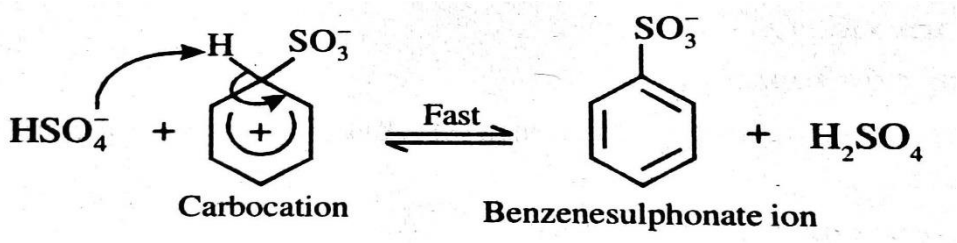
- Step 2- formation of σ complex.

  SO_3 attacks benzene to form a carbocation, called σ complex which is stabilized by resonance. This is the rate determining step.



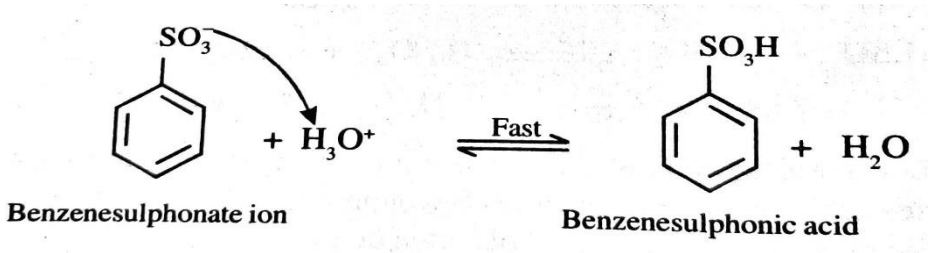
- Step 3- loss of a proton from σ complex.

  HSO_4^- present in the reaction mixture abstract a proton from the carbocation and restore aromaticity to yield benzenesulphonate ion.



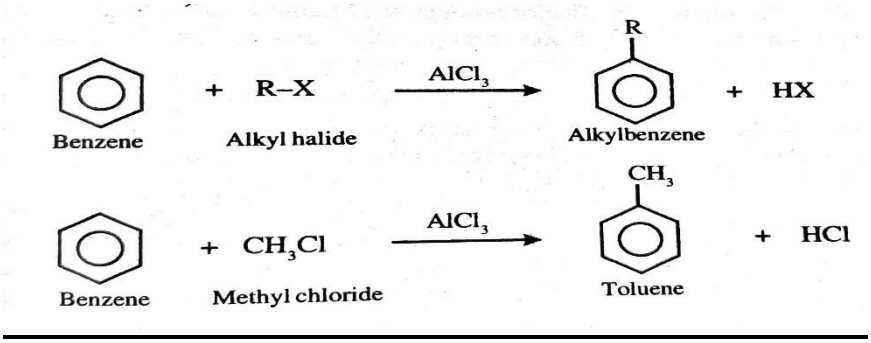
- Step 4- Acceptance of a proton

  The benzenesulphonate ion accepts a proton to yield benzenesulphonic acid.



4. FRIEDEL- CRAFTS ALKYLATION

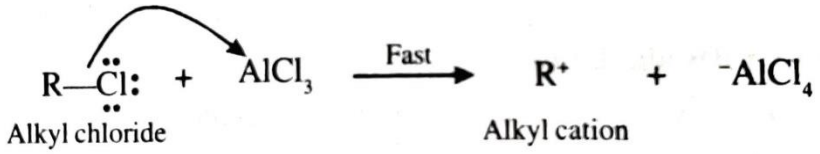
- Benzene reacts with an alkyl halide in the presence of anhy. $AlCl_3$ to yield the corresponding alkylbenzene.



Mechanism of Friedel crafts alkylation

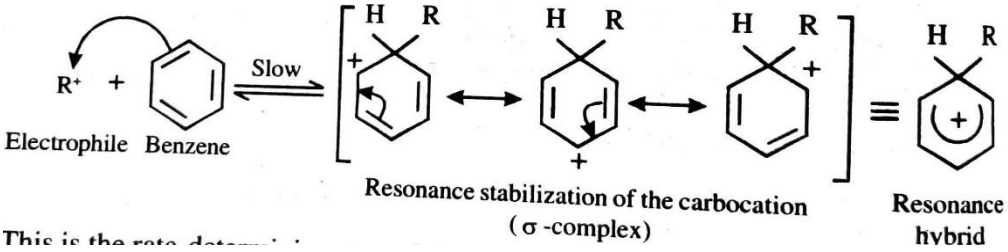
- Step 1- Generation of electrophile.

  Alkyl halides (R-X) reacts with anhydrous $AlCl_3$ to yield a carbocation which acts as electrophile.



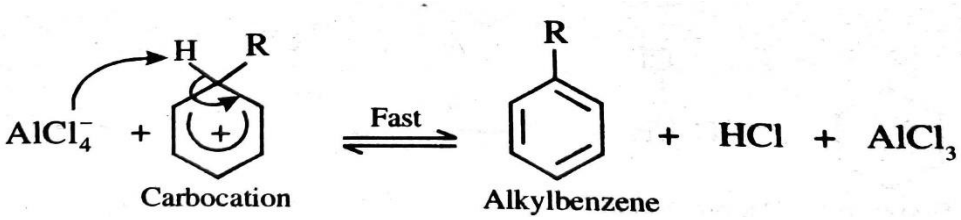
- Step 2- Formation of σ complex.

  The electrophile attacks benzene to form another carbocation, called σ complex, which is stabilized by resonance.



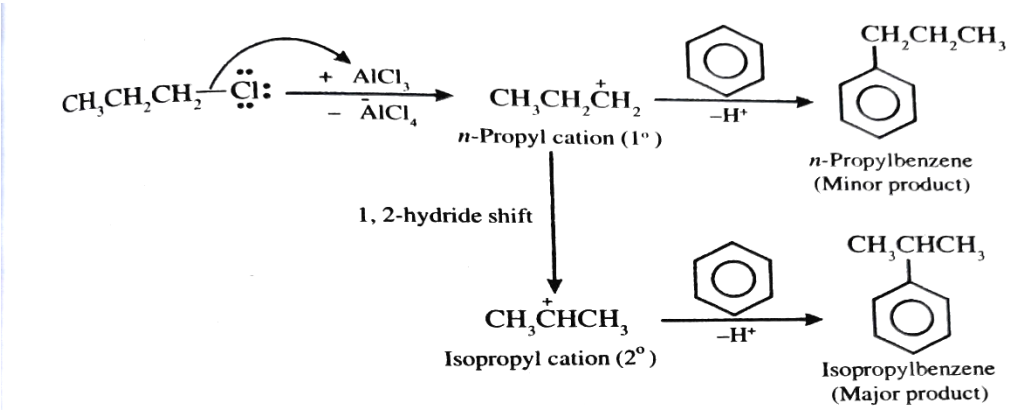
- Step 3- loss of a proton from the σ complex.

  $AlCl_4^-$ present in the reaction mixture abstract a proton from the carbocation and restores the aromaticity to yield the alkylbenzene.



- If the carbocation R+ initially produced rearranges to a more stable one, then the product from the more stable carbocation is the major product.

  Eg: when benzene is treated with n-propyl chloride in the presence of anhy. $AlCl_3$, the major product is isopropyl benzene because the n- propyl cation (1^o) produced rearranges to the more stable isopropyl cation(2^o).



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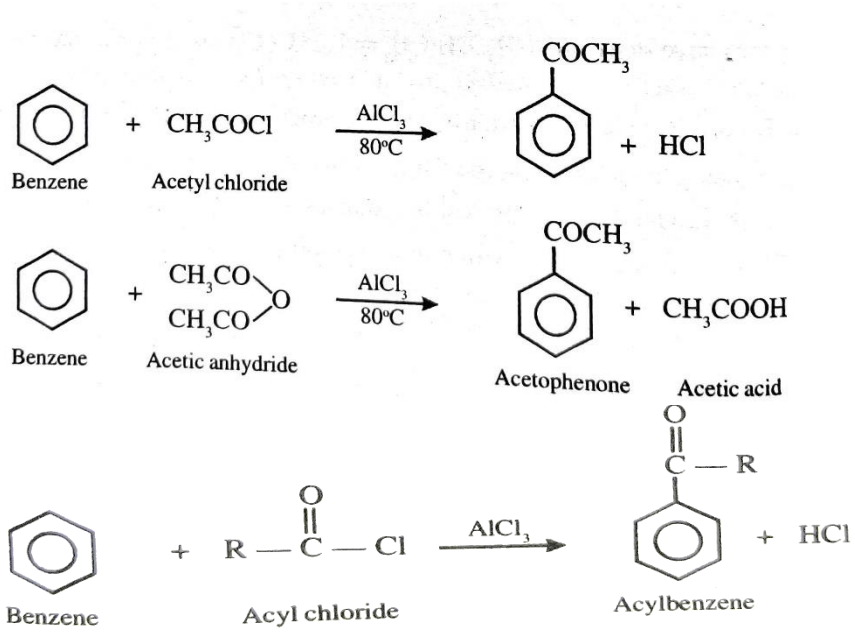
5. FRIEDEL- CRAFTS ACYLATION

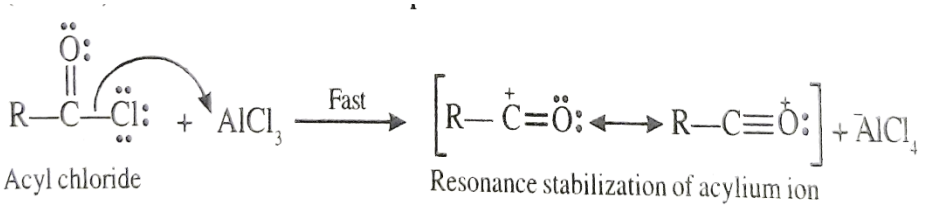
- Benzene react with an acyl halide or an acid anhydride in the presence of anhydrous $AlCl_3$ to yield corresponding acylbenzene.



Mechanism of Friedel- crafts acylation

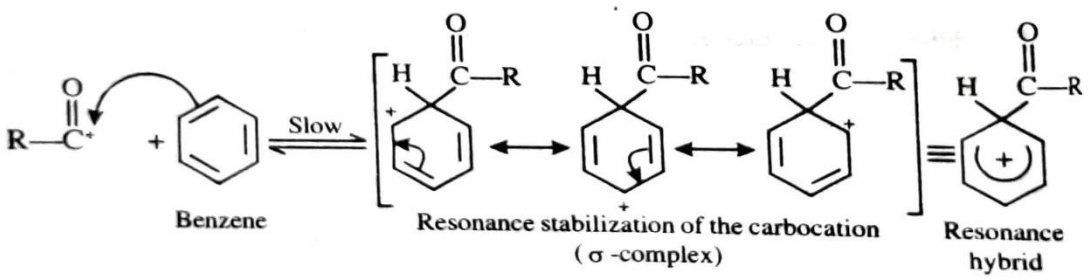
- Step 1- Generation of electrophile.

Acyl chloride reacts with anhy. $AlCl_3$ to yield acylium ion($R\text{-}CO^+$) which acts as electrophile.



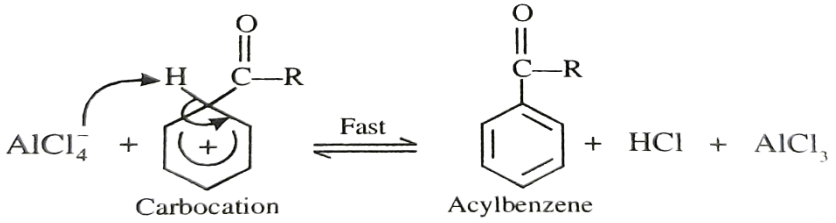
- Step 2- Formation of σ complex.

  The carbocation $R\text{-}CO^+$ attacks benzene to form a carbocation called σ complex which is stabilized by resonance. This is the rate determining step.



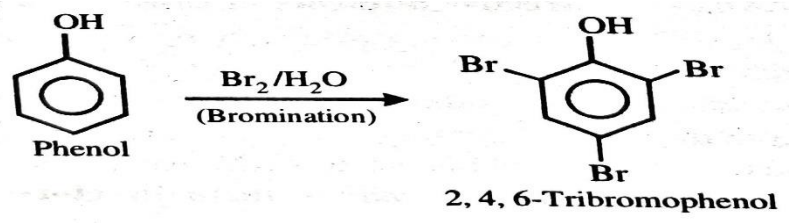
- Step 3- Loss of a proton from the σ complex.

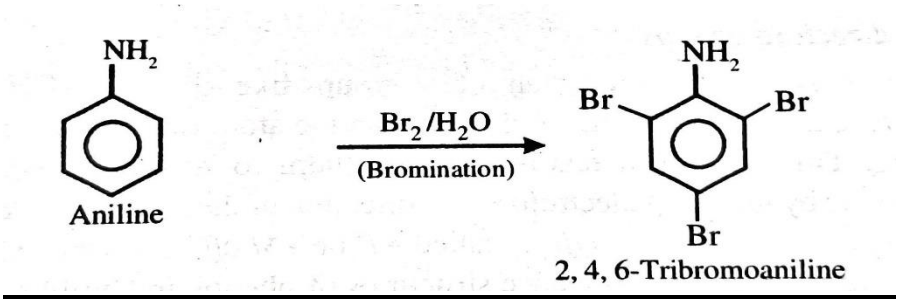
  $AlCl_4^-$ present in the reaction mixture abstract a proton from the σ complex and restores aromaticity to yield acylbenzene.

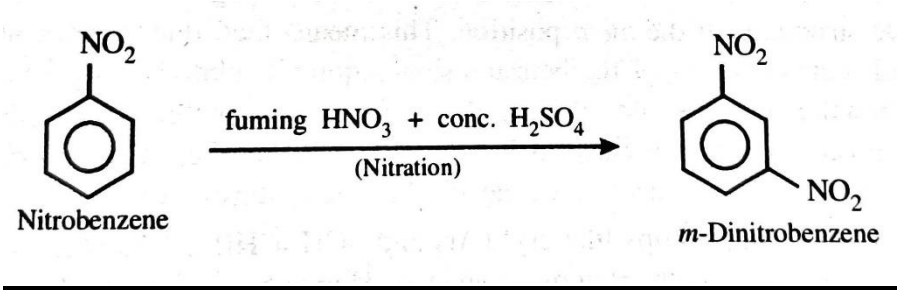


ORIENTATION EFFECTS OF SUBSTITUENTS- DIRECTIVE INFLUENCE OF GROUPS

- When a monosubstituted benzene undergoes further electrophilic attack, the substituent already present on the aromatic ring influences the orientation of further electrophilic substitution. This is known as directive influence of substituents.







- The substituent already present affect both the rate of reaction and site of electrophilic attack.
- Based on the way in which the substituent groups influence the incoming electrophile, they are classified into two classes-

  i. **Ortho-para directors-**

  Substituents that direct the incoming group into ortho and para positions are called ortho- para directors.

  ii. **Meta directors-**

  Substituents that direct the incoming group to meta position are called meta directors.

- Based on the manner in which the substituent influence the reactivity of aromatic ring, they are classified into two-

  i. **Activating groups-**

  Substituent groups that cause the benzene ring to be more reactive than benzene towards electrophilic substitution are called activating groups.

  Eg: strongly activating groups- $-NH_2$, -NHR, -OH, -OR

  Moderately activating groups- -NH-CO-R, -O-CO-R

  Weakly activating groups- -R, -Ar, -CH=CHR

  ii. **Deactivating groups-**

Substituent groups that cause the benzene to be less reactive than benzene towards electrophilic substitution are called deactivating groups

Eg: strongly deactivating groups- -CN, -SO_3H, -NO_2

Moderately deactivating groups- -CHO, -CO-R, -COOR, -COOH, -COCl

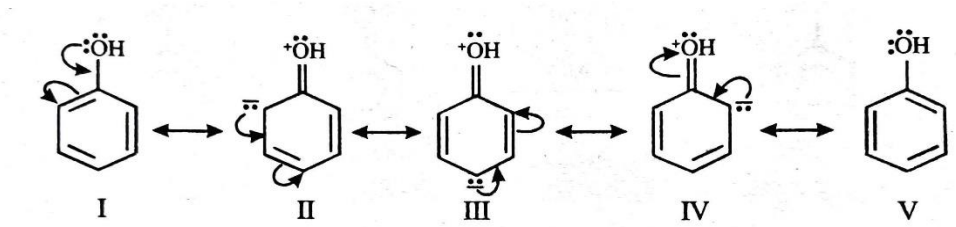
Weakly deactivating groups- -F, -Cl, -Br, -I.

- All the activating groups and weakly deactivating groups are ortho- para directors whereas the moderately and strongly deactivating groups are meta directors.

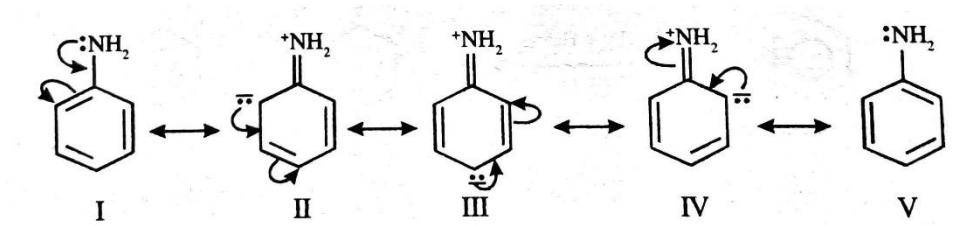
<u>Ortho- para directing groups</u>

- The ortho- para directing groups with unshared pair of electrons on the atom directly attatched to the benzene ring releases electron to the ring by resonance. This electron releasing resonance or mesomeric effect causes a higher electron density at ortho and para positions.

Eg: 1.phenol



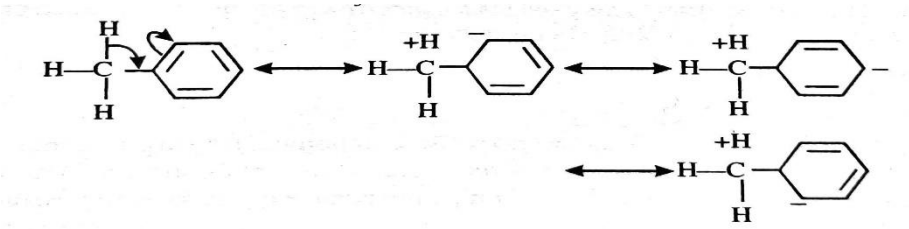
2. Aniline



- Weakly activating groups like Aryl and –CH=CHR are slightly electron donating than electron withdrawing. They can donate electrons by resonance. Hence they are ortho-para directing.

- In halogens, there are two effects- Electron withdrawing inductive effect (-I effect) and electron releasing resonance effect (+M or +R effect). The –I effect is prominent one. The halogens are slightly deactivating because of the fact that they withdraw electrons by –I effect. That is, they deactivate all positions. But the deactivation at ortho and para positions are opposed by the +R effect of halogen atom. Hence, they are ortho- para directors.

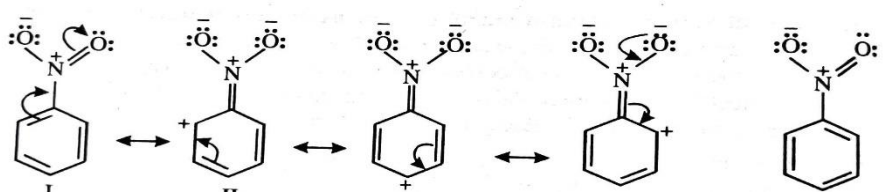
- Weakly activating alkyl groups (–R) can donate electrons by electron donating inductive effect (+I effect). They can also increase the electron density at ortho and para positions through hyperconjugation.



Meta directing groups

- Meta directing groups withdraws electron from the ring through resonance. The electron withdrawing resonance effect (-R or –M effect) causes electron density to be depleted from ortho and para positions. That is,meta positions have more electron density than ortho and para positions.

  Eg: Nitrobenzene.



AROMATICITY

- Criteria for a compound to be aromatic.

  1. Molecule must have a planar ring system having a continuous cyclic cloud of delocalized π electrons above and below the plane
  2. The π electron cloud must contain a total of (4n+2) π electrons, where n is an integer.

     The criteria for aromaticity can be summarized in the form of huckel rule.

- **Huckel's rule**

  Huckel's rule states that a planar cyclic conjugated polyene will be aromatic if and only if it contains a continuous π electron cloud and contains (4n+2) π electrons, where n is an integer (n=0, 1, 2, 3…).

  Significance-The number of π electrons required for a stable closed shell configuration with respect to the complete filling of bonding molecular orbitals in a planar conjugated cyclic system corresponds to (4n+2) π electrons.

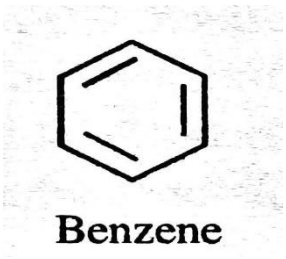
Benzenoid aromatic compounds

- Benzenoid aromatic compounds are those which contain benzene rings or fused benzene rings in the structures.

  Eg: benzene (C_6H_6) , naphthalene($C_{10}H_8$) anthracene($C_{14}H_{10}$)

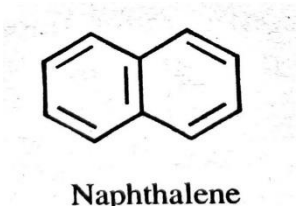
- Benzene- benzene is a planar, cyclic and completely conjugated molecule containing delocalized system of 6π electrons.

  4n+2=6 where n=1. Thus, according to Huckel's rule benzene is an aromatic compound.



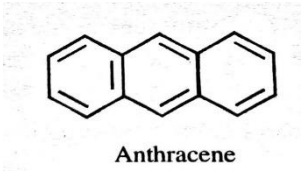
- Naphthalene- naphthalene is a planar, bicyclic and completely conjugated molecule containing delocalized system of 10π electrons.

  4n+2= 10 where n= 2. Thus, according to Huckel's rule naphthalene is an aromatic compound.



- Anthracene- Anthracene is a planar, tricyclic and completely conjugated molecule containing delocalized system of 14π electrons.

  4n+2= 14 where n=3. Thus, according to Huckel's rule anthracene is an aromatic compound.



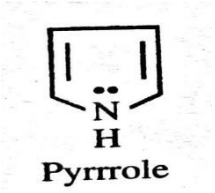
Non- Benzenoid aromatic compounds

- Non- benzenoid aromatic compounds does not have benzene ring in their structures.

  Eg: pyrrole(C_4H_5N), pyridine(C_5H_5N), Indole(C_8H_7N)

- Pyrrole- pyrrole is a planar, cyclic and completely conjugated five membered heterocycle containing delocalized system of six π electrons. The lone pair on N, which is in unhybridized p orbital, forms a part of delocalized system.

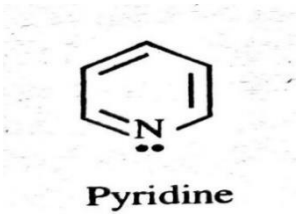
  4n+2= 6, where n=1. Thus, according to Huckel's rule, pyrrole is aromatic.



Pyrrrole

- Pyridine – pyridine is a planar, cyclic and completely conjugated six membered heterocyclic, containing delocalized system of six π electrons. Here, the lone pair on nitrogen is in sp^2 hybrid orbital. It is not the part of delocalized π system.

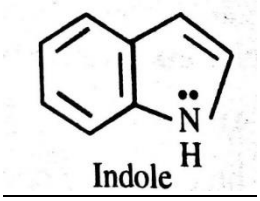
  4n+2=6, where n=1. Thus, according to Huckel's rule, pyridine is aromatic.



Pyridine

- Indole –Indole is a planar,bicyclic and completely conjugated heterocycle containing delocalized system of 10 π electrons. The lone pair on nitrogen is in unhybridised p orbital. It forms a part of delocalized π electron system.

  4n+2=10, where n=2. Thus according to Huckel's rule, Indole is aromatic.



Indole

MODULE 4: CHEMISTRY OF FUNCTIONAL GROUPS-1

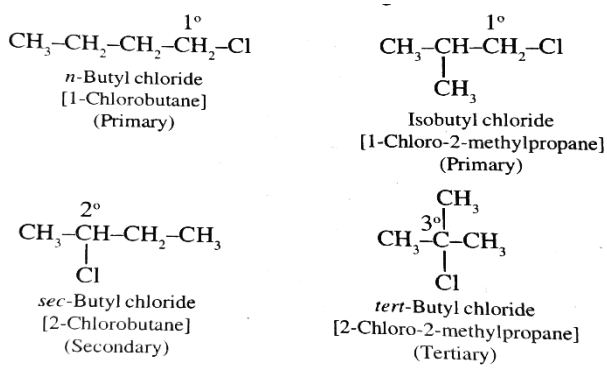
INTRODUCTION

- Three classes- Halogen compounds, alcohols, phenols.

HALOGEN COMPOUNDS

- Replacement of a hydrogen of an alkane by a halogen gives alkyl halide.
- Three types of alkyl halides- primary (1°), secondary (2°) and tertiary (3°).

Eg:



PREPARATION OF ALKYL HALIDE

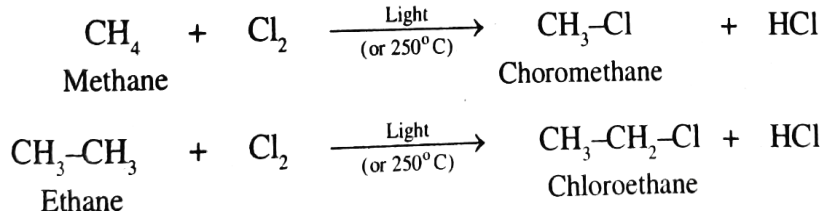
a) ***From alkanes by radical halogenation***

- Alkanes when treated with halogen either in the presence of UV light or upon heating at a temperature of 250-400°C gives alkyl halides.
- The order of reactivity of halogens is $F_2 > Cl_2 > Br_2 > I_2$.

(i)Chlorination:

- In chlorination, alkanes reacts with chlorine either in the presence of UV light or upon heating at 250-400°C.

Eg:



- Extend of chlorination depends on amount of Cl_2 used. Accordingly, monochloro, dichloro, trichloro, tetrachloro derivatives are possible.

Eg:

$$CH_4 + Cl_2 \xrightarrow[(or\ \Delta)]{UV\ light} \underset{Choromethane}{CH_3Cl} + HCl$$

$$CH_3Cl + Cl_2 \xrightarrow[(or\ \Delta)]{UV\ light} \underset{Dichloromethane}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow[(or\ \Delta)]{UV\ light} \underset{Trichloromethane}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow[(or\ \Delta)]{UV\ light} \underset{Tetrachloromethane}{CCl_4} + HCl$$

- In higher alkanes, isomeric products will be obtained.

(***ii) Bromination:***

- In bromination, alkanes reacts with bromine in the presence of UV light or upon heating at 250-400°C.

  Eg:

$$\underset{Methane}{CH_4} + Br_2 \xrightarrow[(or\ \Delta)]{Light} \underset{Bromomethane}{CH_3Br} + HBr$$

$$\underset{Ethane}{CH_3{-}CH_3} + Br_2 \xrightarrow[(or\ \Delta)]{Light} \underset{Bromoethane}{CH_3{-}CH_2Br} + HBr$$

(b)From alkenes:

- A halogen acid, HX (HCl, HBr, HI) adds to an alkene to yield corresponding alkyl halide.

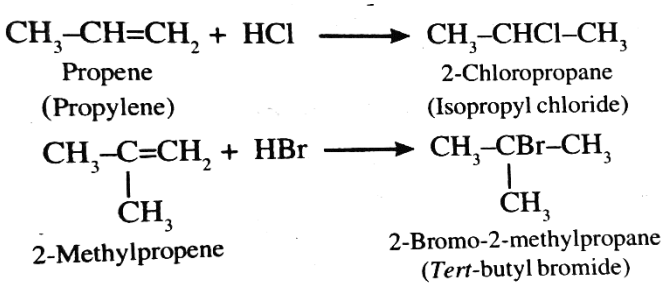
  Eg:

$$\underset{\substack{Ethene\\(Ethylene)}}{CH_2{=}CH_2} + HBr \longrightarrow \underset{\substack{Bromoethane\\(Ethyl\ bromide)}}{CH_3{-}CH_2{-}Br}$$

$$\underset{But\text{-}2\text{-}ene}{CH_3{-}CH{=}CH{-}CH_3} + HI \longrightarrow \underset{\substack{2\text{-}Iodobutane\\(\textit{Sec}\text{-}butyl\ iodide)}}{CH_3{-}CH_2{-}CHI{-}CH_3}$$

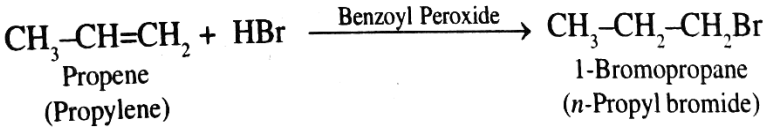
- Addition of HX to alkene takes place according to **Markonikov's rule**. The rule states that "***In the ionic addition of an unsymmetrical reagent to an unsymmetrical alkene, the positive part of the adding molecule goes to that carbon which bears the greater number of hydrogen atoms***".

Eg:



- When addition of HBr to an unsymmetrical alkene takes place in the presence of a peroxide, the addition occurs in accordance with **Anti-Markanikov's rule**. This is known as **peroxide** or **Kharasch** effect.

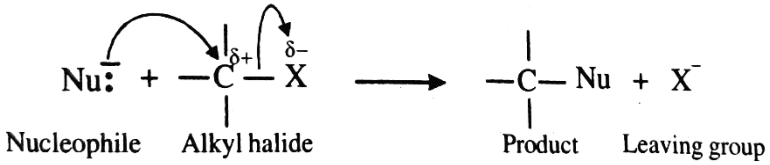
Eg:



REACTIONS OF ALKYL HALIDES

NUCLEOPHILIC SUBSTITUTION REACTIONS

- A substitution reaction in which the attacking reagent is nucleophile is called nucleophilic substitution reaction.



Eg: 1) Formation of alcohols:

Alkyl halides on treatment with boiling aq. NaOH/KOH or AgOH undergo hydrolysis

R-X + KOH $\xrightarrow{\Delta}$ **R-OH + RX**

2) Formation of ether: (**Williamson's synthesis**)

When alkyl halides are heated with sodium or potassium alkoxide, ethers are obtained.

R-X + NaOR' $\xrightarrow{\Delta}$ **R-O-R' + NaX**

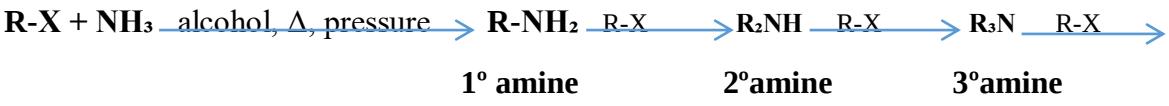
3) Formation of ester:

When alkyl halides are heated with alcoholic solution of silver salts of fatty acids, esters are obtained.

R'-COOAg + X-R $\xrightarrow{\text{alcohol,}\Delta}$ **R'-COO-R + AgX**

4) Formation of amines:

When heated with excess of alcoholic ammonia under pressure, alkyl halides yields primary amines. Further alkylation may results in a mixture of primary,secondary and tertiary amines and quarternary ammonium salt.



$R_4N^+X^-$

Quarternary salt

MECHANISM OF ALIPHATIC NUCLEOPHILIC SUBSTITUTION REACTIONS

- Depending upon kinetics, nucleophilic substitution reactions are of two types- S_N1 and S_N2.

A) *BIMOLECULAR NUCLEOPHILIC SUBSTITUTION REACTION- S_N2*

- A nucleophilic substitution reaction which is kinetically second order is known as bimolecular nucleophilic substitution reaction or S_N2.

Kinetics

- Rate depends on the concentrations of both the substrate and the nucleophile.

  Rate= k [substrate][nucleophile]

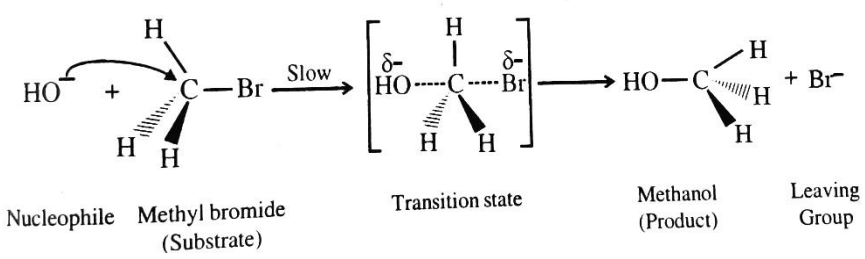
  k is the rate constant.

- Eg:

Rate= k [CH_3- Br][OH^-]

Mechanism

- S_N2 mechanism involves single step. It is a direct displacement reaction in which bond-breaking and bond-making occur simultaneously.

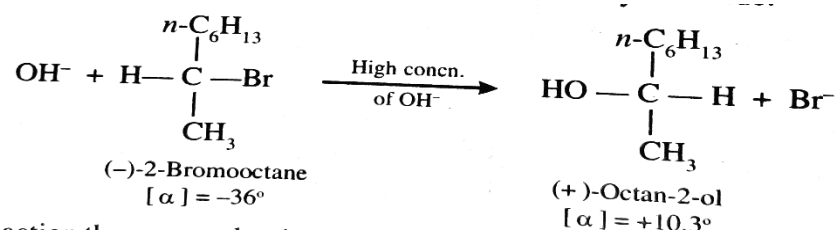


- The nucleophile attacks the carbon from sterically favourable rear side (back side attack) and the reaction proceeds through a transition state. The transition state is one

in which the carbon is partially bonded to both the incoming nucleophile and the leaving group. In this state, the three hydrogens and the carbon lie in a single plane making a bond angle of 120º. OH and Br lie on either sides of the plane perpendicular to it. Gradually, the bond between the Carbon and nucleophile is fully formed and that between carbon and bromine is completely broken to form the products.

Stereochemistry

- S_N2 mechanism proceeds with complete stereochemical inversion. Such an inversion is referred to as Walden inversion.
- Eg: The S_N2 reaction of (-)- 2-Bromooctane with concentrated NaOH yields (+)-2-octanol.



(–)-2-Bromooctane
[α] = –36º

(+)-Octan-2-ol
[α] = +10.3º

- S_N2 mechanism involves back side attack. In MO terms, this is the favoured mode of attack because as one lobe of the sp^3 orbital of C is overlapping with a p-orbital of Br, the orbital of nucleophile can overlap only with the other lobe on opposite side.
- The hybridisation of C goes from sp^3 to sp^2 and then again to sp^3.

Factors affecting reactivity in S_N2 reactions of alkyl halides.

A) Nature of substrate(alkyl halides)

- The relative reactivities of alkyl halides in S_N2 reactions are in the order

  Methyl halide> 1º alkyl halide > 2º alkyl halide > 3º alkyl halide

  Eg: CH_3-X > CH_3-CH_2-X > $(CH_3)_2CH$ > $(CH_3)_3C$-X

- The order of reactivity is explained on the basis of steric factors.

  In methyl halide, the methyl group offers no steric hindrance to the back side attack of incoming nucleophile. Thus methyl halide readily undergoes S_N2 reaction. Steric hindrance increases with increasing number of alkyl groups. In tertiary halides, the steric hindrance is so great that they are unable to undergo S_N2 reactions.

- The steric hindrance also increases with an increase in size of alkyl group. The order of reactivity of ethyl halide and n-propyl halide is

  CH_3-CH_2-X > CH_3-CH_2-CH_2-X

  Ethyl halide n-propyl halide

(B)Nature of nucleophile

- The greater the nucleophilicity of a nucleophile, greater is its S_N2 reactivity. Nucleophilicity is a measure of the tendency of a nucleophile to share its non-bonding electrons with an electron- deficient centre. Stronger bases are better nucleophiles.

Eg: In the case of CH_3^-, H_2N^-, OH^- and F^-, the basicity order is

$$CH_3^- > NH_2^- > OH^- > F^-$$

Which is also the order of nucleophilicities.

(C)Nature of leaving group

- Weaker the basicity of the leaving group, the better is its leaving ability.

  Eg: The relative basicities of the halide ions are in the order

  $I^- < Br^- < Cl^- < F^-$

  Hence the relative leaving abilities of halide ions are in the order

  $I^- > Br^- > Cl^- > F^-$

  The relative reactivities of alkyl halides are in the order

  RI > RBr > RCl > RF

B) **UNIMOLECULAR NUCLEOPHILIC SUBSTITUTION REACTIONS- (SN1)**

- A nucleophilic substitution reaction which is kinetically first order is known as unimolecular nucleophilic substitution reaction or S_N1.

Kinetics

- Rate depends only on the substrate concentration and is independent of concentration of nucleophile. Rate determining step involves only one molecule.

  Rate law for an S_N1 reaction is

  Rate = k [substrate]

  Where 'k' is the rate constant.

- Eg: Reaction between tert-butyl bromide and hydroxide ion to yield tert- butyl alcohol.

  $(CH_3)_3C\text{-}Br + OH^- \longrightarrow (CH_3)_3C\text{-}OH + Br^-$

  Tert-butyl bromide *Tert-butyl alcohol*

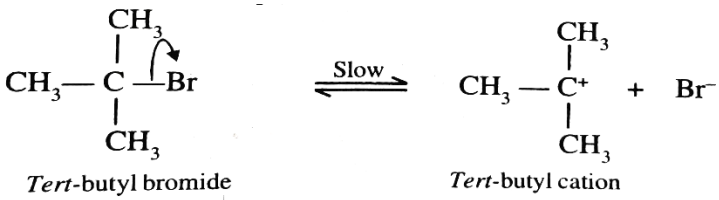
  Rate = k [$(CH_3)_3C$-Br]

Mechanism

- S_N1 mechanism involves two steps-

  Step-1

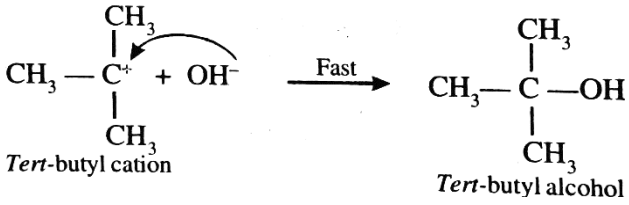
  The leaving group breaks away by the heterolytic fission of the carbon-halogen bond producing carbocation. This step is the slow step and hence the rate-determining step.



Tert-butyl bromide — *Tert*-butyl cation

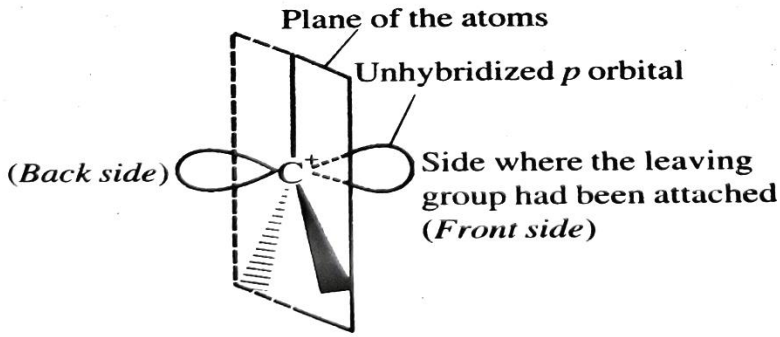
Step-2

The carbocation rapidly reacts with the nucleophile to yield the product.



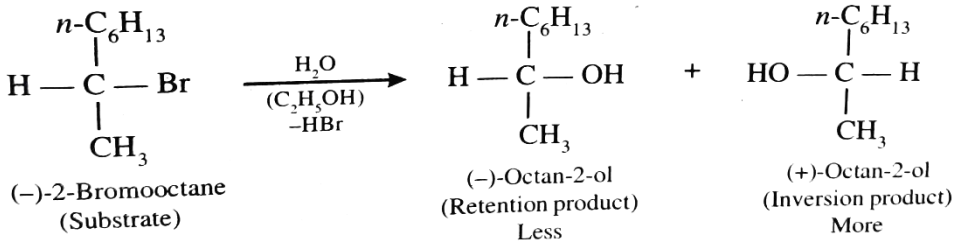
Tert-butyl cation — *Tert*-butyl alcohol

Stereochemistry of SN1 reaction



- Carbocation is formed in the initial step of SN1 reaction by breaking carbon-halogen bond. The carbocation has a planar structure. The nucleophile can attack from both front side and back side. The front side attack leads to retention of configuration whereas back side attack would leads to inversion of configuration. Since both are equally probable, we expect the formation of racemic mixture (in case of chiral carbon). But, it is seen that the inversion products predominates over retention product.

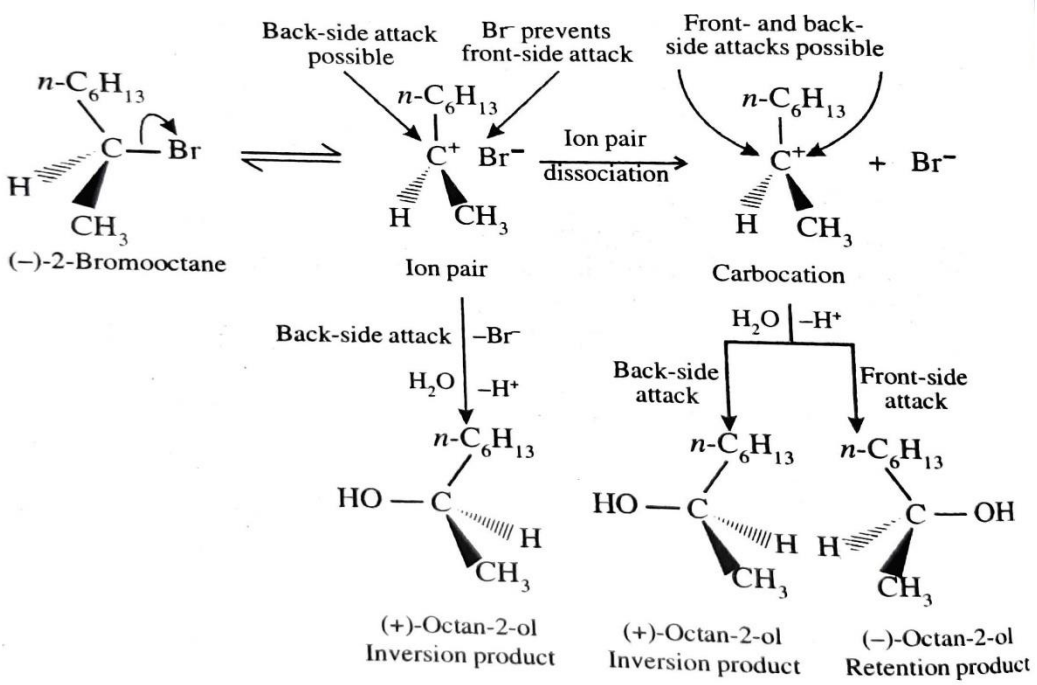
  Eg:



(–)-2-Bromooctane (Substrate) — (–)-Octan-2-ol (Retention product) Less — (+)-Octan-2-ol (Inversion product) More

- The front side is shielded from the approach of nucleophile by the departing leaving group. The leaving group is under the influence of an electrostatic attraction with the carbocation for a period of time. This combination is called ion-pair. During this period, the nucleophile can attack only from back side leading to inversion product. After the

ion- pair are separated, both front side and back side attack is possible, yielding both the inversion and retention products. So, in overall reaction, inversion products predominates.



FACTORS AFFECTING REACTIVITY IN THE S_N1 REACTIONS

(A)Nature of alkyl group:

- The relative reactivities of alkyl halides in an S_N1 reaction is

  3º alkyl halide > 2º alkyl halide >1º alkyl halide > methyl halide

  Eg:

  $(CH_3)_3C\text{-}X > (CH_3)_2CH\text{-}X > CH_3\text{-}CH_2\text{-}X > CH_3\text{-}X$

- The greater the stability of carbocation, greater is its ease of formation and greater the S_N1 reactivity of alkyl halides.

(B)Nature of the leaving group:

- The weaker the basicity of the group, better is its leaving ability. This is because weaker the base, weaker is its bond with carbon atom.

  Eg: The order of basicity of halide ions is

  $I^- < Br^- < Cl^- < F^-$

  Therefore, the order of leaving abilities of halide ions is in the order

  $I^- > Br^- > Cl^- > F^-$

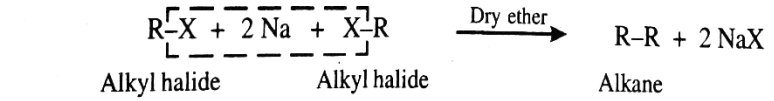
(C) **Nature of nucleophile**

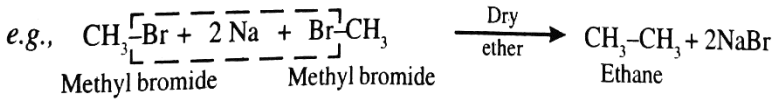
- Reactivity of nucleophile has no effect on the rate of S_N1 reaction. When solvent act as nucleophile in S_N1 reaction, the reaction is called solvolysis.

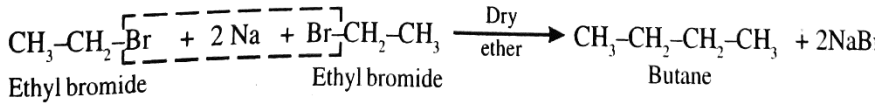
REACTIONS OF ALKYL HALIDES

WURTZ REACTION:

- Alkyl halides when treated with sodium metal in dry ether solution yield higher alkanes.This reaction is called Wurtz reaction.

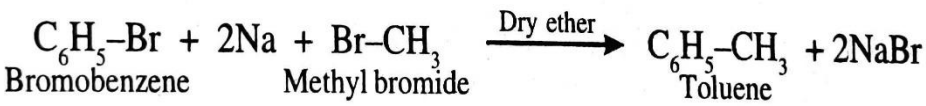






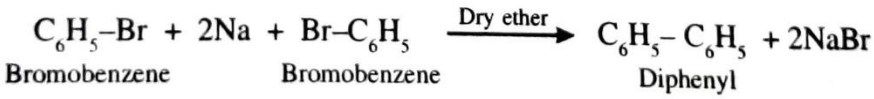
WURTZ- FITTIG REACTION:

- When an aryl halide is heated with alkyl halide in the presence of sodium in dry ether solution, alkyl arenes are obtained. This reaction is called Wurtz- Fittig reaction.



FITTIG REACTION:

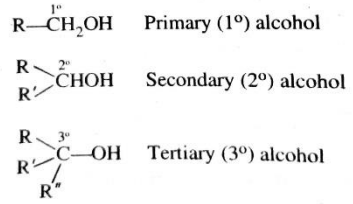
- When an aryl halide is heated with sodium in dry ether, diaryls are obtained. This reaction is called Fittig reaction.



ALCOHOLS

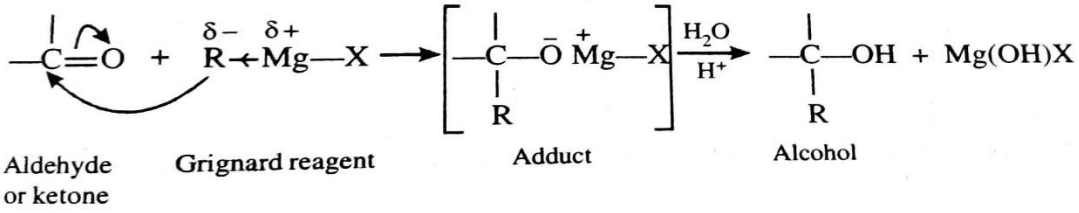
- Alcohols are compounds having general formula C_nH_{2n+1}–OH.
- Alcohols are classified into primary, secondary and tertiary.

  Eg:

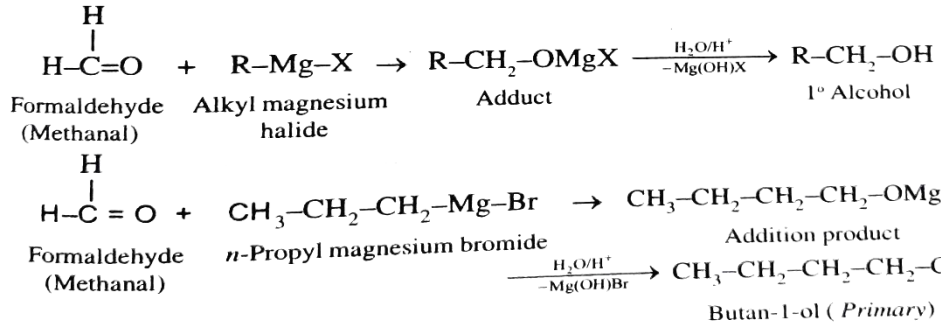


PREPARATION OF ALCOHOLS FROM GRIGNARD REAGENTS

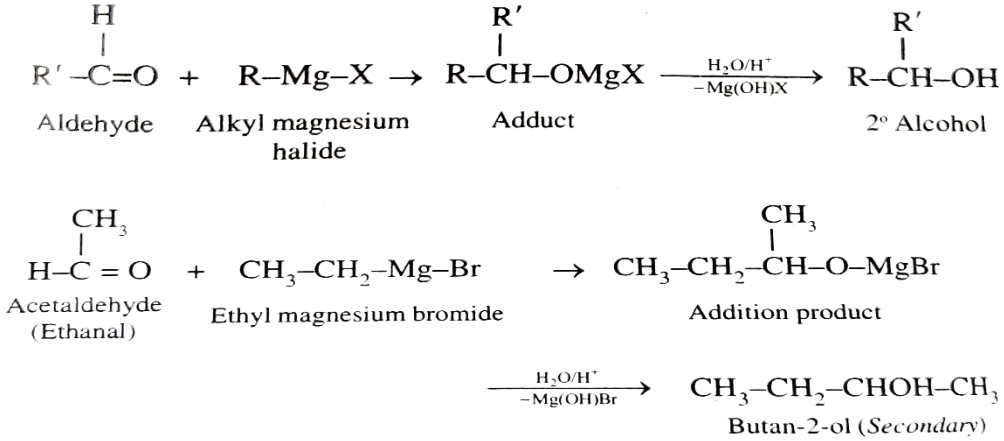
- Grignard reagents are organomagnesium halides having general formula R-Mg-X.
- Alcohols are prepared by the reaction of Grignard Reagents with aldehydes and ketones, followed by acidic hydrolysis.
- The mechanism involves two steps. First step involves the nucleophilic addition of Grignard reagent to the carbonyl group to form an adduct. Second step is the hydrolysis of adduct to yield alcohol.



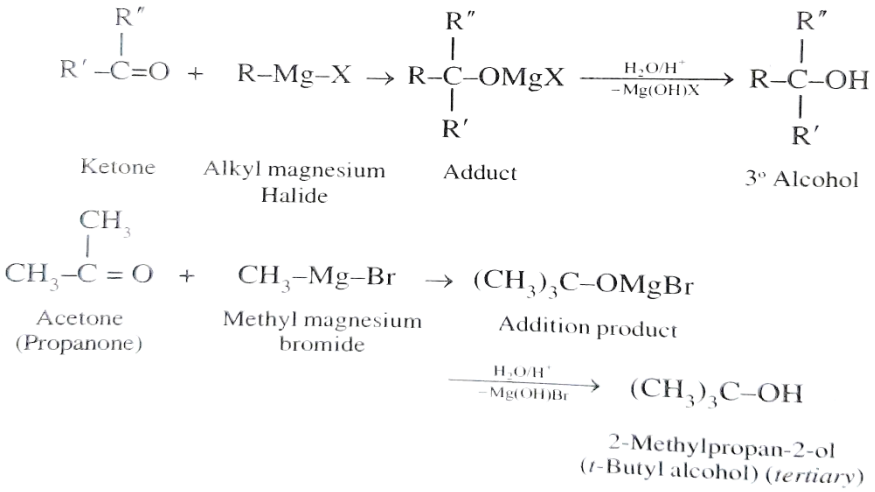
- Formaldehyde reacts with Grignard reagent to form adduct which on acidic hydrolysis yield primary alcohol.



- Aldehydes other than formaldehyde react with Grignard reagent to form adduct which on acidic hydrolysis yield secondary alcohol.

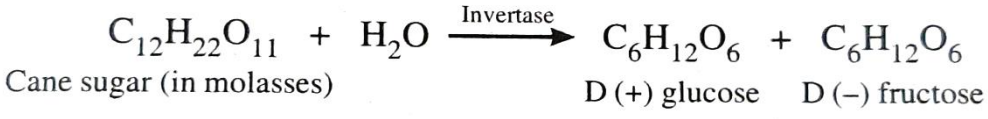


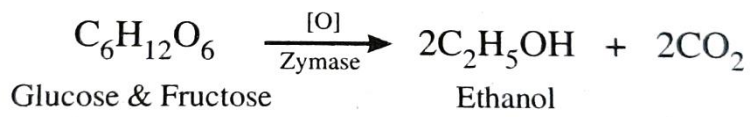
- Ketone react with Grignard reagent to form an adduct which on acidic hydrolysis yield tertiary alcohol.



MANUFACTURE OF ETHANOL FROM MOLASSES

- Ethanol is manufactured from molasses by the fermentation process. Molasses is diluted with water to get 10% solution of sugar. Yeast is added to it and kept at 303-308K for 2-3 days. The enzyme invertase present in yeast hydrolysis sucrose (sugar) to glucose and fructose. The enzyme zymase present in the yeast convert glucose and fructose into ethanol.





- 8-10% solution of ethanol obtained by the fermentation of carbohydrates is called Wash.
- 95.6% solution of ethanol obtained by fractional distillation of wash is called rectified spirit.
- 100% ethanol solution obtained by distillation of rectified spirit over quick lime(CaO) and over a few pieces of calcium is called absolute alcohol.
- Alcohol for industrial purpose is made unfit for drinking by adding some copper sulphate and poisonous substances like methanol, pyridine etc. This process is called denaturation of alcohol and the alcohol thus obtained is called denatured spirit.
- Ethanol denatured with small quantity of methanol(5%) is called methylated spirit.
- Proof spirit is used to represent an alcohol-water mixture or a beverage containing a standard amount of alcohol. It is used a standard of strength of distilled alcohol and is denoted as 100 proof.

- Ethanol is used as an additive to the fuels for automobiles or other internal combustion engines. Ethanol used for generation of power is called power alcohol.

ACIDITY OF ALCOHOLS

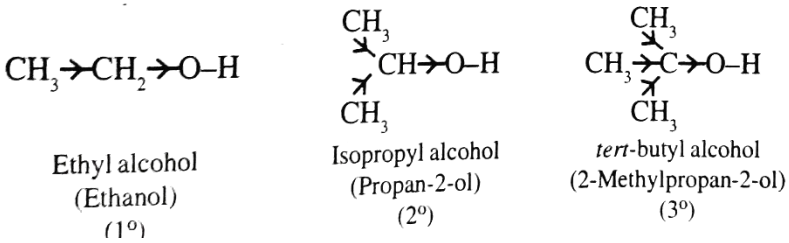
- Alcohols show feeble acidic property. They react with active metals (Na, K etc) to yield alkoxides.

Alcohol sodium alkoxide

- The acidic character of alcohols is due to polar nature of O-H bond. But, they are weakly acidic because the electron density on oxygen increases by +I effect. This decreases the polarity of OH bond and thereby decreases the acidic strength.
- The greater the number of electron-releasing alkyl groups attached to the carbon carrying OH group, the polarity of O-H bond decreases due to +I effect. This results in decrease of acidic character. Hence, the acidic strength of the alcohols decreases in the order

Primary> secondary> tertiary

Eg:



Ethyl alcohol (Ethanol) (1^o)

Isopropyl alcohol (Propan-2-ol) (2^o)

tert-butyl alcohol (2-Methylpropan-2-ol) (3^o)

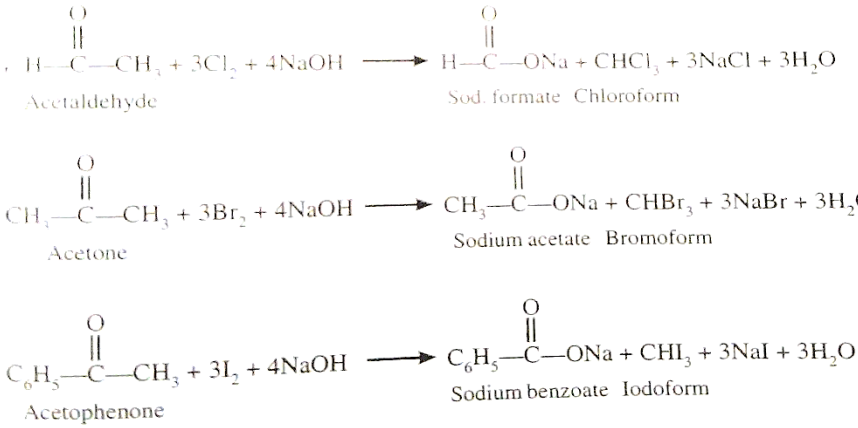
HALOFORM REACTION

- Acetaldehyde (CH_3-CHO) and methyl ketones (R-CO-CH_3) when oxidised by halogen (Cl_2,Br_2,I_2) and alkali (NaOH) results in the formation of haloform and salt of carboxylic acid. This reaction is called haloform reaction.

Methyl ketone Trihalocompound

Trihalocompound Sodium carboxylate Haloform

- When halogen is Chlorine, chloroform is formed. Bromoform and Iodoform are formed when halogens are Bromine and Iodine respectively.



- Compounds like ethanol(CH_3-CH_2-OH),propan-2-ol(CH_3-CHOH-CH_3)etc get oxidised when treated with halogen and alkali to aldehydes or ketones containing CH_3-CO- group. They also give haloform reaction.
- *IODOFORM TEST*- Iodoform test is used to detect the presence of CH_3-CO- group in ketone or CH_3-CHOH- group in alcohol. If I_2 and alkali are the reagents used in the haloform reaction, Iodoform is formed, which is a yellow precipitate having characteristic odour. It is an easily recognizable compound.

LUCAS TEST

- Lucas test is used to distinguish primary, secondary and tertiary alcohols.
- Alcohols on treating with lucas reagent forms alkyl halides. Lucas reagent is a mixture of conc.HCl and anhy.$ZnCl_2$. The time required for the formation of alkyl halides (indicated by the presence of turbidity) is different for different alkyl halides.
- A tertiary alcohol produces turbidity immediately. Secondary alcohol produces turbidity only in about 5mts. Primary alcohol does not produce any turbidity at all.

CHEMISTRY OF METHANOL POISONING

- Methanol absorption in humans can cause severe metabolic disturbances,blindness and permanent neurological dysfunction leading to coma and death.
- Methanol is metabolized in the liver through dehydrogenation by the enzyme alcohol dehydrogenase to toxic formaldehyde and then to highly toxic formic acid.

  CH_3-OH ~~Alcohol dehydrogenase~~→ H-CHO ⟶ H-COOH

  Methanol Formaldehyde Formic acid
- Formic acid inhibits mitochondrial cytochrome c oxidase, causing hypoxia. It also causes metabolic acidosis.

HARMFUL EFFECTS OF METHANOL IN HUMAN BODY

1. ***Central nervous system***:

- Alcohol depresses central nervous system.

- It interfers with brain communication pathway causing changes in mood and harder to think.
- Leads to slurred speech, impaired vision and foggy memory.
- Impaires judgement and leads to accidents.
- Adversely affect normal thought processes and moral judgement, leading to domestic violence and sexual assaults.
- Long term drinking causes permanant damage to brain.

2. ***Heart:***

- Heavy drinking and long term drinking can lead to cardiomyopathy(weakening and stretching of heart muscle),cardiac arrhythmia (irregular heart beat) and blood pressure.

3. ***Liver:***

- Drinking leads to a variety of chronic liver problems like steatosis(fatty liver),alcohol hepatitis, liver fibrosis, liver cirrhosis.

4. ***Pancreas:***

- Alcohol causes the pancreas to produce toxic substances that can lead to inflammation and swelling of blood vessels in the pancreas which affects digestion. Alcohol reduces the amount of digestive enzymes produced by pancreas.

5. ***Stomach:***

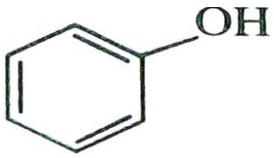
- Drinking alcohol makes the stomach more acidic, leading to gastritis. Alcohol consumption can also lead to peptic ulcer. Chronic irritation may lead to damage of lining of the stomach. Alcohol can affect digestive process, depriving the essential vitamins and minerals required.

6. ***Kidney:***

- Chronic alcohol consumption can interfere with kidney function directly and indirectly. Alcohol has diuretic effect, it causes an increase in the production of urine. This can change the body fluid level and disturb the electrolytic balance. Alcoholic liver disease impairs the rate of plasma flow and filtration in kidneys.
- Long term drinking may lead in developing cancers. Drinking too much alcohol weakens the immune system.

PHENOLS

- Phenols are organic compounds containing at least one –OH group attached directly to a benzene ring.

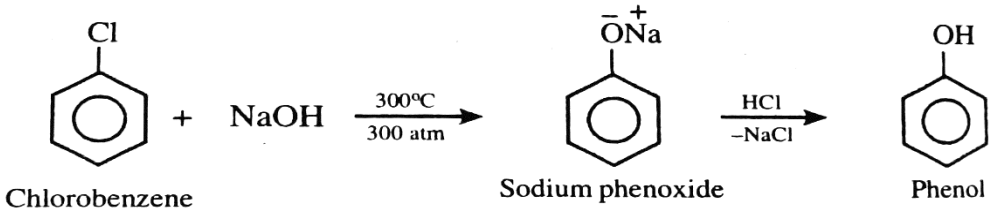


Phenol

PREPARATION OF PHENOL FROM CHLOROBENZENE

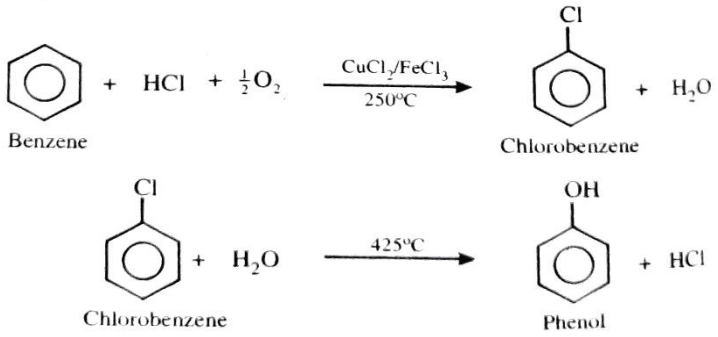
1. Dow process:

Chlorobenzene is heated with NaOH at 300ºC and 300 atm pressure to get sodium phenoxide which upon acidification yields phenol.



2. Raschig's process:

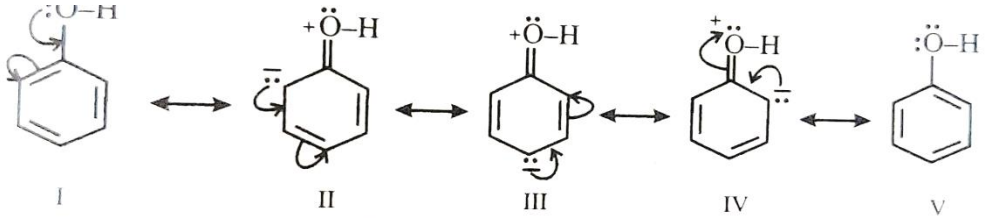
Chlorobenzene, obtained by the interaction of benzene, hydrogen chloride and air at 250ºC in the presence of a mixture of cupric chloride and ferric chloride as catalyst, is hydrolysed by superheated steam at 425ºC to get phenol and HCl.



ACIDITY OF PHENOLS

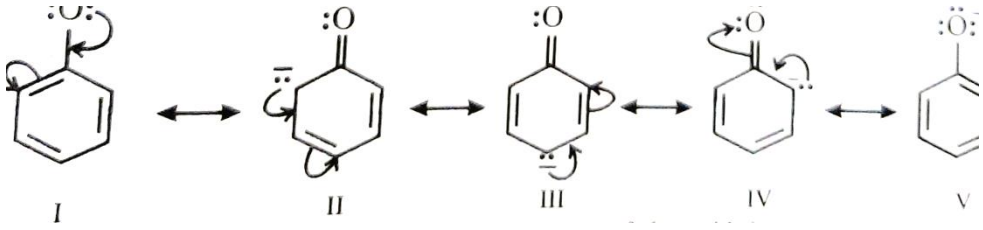
- Phenols are acidic in nature. The acidicity is due to two reasons.

1. Due to resonance, the oxygen atom of the –OH group acquires a positive charge which helps in the release of a proton.



Resonating structures of phenol

2. The phenoxide ion is more stabilized by resonance than phenol. In phenoxide ion there is no charge separation and also there is delocalization of negative charge over the ring.

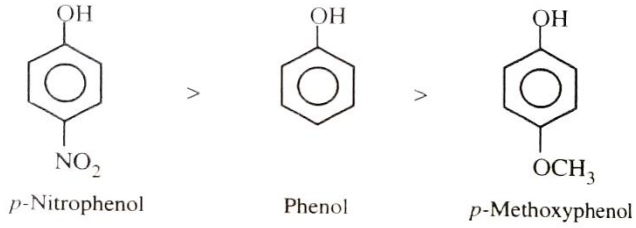


- Resonance stabilization is not seen in alcohols. Therefore, phenols are more acidic than alcohols.

EFFECTS OF SUBSTITUENTS ON ACIDITY OF PHENOL

- The presence of electron withdrawing groups such as NO_2, CN, CHO, COOH enhances the acidic strength of phenol when present at ortho or para positions. This is because of the effective dispersal of its negative charge through negative resonance effect.
- The presence of electron donating groups such as alkyl groups,-NH_2, -OH, -OR etc at ortho or para positions destabilize the phenoxide ion by intensifying negative charge through positive resonance effect. This results in decrease of acid strength.
- When groups like -NH_2, -OH,-OR etc when present in meta position increase the acidity of phenols by **–I** effect.

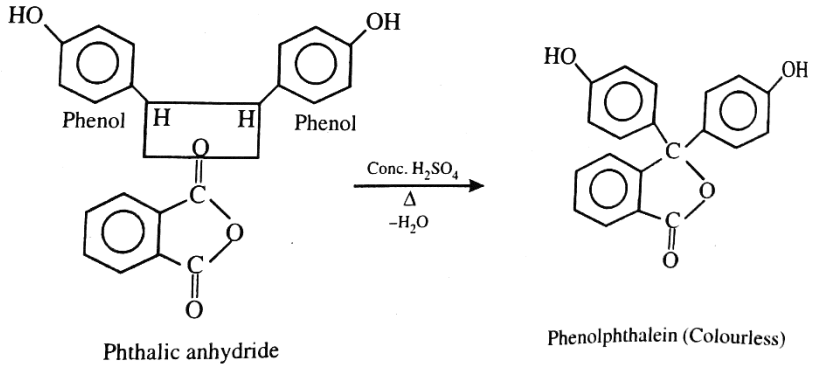
Eg: The acidic strength of phenol, p-nitrophenol, p-methoxyphenol is in the order



p-Nitrophenol Phenol *p*-Methoxyphenol

PHENOLPHTHALEIN

- **Preparation:** When phenol is heated with pthalic anhydride in the molar ratio 2:1 in the presence of conc.H_2SO_4, phenolphthalein is obtained.



Phthalic anhydride Phenolphthalein (Colourless)

- **Uses:**

1. Phenolphthalein is used as an indicator in acid-base titrations.
2. It is a component of universal indicator.

3. Phenolphthalein powder is used to trap corrupt officials. The powder is applied on currency notes given to them, objects which come in close contact with the above marked notes turn pink upon washing with alkali solution.
4. Phenolphthalein has been used as a laxative in early days.

MODULE: 5- CHEMISTRY OF FUNCTIONAL GROUPS-II

INTRODUCTION-

- Aldehydes and ketones, Carboxylic acids, Amines, Diazonium salts.

ALDEHYDES AND KETONES

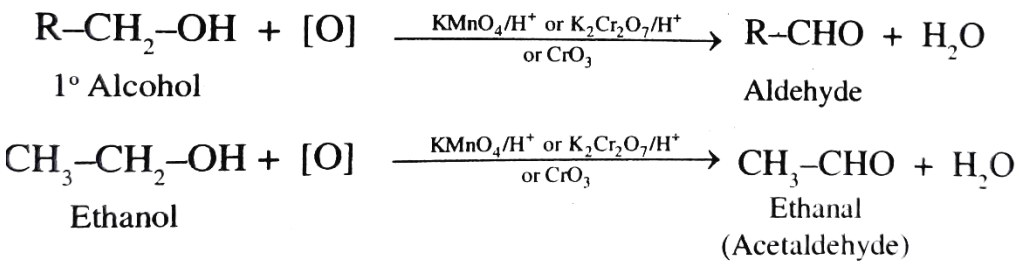
- Aldehydes and ketones are compounds containing the carbonyl group or oxo group (C=O group).

PREPARATION OF ALDEHYDES

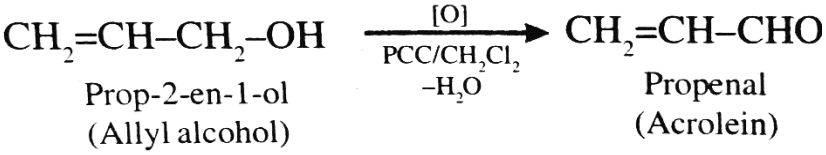
1. By oxidation of primary alcohols-

- Primary alcohols are oxidised to the corresponding aldehyde on treatment with strong oxidizing agents such as acidified $KMnO_4$ or $K_2Cr_2O_7$ or CrO_3 in an anhydrous medium.

  Eg:

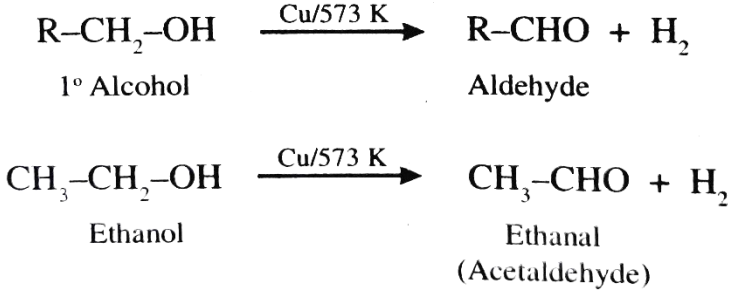


- Primary alcohols are also oxidized to aldehydes by pyridinium chlorochromate(PCC). The advantage of using PCC is that it leaves any carbon- carbon multiple bond uncleaved and unoxidised.



2. By dehydrogenation of primary alcohols-

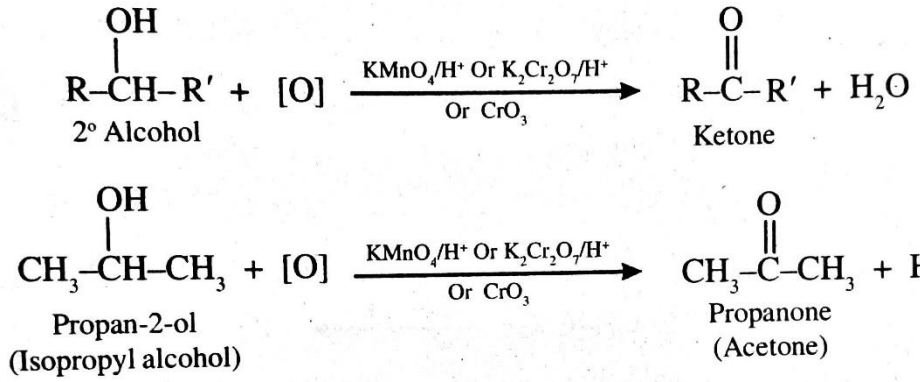
- When vapours of primary alcohol are passed over heated copper, dehydrogenation of alcohol occurs to yield corresponding aldehyde.



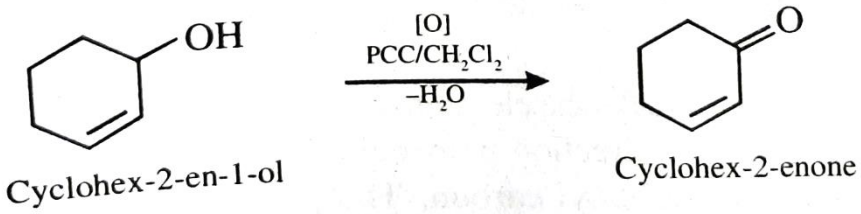
PREPARATION OF KETONES

1. By oxidation of secondary alcohols-

- Secondary alcohols are oxidised to corresponding ketone on treatment with acidified $KMnO_4$ or $K_2Cr_2O_7$ or CrO_3 in anhydrous medium.

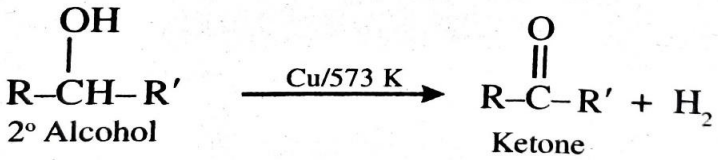


- Secondary alcohols are also oxidised to ketones by PCC. It will leave the C-C multiple bond unaffected.



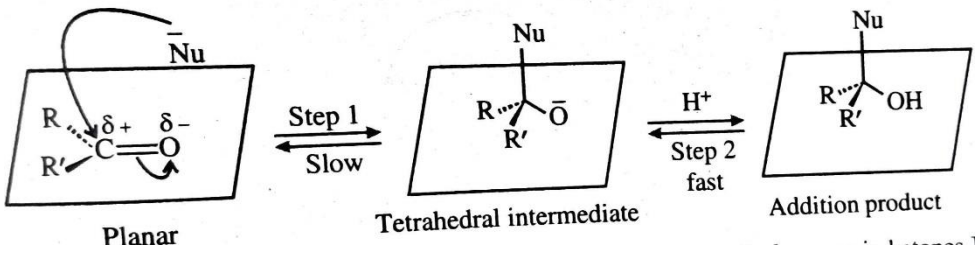
2. <u>By dehydrogenation of secondary alcohols-</u>

- When vapours of secondary alcohols are passed over heated copper, dehydrogenation of alcohol occurs to yield corresponding ketones.



NUCLEOPHILIC ADDITION REACTIONS OF ALDEHYDES AND KETONES

- **<u>General mechanism</u>**-



<u>Step-1</u>: The nucleophile attacks the electron deficient carbon atom of carbonyl group in a direction perpendicular to the plane of three sigma bonds attached to the carbonyl carbon. There is a change of hybridisation from sp^2 to sp^3 and intermediate is tetrahedral.

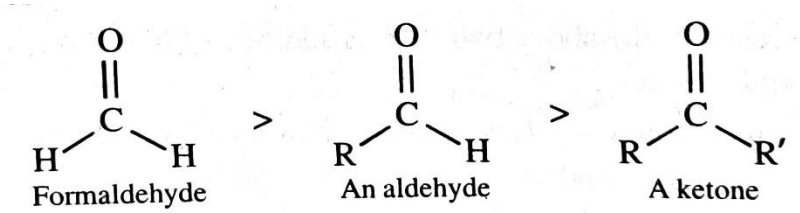
Step-2: The intermediate formed capture a proton from the reaction medium to yield addition product.

- Ketones are less reactive than aldehydes in nucleophilic addition reactions because

(i) The approach of nucleophiles to carbonyl carbon is sterically more hindered in ketones than in aldehydes.

(ii) The electron releasing nature (+I) of alkyl group decreases the electrophilicity of carbonyl carbon.

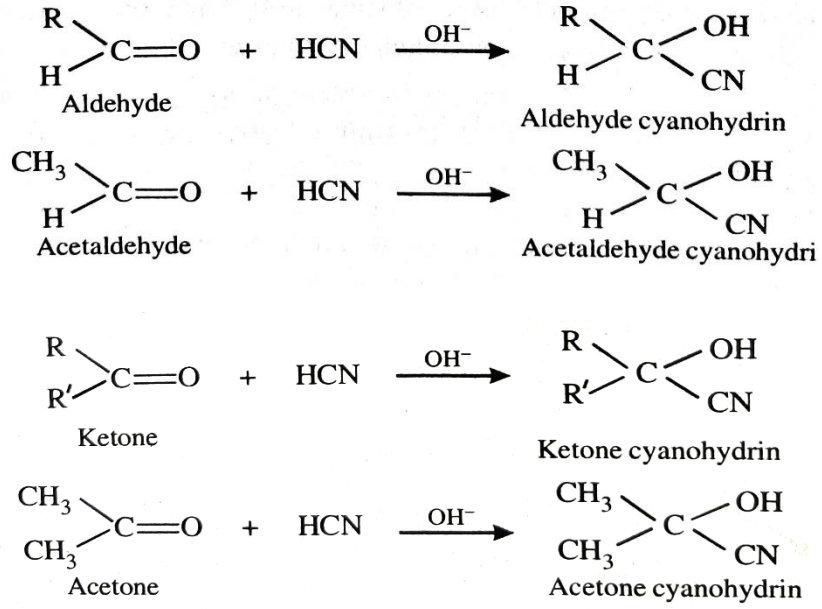
(iii) The transition state is tetrahedral with bond angle 109.5° while the original compound was trigonal planar (bond angle 120°). In ketones the steric crowding will be more in transition state.



- **Examples for nucleophilic addition reactions-**

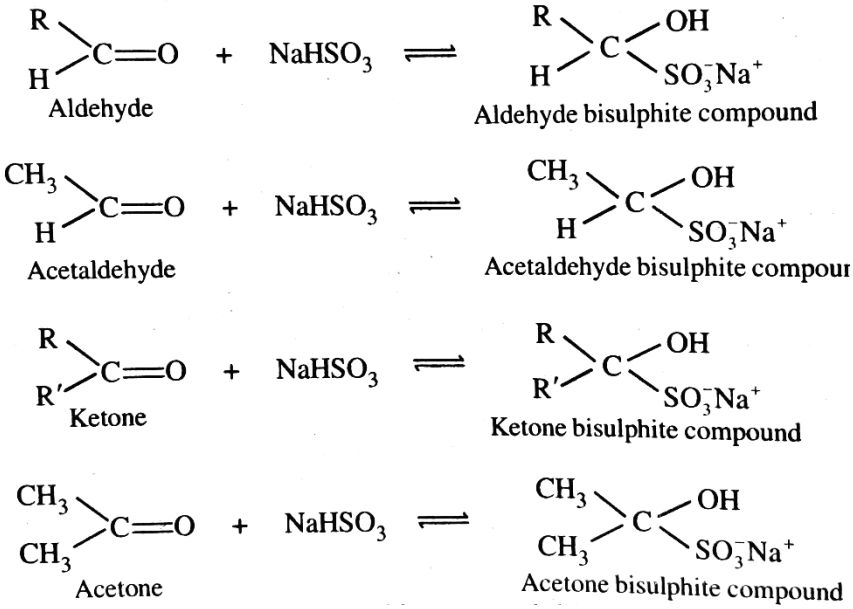
1. Addition of HCN:

- Aldehydes and ketones add HCN in the presence of a base to form cyanohydrins.



2. Addition of sodium bisulphite-

- Aldehydes and ketones add sodium bisulphite ($NaHSO_3$) to form crystalline bisulphite addition compound.

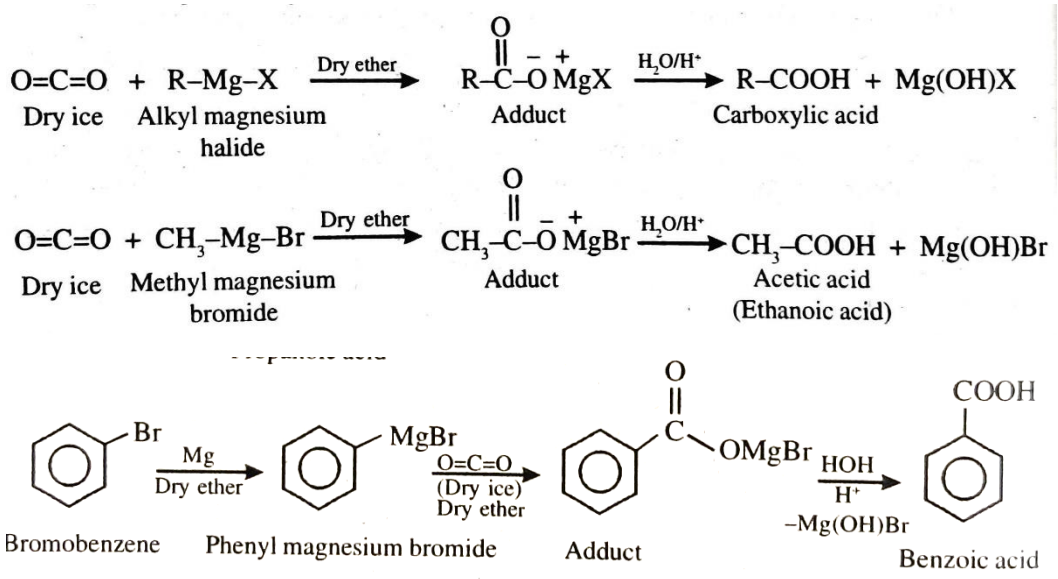


CARBOXYLIC ACIDS

- Organic compound containing carboxyl group(- COOH) are called carboxylic acids.

PREPARATION OF CARBOXYLIC ACIDS

- From Grignard reagent-
- Grignard reagents react with solid carbon dioxide in equimolar amounts in dry ether medium to form addition product which on acidic hydrolysis give the corresponding carboxylic acids.

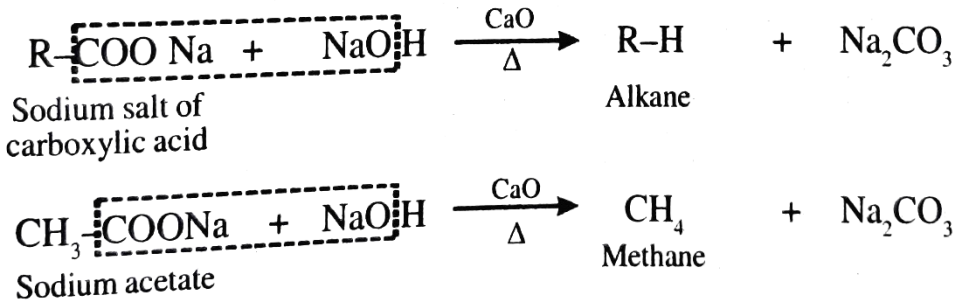


REACTIONS OF CARBOXYLIC ACIDS

1. **Decarboxylation**-

(a) Action of soda lime on sodium carboxylates-

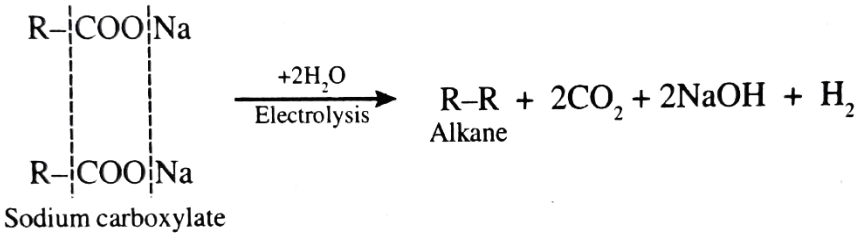
- When sodium salt of aliphatic carboxylic acid is fused with soda lime, an alkane with one carbon atom less than the parent carboxylic acid is obtained. The reaction involves the removal of CO_2 group and is called decarboxylation.

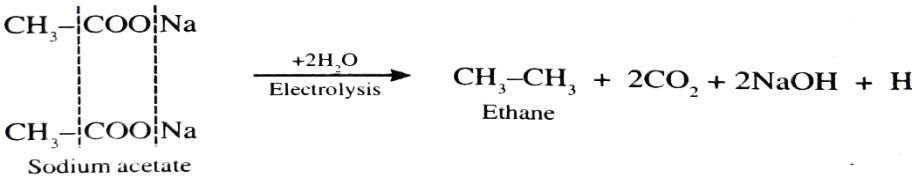


- When sodium salt of aromatic carboxylic acids is fused with dry soda lime, an arene with one carbon less is obtained.

2. <u>Kolbe's electrolyltic method –</u>

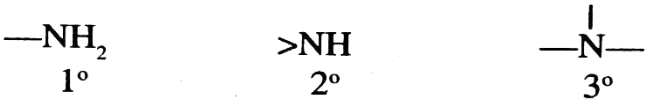
- Concentrated aqueous solution of sodium or potassium salt of a carboxylic acid on electrolysis gives an alkane containing even number of carbon atoms at anode. This process is called Kolbe's electrolytic method.





AMINES

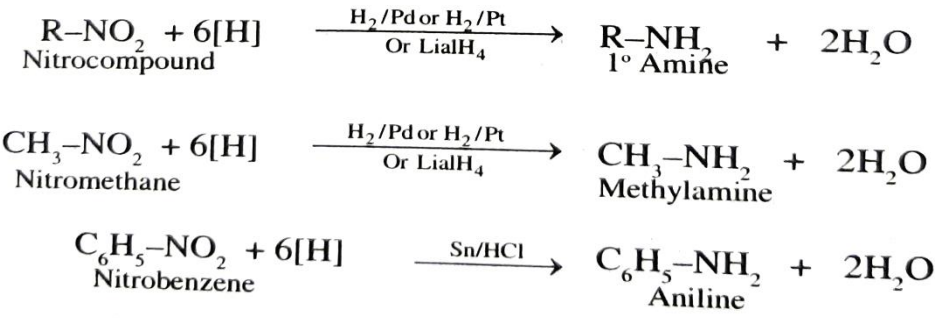
- Amines are derivatives of ammonia in which one, two or all the three hydrogen atoms of hydrogen are replaced by alkyl or aryl substituents.



PREPARATION OF AMINES

1. <u>By reduction of nitro compounds:</u>

- Nitro compounds can be reduced by catalytic hydrogenation (H_2/Pd or H_2/Pt)to the corresponding primary amines. Or by using reducing agents Fe/HCl or Sn/HCl or $LiAlH_4$.



2. <u>By Hoffmann's bromamide reaction:</u>

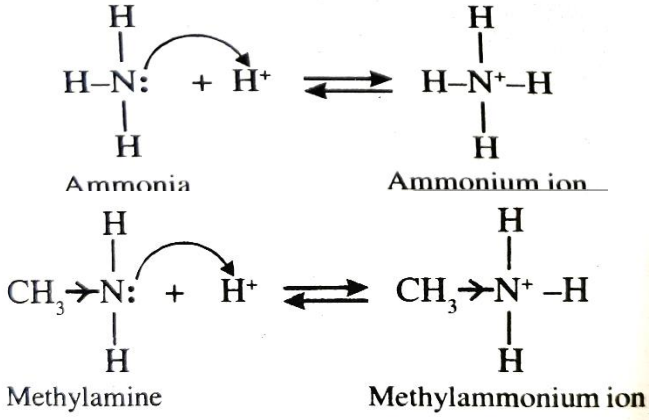
- Primary amides on reaction with bromine and KOH at 70°C yield primary amines having one carbon atom less than parent amides. This reaction is called Hoffmann's bromamide reaction or Hoffmann's hypobromite reaction.

<u>BASICITY OF AMINES</u>

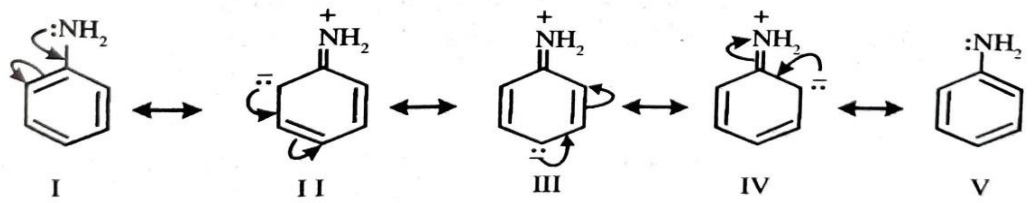
- The basic strength of ammonia, methylamine, and aniline varies in the order :

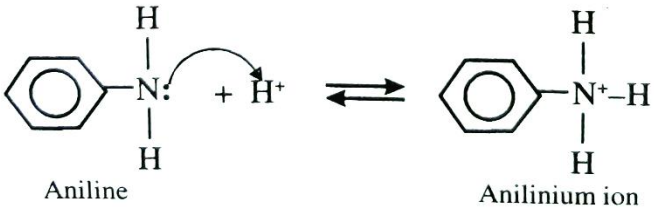
  Methyl amine > Ammonia > Aniline

- In methylamine, the electron-donating inductive effect (+I effect) of the methyl group increases the electron availability on nitrogen. Also, the methyl ammonium ion formed gets stabilized due to the dispersal of the positive charge by the +I effect of methyl group. So it is more basic than ammonia.



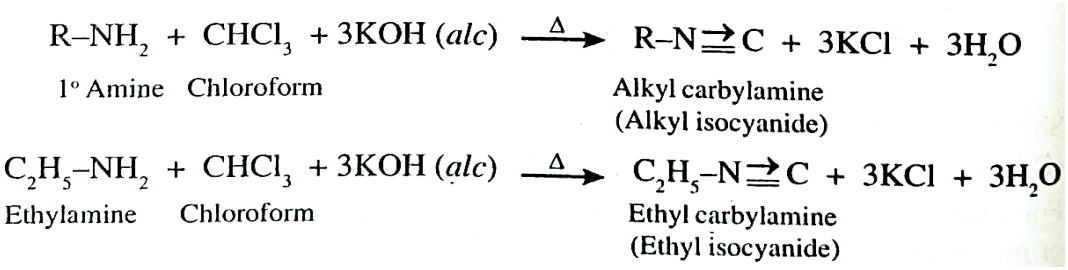
- In aniline, the +R effect of -NH_2 group makes the electron pair on N less available for protonation. The small positive charge on nitrogen repel the proton. Also, the anilinium ion (C_6H_5- NH_3^+) is not as stabilized through resonance as aniline.





HOFFMANN'S CARBYLAMINE REACTION

- Aliphatic and aromatic primary amines when warmed with chloroform and alcoholic KOH yield corresponding carbylamines (isocyanides) which have characteristic foul smell. This reaction is called carbylamine reaction.

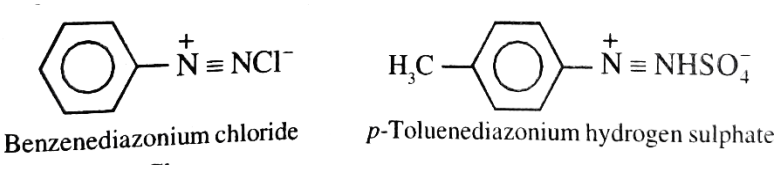


- Secondary and tertiary amines do not give this reaction. Hence, this test can be used to distinguish primary amines.

DIAZONIUM SALTS

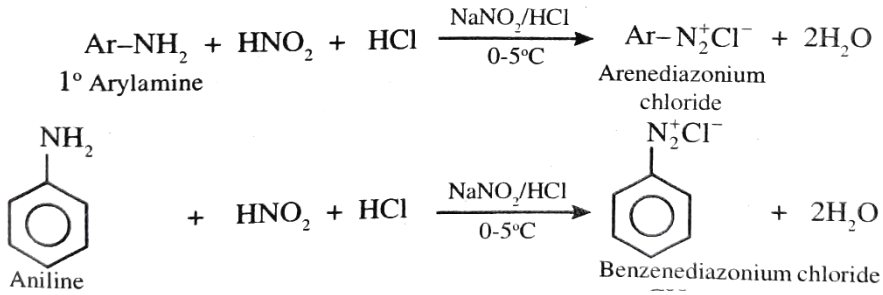
- Aromatic diazonium salts possess the general formula $ArN_2^+X^-$ where X^-= Cl^-, Br^-, HSO_4^- etc.

  Eg:



PREPARATION OF ARYL DIAZONIUM SALTS

- Aromatic primary amines on treatment with nitrous acid at low temperatures, yield aryl diazonium chloride. This reaction is called diazotization reaction.

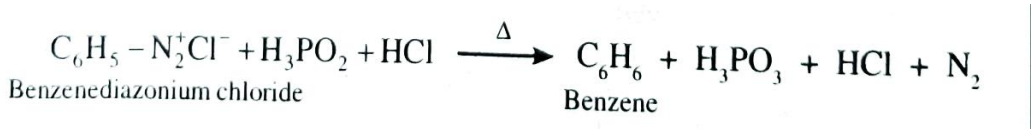


- The reaction is done at low temperature because the diazonium salts decompose at higher temperatures.

SYNTHETIC APPLICATIONS OF BENZENEDIAZONIUM CHLORIDE

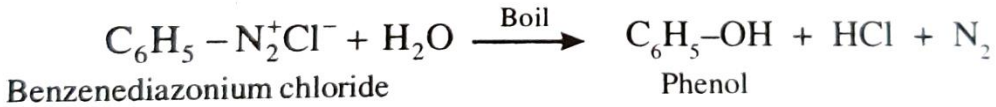
1. **Replacement by –H:**

When aq. Benzenediazonium chloride is heated with hypophosphorous acid(H_3PO_2), benzene is obtained.



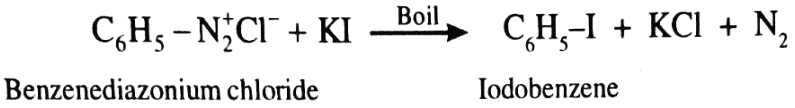
2. Replacement by –OH:

When aq. Benzenediazonium chloride is boiled or steam distilled, phenol is obtained.



3. Replacement by –I:

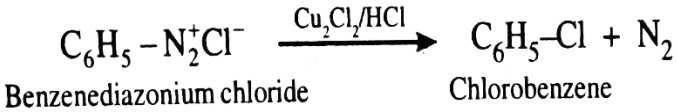
When aq. Benzenediazonium chloride is boiled with potassium iodide solution, iodobenzene is obtained.



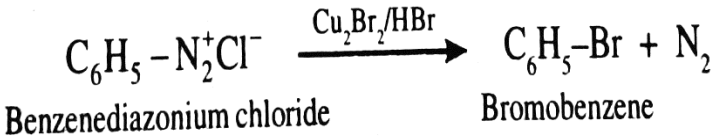
4. **Replacement by –Cl and –Br:**

a) Sandmeyer reactions:

i) When aq. Benzenediazonium chloride solution is warmed with cuprous chloride dissolved in HCl , chlorobenzene is obtained.

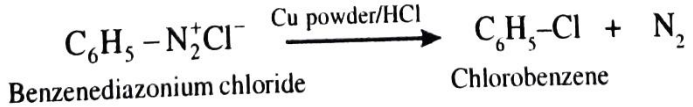


ii) When aq. Benzenediazonium chloride solution is warmed with cuprous bromide dissolved in HBr, bromobenzene is obtained.

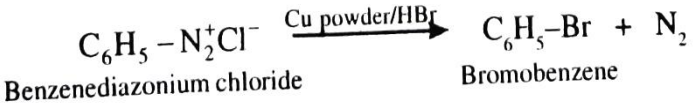


b) Gattermann reactions:

i) when aq. Benzenediazonium chloride solution is warmed with copper powder and HCl, chlobenzene is obtained.

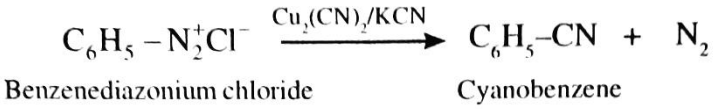


ii) When aq. Benzenediazonium chloride solutions is warmed with copper powder and HBr, Bromobenzene is obtained.

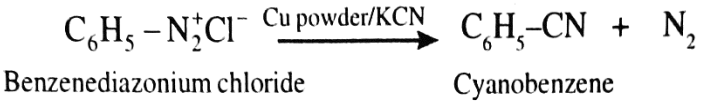


5. Replacement by –CN:

i) When aq. Benzenediazonium chloride solution is warmed with cuprous cyanide dissolved in aq. KCN, cyanobenzene is obtained.(Sandmeyer reaction)

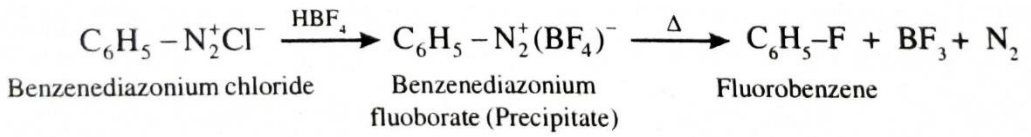


ii) When aq. Benzenediazonium chloride solution is warmed with copper powder and KCN, cyanobenzene is obtained.(Gattermann reaction)



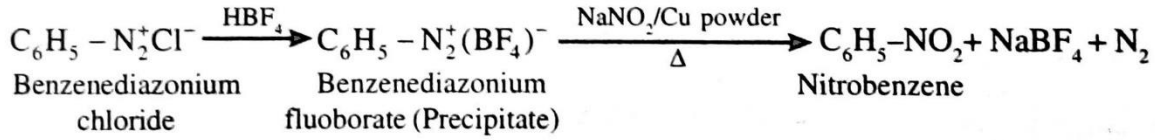
6. Replacement with –F:

When aq. Benzenediazonium chloride is treated with fluoroboric acid (HBF_4), benzenediazonium fluoroborate is precipitated, which on filtration and heating decomposes to fluorobenzene. This reaction is called Balz-Shiemann reaction.



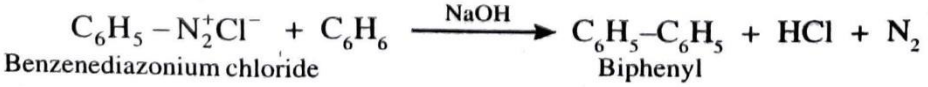
7. Replacement by -NO_2:

When aq. Benzenediazonium chloride solution is treated with fluoroboric acid,benzenediazonium fluoroborate is precipitated, which on filtration and heating with sodium nitrate ($NaNO_2$) and copper powder gives nitrobenzene. This reaction is known as Balz- shiemann reaction.



8. Replacement by phenyl group:

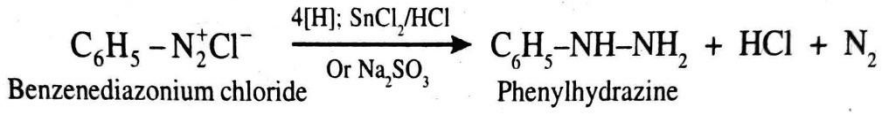
When benzenediazonium chloride solution is made alkaline and treated with benzene, biphenyl is obtained. This reaction is called Gomberg- Bachmann reaction.



REDUCTION

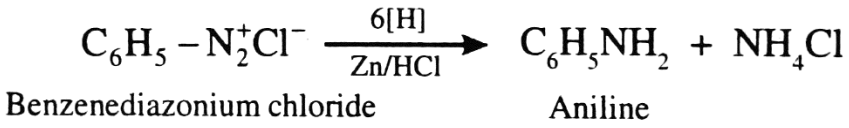
1. **Mild reduction:**

Reduction of benzenediazonium chloride using a reducing agent like Na_2SO_3 or $SnCl_2$/HCl yields phenylhydrazine.



2. Strong reduction:

Reduction of benzenediazoniumchloride using Zn /HCl yields aniline.

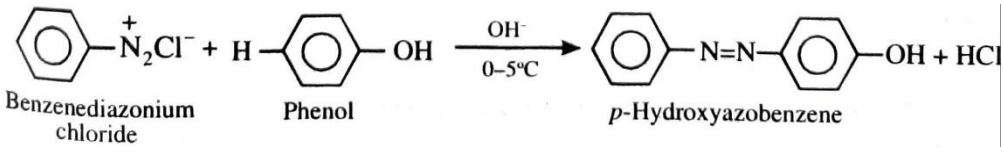


COUPLING REACTIONS

- Aryl diazonium salts react with aromatic amines and phenols to yield brightly coloured azo compounds, containing the azo group(-N=N-). These reactions are called coupling reactions.
- Azo dyes can be prepared through these reactions.
- For coupling to occur, the aromatic amines must contain electron donating and activating groups like –OH ,-OR, NH_2, etc. coupling normally occurs at para position with respect to activating groups.

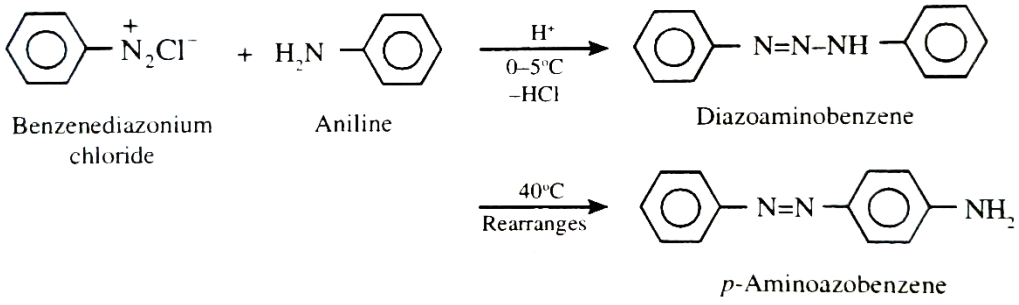
Eg: i)**Coupling with phenol:**

Benzenediazonium chloride couples with phenol in alkaline medium at 0-5° to yield azo dye *para*-hydroxyazobenzene.



ii)**Coupling with aniline:**

Benzenediazonium chloride couples with aniline in acidic medium at 0-5° to yield diazoaminobenzene which when warmed at 40° rearranges to yield azo dye *para*-aminoazobenzene.



Benzenediazonium chloride

Aniline

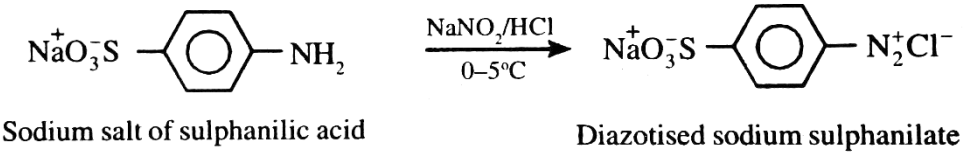
Diazoaminobenzene

p-Aminoazobenzene

METHYL ORANGE

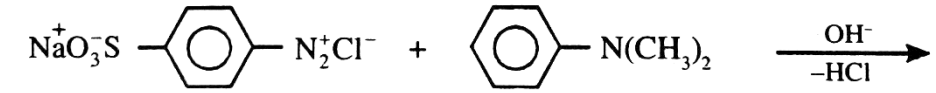
- **Preparation:**

When Diazonium salt of sulphanilic acid is coupled with N,N- dimethyl aniline in mild alkaline medium at 0-5° , Methyl orange is obtained.



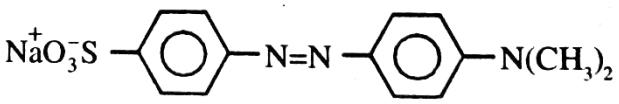
Sodium salt of sulphanilic acid

Diazotised sodium sulphanilate



Diazotised sodium sulphanilate

N, N-dimethylaniline



Methyl orange

- **Uses:**

Methyl orange is used as indicator in strong acid- strong base titrations and also in strong acid- weak base titrations. Its colour change interval is from pH 3.2 to 4.4.

MODULE: 6-BIOMOLECUES

INTRODUCTION

- Biomolecules are the most essential organic molecules, which are involved in the maintenance and metabolic processes of living organisms.
- They include simple molecules like vitamins and mineral salts and also complex molecules like carbohydrates, proteins, nucleic acids and lipids.

CARBOHYDRATES

- Carbohydrates are polyhydroxy aldehydes or polyhydroxy ketones or compounds which yield these on hydrolysis.

Classification: Carbohydrates are broadly classified into two-

1. **Sugars:** These carbohydrates are crystalline in nature, sweet and water soluble.

   Eg: Glucose, Fructose, Sucrose etc.

2. **Non-sugars:** These carbohydrates are amorphous in nature, tasteless and water insoluble.

   Eg: Starch, cellulose etc.

- On the basis of the behaviour of carbohydrates towards hydrolysis, they are classified into three-

a) **Monosaccharides:**

- Carbohydrates which cannot be hydrolysed into simpler compounds are called monosaccharides.
- Most of them have general formula $(CH_2O)_n$.
- Monosaccharides containing aldehyde group are called aldoses and those containing keto group are called ketoses.
- Eg: Glucose, fructose

b) **Oligosaccharides:**

- Carbohydrates which upon hydrolysis give 2 to 9 monosaccharides are called oligosaccharides.
- Disaccharides- yield 2 monosaccharides upon hydrolysis. Eg: sucrose, maltose

  Trisachharides-yield 3 monosaccharides upon hydrolysis. Eg: maltotriose.

c) **Polysaccharides:**

- Carbohydrates which upon hydrolysis yield a large number of monosaccharide molecules upon hydrolysis are called polysaccharides.

- In polysaccharides, monosaccharides are joined through glycosidic linkages.

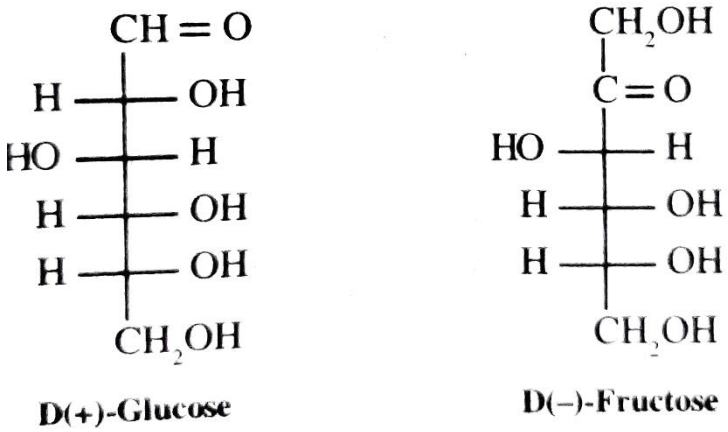
  Eg: starch, cellulose

REPRESENTATION OF MONOSACCHARIDES

Fischer projection:

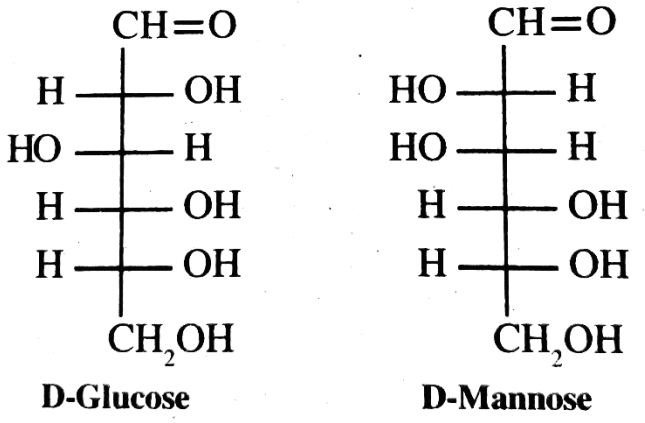
- Monosachharides can be represented by Fischer projections. They are 2-D representation of structures which contain at least one carbon atom. Four different groups attached to a chiral centre are placed at the four ends of a cross. The chiral carbon atom is assumed to be located at the centre of cross. If there are more chiral centres, more than one cross will be there. Horizontal lines represent bonds directed towards the observer.

  Eg: Fischer projection of D(+) Glucose and D(-) Fructose



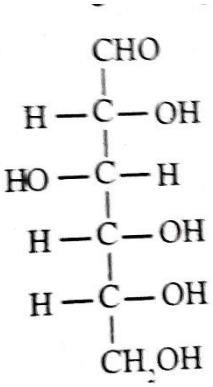
- **Epimers-** Diastereoisomers which differ from each other in configuration at only one chiral centre are called epimers.

  Eg**:** D- glucose and D- mannose

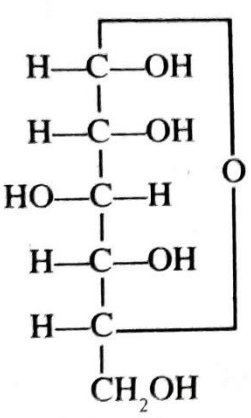


<u>Cyclic structures of glucose and fructose:</u>

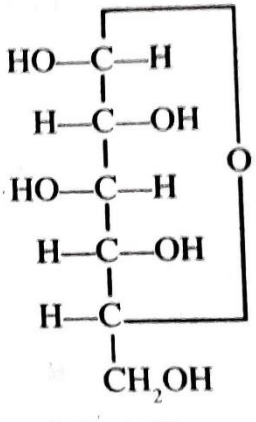
- Aldehydes and ketones can react with an equivalent amount of alcohol to form an addition product called hemiacetal and hemiketals respectively.
- The open chain form of glucose D-glucose is



- The OH group attached to C-5 can interact intramolecularly with CHO group to form a hemiacetal. A new chiral centre is formed at the carbonyl carbon.

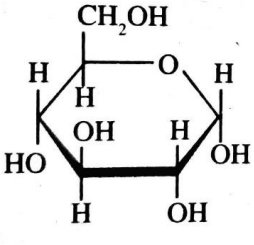


α -D(+)-Glucose

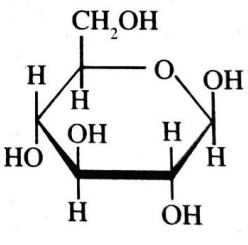


β -D(+)-Glucose

- Two cyclic forms of D-glucose are formed. One in which OH group on new chiral carbon to the right called α-D glucose and the other in which OH group is to the right called β-D Glucose
- The six membered cyclic structure of glucose can be represented by Haworth representation. They are called pyranose structures. The groups on the right of Fischer projection are down in Haworth projection and the groups on the left are up. For D-sugars the terminal -CH_2OH group is up and for L-sugars it is down.

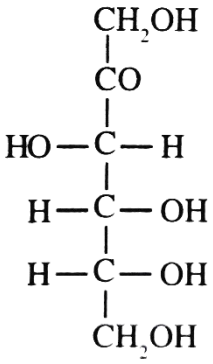


α -D(+)-Glucopyranose



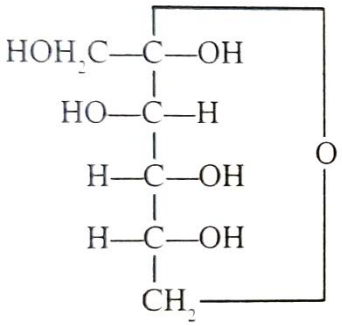
β -D(+)-Glucopyranose

- The open chain form of D- fructose is

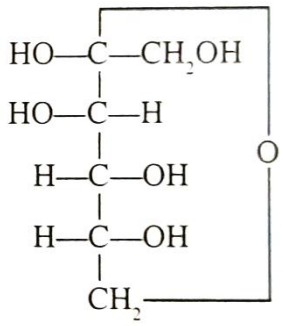


D-Fructose

- The two cyclic form of Fructose are α-D- Fructose and β-D-Fructose

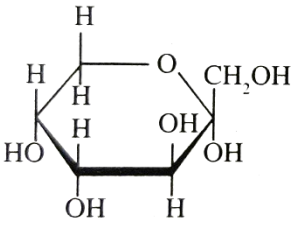


α -D(–)-Fructose

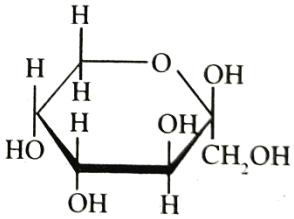


β -D(–)-Fructose

- The Haworth structures of the two forms of D-Fructose are



α -D(–)-Fructopyranose



β -D(–)-Fructopyranose

- Anomers- Diastereomeric ring forms differing in configuration only at chiral centre produced due to cyclisation are called Anomers.

APPLICATIONS OF CARBOHYDRATES

- Carbohydrates are essential to the existence of living organisms. Plants and animals synthesize and metabolize carbohydrates, using them they store energy and deliver it to the cells. Cellulose makes up the cell walls of the plants.

Glucose:

- Food for growing children and sickly person.
- Reducing agent in silvering of mirrors and vat dyeing.
- As a sweetening agent in drinks, sweets, jams etc.

- In fruit preservation.
- In wine manufacture.
- In vitamin-C synthesis.

Fructose:

- As a sweetening agent in drinks, sweets, syrups etc.
- As a sweetening agent in food for diabetic patients.

Sucrose:

- As a sweetening agent in food. Drinks, sweets, syrups.
- In the preparation of oxalic acid.
- In the preservation of food and fruits.
- Used in the preparation of non-aqueous adhesives.

Starch:

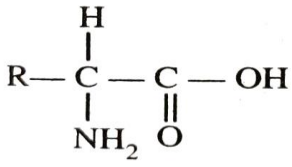
- Important constituent of food.
- Manufacture of Glucose and ethanol.
- Manufacture of dextrin, which is used as an adhesive.
- As an indicator in iodometric and iodimetric titrations.
- Used for preparation of nitrostarch, an explosive.

Cellulose:

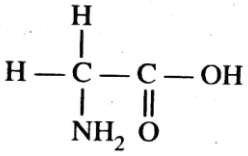
- ***Industrial applications:***
    1. Cotton is used in the manufacture of textiles.
    2. Rayon, a cellulose fibre is widely used in the manufacture of textiles. Viscous solution of cellulose in NaOH is passed through the holes of spinneret into a bath of dil. H_2SO_4. Cellulose is regenerated in the form of viscous rayon.
    3. Complete nitration of cellulose yield cellulose trinitrate, known as gun cotton. It is used as explosive
    4. Acetylation of cellulose yields cellulose acetate which is use in the manufacture of fibres known as acetate rayon. Cellulose acetate is also used in paints and varnishes.
    5. When cotton is stretched, heated with conc. Caustic soda solution and then washed with water, mercerised cotton is obtained These fibres are lustrous than cotton, possess greater capacity to absorb dyes.
    6. Cellulose present in wood, bamboo, straw etc are widely used in the manufacture of paper.

AMINO ACIDS

- An amino acid is a bifunctional organic molecule containing a carboxyl(COOH) and an amino group(-NH_2).
- The α-amino acids may be represented by the following general formula



Eg: Glycine



CLASSIFICATION OF AMINO ACIDS

- There are three types of Classification

1. **Structural classification:**

- Amino acids are classified according to nature of side chain group R. This class can be subdivided into

a) ***Acyclic amino acids:***

These are amino acids in which side chain is an aliphatic group. They include

i) Aliphatic unsubstituted amino acids- R is an alkyl group.

Eg: Glycine, Alanine

ii) Hydroxy amino acids: R contains –OH group.

Eg: Serine

iii) Thioamino acids: R contains S atom.

Eg: Cysteine

iv) Carboxy amino acids: R contains an acid group or its derivative.

Eg: Aspartic acid

v) Diamino acids: R contains an -NH_2 group.

Eg: Lysine

b) ***Cyclic amino acids:*** The amino acid contains a cyclic group in R. This includes

i) Aromatic amino acids: R contains an aromatic group.

Eg: Phenyl alanine:

ii) Heterocyclic amino acids: R contains a heterocyclic ring system.

Eg: Tryptophan.

iii) Rare amino acids: Amino acids found rarely in proteins.

Eg: Hydroxyproline.

2. Electrochemical classification:

- This classification is based on the acidic- basic properties of amino acids and they are classified into 3 groups.

i) ***Acidic amino acids –*** Contains an additional carboxyl group in the side chain. This provides acidic properties to them.

Eg: Aspartic acid, glutamic acid.

ii) ***Basic amino acids***- Contains an additional basic group in the side chain. This provides basic properties to them.

Eg: Lysine, arginine, histidine.

iii) ***Neutral amino acids-*** Contain only one acid and one basic group. They side chain shows neither acidic nor basic properties.

Eg: Glycine, Alanine.

3. Biological classification:

Based on the functional priority of amino acids, they are classified into two-

i) ***Essential amino acids***- Those amino acids which cannot be synthesized by human body from other compounds and hence must be supplied in the diet are called essential amino acids. There are 10 essential amino acids.

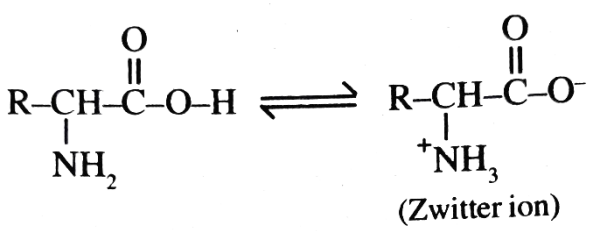
Eg: valine, leucine, isoleucine

ii) ***Non- essential amino acids-*** Those amino acids that can be synthesized by human body from other compounds that are suppled through diet are called non- essential amino acids.

Eg: Glycine, Alanine, Aspartic acid etc.

<u>Amphoteric nature of amino acids</u>:

- **Zwitter ions:** Zwitter ion or dipolar ion is an internal salt formed by the interaction between an acidic and a basic group that are part of the same molecule. As a result of Zwitter ion formation, amino acids are colourless, water soluble, high melting crystalline solids. Zwitter ions show amphoteric character.



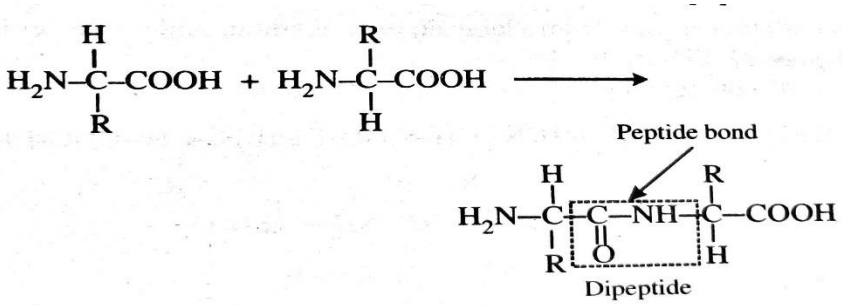
(Zwitter ion)

- **Isoelectric point-** The pH at which an amino acid zwitter ion is neutral and hence shows no tendency to migrate towards the cathode or the anode when placed in an electric field is known as isoelectric point of amino acid. This is the characteristic of an amino acid.

  Eg: The isoelectric point of alanine and phenyl alanine are 6.1 and 5.5 respectively.

PEPTIDES

- The –CO-NH linkage formed by the condensation of α-amino acids is called peptide linkage or peptide bond. The product of condensation are called peptides.
- The peptide linkage is formed between –COOH group of one amino acid and the -NH_2 group of another.



- Peptides and proteins are written with N-terminal amino acid on the left and C-terminal amino acid on the right. Generally, 3 letter symbols of amino acids separated by hyphen are used to write the sequence in a peptide.

  Eg: The condensation of glycine and alanine yields dipeptide glycylalanine represented as Gly-Ala

- When two amino acids condense, the product is called dipeptide. When three amino acids condense, the product is called tripeptide.

Polypeptides:

- The condensation product from a large number of amino acid molecules (ten or more) is referred to as polypeptide. Proteins are polypeptides.

PROTEINS

- Proteins are polypeptides of high molar mass formed from the condensation of a very large number of α- amino acids.

Classification of proteins

- Based on the molecular shape and solubility in water, proteins can be classified into two-

  a) **Fibrous proteins:** They consist of long helical thread like polypeptides which lie parallel to each other and are held together by hydrogen bonds and disulphide bonds. They are generally insoluble in water.

  Eg: keratin in hair, myosin in muscles etc.

b) **Globular proteins:** Globular proteins are those in which molecules are looped, twisted and folded together to form ball like structures. They are generally soluble in water.

Eg: Enzymes, hormones like insulin, albumins

Structure of proteins

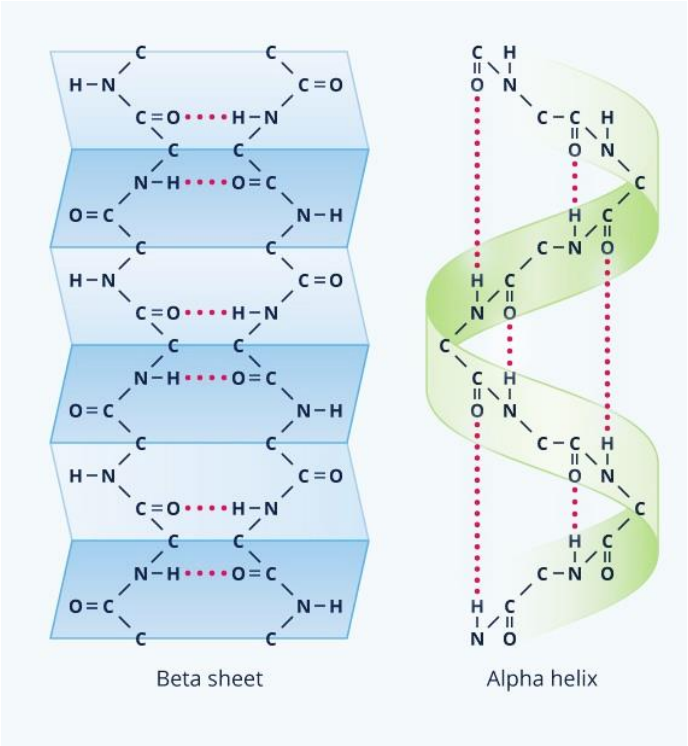
A) Primary structure:

- The specific sequence in which various amino acids are arranged in a protein is called its primary structure.

Eg: Haemoglobin contains 574 aminoacid units arranged in a specific sequence.

B) Secondary structure

- The conformation which the polypeptide chain assume as a result of intramolecular or intermolecular hydrogen bonding is called its secondary structure. Two common types of secondary structure are α-helix structure and β- pleated structure.



i) α – helix structure:

- The polypeptide chain in a protein coils up into a spiral structure. The turns are held together by intramolecular hydrogen bonds between –C=O bond of one amino acid and –N-H bond of fourth one in the same chain.
- The axial pitch of α-helix is 0.54 nm and it contains 3.6 amino acid residues.
- α – helix structure is found in many fibrous proteins like keratin in hair, myosin in muscles etc.

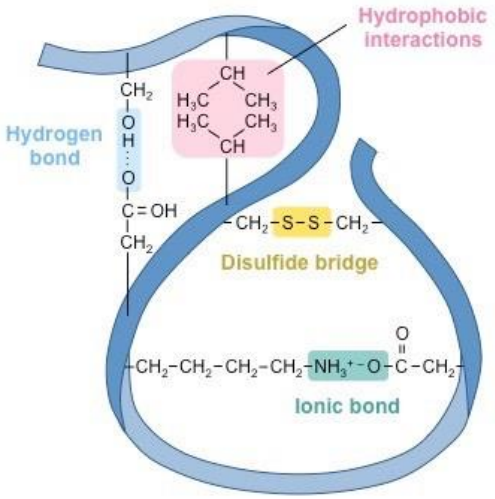
ii) β – pleated structure:

- The long polypeptide chains lie side by side in a zig- zag manner and are held together by intermolecular hydrogen bonds to form a flat sheet.
- The sheets are stacked one above the other to form 3-D structure.

  Eg: Silk protein fibroin has β- structure.

C) Tertiary structure:

- The 3-D structure which arises due to folding and superimposition of different secondary units. This give rise to two major molecular shapes- globular and fibrous proteins.



- The forces that stabilize the tertiary structure are

a) Hydrogen bonds between -NH_2, -OH or SH in the side chain of one amino acid and carboxylic acid of the other.

b) Ionic or electrostatic bonds formed between the charged side chain groups -NH_3^+ and COO^-.

c) Disulphide bonds (-S-S-) between the side chains of cysteine residues.

d) Vanderwaals bonds or hydrophobic interactions between the hydrocarbon radicals of amino acids.

- At normal pH and temperature, the protein take a shape that is energetically the most stable and this state is called native state.
- In fibrous protein, the tertiary structure has same secondary structure throughout, where as in globular protein, some parts have α- helix structure and some other parts have β- structure and the rest may be randomly coiled.

D) Quaternary structure:

- Some proteins are composed of two or more polypeptide chains referred to as sub-units. The spatial arrangement of sub-units with respect to each other is known as quaternary structure.

  Eg: Haemoglobin is a protein which has a quaternary structure with four globular polypeptide structures.

- The forces that stabilize the quaternary structure include hydrogen bonds, disulphide linkages, van der Waals and electrostatic interactions.

DENATURATION OF PROTEINS

- At normal pH and temperature, each protein will take a shape that is energetically most stable. This state is called native state and it is specific to an amino acid sequence.
- Disruption of the native conformation of a protein by external agents is called denaturation. Denaturation does not change the primary structure, but brings about changes in secondary and tertiary structure.
- As a result of denaturation, the protein molecule uncoils from the ordered and specific conformation and precipitates from the solution.

  Eg:

  1. The soluble globular proteins present in the egg white undergo denaturation into fibrous form and gets coagulated, on hard boiling.

  2. When milk is heated with acid, the globular milk protein lactoalbumin undergoes denaturation into fibrous form and gets coagulated to form cheese.

ENZYMES

- Enzymes are biological catalysts which catalyse various biochemical reactions in the cells.
- Enzymes which function inside the same cells which produce them are called endoenzymes or intracellular enzymes. Eg: Respiratory enzyme. Enzymes which function outside the cells which produce them are called exoenzymes or extracellular enzymes. Eg: Digestive enzymes.

Examples for enzyme- catalysed reactions

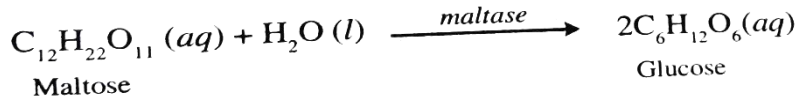
1. Inversion of cane sugar: The enzyme invertase catalyses the hydrolysis of sucrose into glucose and fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{invertase} \underset{\text{Glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{Fructose}}{C_6H_{12}O_6(aq)}$$

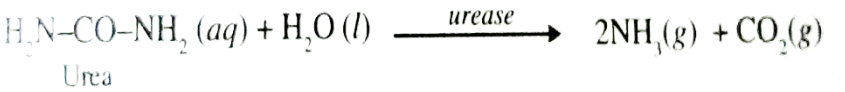
2. Conversion of starch into maltose: The enzyme diastase catalyses the hydrolysis of starch into maltose.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n\,(aq)} + nH_2O\,(l) \xrightarrow{diastase} \underset{\text{Maltose}}{n\,C_{12}H_{22}O_{11}\,(aq)}$$

3. Conversion of maltose into glucose: The enzyme maltase catalyses the hydrolysis of maltose into glucose.



4. Decomposition of urea: The enzyme urease catalyses the decomposition of urea into ammonia and carbon di oxide.



5. Conversion of proteins into peptides: In stomach, the enzyme pepsin catalyses the conversion of protein into peptides. In the intestine, the enzyme trypsin catalyses the hydrolysis of proteins into amino acids.

CHARACTERISTICS OF ENZYME CATAYSIS

(A) Functional characteristics

1. Enzymes are highly efficient catalysts. They increase the speed of reaction by ten million or more times.
2. Even a small amount of catalyst can speed up the reaction to a great extent.
3. Enzymes are highly specific in their catalytic action.
4. Enzymes are not broken down or changed in the process of their catalytic functions.
5. Enzymes speed up the attainment of equilibrium in biochemical reactions but however they do not alter the position of equilibrium.

(B) Condition characteristics

6. The characteristic temperature at which an enzyme shows maximum catalytic activity is called optimum temperature.
7. The characteristic pH at which an enzyme shows maximum catalytic activity is called optimum pH.
8. The non- protein part attached to the protein part of an enzyme, which enhances its catalytic activity are called cofactor. They act as bridge between the enzyme and substrate or they take part in reaction.

   If the cofactor is an inorganic moiety like a metal ion, it is called an activator.

   Eg: Enzyme alcohol dehydrogenase is activated by Zn^{2+}.

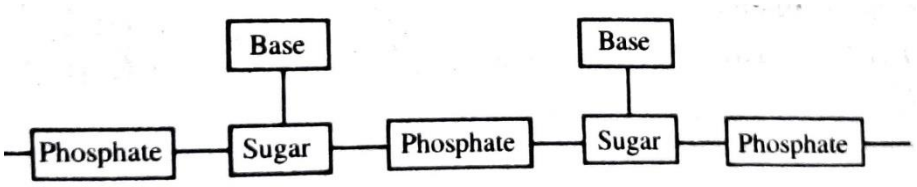
   If the cofactor is an organic moiety, it is called coenzyme.

   Eg: Thiamine pyrophosphate(TPP)
9. Catalytic activity of an enzyme is decreased by the presence of certain substances. They are called inhibitors. They interact with the active functional group on the enzyme and thereby inhibits its activity.

   Eg: Heavy metals like Hg^{2+}, Ag^{+}, Pb^{2+} inhibit the activity of enzyme urease

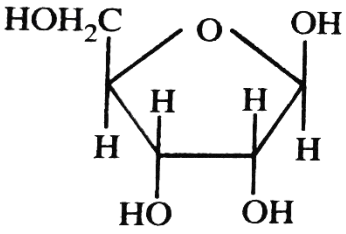
NUCLEIC ACIDS

- Nucleic acids are polynucleotides of very high molecular masses in which the nucleotide units are linked through phosphate ester linkages.
- Each nucleotide is made up of three components- a pentose sugar, a heterocyclic nitrogenous base and a phosphate group.

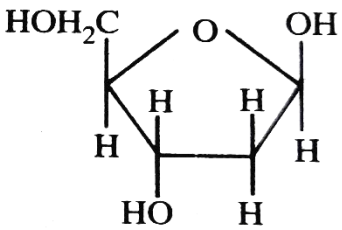


Structure of pentose sugar:

- The pentose sugar present in a nucleic acid is either ribose or 2-deoxy ribose. Their structures are



D-Ribose

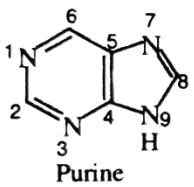


2-Deoxy-D-ribose

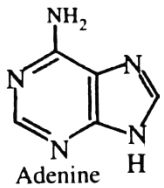
Structure of heterocyclic nitrogenous base:

- The heterocyclic nitrogenous base is either a substituted purine or a substituted pyrimidine.

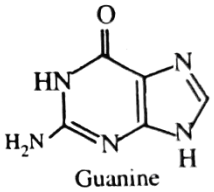
- The purine bases are adenine and guanine and the pyrimidine bases are cytosine, thymine and uracil.



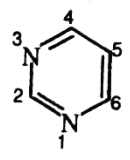
Purine



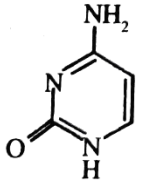
Adenine



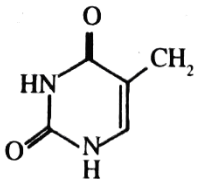
Guanine



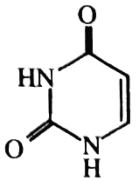
Pyrimidine



Cytosine



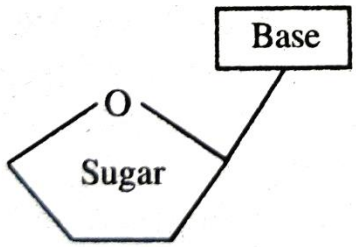
Thymine



Uracil

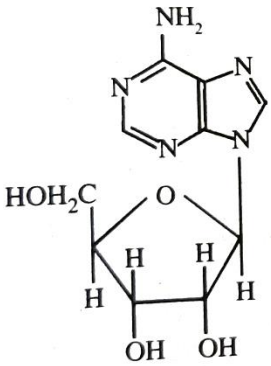
NUCLEOSIDES

- The compounds containing two component units, pentose sugar and a heterocyclic nitrogenous base is called nucleoside.

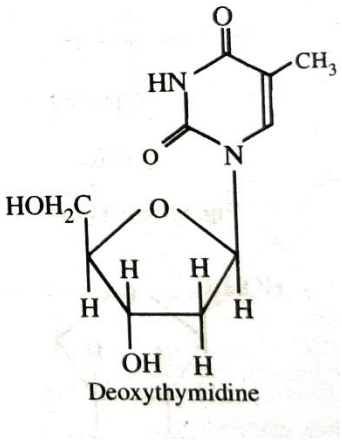


- A nucleoside containing ribose as the sugar unit is termed as a ribonucleoside while one containing 2- deoxyribose as sugar unit is called deoxyribonucleoside.
- The nitrogenous base is either adenine or guanine if it is purine and either cytosine or uracil or thymine if it is pyrimidine.
- In the purine nucleoside, the pentose sugar unit is linked to the base by a β- glycosidic link from C-1' of sugar to N-9 of purine base. In the pyrimidine nucleoside, the C-1' of pentose sugar is connected through a β- glycosidic link to N-1 of pyrimidine base.

  Eg:



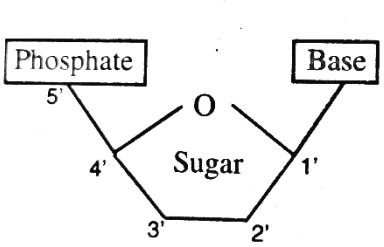
Adenosine



Deoxythymidine

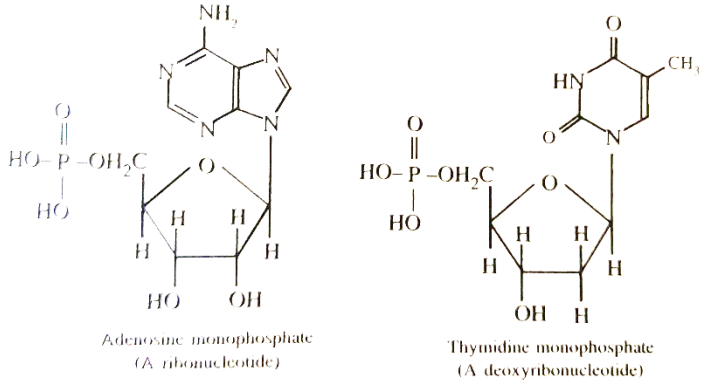
NUCLEOTIDES

- A compound containing three component units- a pentose sugar, a heterocyclic nitrogenous base and a phosphate group is called a nucleotide.



- A nucleotide containing ribose as sugar unit is called ribonucleotide while that containing 2- deoxy ribose are called deoxyribonucleotide.

  Eg:

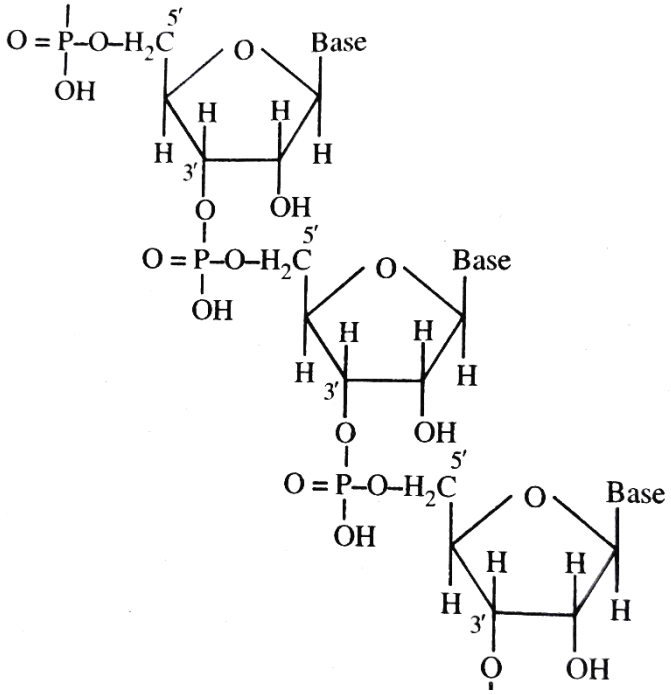


TYPES OF NUCLEIC ACIDS

- Depending upon the type of pentose sugar units present, there are 2 types of nucleic acids-

1. **Ribonucleic acid(RNA):**

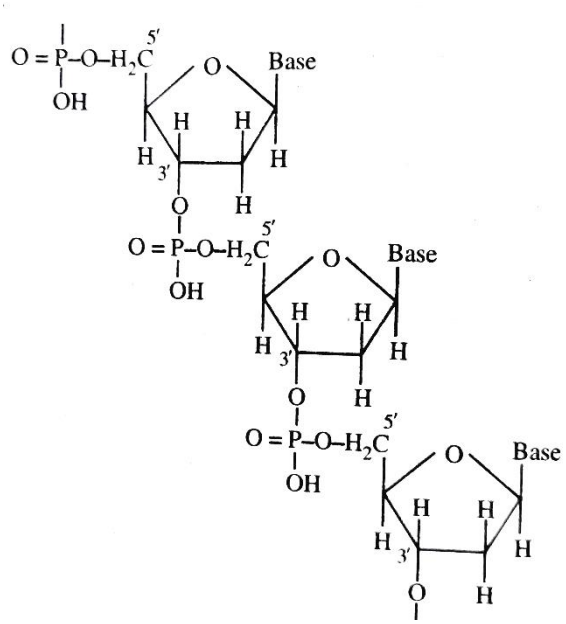
- Nucleic acid containing ribose as the pentose sugar unit is called Ribonucleic acids.
- The nitrogenous base found in RNA are adenine, guanine, cytosine and uracil. Thymine is not found in RNA.
- In RNA, the C-5' of one ribose unit is linked through phosphodiester to the C-3' of next ribose in the polynucleotide chain.



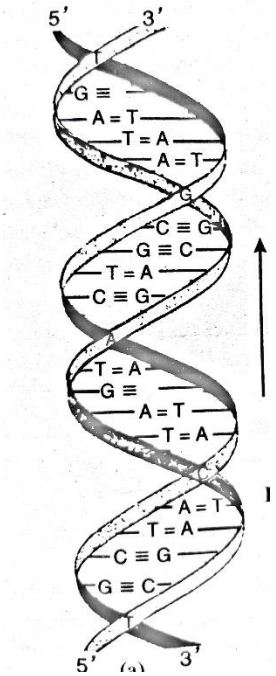
- RNA molecule has a single-stranded structure.
- In some RNA molecules, the single strand may fold up. This is due to intra molecular hydrogen bonding. Here, adenine pairs only with uracil while guanine pairs only with cytosine.

2. <u>Deoxyribonucleic acid(DNA):</u>

- Nucleic acid containing 2-deoxyribose as the pentose sugar unit is called deoxyribonucleic acid or DNA.
- The nitrogenous bases found in DNA are adenine (A), guanine(G), cytosine(C) and thymine(T). Uracil is not found in DNA.
- The DNA molecule consist of two strands of polynucleotide chains coiled around each other about a common axis in the form of a right handed double helix. The nucleotides are connected by phosphodiester bonds. This bond connects C-5' of one deoxy ribose sugar to C-3' of the adjacent one. The bases are attached to C-1' of sugar. The sugar-phosphate backbone forms the periphery of the spiral structure whereas bases are on inside of helix.



- The two chains are in opposite direction. The sugar units are oriented in opposite directions.
- The bases in one strand of DNA are paired with the bases of other strand by means of hydrogen bonding. The hydrogen bonding is specific such that only adenine- thymine pairing and guanine-cytosine pairing happens. This is energetically and sterically more favoured. This is called base- pairing principle or base complementarity.



- The two strands of DNA are complementary to each other. If the sequence of one strand is known, automatically the other can be determined.
- DNA molecule contains equal number of A and T units and equal number of G and C units. The molecule is about 20 Å in diameter. The bases lie in planes approximately perpendicular to the helix axis. The average distance between two base pairs is 3.4Å. A complete turn is 34Å. There are 10 base pairs per turn of the double helix.

- The specific sequence of bases carry genetic information and is called primary structure.

DNA Fingerprinting and its applications

- The process of acquiring the pattern of unique base sequence of DNA in a person is called DNA fingerprinting.
- In DNA fingerprinting, a sample of DNA is extracted from the sample of blood, saliva, semen, skin or other tissues. Then, amount of DNA is amplified by using special enzymes. This is known as polymerase chain reaction method. After that, another set of enzymes referred to as restriction enzymes are used to cut the DNA into smaller fragments. They are separated by size using gel electrophoresis. Each fragment is labelled with a radioactive probe. When a x- ray film is placed over the gel, the radiation from the radioprobe, produces a pattern of light and dark bands. This constitute the representation of base sequence of a person' DNA.

Applications:

- In forensic laboratories for identification of criminals. It can also be used to prove the innocence of persons wrongly convicted of a crime.
- Used to determine biological parents of an individual.
- It is used in establishing the identity of a deceased person.
- It is used in medicine for matching recipients with organ donors.
- It is used to identify racial groups while carrying out research on biological evolution.

MODULE 7: ALKALOIDS AND TERPENES

ALKALOIDS

- Alkaloids are a class of organic nitrogenous bases, generally of plant origin, which have structures containing one or more nitrogen heterocyclic rings and have significant physiological action.

Classification of alkaloids

1. Classification based on the genus in which alkaloids occur.

   Eg: ephedra alkaloids, cinchona alkaloids.

2. Classification based on their physiological action.

   Eg: Analgesic alkaloids, cardioactive alkaloids.

3. Classification based on the prominent heterocyclic ring system present in their molecule. Some important classes are

   1. Phenylethylamine alkaloids.

   Eg: ephidrene, tyramine.

   2. Pyridine alkaloids.

   Eg: ricinine, trigonelline

   3. Pyrrolidine alkaloids.

   Eg: hygrine, cusohygrine

   4. Pyridine- pyrrolidine alkaloids.

   Eg: nicotine, mysomine

   5. Piperidine alkaloids.

   Eg: coniine, piperine.

   6. Quinoline alkaloids.

   Eg: quinine, cinchonine

   7. Isoquinoline alkaloids.

   Eg: narcotine, papaverine.

   8. Indole alkaloids.

   Eg: strychnine, reserpine

   9. Tropane alkaloids

   Eg: cocaine, atropine.

   10. Phenanthrene alkaloids.

   Eg: morphine, codeine

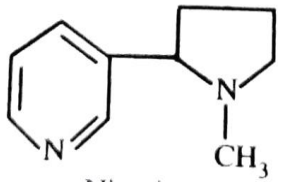
NICOTINE

Source:

- The chief source of nicotine is the tobacco plant. It occurs as its salt of malic and citric acids.

Structure:

- Nicotine ($C_{10}H_{14}N_2$) is N-Methyl-2-β-pyridylpyrrolidine.



Nicotine

Physiological activity:

- Nicotine is extremely poisonous. In very small doses, it temporarily stimulates the central nervous system but afterwards causes depression. It increases the heart beat and causes constriction of the blood vessels, increases the blood pressure and disturb blood distribution. In higher doses, it may cause respiratory paralysis and death.
- Long term inhalation causes serious lung diseases like bronchial asthma and lung cancer.

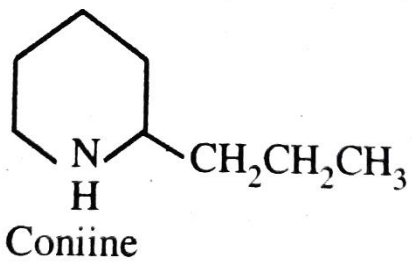
CONIINE

Source:

- The chief source of coniine is the Hemlock herb. It occurs as its salts of malic and caffeic acids.

Structure:

- Coniine ($C_8H_{17}N$) is α-n-propylpiperidine.



Coniine

Physiological activity

- Coniine is highly poisonous to humans. It affect the nervous system causing gradual paralysis followed by convulsions and finally death.

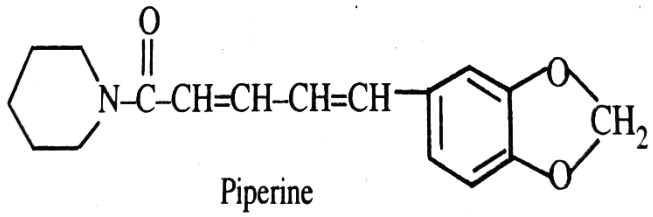
PIPERINE

Source:

- The chief source of piperine is pepper.

Structure:

- Piperine ($C_{17}H_{19}O_3$) is 1-[5-(1,3-benzodioxol-5-yl)-1-oxopenta-2,4-dienyl]piperidine



Piperine

Physiological activity:

- Piperine has beneficial effects. It enhances the digestive capacity by stimulating the digestive enzymes of pancreas. It reduces the gastrointestinal food transmit time.
- Piperine is also an analgesic, antipyretic, anti- inflammatory, anti convulsant and CNS depressant.

TERPENOIDS

- Terpenoids consist of a group of hydrocarbons, most of which have molecular formula $(C_5H_8)_n$ or their oxygen derivatives which possess characteristic pleasant odours.

Essential oils:

- The volatile oils that that can be obtained from the sap and tissues of various parts of plants by steam distillation are called essential oils.
- The chief constituent of essential oils are terpenes and their oxygenated derivatives.
- They have pleasant odours and have been used in perfumes.

Isolation of essential oils:

- Isolation of essential oils from plants by steam distillation.

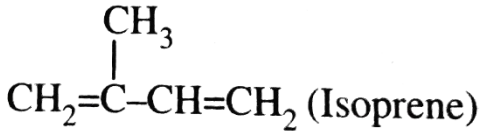
  The plant parts are macerated and then steam distilled. The steam volatile essential oils distils over along with water. They form a layer separate from aqueous layer. The oil layer is separated and collected.

- Separation of the component terpenoids of the essential oils

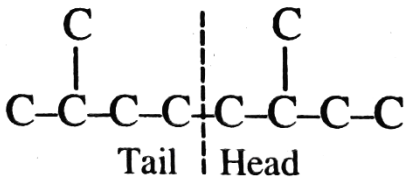
  Fractional distillation and chromatographic techniques can be used for the isolation and separation of terpenoids.

Isoprene rule:

- Almost all terpenoids on thermal decomposition yield isoprene (C_5H_8) units.



- The skeleton structures of all natural terpenoids are built up of isoprene units. This is known as isoprene rule.
- Molecules of all natural terpenoids are built up of isoprene units and these isoprene units are joined head to tail. This is known as special isoprene rule.



Classification of terpenoids:

- Terpenoids are classified on the basis of number of isoprene units they contain.
    1. Monoterpenoids- 2 isoprene units
    2. Sesquiterpenoids- 3 isoprene units.
    3. Diterpenoids- 4 isoprene units.
    4. Sesterterpenoids- 5 isoprene units.
    5. Triterpenoids- 6 isoprene units.
    6. Tetraterpenoids- 8 isoprene unist.
    7. Polyterpenoids- more than 8 isoprene units.
- Terpenoids are also classified as
    1. Acyclic terpenoids- Terpenoids having open chain structures. Eg: myrcene, citral, geraniol etc.
    2. Cyclic terpenoids- Terpenoids having ring in their structures.

       Eg: limonene (monocyclic terpenoid), α- pinene (bicyclic terpenoid)
- Classification on the basis of whether they are hydrocarbons(eg: myrcene, limonene) or oxygenated hydrocarbons(eg: citral, geraniol, menthol)

<u>Uses of some essential oils:</u>

(a) Lemongrass oil:

- Lemongrass oil have analgesic, antimicrobial, antiseptic, carminative, antipyretic, fungicidal and bactericidal properties. It is used

1. In various skin care and cosmetic products, such as soaps, deodorants, shampoo, lotions etc

2. As an ingredient in air fresheners and deodorizers.
3. As an analgesic and anti- inflammatory agent to reduce pain and inflammation due to muscular and rheumatic disease.
4. As an insect repellent to repel insects such as mosquitoes and ants due to its high citral and geraniol content.
5. To treat bacterial and fungal infections, such as ring worm and athlete's foot.

(b) Eucalyptus oil:

- Eucalyptus oil have analgesic, antimicrobial and antiseptic properties. It is used

1. As an antiseptic in treatment of wounds.
2. As an ingredient in perfumes and cosmetics.
3. As an insect repellent.
4. To treat bacterial infections of tooth.
5. In liniments and ointments to relieve pain.

(c) Sandalwood oil:

- Sandalwood oil have antiseptic, anti-inflammatory, antispasmodic, astringent, disinfectant, emollient, expectorant and sedative properties.

1. As an ingredient in skin- care products.
2. As an inhalant in vapour therapy to provide relief to coughs, chest infections, asthma, Bronchitis.
3. As an antispasmodic in relaxing nerves, muscles as well as blood vessels
4. As an internal and external antiseptic in the treatment of wounds and ulcers.
5. As an insect repellent.

MONOTERPENOIDS

1. CITRAL ($C_{10}H_{16}O$)

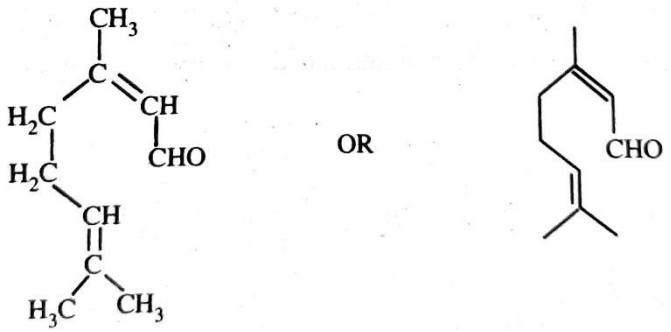
Source

- Citral occurs mainly in lemongrass oil. It also occurs in the oils of lemon, oranges etc.

  Citral is isolated by fractional distillation of lemongrass oil under reduced pressure. It is then treated with saturated sodium bisulphite solution and then decomposed by sodium carbonate solution to get citral in pure form.

Structure:

- Citral is an acyclic diolefinic aldehyde.



Uses:

- In the preparation of synthetic lemon flavours.
- In the manufacture of soaps, perfumes and other cosmetics to produce the odour of lemons.
- As a starting material for the synthesis of vitamin A.
- In the preparation of geraniol used in synthetic rose perfumes.

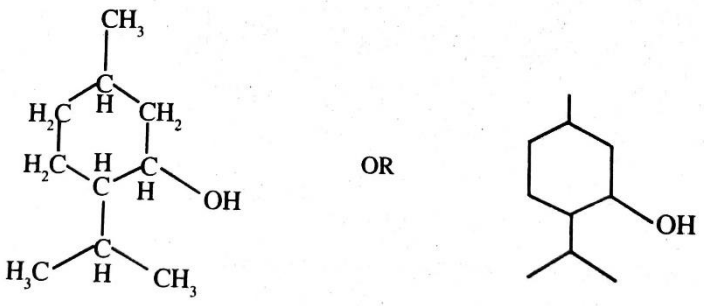
2. MENTHOL($C_{10}H_{20}O$)

Source:

Menthol occurs in peppermint oil.

Structure:

Menthol is a cyclic terpenoid alcohol.



Uses:

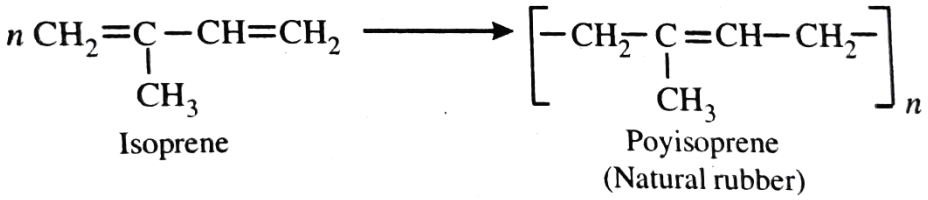
- Menthol has antiseptic, analgesic and mild anaesthetic properties. It is used

1. In throat lozenges, chewing gums and inhalers.
2. In gargles, mouthwashes and toothpastes.
3. In pain relieving ointments and liniments.
4. In face creams and shaving creams.
5. In certain brands of cigarettes and candles.

POLYTERPENOIDS

NATURAL RUBBER $(C_5H_8)_n$

- Natural rubber occurs as latex obtained from the barks of rubber trees. Latex is diluted, filtered and treated with formic acid or acetic acid when rubber gets coagulated as a soft, white mass. This is separated, rolled into sheets and smoked at a temperature of 40-50°C.
- Natural rubber is a polymer of isoprene.



Vulcanization:

- Vulcanization of rubber is a process of improvement of properties of rubber such as elasticity, tensile strength, viscosity, hardness and weather resistance. Rubber is heated in the presence of sulphur, accelerators and activators at 110- 140°C. This results in three- dimensional cross linking of the chain by sulphur atoms.

Advantages of vulcanization-

- Vulcanization introduces stiffness to the material and improves its strength and resilience.
- Vulcanized rubber has great tensile strength, extendability, resilience, resistance to wear and tear and mouldability.
- Increase in sulphur content decreases elasticity of rubber. Ebonite rubber contains about 32% of sulphur. It has toughness, abrasion resistance and very good insulation properties.