PREFACE

With its grounding in the "guiding pillars of Access, Equity, Equality, Affordability and Accountability," the New Education Policy (NEP 2020) envisions flexible curricular structures and creative combinations for studies across disciplines. Accordingly, the UGC has revised the CBCS with a new Curriculum and Credit Framework for Undergraduate Programmes (CCFUP) to further empower the flexible choice based credit system with a multidisciplinary approach and multiple/ lateral entry-exit options. It is held that this entire exercise shall leverage the potential of higher education in three-fold ways – learner's personal enlightenment; her/his constructive public engagement; productive social contribution. Cumulatively therefore, all academic endeavours taken up under the NEP 2020 framework are aimed at synergising individual attainments towards the enhancement of our national goals.

In this epochal moment of a paradigmatic transformation in the higher education scenario, the role of an Open University is crucial, not just in terms of improving the Gross Enrolment Ratio (GER) but also in upholding the qualitative parameters. It is time to acknowledge that the implementation of the National Higher Education Qualifications Framework (NHEQF) and its syncing with the National Skills Qualification Framework (NSQF) are best optimised in the arena of Open and Distance Learning that is truly seamless in its horizons. As one of the largest Open Universities in Eastern India that has been accredited with 'A' grade by NAAC in 2021, has ranked second among Open Universities in the NIRF in 2024, and attained the much required UGC 12B status, Netaji Subhas Open University is committed to both quantity and quality in its mission to spread higher education. It was therefore imperative upon us to embrace NEP 2020, bring in dynamic revisions to our Undergraduate syllabi, and formulate these Self Learning Materials anew. Our new offering is synchronised with the CCFUP in integrating domain specific knowledge with multidisciplinary fields, honing of skills that are relevant to each domain, enhancement of abilities, and of course deep-diving into Indian Knowledge Systems.

Self Learning Materials (SLM's) are the mainstay of Student Support Services (SSS) of an Open University. It is with a futuristic thought that we now offer our learners the choice of print or e-slm's. From our mandate of offering quality higher education in the mother tongue, and from the logistic viewpoint of balancing scholastic needs, we strive to bring out learning materials in Bengali and English. All our faculty members are constantly engaged in this academic exercise that combines subject specific academic research with educational pedagogy. We are privileged in that the expertise of academics across institutions on a national level also comes together to augment our own faculty strength in developing these learning materials. We look forward to proactive feedback from all stakeholders whose participatory zeal in the teaching-learning process based on these study materials will enable us to only get better. On the whole it has been a very challenging task, and I congratulate everyone in the preparation of these SLM's.

I wish the venture all success.

Professor Indrajit Lahiri
Vice-Chancellor

NETAJI SUBHAS OPEN UNIVERSITY

Four Year Undergraduate Degree Programme

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CONTENT Page No.

Unit 1: Fundamentals of Organic Chemistry

1.0. Objectives

By the end of this unit learners will be able to

- Gather information about the basic fundamentals of the organic chemistry.
- Know about various physical Effects, Electronic Displacements like Inductive Effect, Electromeric Effect. Resonance and Hyperconjugation.
- Know the types of cleavage of Bonds e.g. Homolysis and Heterolysis Know about the nucleophiles and electrophiles.
- Know about the structure, stability and reactivity of the reactive Intermediates like Carbocations. Carbanions and free radicals.
- Know about the strength of organic acids and bases and Comparative study with emphasis on factors affecting pK values.
- Understanding of the fundamental concepts of Aromaticity, Benzenoids and Huckel's rule.

1.1. Introduction

Organic Chemistry is the subclass of chemistry that involves the study of carbon and its compounds. It is established (act now that carbon can forms unlimited number of compounds. Thus the domain of organic chemistry is continuously growing synthetic research finding being made around the globe. As a consequence, impact and role of organic compounds in our daily lives is expanding from medicine to agriculture and polymers to petroleum etc. Today, organic chemistry is well developed science which has great deal of scope for further developments. Therefore, plethora of information and theories are available on organic chemistry. This implies that NSOU students of organic chemistry require a great deal of study to understand

the latest developments in the field. The study of organic chemistry seems involved; however it is very interesting and in this course begins with concise details on the concepts on fundamentals of in organic compounds

1.2. Inductive effect

It is the permanent dipole induced in a bond by another bond directly along a chain of atoms within a molecule. Inductive effect can also operate through solvent molecules or through space and referred as field effects, or I effect.

In simple word when an electronegative atom is attached to a carbon chain permanent bond polarisation is occurred by displacement of electron this polarisation is transmitted through out the carbon chain is inductive effect.

$$CH_3 \xrightarrow{\delta\delta\delta+} CH_2 \xrightarrow{\delta\delta+} \overset{\delta+}{C}H_2 \xrightarrow{\delta-} Cl$$

Inductive effect is of two type:

(i) + I effect
(ii) - I effect

(i) +1 effect: Groups having +1 effect attached to a molecule increases the overall electron density on the molecule.

$$\text{e.g.} \Rightarrow O^-, -COO^-, (CH_3)_3C-(CH_3)_2CH, CH_3CH_2, CH_3$$

$$\text{order will be } -\bar{O} > C\bar{O}O > (CH_3)C- > (CH_3)_2CH > CH_3CH_2 > -CH_3$$

(ii) **-I effect:** The electron withdrawing nature of atoms or groups is called as -I effect.

$$\text{Such as } -\overset{\oplus}{N}\equiv N, -NO_2, -CN, -F, -Cl, \ Br, \ -1$$

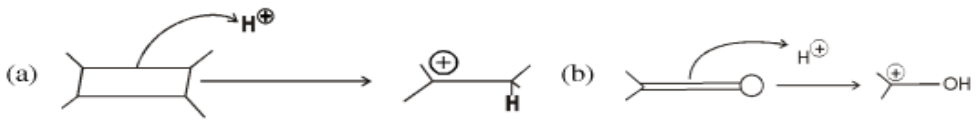
$$\text{Order will be : } -\overset{\oplus}{N}\equiv N > -NO_2 > -CN - F > -Cl > -Br > -I$$

Inductive effect is very helpful to detect the basicity of base, acidity of acids, dipole moment, chemical reactivity, and stability of carbocation.

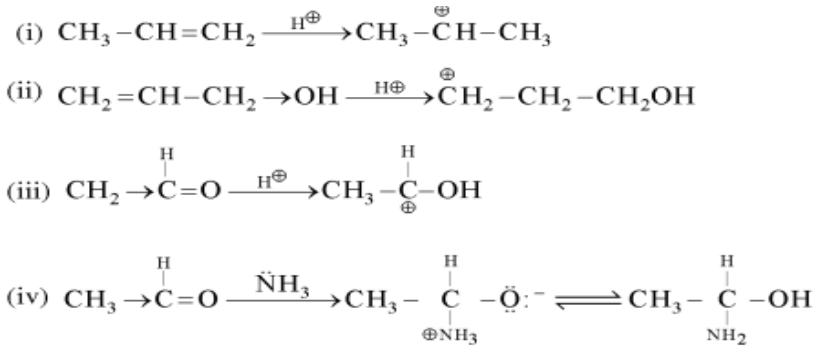
1.3 Electromeric effect

The temporary or time variable effect involving the complete transfer of a shared pair of electrons to one of the atoms joined by a multiple bond (double bond or triple bond) at the requirement of an attacking reagent is known as electromeric effect or E effect.

As soon as the attacking reagent is removed the transferred K electron pair again from the bond and the molecule reverts to its ground state electronic configuration. For this reason electromeric effect is sometime called as polarisability of multiple bond. Such as



In the presence of H^+ the π electrons are completely transferred to one of the two carbon atoms and H^+ gets attached. In the absence of H^+ (external – attacking reagent) the π electrons assume their original position. (-) or (+) I effect containing group determined the direction of electromeric effect.



Electromeric effect being temporary in nature does not influence the physical properties like melting point, boiling point etc. Electromeric effect is (+E) when the transfer of electron pair occurs towards the carbon atom and it is (-E) when it is away from the carbon atom.

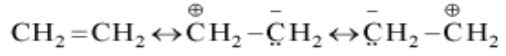
1.4. Resonance

Resonance is a hypothetical state of a chemical entity in which its electronic Structure can be hypothetically represented by two or more structures, each differing in distribution of shell electrons. The properties of the concerned molecule cannot be explained fully from any of those structures but the properties may be explained from a combination of the structures. The combination of these hypothetical structures is known as resonance hybrid. Each of the contributing structures to the resonance hybrid is known as a resonating structures and though non-existent can be written on a paper placing a double headed arrow (⟷) between the each pair. The actual structures of the molecule cannot be written on a pair.

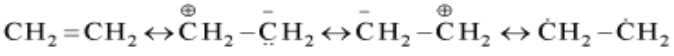
Rules of resonating structures:

(1) All the cannonical from/structure must be written with proper bonds, lone pair, electron, formal charge etc.

(2) Only the movement of π elections are allowed σ elections are not distributed.



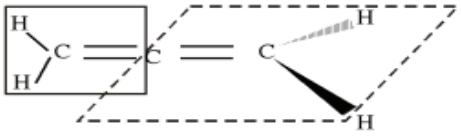
(3) The number and mode of unpaid electrons in each resonating structures must be the same.



(4) The resonating structure should have comparable energy. If any structure has high energy content the contribution of it to the resonance hybrid becomes minimum.

(5) All the atom Involved in resonance should be in the same plane. Any charged structure which prevent attaining planarity will diminish the resonance because maximum overlap of p orbitals

is then becomes impossible. For example allene molecule have no extended resonance is possible as the two $=CH_2$ Units are not be in the same plane they be perpendicular to each other.



(Not in same plane)

Contributing resonating Structures:

There are many contributing factors present that can stabilize the resonance structures and make the structure more contributing such as more covalent bond, charged uncharged structure, aromaticity, and equivalent resonating structure. Resonance is very effective on acidity or basicity of acid and bases, respectively.

Resonance energy:

The difference in energy between two most contributory resonating structure (Ec) and the experimentally obtained energy of resonance hybrid (Eo) for lg mole of a molecule is known as the resonance energy.

$$\boxed{E_R = E_C - E_O} \qquad [\ E_R = \text{Resonance energy}\ ]$$

Some point:

(i) Aromatic resonance structure have more contribution then non aromatic structure.

(ii) R.E. increase with the number of stable resonating structure.

Application:

(1) Acid strength, (2) Basic strength, (3) Bond length.

But there are a number of exceptions, one of them is the steric inhibition of resonance which opposed the resonance structure contribution and failed to maintain the co-planarity in the molecule.

1.5 Hyperconjugation

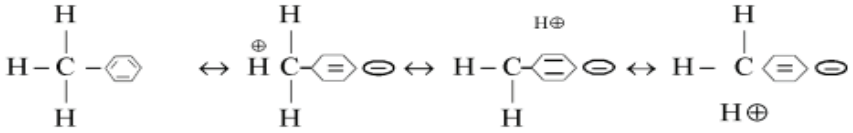
Hyperconjugation process is also known as no bond resonance or Baker Nathan effect. It is defined as it is involved the delocalization or a molecule contains at least one α-hydrogen atom with respect to a multiple bond or an unshared orbital. Canonical or resonance forms of the following types can be drawn as follows.

$$R-\underset{H}{\overset{R}{\underset{|}{\overset{|}{C}}}}-\overset{R}{\overset{|}{C}}=CR_2 \leftrightarrow B-\underset{H\oplus}{\overset{R}{\underset{|}{\overset{|}{C}}}}=\overset{R}{\overset{|}{C}}-\ddot{\overline{C}}R_2$$

Hyperconjugation in the above example may be regarded as an overlap of the orbital of the C-H bond and the π - orbital of C - C double bond.

Concept of Hyperconjugation arose from the discovery of (+)I effect alone. On that basic we can a similar order of an Unsaturated system.

tertiary butyl > isopropyl > ethyl > Methyl + I effect decreased. Baker and Nathan observed that reaction rate with pyridine and p-substituted benzylbromide were opposite than expected from electron release by I-effect. The methyl substituted compound reacted fastest and tertiary - butyl substituted compound reacted at slowest.



Three hyperconjugative structures are possible for toluene.

Application :

Hyperconjugation is the effect can stabilize the greater thermodynamic stability in which the double bond is terminal. Such stability is gain-

$$Me_3C^{\oplus} > Me_2C^{\oplus}H > Me^{\oplus}CH_2 > Me^{\oplus}$$

$\longrightarrow$ Stability decreases.

$$Me_3\dot{C} > Me_2\dot{C}H > Me\dot{C}H_2 > M\dot{e}$$

Dipole moment also controlled by Hyperconjugation.

1.6. Cleavage of bonds:

Bond cleavage is the Splitting of bond (Chemical bonds) in general word. This can be generally referred to as dissociation of bond, when a molecule get divided into two fragments.

There are two types of bond cleavage—

(i) Homolysis (homolytic bond cleavage)

(ii) Heterolysis (heterolytic bond cleavage)

(1) Heterolytic cleavage:

It is the breaking of a covalent bond in such a way that one gets both of the shared electrons. The heterolytic comes from 'greek' word heteros 'different' and lysis 'loosening'.

In polar bond this types of bond cleavage occurs. If the compound is originally uncharged then the cleavage make the atoms one cation and one anion.

Such as $H_3C - Br \longrightarrow H_3C-C\oplus \quad + Br^-$

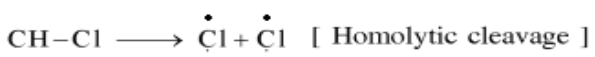
Since Br is more E.N. then 'C' so Br gets '-'ve charge and CMe3 get +'Ve' charge.

(2) Homolytic Cleavage:

Homolytic cleavage is the breaking of a covalent bond in such a way that each fragment get one of the shared electrons.

The word homolytic comes from Greek homoi 'equal' and lysis 'loosening' the words are same homolysis/homolytic.

Such that, Homolytic cleavage produce free radical atom with unpair valence electron.

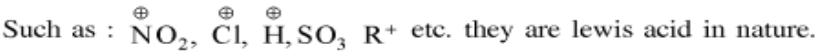


The very common difference between the homolysis and heterolysis bond cleavage is in homolysis electron from bond pair are received from one bonded atom and produce free radicals reactive intermediate.

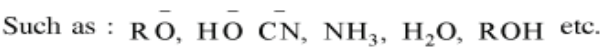
But heterolytic cleavage leads to the formation of two ions, anion and cation not the free radical.

1.7 Reacting Species

The group which possess formal positive charge on it or are electron deficient, are known as 'Electrophilies', which can act as species prone to combine with an electron rich centre.



Nucleophiles: The attacking reagents which have formal negative charge on them or possess available unshared electron pairs are termed as nucleophiles they are Lewis basic in nature.



Nucleophiles are nucleolus loving and electrophiles are electron loving.

Nucleofuge : Leaving groups having a formal negative charge on them possessing unshared electron pairs are called 'Nucleofuge' and the tendency of a group to leaves an anion is termed as 'Nuclcofugacity' some common nucleofuges are :

HO^-, NH^-_2, RO^- etc.

Electrofuges: Leaving group having a formal +'ve' charge on them or possessing/ or electron deficient are known as 'Electrofuges'.

Some electrofuges are H^+, R^+, SO_3

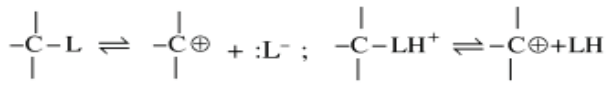
The tendency of group to leave as a cation is called electrofugacity.

1.8. Carbocation

If a positively charged atom contains covalent bonds more than that present in the same neutral atom known as carbocation.

e.g. NH_4^+, H_3O^+, $C_2H_5^+$, R_3O^+ etc.

When a bond of a substrate molecule or its conjugate acid dissociates and the bonded pair of electron get transferred to the leaving group then a carbocation is formed.



Carbocation forms by (i) heterolytic fission of neutral species, (ii) By Olah's super acid (SbF_5), (iii) by protonation of lone pair, (iv) Ionisation induced by Lewis acid etc. e.g.—

(i) $Me_3CBr \rightleftharpoons Me_3C^+ Br^-$

(ii) $R-F + SbF_5 \rightleftharpoons R^+ SbF_6^-$

(iii) $Ph_3C-OH \overset{H_2SO_4}{\rightleftharpoons} HSO_4^- + Ph_3C-\overset{H}{\overset{|}{O}}H \overset{H_2SO_4}{\rightleftharpoons} Ph_3C^+ + H_3O^+ + 2HSO_4^-$

(iv) $MeCOF + BF_3 \rightleftharpoons MeC^{\oplus}O\ BF_4^{\ominus}$

From other cation $R-NH_2 \xrightarrow[\text{dil HCl}]{NaNO_2} R^+ + N_2\uparrow$

Stability of Carbocation:

(i) Stability of Carbocation increases with the increase in delocalization of positive charge, e.g., +R, +I effect stabilizes carbocation

Similarly -I, -R effect decreases the Stability of carbocation.

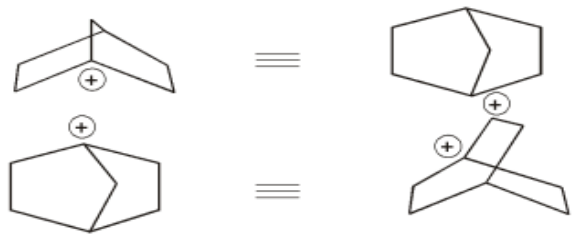
(ii) The bond angle increases in a carbocation i.e. increase in Stability.

(iii) Solvent make a great role in stability such as polar solvent is the cause of greater stability compare to non polar solvent.

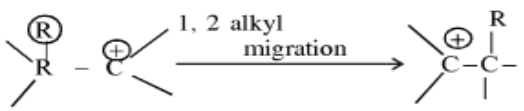
Some other effect aromaticity, steric relief are also the cause of the stability of carbocation.

Some other type carbocation—

(i) Bridge head carbocation

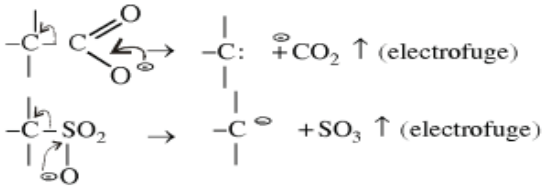


(ii) Non classical carbocation



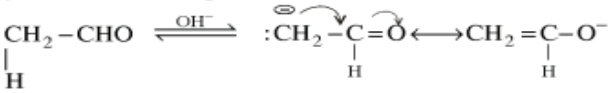
1.8 Carbanions

In simple way, carbanion is a base and it can form a conjugate acid with an acid say proton. The less is strength of conjugate acid the more stability of carbanions or vice versa.

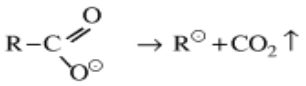


Formation of Carbanions:

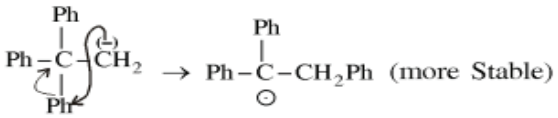
(i) By abstruction of proton.



(ii) By the decomposition of anion.



(iii) less stable to more stable



(less stable)

(iv) By Grignard synthesis

1.10 Aromaticity

Aromatic compound: In a more specific chemical sense aromatic compounds are defined as those which meet the following criteria—

(1) The structure must be cyclic and must contain some number of conjugated bonds.

(2) Each atom in the ring must have an unhybridised p-orbital.

(3) The hybridized π-orbitals must have overlap to form a continuous ring of parallel orbitals, usually reached / achieved planar (almost planar) arrangement allowing the most efficient overlap.

(4) Delocalization of the electron (π) over the ring must result in a lowering of the electronic energy.

An antiaromatic compound is which meets the first three criteria but delocalization of the π electrons over the ring results in increase in electronic energy.

Acyclic compound that does not have a continuous overlapping of ring of p orbitals is can't be aromatic or antiaromatic is the compound known as non aromatic.

** Aromatic compound is more stable then antiaromatic or non aromatic. Some examples of aromatic and antiaromatic also non aromatic compounds :


Aromatic


Antiaromatic


non aromatic

Huckel aromaticity:

Huckel develop a quick way to predict which would be aromatic and which be antiaromatic. If (and only if) the molecule in question meets the criteria for being either aromatic or antiaromatic (i.e., it must have a continuous rings of overlapping p-orbitals arranged in planar or almost planar fashion then the Huckel rule is applied.

Rule: It is the rale that states that if the number of π electron in the cyclic system is equal to (4N+2) where N is a whole number integer then the system is aromatic.

If the number of π electron in the cyclic system is 4N where 'N' is a whole integer then the system is antiaromatic.

So, the system 2, 6, 10, 14 ... π -electron are aromatic and 4, 8, 12 π-electron system are antiaromatic.

Examples of the compounds :

(1) 

5 × C —— 5 π e

1 × N —— 1 π e

Total = 6 π e Aromatic

(2) 

3 × C —— 3 π e

1 negative charge 1 π e

Total = 4 π e Antiaromatic

Benzenoids:

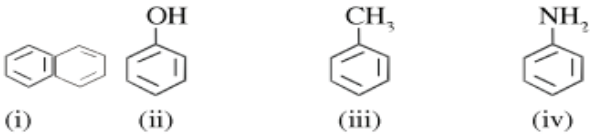
In a single word benzenoids are those compounds which have at least one benzene ring in the structure of the molecule.

According to Huckel's aromatic compounds must contain (4n+2) n electrons. Benzene is an ideal example which fulfil all the criteria of aromaticity.

 6π electron Perfectly aromatic

(4x+2) n = 1 aromatic

example of benzenoids :



(i) (ii) (iii) (iv)

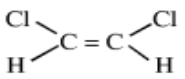
1.11 Summary

Tins chapter provides with the concise description of fundamental concepts of the organic chemistry. The description on topics such as hybridization, localized and delocalized chemical bond, resonance, hyperconjution, aromaticity, steric effect and electronic effects make base to comprehend organic chemistry. Introduction to the topics such as structure, shape and reactivity of organic molecules e.g. nucleophiles and electrophiles and reactive intermediates stimulate the interest of reader to the basic studies in organic chemistry. Other significantly important topics such as strength of organic acids and bases are also given with lucid diagrams.

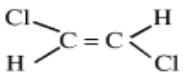
1.12 Solved problems

(1) Explain why in the following pair one has dipole moment but the other compound has no dipole moment— (i) Cis and trans ClCH = CHCl.

Ans. The cis isomer has both chlorine groups on the same side whereas the trans isomer has them on opposite sides. Dipole moment depends on the variation in distribution of electrons along the bond. In the trans isomer the dipole moments of the two C-Cl bonds cancel each other as they are in opposite directions. Where as in the cis isomer the polar C-Cl bonds are on the same side of the double bond, thus the resultant has a (+)ve value.



Cis structure



Trans structure

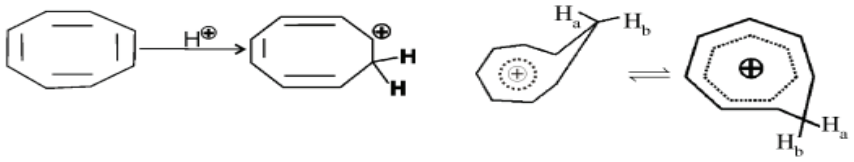
(2) Write down the difference between inductive effect and electromeric effect?

Ans.

Inductive effect	Electromeric effect
(1) If is the permanent polarisation of single bond.	(1) It is the polarisability of multiple bond.
(2) only electron displacement takes place in the inductuctive effect.	(2) Complete transfer of π electrons take place in the electromenric effect.
(3) σ electrons are involved.	(3) π electrons are involved.
(4) It effect both physical and chemical properties as well as the reactivity of the molecule.	(4) It does not effect the physical properties but enhance the chemical reactivity of the molecule.

(3) What is called Homoaromatic compound? Give an example.

Ans. If a stabilized cyclic conjugated system (4n+2) electrons can be formed by passing one saturated atom, the system is called homoaromatic compound. Homotropylium ion is formed when cyclooctaene is dissolved in concentrated sulphuric acid is the best example to demonstrate homoaromaticity. Here, Six electrons are spread over seven carbon atoms.



(4) Why carbocations are highly reactive species ?

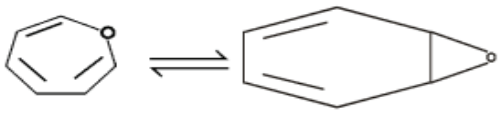
Because of having a strong tendency to complete the octet of the electron-deficient carbon. Thus carbocations are highly reactive species.

(5) What do you mean by ring chain and valence tautomerism?

Ans. The type of tautomerism where one tautomer is acyclic and other is cyclic is denoted as ring chain tautomerism. The ring and open chain form of tautomers are possible when one functional group of a bi-functional acyclic molecule react with other and forms a cyclic system e.g. D-glucose, D-Mannose, etc. exhibit ring chain tautomerism.

In such cases open chain aldehyde is converted to the cyclic hemiacetal form by inter molecular reaction between -OH and -CHO group.

Valence tautomerism is a type of tautomerism in which single and/or double bonds are rapidly formed and ruptured, without migration of atoms or groups. Oxepin and Benzeneoxide represent a pair of valence tautomers.



Oxepin Benzene Oxide

(9) Although there are eight free electrons phenyl anion $C_6H_5^-$ is aromatic.

Ans. The unshared electron pair of the phenyl anion is located in an sp^2 orbital which is co-planar with the ring and perpendicular to the π electron cloud. The negative charge therefore can't be delocalized through resonance interaction with π electron cloud of the aromatic nucleus. Thus the species (Planar) is a closed loop of six [(4x+2)π, n = 1] π electrons and It is aromatic.

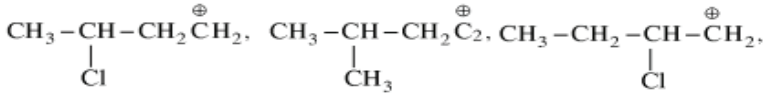
This species is aromatic because it is planar and contain (4n+2)π electrons.

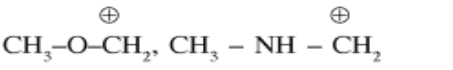
(10) An nucleophilicity order in protic solvent.

$$RS^{\ominus} > R_3P > I^{\ominus} > CN^{\ominus} > R_3N > OH^{\ominus} > Br^{\ominus} > NH_3 > Cl^{\ominus} > CH_3COO^{\ominus} > F^{\ominus} > CH_3OH$$

1.13 Exercise

(1) Which carbocation is more stable and why ?

(a) 

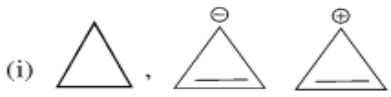
(b) 

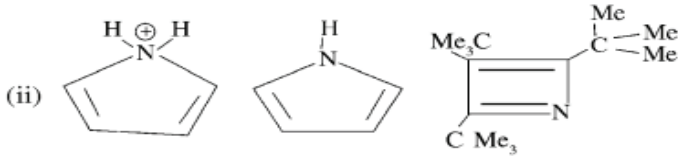
c) 

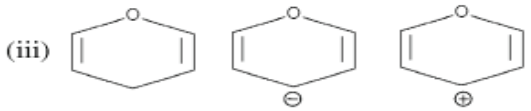
(2) Hydrazine (NH_2- NH_2) is considerably more nucleophilic than NH_3 although it is less basic? Why?

(3) Which species is the smallest aromatic substance?

(4) Classify the following molecule ions as aromatic non-aromatic and antiaromatic.

(i) 

(ii) 

(iii) 

(5) What is resonance energy? What is the salient feature of resonance energy?

(6) Acidity order can be determined by carbanion stability - arrange of the given acids with increasing acidity?

$ClCH_2COOH$, $HCOOH$, CH_3COOH

(7) What is hyperconjugation or Baker-Nathan effect? why hyperconjugation is called as Baker Nathan effect?

(8) Give the suitable stability order of the given carbocations, methyl, isopropyl, tertiary butyl, ethyl carbacations.

(9) Dipole moment of CO have both a-moment and π-moment show that?

(10) Explain why CCl_4, CO_2, NF_3 has no dipole moment and why?

But some other compounds have dipole moment e.g. CH_3Cl, SO_2, NF_3 – give explanation.

(11) Acetone exist almost exclusively in the keto form-Why?

(12) For phenol there is no evidence for the existence of the keto form (the cyclohexadienone)?

(13) Explain why carboxylic acids behave as acidic in aqueous medium and they are much stronger acids than alcohol?

(14) State the nucleophilicity order of the following nucleophiles with explanation—

(a) NH_3, H_2O_2, NH_2 , $\bar{N}H_2$
(b) Cl^- , NH_2, OR^-, CH_3^-

(15) What is the free radical? Give a process by which you can detect the free radicals?

(16) What is the Neighbouring group participation?

Unit 2: Stereochemistry

2.0 Objectives

By the end of this unit learners will be able to

- Describe isomers and explain the structural formulae for a variety of isomeric organic compounds
- Explain various kinds of structural and stereo isomerism along with their representation. 'Differentiate geometrical and optical isomers
- Represent three dimensional organic molecules in two dimensions
- Leant chirality, enantiomers, diastereomers and their relative/absolute configurations
- Leant the nomenclature (cis-trans, E/Z, D/L, d/1, erythro/threo and R/S) of different stereo isomers

2.1 Introduction

Stereochemistry deals with three dimensional representation of molecule in space. This has sweeping implications in biological systems. For example, most drugs are often composed of a single stereoisomer of a compound. Among stereoisomers one may have positive effects on

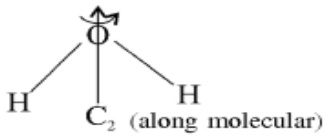
the body and another stereoisomer may not or could even be toxic. For an example human body can digest D-Glucose whereas L-Glucose cannot be digested and is toxic. The study of stereochemistry focuses on stereoisomers and spans the entire spectrum of organic, inorganic, biological, physical and especially supramolecular chemistry. Stereochemistry includes method for determining and describing these relationships; the effect on the physical or biological properties.

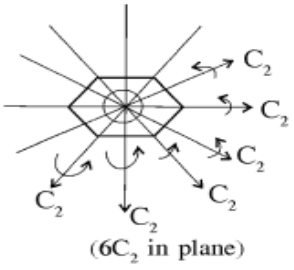
2.2 Optical Isomerism

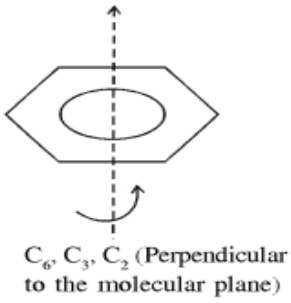
When isomers of a compound are capable of rotating the plane of plane-polarized light, are known as optical isomers and the phenomenon is known as optical isomerism. A molecule is optically active, when it is non-superimposable with its mirror image.

2.4 Elements of Symmetry

There are two fundamental elements of symmetry (I) Proper or rotational axis of symmetry and (II) Alternating axis of symmetry. (I) Proper or rotational axis of symmetry It is an imaginary axis, passing through a molecule, such that the molecule rotates about the axis through an angle $\frac{360^\circ}{n}$ results in an equivalent molecule. It is denoted by C, where 'n' is called fold or order. If a molecule possess multiple C_n axis with different values of n, the axis with maximum 'n' value is called principal axis of symmetry.

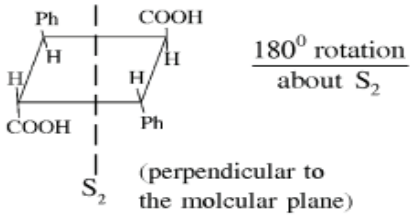


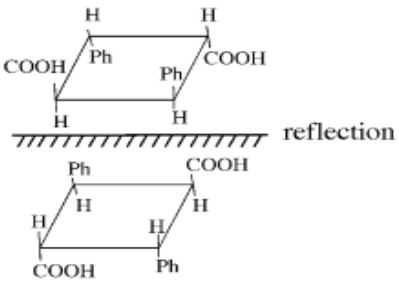




(II) Alternating axis of symmetry

Rotation about this axis by $\frac{360^\circ}{n}$, followed by reflection through a plane perpendicular to this axis produces an indistinguishable structure. It is denoted by S_n, of order n.





Plane of symmetry (σ or S1)

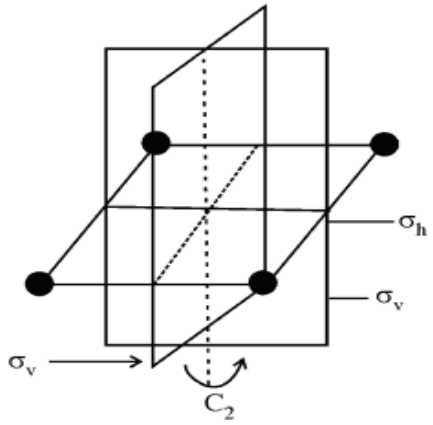
It is a plane bisecting a molecule such that each atom on one side of the plane, when reflected through the plane encounters an equivalent atom on the other side.

*Every linear and planar molecule necessarily have a σ-plane, i.e. the molecular plane.

σ_h — σ-plane perpendicular to principal axis C_n (h = horizontal)

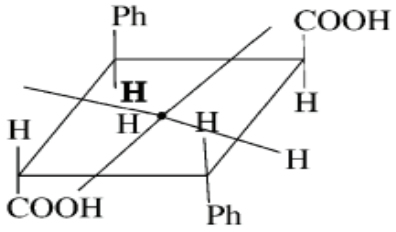
σ_v — σ-plane containing the principal axis C_n (v = vertical)

σ_d — σ-plane containing principal C_n and bisecting the angle between two C_2 (d =diagonal)



Centre of symmetry (i or S_2)

It is a point within a molecule such that if a straight line is drown from any part of the molecule through the point and extended an equal distance by a straight line on the other side, a like atom or part is encountered.



Equivalent symmetry operations

(i) $C_n^n = E$ (E stands for operation of identity or I)

ii) $\sigma^2 = E$

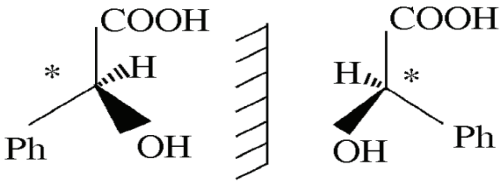
iii) $i^2 = E$

iv) $S_n^n = E$ (n = even)

v) $S_n^{2n} = \sigma^2 = E$ (n = odd)

2.5 Enantiomers

A pair of stereoisomers having non-superimposable mirror image.

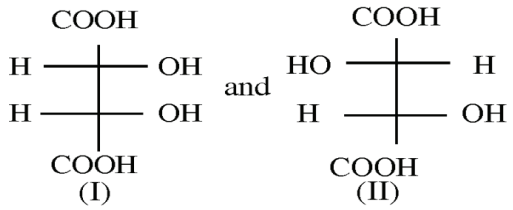


Enantiomers are chemically alike

(* chiral centre)

2.6 Diastereomers

A pair of stereoisomers having no mirror-image relationship

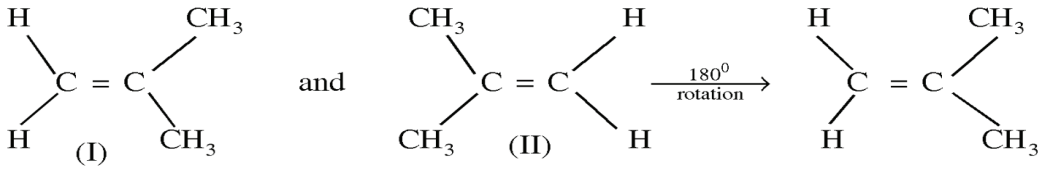


Diastereomers are chemically different. (eg. mp, bp, solubility optical activity)

I and II are diastereoisomers

2.7 Homomers

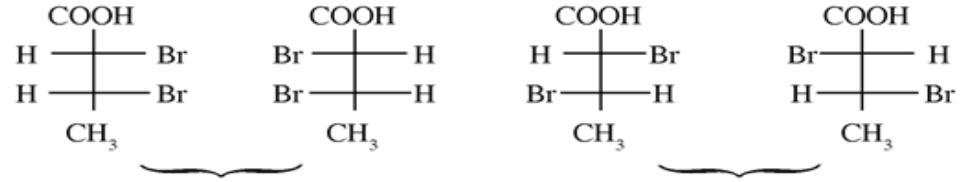
Any two structures, that are superimposable.



(I) and (II) are homomers

Optical properties of molecules containing two chiral centres

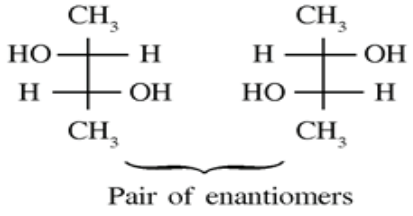
Example 1. $CH_3CH(Br)\ CH(Br)\ COOH$



Pair of enantiomers

pair of enantiomers

Example 2. $CH_3\dot{C}H(OH)\,\dot{C}H(OH)\,CH_3$



Meso Compound

A stereoisomer, i.e, faint to be optically inactive, inspite of the presence of multiple chiral centres, due to presence of σ, i or S_n

2.8 Stereochemical nomenclature of configurational stereoisomers

A) Relative nomenclature— It depends on some standard compound.

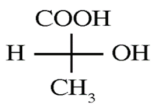
1. D/L nomenclature

Here, glyceraldehyde is taken as a standard compound.

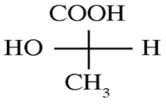
Now, D isomer = In the true Fischer projection, hetero-atom/group in on Right hand side.

L isomer = In the true Fischer projection, hetero-atom/group in on Left hand side

e.g.



(–) ≡ laevorotatory i.e. rotates the plane of plane polarised light anti-clockwise

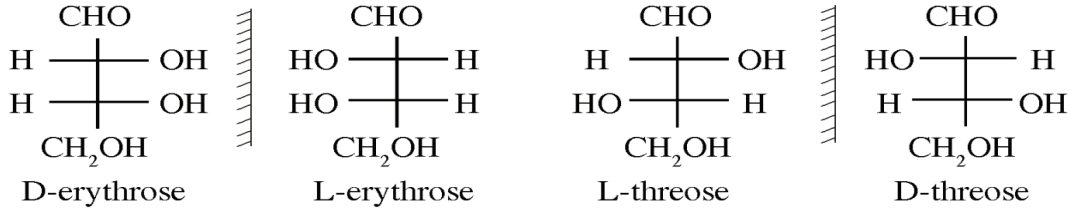


Here, (+) ≡ dextrorotatory i.e. rotates the plane of plane plarised light clockwise

N.B. A compound, whether it is dextrorotatory or laevorotatory has no relationship with its configuration. It is determined experimentally.

2. Erythro / Threo nomenclature

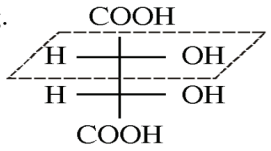
Here, CH-C(OH)-C(OH)-CH_2OH is taken as a standard compound



Now, Erythro isomer = two sets of like atoms are on the same side

Threo isomer = two sets of like atoms are on the opposite side

eg.



σ-plane (meso compound)

erythro-tartaric acid

B) **Absolute** nomenclature — It doesn't depend on any standard compound.

1. R/S nomenclature

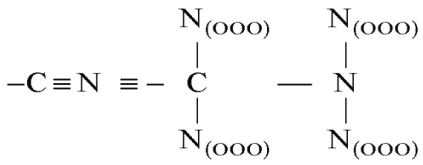
This method of configuration was introduced by three scientist Calm, Ingold, Prelog, known as CIP rule.

i) For molecules with chirality, near groups get priority over far groups.

ii) Priority of atoms increases with atomic number.

iii) If same atoms are attached directly to the chiral centre, then β-atoms are considered. If β-atoms are also same, then γ-atoms and the δ-atoms and further, until priority is decided.

iv) Double and triple bonds are considered as 2 and 3 bonds separately joined to same atoms (imaginary, phantom).



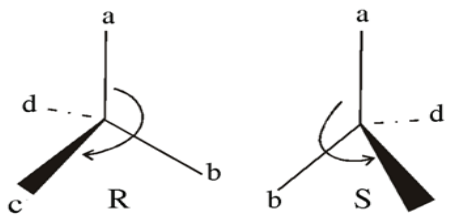
v) If still no conclusion is reached, then mass number is taken into consideration.

vi) Groups with different configuration follow the sequence rules as follows,

a. cis > trans , Z > E

b. R > S , R-R or S-S > R-S

Now, **assignment of R/S**

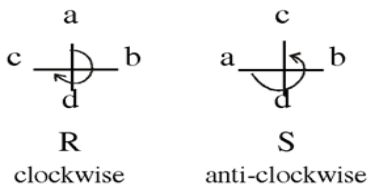


(rectur, clockwise)

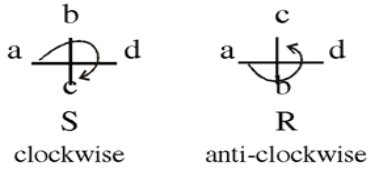
(sinister, anti-clockwise)

priority → a > b > c > d

(lowest priority group is below the plane)



(When,
lowest prierity group is at vertical axis)



(When,
lowest prierity group is at horizontal axis)

2.9 Geometric Isomerism

This type of isomerism is exhibited by molecules having a planar, rigid part (i.e. rotation of that part is restricted). Compounds having double bonds are most common examples. When each double bonded atom is bonded to two different atoms/groups, then there arises two configurations. These are called geometric isomers. As, these isomers do not have mirror image relationship, they are also now called diastereomers.

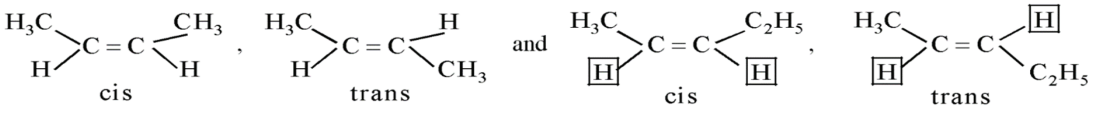
2.10 Cis/trans Nomenclature

This nomenclature applies only if at least one same atom/group or like atom/group reside on both sides of the double bond (or the rigid part)

Cis-isomer = the two like atoms or groups are on the same side of the double bond

trans-isomer = the two like atoms or groups are on the opposite side of the double bond

e.g.



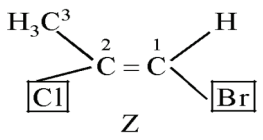
2.11 E / Z Nomenclature

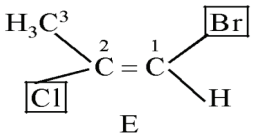
This nomenclature can be applied to any geometric isomers. First, we have to assign priority to the two atoms/groups, bonded to both the double bonded atoms by CIP rule (calm, Ingold, Prelog)

E isomer = the two superior atom or groups are on the same of the double bond.

Z isomer = the two superior atom or groups are on the opposite of the double bond.

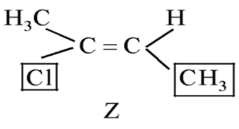
e.g.

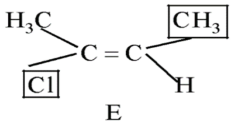


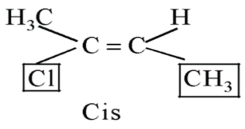


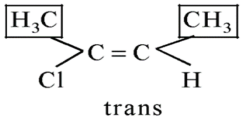
priority order for C-1
Br 〉 H
priority order for C-2
Cl/CH_3

more examples







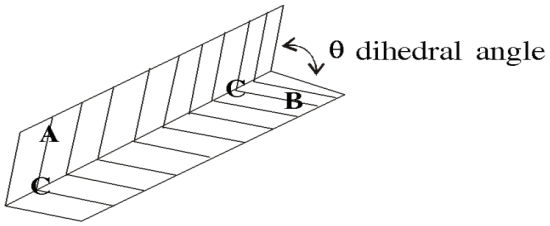


2.12 Conformational isomerism

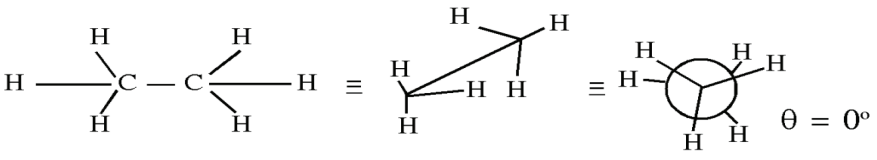
Stereo isomers that can be interconverted by mechanical process (free rotation about a single bond) without involving any chemical process (making or breaking of bonds), are known as conformational isomers / rotational isomers /rotamers.

Conformational isomers / conformers reduce about 16-25 kJ/mole of energy due to interconversion.

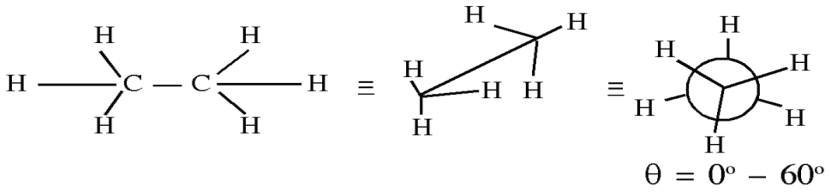
Dihedral angle: Dihedral angle of a molecule of die type (A-C-C-B) is the angle between planes ACC and CCB.



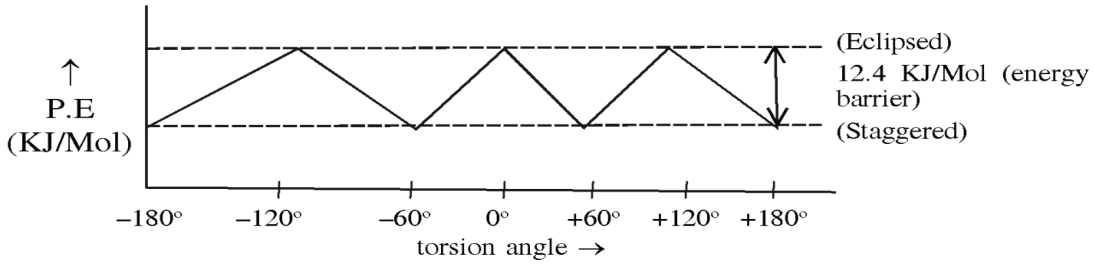
Torsion angle: In a system of attached atoms X-A-B-Y, where neither X nor Y is collinear with A and B, smaller angle subtended by the bonds X-A and Y-B in a plane projection obtained by looking at the system along the axis A-B. It is positive (+) when clockwise and negative (-) when anticlockwise.



staggered conformation more stable :



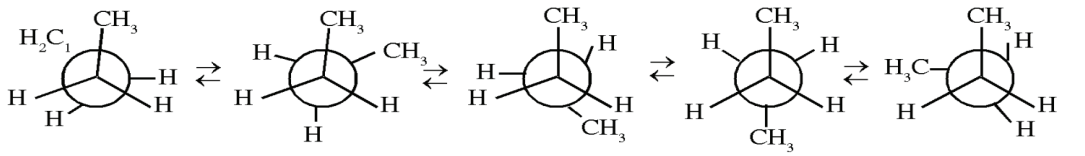
skew conformations : any conformation between these two entries



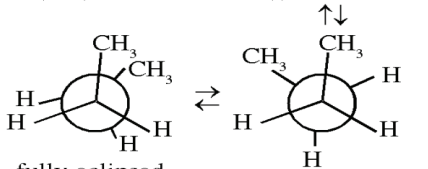
2.12.2. Conformational analysis of n-butane

1. about C1 - C2 rotation— This is very similar to the situation with ethane, but the energy barrier is much higher.

2. about C2- C3 rotation— There are two energy-minima's— gauche-staggered & anti-staggered and also two energy-maxima's-partially eclipsed & fully eclipsed.

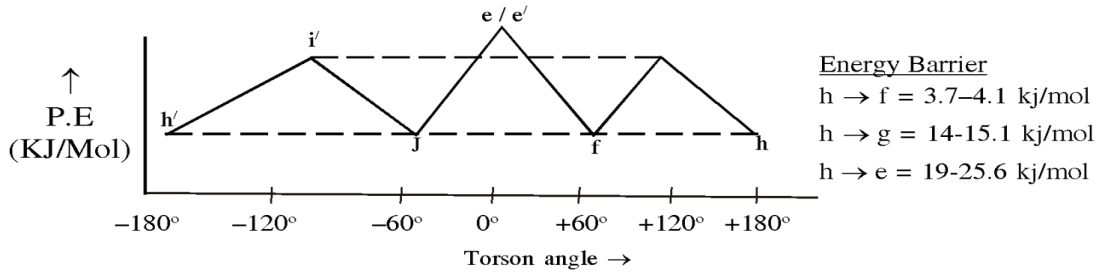


fully-eclipsed (e) w = o° | ganche staggered (f) w = + 60° | partially eclipsed (g) w = +120° | anti staggered (h/h′) w = ±180° | partially eclipsed (i) = –120°



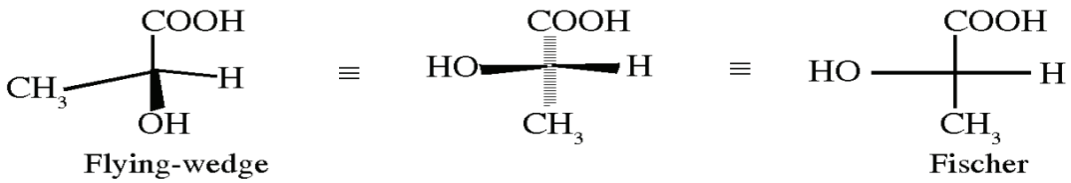
fully eclipsed (e′) w = 0° | gauche staggered (j) w = –60°

All other possible conformers between these entries are called skew conformers.

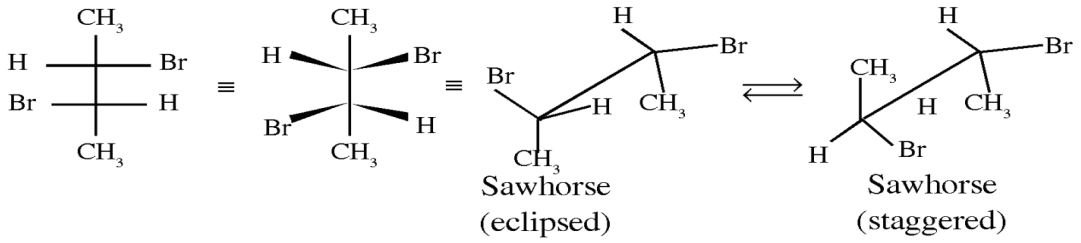


2.13 Interconversion between various projection formulas

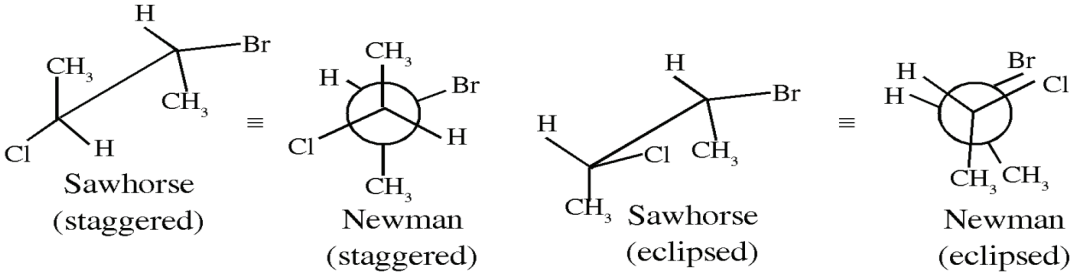
1. Flying wedge to Fischer projection and vice versa



2. Fischer to Sawhorse projection and vice versa



3. Sawhorse to Newman projection and vice versa



2.14 Summary

- Stereochemistry is all about the three Dimensional spatial aspects, properties of molecules and reactions.
- Molecules that differ only in the arrangement of bonds in three Dimensional space are called" stereoisomers"

- An object that has a non-superimposable mirror image relationship is said to be " chiral" (Greek = " handedness") and one that has a superimposable mirror image is called " achiral" .
- Pairs of molecules that are non-superimposable mirror images relationship with each other are called " enantiomers"
- The most common type of " chirality" is observed when a carbon atom has four different groups attached to it This carbon atom is then described as a chiral or asymmetric or stereogenic center. This later term can also be contracted to a stereocenter.
- Chiral molecules cause the plane of polarized light to rotate in some directions (clockwise = +ve, anticlockwise = -ve). This can be measured using a polarimeter. An achiral molecule is optically inactive.
- Enantiomers have the same chemical and physical properties (melting points, boiling points, heat of combustion etc.), except for their interaction with plane polarized light or with other chiral molecules (reagents, solvents, catalysts, etc).
- Diastereomers are stereoisomers that have the same molecular formula and sequence of bonded elements but which are non-superimposable and have no mirror image relationship with each other.
- Cis-Trans and E-Z forms of molecules shows geometrical isomerism i.e. these isomers are diastereomers to each other, Trans- or E- isomer is more stable than Cis-or Z- isomer respectively.
- Conformational isomers (or conformers or rotational isomers or rotamers) are stereoisomers produced by rotation (twisting) about o bonds, and are often rapidly interconverting at room temperature.

2.15 Solved Problems

1. Indicate the simple axes of symmetry present in the following molecules/ions :

(a) ethylene (b) methyl cation, (c) allene (d) cyclohexane.

Ans. (a) Ethylene ($CH_2 = CH_2$)

It has three C_2 axes.

(b) Methylcation

It has one C_3 axis and three C_2 axes.

(c) Allene ($CH_2= C = CH_2$)

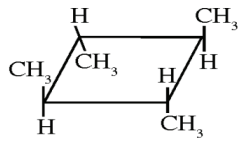
It has three C_2 axes.

(d) Cyclohenane (C_6H_{12})

It has one C_3 axis and three C_2 axes.

2. Indicate the elements of symmetry (other than C_n) present in the following molecules :

(a) anti conformation of meso-tartaric acid (b) 8-chlorospiro [4,5] decane

(c) 

Ans. (a) anti conformation of meso-tartaric acid

It has a centre of symmetry (i)

(b) 8-chlorospiro [4,5] decane

It has a plane of symmetry (σ)

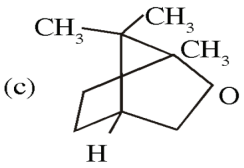
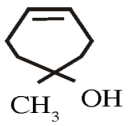
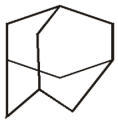
(c) The molecule has a four-fold

alternating axis of symmetry (S_4)

3. Identify the chiral centre(s), if any, in each of the following compounds and indicate each of them with an asterisk :

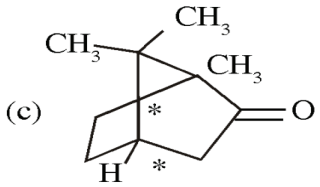
(a) $CH_3CH = CH\text{-}CHC1CH_2CH_3$

(b) $CH_3CH_2\underset{\underset{O}{\downarrow}}{N}(CH_3)CH_2CH(CH_3)C_2H_5$

(c)  (d)  (e) 

Ans. (a) $CH_3CH{=}CH{-}\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C^*}}{-}CH_2CH_3$ (b) $CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{O}{\downarrow}}{N^*}}-CH_2-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C^*}}-CH_2CH_3$

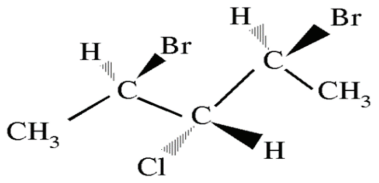
$* \equiv$ chiral centre

(c) 

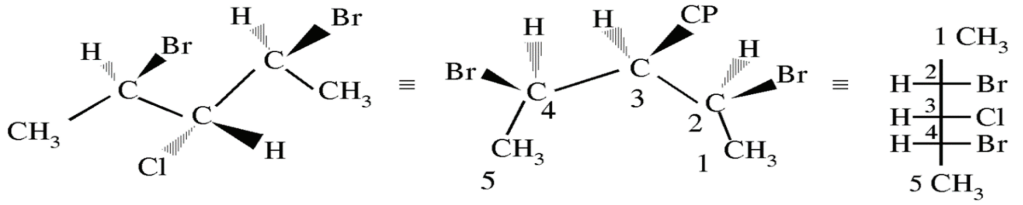
(d) There is no chiral centre in the molecule

(e) There is no chiral centre in the molecule.

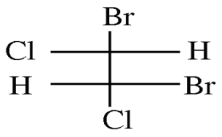
4. Convert the following flying wedge projection into Fischer projection :



Ans.

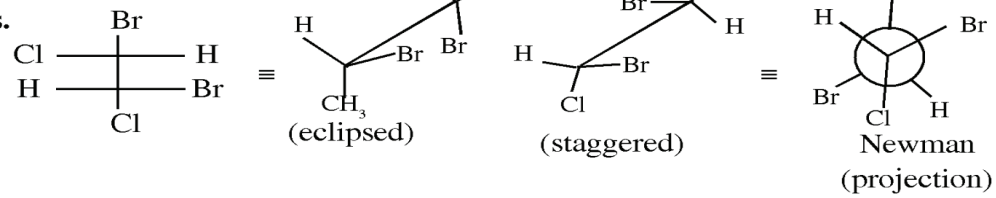


5. Convert the following Fischer projection into sawhorse and Newman projection as directed:



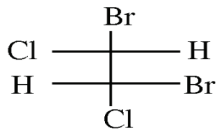
(Projection having a centre of symmetry)

Ans.



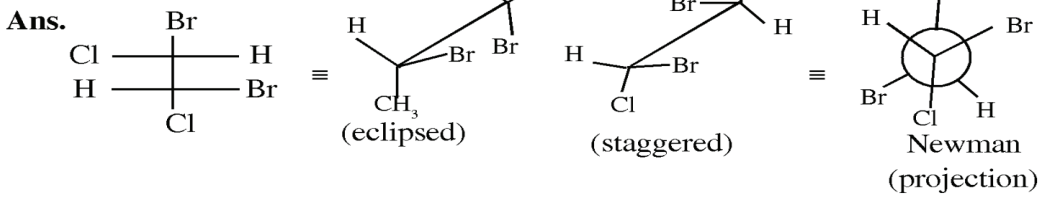
(eclipsed) (staggered) Newman (projection)

5. Convert the following Fischer projection into sawhorse and Newman projection as directed:



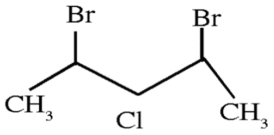
(Projection having a centre of symmetry)

Ans.

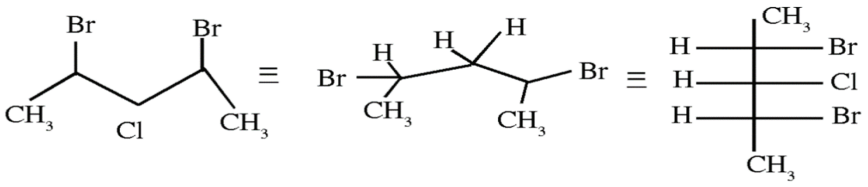


(eclipsed) (staggered) Newman (projection)

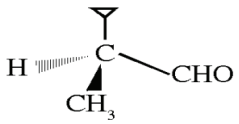
6. Convert the following Zigzag projection to Fischer projection :



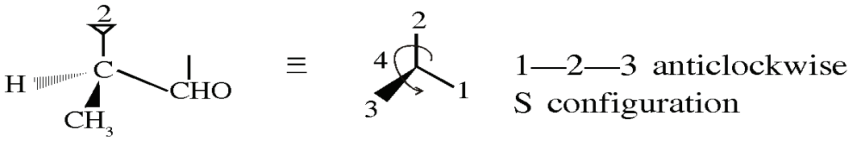
Ans.



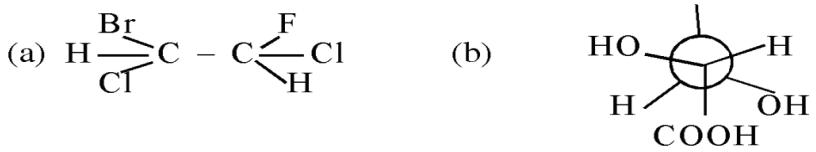
7. Assign R/S designation to the following compounds :



priority order : CHO > –◁ > $–CH_3$ > –H

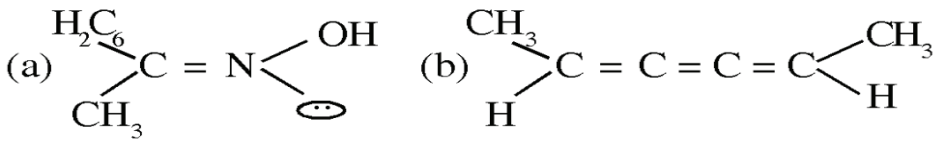


8. Designate the following structures with threo/erythro prefix :



Ans. (a) threo form, (b) erythro form

9. Specify the configuration (E or Z) of each of the following compounds :



10. (a) Calculate the ee and the specific rotation of a mixture containing l0g of (+) 2-butanal and 6g of (-) 2-butanol. The specific rotation of enantomerically pure (+) – 2-butanol is +13.5°.

(b) What is the percentage composition of a mixture of two enantiomers of 2-butanol whose rotation is +2.7°?

Ans. (a) In (10+6)g = 16g mixture, there is 4g excess of the (+) enantiomer.

$$\therefore \text{OP} = \text{ee} = \frac{\frac{10}{74} - \frac{6}{74}}{\frac{10+6}{74}} \times 100\% = \frac{(10-6)}{(10+6)} \times 100\% = \frac{4}{16} \times 100\% = 25\%$$

$$\therefore \text{OP} = \text{ee} = \frac{\frac{10}{74} - \frac{6}{74}}{\frac{10+6}{74}} \times 100\% = \frac{(10-6)}{(10+6)} \times 100\% = \frac{4}{16} \times 100\% = 25\%$$

$\therefore$ observed specific rotation = specific rotation of the pure enantiomer $\times \frac{\text{OP}}{100}$

$$= \frac{(+13.5^0) \times 25}{100} = +3.37^o$$

(b) $\text{OP} = \frac{+2.7}{+13.5} \times 100\%$ = 20% [with respect to the (+) enantiomer]

$\therefore$ The mixture consists of 20% (+) enantiomer and 80% racemic modification.

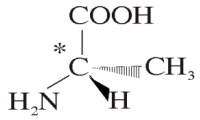
$\therefore$ The total of (+) eneantiomer is thus $\left(20 + \frac{80}{2}\right)\%$ or 60%

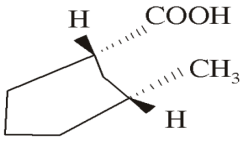
and the renaining 40% is (–) enantiomer.

2.16 Exercises

1. Are D, L - symbols related to the sign of rotation of the optically active compounds?

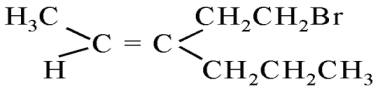
2. Assign R/S designation to the following compound :

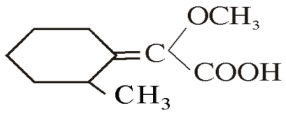
(a) 

(b) 

3. How can you draw flying wedge structures for the following compound : (R) - 2-butanal

4. Specify the configuration (E or Z) of the following compounds :

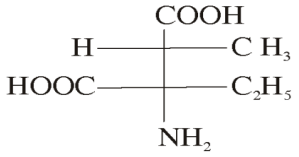
(a) 

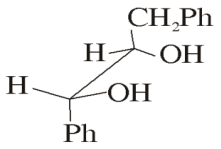
(b) 

5. Write the structural formula for the following compounds

(a) (Z) - 3 - methyl - 2 - hexane (b) (Z,E) - hepta-2, 4-diene

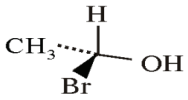
6. Designate each of the following structures with erythro or threo prefix

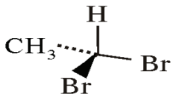
(a) 

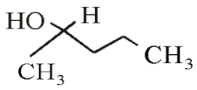
(b) 

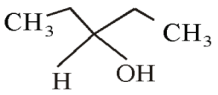
7. Which of die following compounds has a stereoisomer that is a meso compound : (a) 1, 3-dimethylcyclopenlane, (b) pentane 2, 3, 4 triol

8. Identify chiral and achiral molecules in each of the following pairs of molecules :

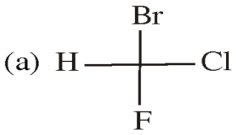
(a) 

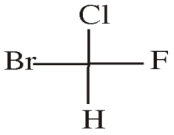
and 

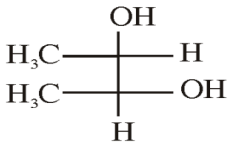
(b) 

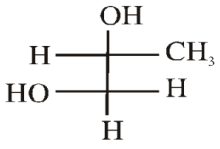
and 

9. Label the following pairs of structures as homomers, enantiomers or diastereomers :

(a) 

and 

(b) 

and 

10. The dipole moment of active 2, 3-dibromobutane is larger than meso-2, 3,dibromobutane. Explain the observation.

Unit 3: Chemistry of Alkanes

3.0 Objectives

By the end of the unit the learner should be able to:

- Recognize the hydrocarbon families, functionally substituted derivatives of alkanes.
- Know the method of preparation of alkane.
- Understand the different types of reactions in alkane.
- Mechanism of free radical substitution with reference to halogenations.

3.1 Introduction

Alkanes are saturated open-chain hydrocarbons containing carbon-carbon single bonds. Methane is the first member of this family. Methane is a gas found in coal mines and marshy places. If we replace one hydrogen atom of methane by carbon we get hydrocarbon with molecular formula C_2H_6 called ethane.

Alkanes are organic compounds with only C-C and C-H single (σ) bonds.

General formula for alkanes : C_nH_{2n+2}

Some common names of alkanes :

Name	Formula	n value
Methane	CH_4	1
Ethane	$CH_3–CH_3$	2
Propane	$CH_3–CH_2–CH_3$	3
Butane	$CH_3–CH_2–CH_2–CH_3$	4
Pentane	$CH_3–CH_2–CH_2–CH_2–CH_3$	5

3.2 Preparation

Petroleum and natural gas are the main sources of alkanes. However, alkanes can be

prepared by following methods :

3.2.1 From Hydrogenation of unsaturated hydrocarbon :

Dihydrogen gas adds to alkene and alkynes in the presence of finely divided catalyst like platinum, palladium or nickel to form alkanes. This process is called hydrogenation. These metal adsorb dihydrogen gas on their surfaces and activate the hydrogen-hydrogen bond. Platinum and palladium catalyse the reaction at room temperature but relatively higher temperature and pressure are required with Ni catalyst.

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

$$\underset{\text{Propene}}{CH_2=CH_2}+H_2 \xrightarrow{Pt/Pd/Ni} \underset{\text{Propene}}{CH_3-CH_2-CH_3}$$

$$\underset{\text{Propyne}}{CH_3-C\equiv C-H}+H_2 \xrightarrow{Pt/Pd/Ni} \underset{\text{Propane}}{CH_3-CH_2-CH_3}$$

3.2.2 From alkyl halides

Alkyl halides (except fluorides) on reduction with zine and dilute hydrochloric acid give alkanes.

$$\underset{\text{Chloromethane}}{CH_3-Cl}+H_2 \xrightarrow{Zn,H^+} \underset{\text{Methane}}{CH_4}+HCl$$

Basically :

$$\underset{\text{Alkyl halides}}{R-X} \xrightarrow{Zn,H^+} \underset{\text{Alkane}}{R-H}+H-X$$

3.2.3 Wurtz reaction

Alkyl halides on treatment with Na (sodium) metal hi dry ethereal (free from moisture) Solution give higher alkanes. This reaction is known as Wurtz reaction and is used for the preparation of higher alkanes containing even number of carbon atoms.

$$R\overline{-X+2Na+X-}R \xrightarrow[ether]{dry} R-R+2NaX$$

$$H_3C\overline{-Br+2Na+Br-}CH_3 \xrightarrow[ether]{dry} H_3C-CH_3+2NaBr$$

$$C_2H_5\overline{-Br+2Na+Br-}C_2H_5 \xrightarrow[ether]{dry} CH_3-CH_2-CH_2-CH_3+2NaBr$$

When different alkyl halides are used, a mixture of three alkenes are obtained as shown below

$$CH_3-Br+C_2H_5Br \xrightarrow[dry\,ether]{Na} ??$$

$$\Rightarrow \underset{\text{Methyl bromide}}{CH_3Br} + 2Na + \underset{\text{Ethylbromide}}{Br - C_2H_5} \rightarrow \underset{\text{Propane (A)}}{CH_3 - CH_2 - CH_3} + 2NaBr$$

$$CH_3Br + 2Na + Br - CH_3 \rightarrow \underset{\text{Ethane (B)}}{CH_3 - CH_3} + 2NaBr$$

$$C_2H_5Br + 2Na + Br - C_2H_5 \rightarrow \underset{\text{Butane (C)}}{C_2H_5 - C_2H_5} + 2NaBr$$

So the product is mixture of (A), (B) and (C).

Mechanism : Two mechanism have been suggested for the reaction :

Mechanism I : The reaction takes place in two steps as shown below :

$$R - X + 2Na \rightarrow R - Na + Na - X$$
$$R - Na + X - R \rightarrow R - R + Na - X$$

Mechanism II : Again the reaction takes place under two steps :

$$R - X + Na \rightarrow \dot{R} + NaX$$
$$\dot{R} + \dot{R} \rightarrow \underset{\text{hydrocarbon}}{R - R}$$

3.2.4 Kolbe's electrolytic method

An aqueous solution of sodium or potassium salt of a carboxylic acid on electrolysis gives alkane containing even number of carbon atoms at the anode for examples :

$$2CH_3COO^{\ominus}\,Na^{\oplus} + 2H_2O \xrightarrow{electrolysis} CH_3-CH_3+2CO_2+2NaOH+H_2$$

The reaction is supposed to follow the following path :

$$2CH_3COONa \longrightarrow 2CH_3COO^{\ominus} + 2Na^{\oplus}$$

At anode

$$2CH_3-\overset{\overset{O}{\|}}{C}-O^{\ominus} \xrightarrow{2e^{\ominus}} 2CH_3-\overset{\overset{O}{\|}}{C}-\dot{O}: \rightarrow 2CH_3 + 2CO_2\uparrow$$

$$\dot{C}H_3 + \dot{C}H_3 \rightarrow C_2H_6$$

At Cathode

$$H_2O + e^- \longrightarrow OH^{\ominus} + \dot{H}$$

$$2\dot{H} \longrightarrow H_2\uparrow$$

Methane can not be prepared by this method.

3.2.5 From Grignard reagent

Organic compounds in which a metal atom is directly linked to carbon atom are known as organometallic compound e.g. HC = CNa, $(C_2H_5)_4Pd$, $(C_2H_5)_2$ Zn etc. Alkyl or aryl magnesium halide (R-MgX) are also called Grignard reagent or organometallic compounds Basically, Alkyl halides react with magnesium in dry ether to form alkyl magnesium halides (Grignard reagent. Grignard reagent on double decomposition with water or with other compounds having active H (The hydrogen attached on O, N, F or triple bonded carbon atom are known as active H) give alkane.

$$\underset{\text{Alkyl halide}}{R-X} + Mg \xrightarrow[\text{ether}]{\text{dry}} \underset{\text{Grignard reagent}}{R-MgX}$$

$$R-MgX + H-OH \longrightarrow R-H + Mg\begin{matrix}OH\\X\end{matrix}$$

$$R-MgX + HNH_2 \longrightarrow R-H + Mg\begin{matrix}NH_2\\X\end{matrix}$$

$$CH_3MgBr + H-OH \longrightarrow CH_4 + Mg\begin{matrix}OH\\X\end{matrix}$$

Methyl magnesium bromide

3.3 Reaction

3.3.1 Free radical Substitution

One or more hydrogen atoms of alkanes can be replaced by halogens, nitro group and sulphonic acid group. Halogenation takes place either at higher temperature (573-773K) or in presence of diffused sunlight or ultraviolet light. Lower alkanes do not undergo nitration and sulphonation reactions. These reactions in which hydrogen atom of alkanes are substituted are known as substitution reaction. When substitution occurs through free radical mechanism then the reaction is named as Free radical substitution reaction. As an example, chlorination of methane is given below :

3.3.2 Halogenation

$$CH_4 + Cl_2 \xrightarrow{h\upsilon} \underset{\text{Chloromethane}}{CH_3Cl} + HCl \qquad CH_3Cl + Cl_2 \xrightarrow{h\upsilon} \underset{\text{Dichloromethane}}{CH_2Cl_2} + HCl$$

$$CH_4Cl_2 + Cl_2 \xrightarrow{h\upsilon} \underset{\text{Trichloromethane (Chloroform)}}{CHCl_3} + HCl \qquad CHCl_3 + Cl_2 \longrightarrow \underset{\text{Tetrachloromethane}}{CCl_4} + HCl$$

$$CH_3CH_3 + Cl_2 \xrightarrow{h\upsilon} \underset{\text{chloroethane}}{CH_3 - CH_2Cl} + HCl$$

It is found that the rate of reaction of alkanes with halogens is $F_2 > Cl_2 > Br_2 > I_2$. Rate of replacement of hydrogens of alkanes is: 3° > 2° > 1°.

Fluorination is too violent to be controlled.

Iodination is very slow and a reversible reaction It can be carried out in the presence of oxidizing agents like HIO_3 or HNO_3

$$CH_4 + I_2 \rightarrow CH_3I + HI$$
$$HIO_3 + 5HI \rightarrow 3I_2 + 3H_2O$$

Halogenation is supposed to proceed via free radical chain mechanism involving three steps namely chain initiation, chain propagation and chain termination or given below.

3.3.3 Mechanism of halogenation reaction

(i) **Initiation**: The reaction is initiated by homolysis of chlorine molecule in the Presence of light or heat. The Cl-Cl bond is weaker than the C-C and C-H bond and hence is easiest to break.

$$Cl - Cl \xrightarrow[\text{homolysis}]{h\upsilon} \underset{\text{Chlorine free redicals}}{\dot{Cl} + \dot{Cl}}$$

(ii) **Propagation**: Chlorine free radical attacks the methane molecule and takes the reaction in the forward direction by breaking the C-H bond to generate methyl free radical with the formation of H-Cl.

(a) $CH_4 - \dot{Cl} \xrightarrow{h\upsilon} \dot{C}H_3 + H - Cl$

The methyl radical thus obtained attacks the second molecule of chlorine to form CH_3Cl with the liberation of another chlorine free radical by homolysis of chlorine molecule.

(b) $\dot{C}H_3 + Cl - Cl \xrightarrow{h\upsilon} \underset{(\text{chlorine free radical})}{CH_4 - Cl + \dot{Cl}}$

The chlorine and methyl free radicals generated above repeat steps (a) and (b) respectively and there by setup a chain of reactions. The propagation steps (a) and (b) are those which directly

give principle products, but many other propagation steps are possible and may occur. Two such steps given below explain how more highly halogenated products are formed.

$$\dot{C}H_3Cl + \dot{C}l \longrightarrow \dot{C}H_2Cl + HCl$$

$$\dot{C}H_2Cl + Cl - Cl \longrightarrow CH_2Cl_2 + \dot{C}l$$

(iii) **Termination**: The reaction stops after some time due to consumption of reactants and/or due to the following side reaction : The possible chain termination steps are :

(a) $\dot{C}l + \dot{C}l \rightarrow Cl - Cl$

(b) $H_3\dot{C} + \dot{C}H_3 \rightarrow H_3C - CH_3$

(c) $H_3\dot{C} + \dot{C}l \rightarrow H_3C - Cl$

Though in (C) CH3 - Cl, The one of the products is formed but free radicals are consumed and the chain is terminated. The above mechanism helps us to understand the reason for the formation of ethane as a by-product during chlorination of methane.

3.3.4 Evidence in Support of free radical mechanism :

The following points support the free radical mechanism :

(i) Reaction does not take place in dark at room temperature but requires energy in the form of heat or light. This is due to the fact that the chain initiation step is endothermic and hence needs a large amount of energy to break the Cl-Cl bond into radicals.

(ii) Oxygen acts as an inhibitor. This is due to the fact oxygen combines with the alkyl free radical to form peroxy alkyl radical (R-O-O) The radical is much less reactive than alkyl free radical (R.) to continue the chain. As a result the halogenation of alkyl in the presence of oxygen is slowed or stopped. Thus the role of inhibitors like oxygen in this reaction gives support to the above mechanism.

(iii) The reaction has high Quantum yield of products.

Halogenation of an alkane containing more than one type (1 °, 2°, 3°) of hydrogens, gives a mixture of isomeric products. For example, chlorination of propane, butane and isobutane give the following products.

(i) $CH_3-CH_2-CH_3 \xrightarrow[\text{light}]{Cl_2} CH_3-CH_2-CH_2-Cl + CH_3-\underset{Cl}{CH}-CH_3$

n-propyl chloride (45%) isopropyl chloride (45%)

(ii) $CH_3-CH_2-CH_2-CH_3 \xrightarrow[\text{light}]{Cl_2} CH_3-CH_2-CH_2-CH_2-Cl + CH_3-CH_2-\underset{Cl}{CH}-CH_3$

n-butyl chloride (28%) sec-butyl chloride (72%)

(iii) $CH_3-\underset{CH_3}{CH}-CH_3 \xrightarrow{Cl_2} CH_3-\underset{CH_3}{CH}-CH_2-Cl + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl$

Isobutyl chloride (64%) tert-butyl chloride (36%)

Bromination gives the corresponding bromides but in different proportions:

(iv) $CH_3-CH_2-CH_3 \xrightarrow[\text{light}]{Br_2} CH_3-CH_2-CH_2-Br + CH_3-\underset{Br}{\overset{+}{CH}}-CH_3$

n propyl bromide (3%) Isopropyl bromide (97%)

(v) $CH_3-CH_2-CH_2-CH_3 \xrightarrow[\text{light}]{Br_2} CH_3-CH_2-CH_2-CH_2-Br + CH_3-CH_2-\underset{Br}{CH}-CH_3$

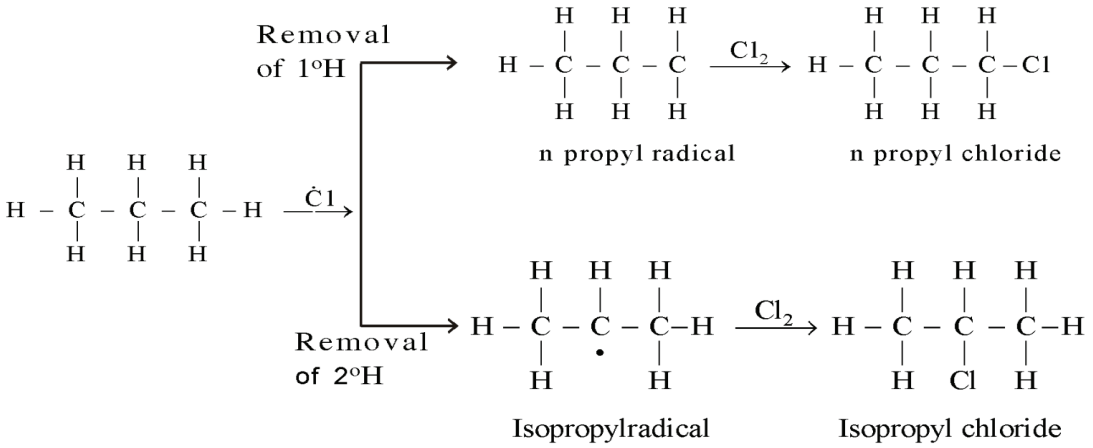
n butyl bromide See-butyl bromide (98%)

(vi) $CH_3-\underset{CH_3}{CH}-CH_3 \xrightarrow[\text{light}]{Br_2} CH_3-\underset{CH_3}{CH}-CH_2-Br + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br$

Iso butane Isobutyl bromide Tert butyl bromide (99%)

The result given above shows that the relative amounts of the different isomeric products differ largely depending upon the halogen used. It is also important to note that the bromination, in contrast to chlorination, leads to the formation of only one of the possible isomeric products. This is reflected in the percentages like 97%, 98% and 99% for one of the products in each reaction. Thus bromine atom is more selective in the site of attack than chlorine.

It is possible to predict the product distribution of different monochloro derivatives resulting from the chlorination of an alkane with non-equivalent hydrogens. Let us take the example of chlorination of propane.



The relative amounts of n-propyl chloride and isopropyl chloride depends upon the relative rates at which the intermediate n-propyl and isopropyl radicals are formed as the rate-determining step is the formation of n-propyl and iso-propyl radicals by the attack of chlorine radical on propane at the proper site.

The relative rates depends on the stability of intermediate radical and the decreasing order of stability of radicals are, Tert radical > see-radical > primary-radical

Thus any single chlorination will favour substitution at the most substituted carbon.

3.4 Summary

- The alkanes are hydrocarbons that only contain single covalent bonds between their carbon atoms. This means that they are saturated compounds, has no specific reactive functional groups and are quite unreactive.
- Alkanes of homologous series have the general formula C H . The simplest alkane has only one carbon atom and is called methane.
- Alkanes are saturated hydrocarbons because they have the maximum number of hydrogen atoms. Alkanes are also called Paraffins because of little reactivity towards reagents.
- An alkyl halide on Wurtz reaction leads to the formation of symmetrical alkane having an even number of carbon atoms.
- Halogenation of an alkane takes place by a free radical reaction. Free radicals are very reactive as they are trying to pair up their unpaired electron. If there is sufficient chlorine, every hydrogen will eventually be replaced.
- The reactivity of the halogens with alkane decreases in the following order: $F_2 > Cl_2 > Br_2 > I_2$

3.5 Solved Problems

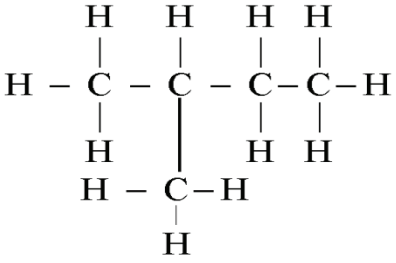
1. The halogenation of alkanes in the presence of tetraethyl lead proceeds at a lower temperature than when it is carried in its absence why?

Ans: Tetraethyl lead decomposes to produce ethyl radical as under,

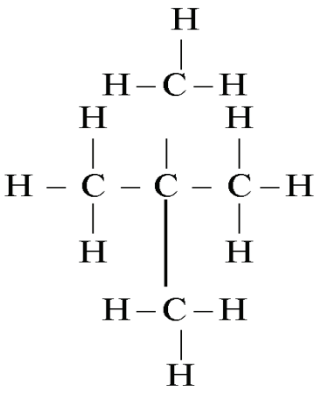
$$Pb(C_2H_5)_4 \xrightarrow{\Delta} Pb + 4\dot{C}_2H_5$$

As the halogenation of alkanes follows a free radical mechanism the reaction can take place at a lower temperature.

(2) Write down the structure of Neo-pentane and Isopentane?



Isopentane



Neo pentane

(3) write down the product.

$$\begin{array}{l} CH_2-CH_2-COOK \\ | \\ CH_2-CH_2-COOK \end{array} + 2H_2O \xrightarrow{\text{Electrolysis}} A+B+C+D$$

It is an example of intermolecular Kolbe electrolysis

$$\begin{array}{l} CH_2-CH_2-COOK \\ | \\ CH_2-CH_2-COOK \end{array} + 2H_2O \xrightarrow[\text{electrolysis}]{\text{kolbe}} \underset{(A)}{\begin{array}{l} CH_2-CH_2 \\ | \quad | \\ CH_2-CH_2 \end{array}} + \underset{(B)}{2CO_2} + \underset{(C)}{2KOH} + \underset{(D)}{H_2\uparrow}$$

(4) Prepare CH_3D from CH_4.

$$CH_4 \xrightarrow[h\upsilon,\Delta]{Br_2} CH_3Br \xrightarrow[\text{Ether}]{Mg} CH_3MgBr \xrightarrow{-\ D_2O} CH_3D + Mg(OD)Br$$

5. Produce Propane from Grignard reagent.

$$CH_3CH_2CH_2MgBr + H_2O \xrightarrow{\text{dil HCl}} CH_3CH_2CH_3 + Mg(OH)Br.$$

3.6 Exercises

Marks : 1

1. Write down general structure of Alkane.

2. What is Grignard reagent?

3. What is aromatisation?

4. Write down the products obtain from substitution of Methane via Cl_2 / hν.

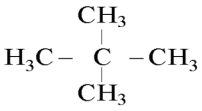
Marks : 5

1. Explain : Bromine is less reactive but more selective whereas chlorine is more reactive and less selective in its attack with alkane.

2. Write short notes on Wurtz reaction.

3. Write short notes on Corey-House synthesis.

4. Which would have a higher boiling point and why?

$CH_3CH_2CH_2CH_2CH_3$ or 

5. Why is Wurtz reaction is not preferred for the preparation of alkanes containing odd number of carbon atoms? Illustrate your answer by taking an example.

Unit 4: Chemistry of Alkenes

4.0 Objectives

By the end of the unit learners should be able to:

- Structure and bonding of alkenes leads to their being unable to rotate around the double bond and results in the formation of cis and trans isomers for disubstituted alkenes.
- Isomerism of alkenes.
- Various methods of alkene preparation Physical and chemical properties of alkene
- Draw the major product of the addition reaction of an alkene with diborane followed by basic hydrogen peroxide.
- Use Marknovnikov's rale to predict the major product of an addition reaction of an alkene.
- Draw the major product of the addition reaction of an alkene with mercuric
- diacetate followed by water

4.1 Introduction

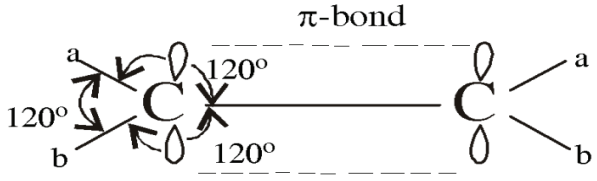
Alkenes are also called olefins.

Alkene is an unsaturated hydrocarbon that contains at least one Carbon-Carbon double bond. The general formula of alkenes are C_nH_{2n} in comparison to alkanes with general formula C_nH_{2n+2}

4.1.1 Structure

The double bond of alkene consists a strong σ-bond and a weak π-bond. Each carbon of the double bond is sp2 hybridized and trigonal planar with bond angles of approximately 120°.

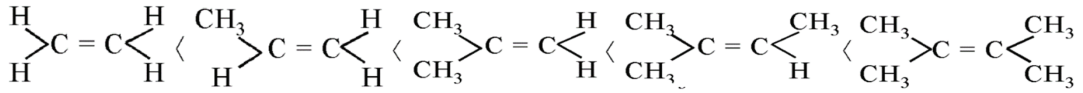
In a double bond, the two carbons are bonded together by overlapping two sp2 orbital head to head, forming a σ-bond. The other two sp2 orbitals are overlapping with the S-orbital of two H-atoms. The two unhybridized p orbital of two carbon atoms are overlapping side to side to form π-bond.



4.1.2 **Isomerism** : Due to restricted rotation around the double bond, geometrical isomerism is possible in alkenes. For the alkene with general formula. R-CH=CH-R, if the two hydrogens stays in the same side is called cis-isomer and if they are in opposite side is called trans isomer for e.g.

4.1.3 Stability of alkenes : A general rule is that, die stability of alkenes increases with increase in the number of alkyl group (containing hydrogen) on the double bond i.e. the more highly substituted an alkene is, the more stable it is. This is also known as Saytzeff's rule.

It is due to increase in the number of contributing hyperconjugative structures with increase in the no of alkyl groups on the double bond. The increasing order of stability of alkenes with increase in the number of methyl groups is depicted below.



This order is also supported by the heat of hydrogenation data of these alkenes. The value of heat of hydrogenation decreases with increase in the stability of alkene. In general, trans isomer is more stable than cis isomer because of decreased steric interactions.

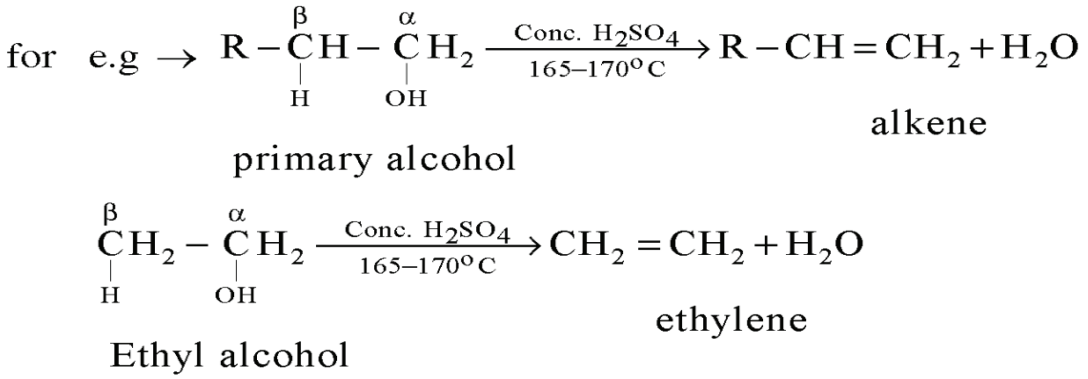
4.2 Preparation of alkenes

4.2.1 by elimination reaction :

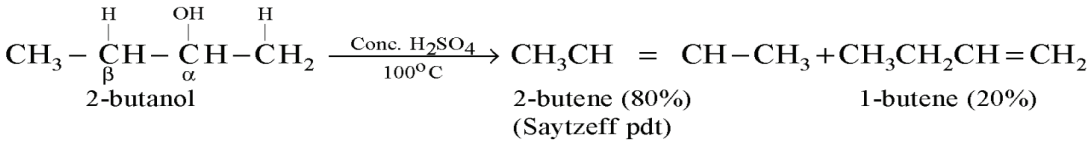
One of the common synthesis of alkene is by the elimination reaction from alkyl halide, alcohol and similar compounds. Alkyl halide undergoes dehydrohalogenation and alcohol undergoes dehydration to form corresponding alkene.

4.2.2 by dehydration of alcohols :

When an alcohol is heated in presence of a strong acid such as cone. H_2SO_4, H_3PO_4, at 165-170°C, removal of one molecule of H_2O takes place in order to obtain the corresponding alkene. In this reaction, an hydroxyl (-OH) group from the α-C and a H-atom from the β carbon are removed.



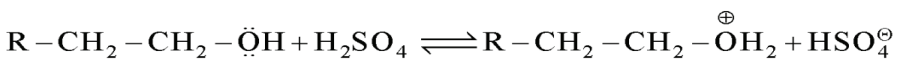
For an unsymmetrical secondary and tertiary alcohols more substituted alkene is the major product.



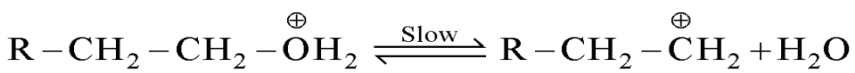
Mechanism:

The reaction proceeds through El mechanism

Step-I : Protonation of alcohol.



Step-II : Elimination of H-,0 and formation of carbocation.



Step-Ill : Elimination of proton from carbocation.

$$R-\underset{\beta}{\overset{H}{\overset{|}{C}}}H-\underset{\alpha}{\overset{\oplus}{C}}H_2 \rightleftharpoons[\quad]{HSO_4^{\ominus}} R-CH=CH_2+H_2SO_4$$

alkene

4.2.3 By dehydrohalogenation of alkyl halide :

When an alkyl halide is heated in presence of ethanolic KOH. alkene is obtained. In this reaction, elimination of H-atom from the β-carbon and halogen atom from the α–carbon take place.

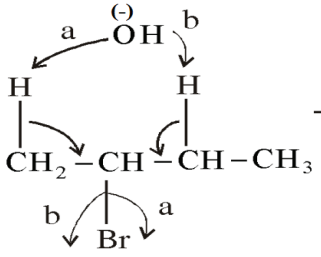
$$R-\overset{\beta}{\underset{H}{CH}}-\overset{\alpha}{\underset{X}{CH_2}} \rightleftharpoons[\Delta]{\text{ethanolic KOH}} R-CH=CH_2+KX+H_2O$$

Alkyl halide (X=Cl, Br, I) Alkene

$$\text{e.g.} \rightarrow CH_3-\underset{H}{CH}-\underset{Br}{CH_2} \xrightarrow[\Delta]{\text{ethanolic KOH}} CH_3CH=CH_2+KBr+H_2O$$

1-bromo propane propene

For an unsymmetrical secondary or tertiary alkyl halide, more substituted alkene is the major product. The product is called Saytzeff product. for e.g. when 2-bromobutane is heated in presence of ethanolic KOH, 2-butene is produced predominantly.



b → $CH_3CH=CHCH_3 + KBr + H_2O$
2 - butene (80%)
Saytzeff product

a → $CH_2=CH-CH_2-CH_3 + KBr + H_2O$
1-butene (20%)
Hofmann product

* If the reaction is carried out in presence of aqueous KOH for 1° alkyl halide. Substitution reaction takes place and an alcohol is obtained.

$$\text{for e.g.} \rightarrow CH_3CH_2CH_2Br \xrightarrow{\text{aqueous KOH, }\Delta} CH_3CH_2CH_2OH$$

1–bromopropane propanol

* The reactivity of different halide in case of dehydrohalogenation reaction Alkyl iodide > Alkyl bromide > Alkyl Chloride

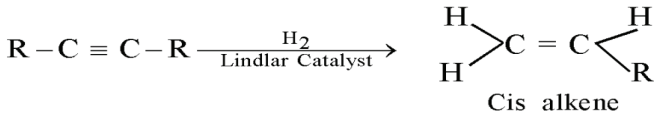
The reactivity of alkyl group— Tertiary > Secondary > Primary

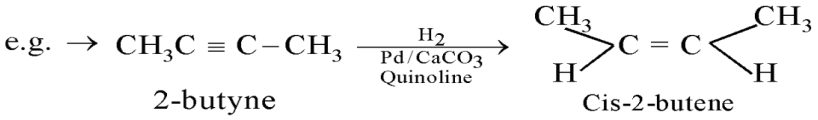
4.2.3 By reduction of alkyne :

(i) Partial catalytic hydrogenation

When an alkyne is reduced by H, in presence of Lindlar catalyst generally cis alkene is obtained. Lindlar catalyst : $Pd/BaSO_4$ or $CaCO_3$, Quinoline

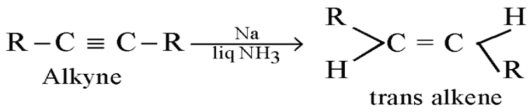
In presence of Lindlar catalyst, the reaction stopped to the alkene and if it is not used further reduction of alkene occurs to produce corresponding alkane.

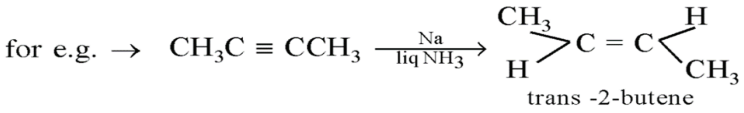




(ii) Birch reduction :

Alkynes can be reduced to trans alkenes with the use of sodium metal in liquid NH_3

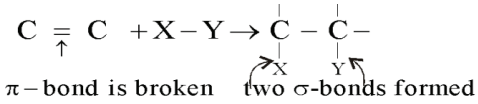




4.3 Reactions of alkene

Introduction to addition reaction :

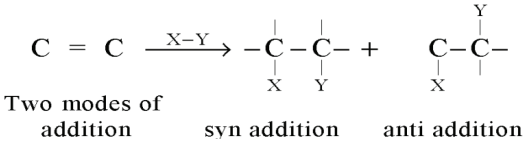
The characteristics reaction of alkene is addition - the π bond is broken and two new σ-bonds are formed.



4.3.1 Addition reaction :

As alkenes are electron rich, simple alkenes do not react with nucleophiles or bases, reagents that are themselves electron rich. Alkenes react with electrophiles.

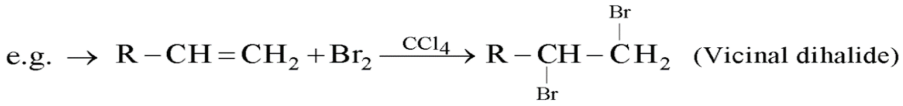
Since the carbon atom of a double bond are both trigonal planar, the elements of X and Y can be added to them from the same side or from opposite side.



Syn addition takes place when both X and Y are added from the same side. Anti addition takes place when X and Y are added from the opposite side.

(a) Addition of Halogen (bromine) to alkene (trans-addition)

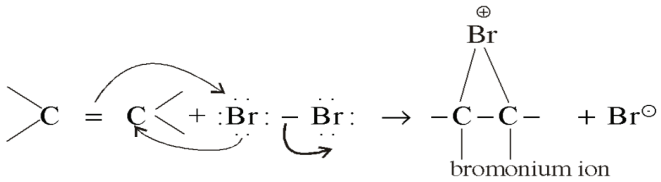
It is a type of anti-addition. Halogens adds to alkene in normal temp in presence of CCl_4 to give vicinal dihalide normally with anti addition



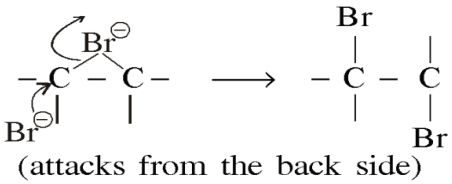
Mechanism

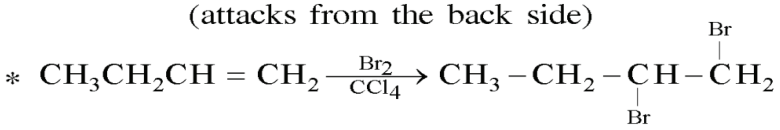
Halogen (bromine) is electrophilic in nature -a nucleophile will attack an one end and displace a halide ion.

Step-I : formation of bromonium ion.



Step-II : Ring opening of bromonium ion by the back side attack of nucleophile to the less hindered site to give the final anti product.





(b) Addition of Halogen Acid :

(i) Addition of HX with alkene produce alkyl halide.

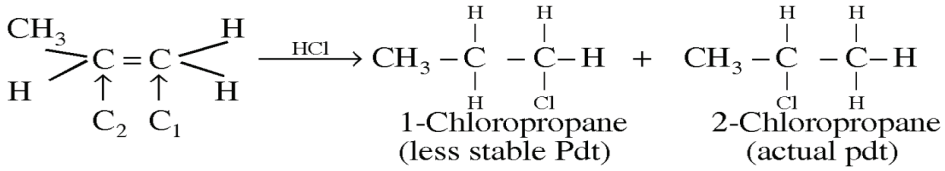
Reactivity of halogen hydracids

$$HI > HBr > HCl > HF$$

$$R-CH=CH-R+HX \rightarrow RCH_2-\underset{\displaystyle X}{\underset{|}{CH}}-R \quad (X = F, Cl, Br, I)$$

$$\text{e.g.} \rightarrow CH_2 = CH_2 + HBr \rightarrow CH_3CH_2Br$$

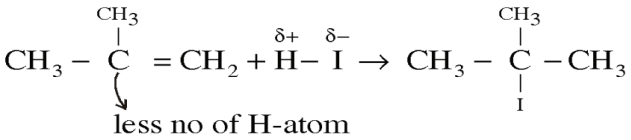
(ii) With an unsymmetrical alkene, HX can add to the double bond to give two constitutional isomer, but only one is actually formed.



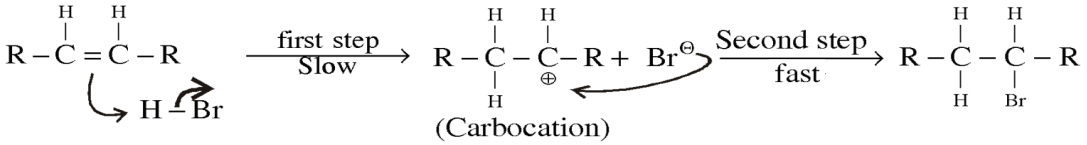
This is a specific example of general trend called Markovnikov's rule.

4.3.2 Markovnikov's rule :

Markovnikov rale states in the addition of HX to an unsymmetrical alkene, the negative part of the addendum goes to carbon of alkene with less no of H-atom.



Mechanism :



Step - I

The alkene abstracts a proton from the HBr and a Carbocation and bromide ion are generated.

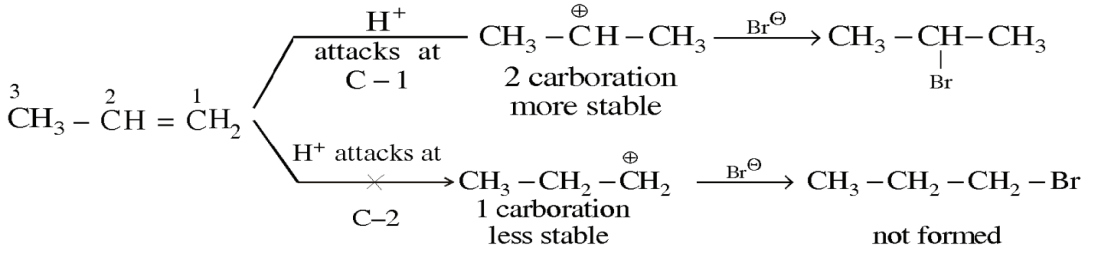
Step - II

The bromide ion quickly attacks the cationic centre and yields the final product.

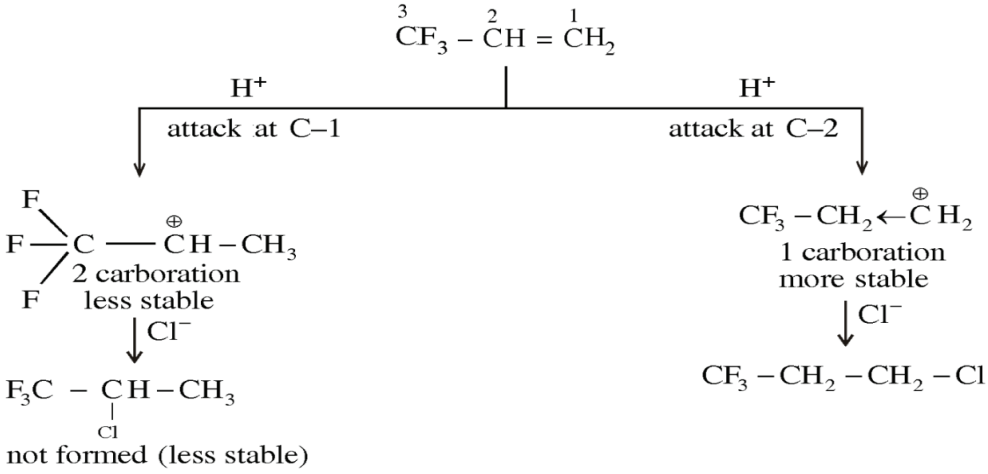
Explanation of Markovnikov's rule :

The basis of Markovnikov's rale is the formation of a carbocation in the rate determining step of the mechanism.

In the addition of HX to an unsymmetrical alkene, the H-atom is added to the less substituted carbon to form the more stable, more substituted carbocation.



Addition of HX to $CH_2 = CH\text{-}CF_3$ takes place opposite to the Markovnikov's rale. This is due to the Electron withdrawing nature of $-CF_3$ group, the carbocation formed by the attack of H^+ at C-l is less stable.



Addition of HI to $CH_2{=}CH{-}N^{(+)}Me_3I^{(-)}$ or $CH_2{=}CH\text{-}COOH$ takes place opposite to the Markovnikov's rale for the same reason.

Peroxide effect :

Addition of HX to an unsymmetrical alkene in presence of 02 or peroxide takes place opposite to the Markovnikov's rale this is called Anti-Markovnikov's addition.

4.3.3 Anti-Markovnikov's rule:

Anti-Markovnikov rale states in the addition of HX to an unsymmetrical alkene, the negative part (X-) of the addendum goes to the carbon of alkene with more number of H-atom. This type of abnormal addition of HX to an alkene in presence of peroxide is called peroxide effect.

Some example of peroxide:

Benzoyl peroxide $(C_6H_5CO)_2O_2$, di-tert-butyl peroxide $(Me_3COOCMe_3)$ etc. e.g., on addition of HBr to propene in presence of peroxide, n-propyl bromide (1-bromopropare) is formed as the major product.

$$\overset{3}{CH_3}\overset{2}{CH} = \overset{1}{CH_2} + \overset{\delta+}{H} - \overset{\delta-}{Br} \xrightarrow{\text{peroxide}} CH_3CH_2 - CH_2 - Br$$

Mechanism : Addition of HX to alkene in presence of peroxide goes through a radical mechanism, whereas the addition of HX to alkene follows the carbocation pathway in absence of peroxide.

Step - I : (i) Homolytic cleavage of peroxide by heat or light.

$$C_6H_5 - \overset{O}{\overset{||}{C}} - O - O - \overset{O}{\overset{||}{C}} - C_6H_5 \rightarrow 2C_6H_5 - \overset{O}{\overset{||}{C}} - \dot{O} \rightarrow 2\dot{C}_6H_5 + CO_2$$

Step - II : formation of bromine radical.

$$\dot{C}_6H_5 + H - Br \rightarrow C_6H_6 + \dot{B}r$$

Step - III : Addition of bromine radical to the alkene to give most stable carbon radical.

$$CH_3 - CH = CH_2 + \dot{B}r$$

$CH_3\underset{\underset{Br}{|}}{C}H - \dot{C}H_2$ — 1^o free radical (less stable)

$CH_3 - \dot{C}H\,CH_2 - Br$ — 2^o freeradical (morestable)

Step - IV : Resulting carbon radical removes a H-atom from HBr, regenerating the bromine radical.

$$CH_3 - \dot{C}H - CH_2 - Br + H - Br \longrightarrow CH_3CH_2CH_2Br + \dot{B}r$$

Bromine radical is regenerated and can then react with another equivalent of alkene the process is recycled. N.B. : peroxide effect is observed in presence of HBr only.

Summary :

$CH_3CH{=}CH_2$

$\xrightarrow{HBr}$ $CH_3\underset{\underset{Br}{|}}{C}H - CH_3$ — Markovnikov product

$\xrightarrow[\text{peroxide}\ \Delta/h\upsilon]{HBr}$ $CH_3CH_2 - CH_2 - Br$ — Anti-Markovnikov product

4.3.4 Hydration : In presence of acid catalyst alkene add with H_2O molecule to form alcohol.

$$\underset{\text{Alkene}}{R - CH = CH - R} + \overset{\delta+}{H} - \overset{\delta-}{O}H \xrightarrow{H^{\oplus}} \underset{\text{Alcohol}}{RCH_2CH\,(OH)\,R}$$

e.g. for an unsymmetrical alkene addition of H_2O takes place according to Markovnikov's rule i.e. H-atom goes to the carbon of double bond which has more no of Hydrogens.

$$\underset{2-\text{methylpropene}}{(CH_3)_2C=CH_2} + \overset{\delta-}{H}-\overset{\delta-}{O}H \xrightarrow{H^{\oplus}} \underset{\text{tert-butyl alcohol}}{(CH_3)_3C-OH}$$

4.3.5 Oxymercuration -demercuration :

(i) In the first step, alkene react with mercuric acetate in a solvent mixture of THF and H_2O to produce p-hydroxy alkylmercuric acetate. This is called oxymercuration.

$$CH_3CH=CH_2 + H_2O + Hg(OAC)_2 \xrightarrow[\text{Oxymercuration}]{H_2O,TH_3F} CH_3-\underset{OH}{\underset{|}{C}}H-\overset{HgOCOCH_3}{\overset{|}{C}}H_2$$

β-hydroxyalkyl mercuric acetate

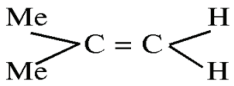
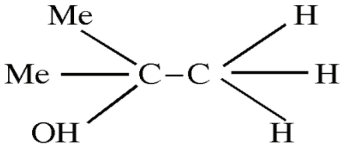
(ii) The 2nd step is the demercuration step which involves the reaction of former addition compound with alkaline NaBH4 to produce alcohol.

$$CH_3-\underset{OH}{\underset{|}{C}}H-CH_2-HgOCOCH_3 \xrightarrow[\text{demercuration}]{NaBH_4+NaOH} CH_3-\underset{OH}{\underset{|}{C}}H-CH_3 + Hg$$

(Propan-2-ol)

It is a type of anti-addition.

H-atom and -OH group in the final product are opposite to each other. For the whole process, we can conclude that H-atom add to the less hindered site and –OH group to the more hindered site to form the final product.

e.g. →  $\xrightarrow[(2)\,NaBH_4,\ NaOH]{(1)\ Hg(OAC)_2,\ THF,\ H_2O}$ 

4.3.6. Hydroboration - Oxidation :

This is a type of syn addition. Alkene react with diborane (B_2H_6) to from trialkylborane (an addition compound). This is called hydroboration.

$$B_2H_6 \rightleftharpoons 2BH_3$$

$$3RCH=CH_2 + BH_3 \rightarrow \underset{\text{trialkylborane}}{(RCH_2CH_2)_3B}$$

Then, oxidation of trialkylborane is earned out by treatment with H_2O_2 in presence of NaOH to produce alcohol.

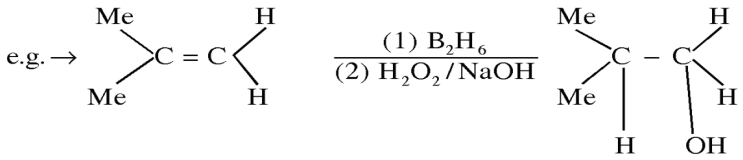
$$(R-CH_2-CH_2)_3B \xrightarrow[NaOH]{H_2O_2} R-CH_2-CH_2-OH$$

for e.g.

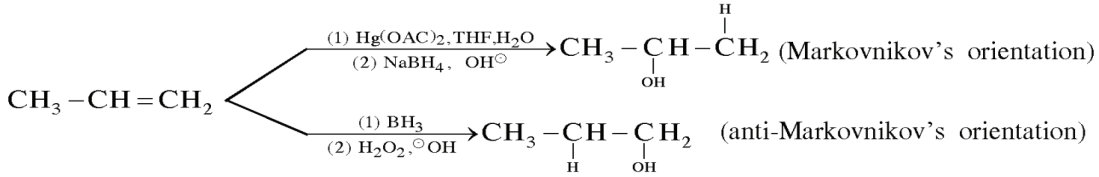
$$CH_3CH=CH_2 \xrightarrow[(2)H_2O_2/NaOH]{(1)B_2H_6} CH_3CH_2CH_2-OH$$

propene 1-propanol

The reaction is reverse to the oxymercuration-demercuration reaction. H-atom and -OH group in the final product are in the same side of double bond. For the whole process, H-atom add to the more hindered site and -OH group to the less hindered site to form final product—



Therefore, from the above two reaction we can conclude that, oxymercuration - demercuation helps to produce more hindered alcohol and on the other hand hydroboration - oxidation helps to produce the less hindered alcohol.



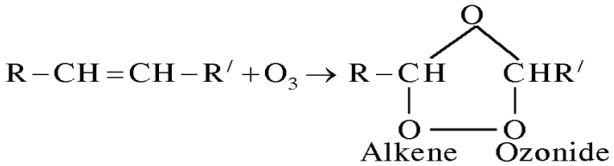
4.3.7 Ozonolysis (Reaction with O_3) :

The Oxidative cleavage of alkenes to form compound containing carbonyl group is called an ozonolysis reaction.

$$\text{e.g.} \rightarrow \underset{\text{Alkene}}{R-CH=CH-R'} + O_3 \xrightarrow[H_2O]{Zn} \underset{\text{Carbonyl compound}}{R-CH=O} + O=CH-R'$$

Mechanism :

Step - I : Treatment of alkene with Ozone to form an addition compound alkene Ozonide.



Step - II :

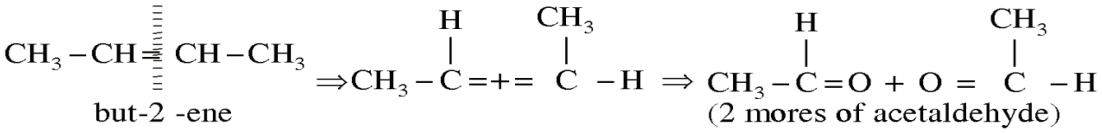
Decomposition of alkene ozonide by water in presence of metallic zine or any other reducing agent like $(CH_3)_2S$ to form carbonyl compound.

Use of powdered Zn

If Powdered-Zn is not used. H909 produced in the reaction medium will oxidize the aldehyde to carboxylic acid. However, in presence of powdered Zinc, it reduce H_2O_2 to H_2O and so there is no chance of oxidation of aldehyde.

$$Zn + H_2O_2 \rightarrow ZnO + H_2O$$

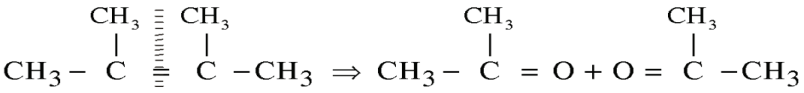
If we know the structure of the alkene, than we can easily determine the structure of the carbonyl compound formed by ozonolysis from the following method for e.g.—



(1) At first draw the structure of alkene.

(2) Cut the alkene across the double bond into two halves.

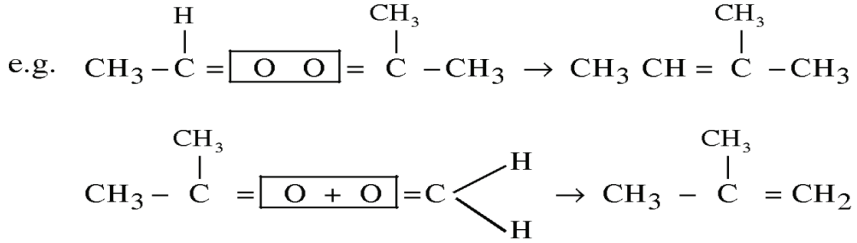
(3) Finally, add oxygen atom to the every double bonded carbon and desired carbonyl product is obtained.



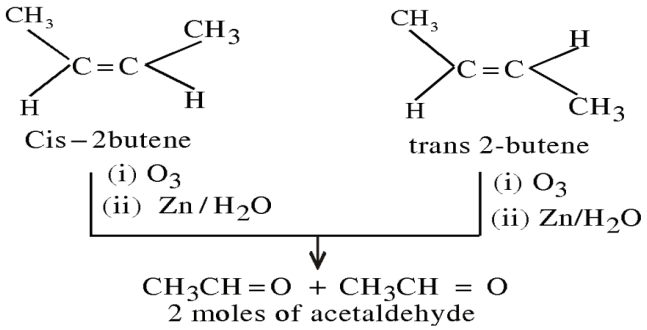
Determination of structure of alkene from the product formed by Ozonolysis.

(i) identify the product formed from ozonolysis.

(ii) Then the products are written in the following fashion to identify the alkene.



* From the Ozonolysis of two geometrical isomer same product is obtained.



ozonolysis of an alkene containing two double bonds produce 1 more of dicarbonyl and 2 mores of carbonyl, for e.g.

$$CH_3 - CH = CH - CH = CH_2 \quad \text{(penta–1, 3–diene)}$$

$$\downarrow \begin{matrix}(i)\ O_3 \\ (ii)\ Zn\ /\ H_2O\end{matrix}$$

$$\underset{\text{acetaldehyde}}{CH_3 - CH=O} \ + \ \underset{\text{glyoxal}}{O=CH - CH=O} \ + \ \underset{\text{formaldehyde}}{O=CH_2}$$

4.3.8. Oxidation reaction :

(1) By alkali $KMnO_4$:

(a) Treatment of alkenes with cold, dilute basic $KMnO_4$ leads to a 1, 2 or vicinal diol. It is called hydroxylation of alkene. Two hydroxyl groups add to the same side of double bond i.e. syn addition occurs.

$$R-CH=CH-R+H_2O+[O] \xrightarrow[\text{basic } KMnO_4]{\text{Cold, dil}} \underset{\text{Vicinal diol}}{R-\underset{OH}{CH}-\underset{OH}{CH}-R} \xrightarrow[+KOH]{+MnO_2} \text{brown precipitate}$$

(b) Treatment of alkene with hot, concentrated basic $KMnO_4$ produced acid, Ketone or both type of compound.

Group present in alkene	oxidised in presence of hot cone alkaline $KMnO_4$
$=CH_2$	CO_2+H_2O
=CH-R	RCOOH
$=CR_2$	$R_2C=O$

e.g.

(i) $(CH_3)_2C=CH_2 \xrightarrow[\text{alkaline } kMnO_4]{\text{Hot, Conc.}} (CH_3)_2C=O + CO_2 + H_2O$
2-methyl propene

(ii) $CH_3CH=CH-CH_3 \xrightarrow[\text{alkaline } kMnO_4]{\text{Hot, Conc.}} CH_3COOH + CH_3COOH$
2-moles of acetic acid

(iii) $(CH_3)_2C=C(CH_3)_2 \xrightarrow[\text{alkaline } kMnO_4]{\text{Hot, Conc.}} (CH_3)_2C=O + O + C(CH_3)_2$
2-moles of acetone

4.4 Summary

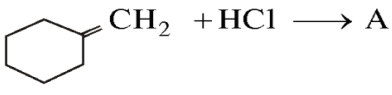
- Alkenes are a class of hydrocarbons (e.g, containing only carbon and hydrogen) unsaturated compounds with at least one carbon-to-carbon double bond. Compounds with two double bonds are called dienes, three double bonds are trienes, etc.
- Stability of alkene is directly proportional to the number of hyperconjugative H-atom or alkyl substitution around the double bond.
- When similar groups or higher priority groups are on the same side of the double bond the alkene is said to be cis. When similar groups are bound to opposite side of the double bond it is said to be trans. Trans isomer is more stable than cis isomer.
- The order of the ease of dehydration of alcohols to produce alkene is, tertiary> secondary > primary
- The characteristic reaction of alkenes is electrophilic addition, because the π bond is both weak and electron rich i.e. nucleophilic.
- The reversal of regiochemistry from Markovnikov's rule through the use of peroxides is called the peroxide effect.
- Oxymercuration-Demercuration produce more hindered alcohol (Markovnikov orientation) and on the other hand hydroboration-oxidation helps to produce the less hindered alcohol (anti-Markovnikov orientation).
- Ozonolysis can be used for the determination of structure of an alkene.
- Alkenes will react with OsO_4 or $KMnO_4$ to form diols.

4.5 Solved Problems

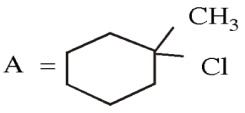
(1) What is Baeyer's reagent.

Ans: Baeyer's reagent is an alkaline solution of cold potassium permanganate (1-2%)

(2) Identify - A of the given reaction-



Ans:



(3) How would you distinguish cis and trans isomers?

Ans: Two main distinguishing properties of geometrical isomers are—

(i) Cis - isomer has higher boiling point than trans isomer.

(ii) The dipole moment of cis-isomer is higher than that of trans - isomers. Generally trans isomer does not possess any dipole moment.

(4) Identify -A of the given reaction

$$CH_2=CH-COOH \xrightarrow{HBr} A$$

Ans: $A = Br-CH_2-CH_2-COOH$

(5) What is peroxide effect.

Ans: The change in the orientation of addition of HBr to alkene or alkyne due to the presence of peroxide is known as the peroxide effect.

(6) Identify A and B of the following reaction.

$$CH_3CH=CH_2 \xrightarrow[\text{peroxide}]{HCl} A$$

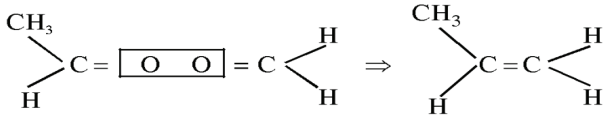
$$\xrightarrow[\text{peroxide}]{HBr} B$$

Ans: $A = CH_3-\underset{\underset{Cl}{|}}{C}-CH_3$; $B = CH_3CH_2CH_2Br$

(7) Identify the alkene (D)

$$\text{Alkene (D)} \xrightarrow{\text{Ozonolysis}} CH_3CHO + HCHO$$

Ans:



(8) Identify A and B of the following reaction :

$$CH_3CH=CH_2 \xrightarrow{H_2SO_4} A \xrightarrow[\Delta]{H_2O} B$$

Ans: $A = CH_3-\underset{\underset{OSO_3H}{|}}{CH}-CH_3$; $B = CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$

(9) Identify the product (D) and E obtained by the following reaction.

$$HC \equiv C-CH_2-CH=CH_2 \xrightarrow[1\,more]{Br_2} D$$

$$C_6H_5CH=CH-CH_3 \xrightarrow{HBr} E$$

Ans:

$$D = HC \equiv C-CH_2\underset{\displaystyle Br}{\underset{|}{C}}H-CH_2-Br$$

As electrophilic addition towards double bond takes place at a faster rate than the triple bond.

$$\underset{\text{more stable}}{C_6H_5-\overset{\oplus}{C}H-CH_2-CH_3} \qquad \underset{\text{less stable}}{C_6H_5CH_2-\overset{\oplus}{C}H_2\ CH_3}$$

$$E = C_6H_5-\underset{\displaystyle Br}{\underset{|}{C}}H-CH_2-CH_3$$

(5) How would you distinguish between acetylene and ethylene?

Ans. Acetylene forms a red precipitate of copper acetylide (Cu_2C_2) when it is passed through ammoniacal cuprous chioride solution while ethylene doer not react with Cu_2Cl_2 solution.

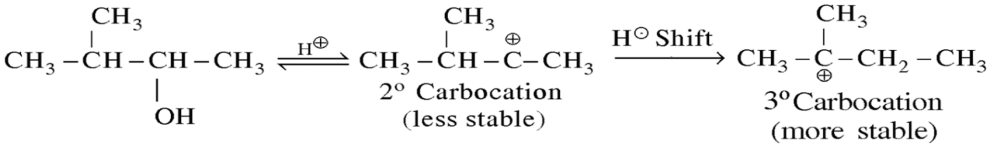
$$HC \equiv CH + Cu_2Cl_2 \xrightarrow{NH_4OH} \underset{\text{red precipitate}}{Cu-C \equiv C-Cu\downarrow}$$

Question Mark - 5 :

(1) Identity A, B, C, D and E of the following reactions

$$CH_3-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}-CH}}-CH_3 \xrightarrow{H^{\oplus}/\Delta} \underset{\text{(Major)}}{A} + \underset{\text{(Minor)}}{B}$$

$$A \xrightarrow{HBr} \underset{\text{(Major)}}{C} + D \qquad A \xrightarrow[\text{presence of peroxide}]{HBr\ in} E$$



A = $CH_3-C(CH_3)=CH-CH_3$ (Major) B = $CH_3-C(CH_3)-CH=CH_2$ (Minor)

C = $CH_3-C(CH_3)(Br)-CH_2-CH_3$ (Major) D = $H_3C-C(CH_3)(H)-CH(Br)-CH_3$ (Minor)

E = $H_3C-C(CH_3)(H)-CH(Br)-CH_3$

Ans:

(2) Identify A, B, C, D and E of the following reaction :

$$CH_2=CH_2 \xrightarrow{Br_2} A \xrightarrow[KOH]{\text{Alcoholic}} B \xrightarrow[(ii)\ H_2O]{(i)\ 20\%\ H_2SO_4,\ HgSO_4} C$$

$$CH_3CH_2-CH=CH_2 \xrightarrow{HBr} D \xrightarrow[KOH]{\text{Alcoholic}} E\ (\textbf{Major})$$

$A = CH_2(Br)-CH_2(Br)$; $B = CH \equiv CH$; $C = CH_3CHO$

$D = CH_3-CH_2-CH(Br)-CH_3$; $E = CH_3CH=CH-CH_3$ (trans-alkene)

Ans:

4.6 Exercises

Mark - 1

(1) what is Lindlar catalyst?

(2) Which one is more stable among cis and trans alkene and why?

(3) $CH_2=CH-\overset{\oplus}{N}Me_3I^{\ominus} \xrightarrow{HBr} A$ (identify)

(4) State Saytzeff's elimination principle.

(5) $CH_3CH_2CH_2-CH_2-OH \xrightarrow[\Delta]{CONC.\ H_2SO_4} B$ (identify)

Mark - 2

(1) Convert : Ethylene — » Acetylene

(2) Identify A and B.

$$CH_3-CH_2-CH_2-Br \xrightarrow[\Delta]{aq.KOH} A$$

$$CH_3-CH_2-CH_2-Br \xrightarrow[\Delta]{alcoholic\ KOH} B$$

(3) Give proper reagent for the following conversions.

$$CH_3-C\equiv C-CH_3 \xrightarrow{?} \begin{matrix} CH_3 \\ \diagdown \\ \quad C \\ \diagup \\ H \end{matrix} = \begin{matrix} CH_3 \\ \diagup \\ C \\ \diagdown \\ H \end{matrix}$$

$$CH_3-C\equiv C-CH_3 \xrightarrow{?} \begin{matrix} CH_3 \\ \diagdown \\ \quad C \\ \diagup \\ H \end{matrix} = \begin{matrix} CH_3 \\ \diagup \\ C \\ \diagdown \\ H \end{matrix}$$

(4) A and B are geometrical isomer with each other in the following reaction. Identify A and B.

$$A \text{ and } B \xrightarrow[(i)\ Zn/H_2O]{(i)\ O_3} CH_3CHO$$

(5) Identify A and B.

$$CH_3-\underset{\underset{N(CH_3)_3}{\oplus}}{CH}-CH_2-CH_3 \xrightarrow{\Delta} \underset{\text{Hofmann pdt}}{\underset{\text{Major}}{A}} + \underset{\text{Saytzeff pdt}}{\underset{\text{Minor}}{B}}$$

Mark – 5

(1) Write a short note on Markovnikov's and Anti Markovnikov's rule.

$$A \text{ and } B \xrightarrow[(i)\ Zn/H_2O]{(i)\ O_3} CH_3CHO$$

(2) Identify A and B.

$$CH_3-\underset{\underset{Br}{|}}{CH}-CH_2-CH_3 \xrightarrow[KOH,\ \Delta]{ethanolic} \underset{\text{Saytzehf}}{A\ (Major)} + \underset{\text{Hoffmann}}{B(Minor)}$$

(3) Convert :

$$\text{Propene } (CH_3CH=CH_2) \rightarrow \text{1-propanol } (CH_3CH_2CH_2OH)$$

$$\text{Propene } (CH_3CH=CH_2) \rightarrow \text{2-propanol } \left(CH_3-\underset{\underset{OH}{|}}{CH}-CH_3\right)$$

(4) Which of the following alkene show geometrical isomer and draw the structure of cis and trans isomers.

(a) $CH_3CH = CH - CH_3$ (b) $CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} = CH_2$ (c) $CH_3CH = CHBr$

(d) $CH_3CH_2CH = CH - CH_3$ (e) $CH_3CH_2CH = CH_2$

(5) What is Ozonolysis?

(6) Identify A, B and C

$$CH_3CH=CH-CH_3 \xrightarrow[\text{Cold and dil}]{\text{Alkaline } KMNO_4} A$$

$$CH_3CH=CH-CH_3 \xrightarrow[\text{Conc. and hot}]{\text{Alkaline } KMNO_4} B+C$$

(7) On reductive ozonolysis an unsaturated hydrocarbon gave the following compounds. (a) HCHO (b) CO_2 (3) CH_3CHO. Write the Structural formula of the hydrocarbon.

Unit 5 Chemistry of Alkynes

5.0 Objectives

By the end of the unit learners should be able to know about:

- Various methods of alkynes preparation
- Physical and chemical properties of alkyne
- Reaction of acidic hydrogen of alkyne with metal to form metal acetylide
- Hydroxylation of alkyne and oxidation with $KMnO_4$
- Ozonolysis of alkyne

5.1 Introduction

Alkynes are unsaturated hydrocarbon having die general formula C_nH_{2n+2}. They contain at least one triple bond between two carbon atoms. The number of hydrogen atoms is still less in alkynes as compared to alkenes or alkanes.

The first stable member of alkyne series is ethyne which is popularly known as acetylene. Acetylene is used for are welding purposes in the form of oxy acetylene flame obtained by mixing acetylene with oxygen gas. Alkynes are stalling materials for a large number of organic compounds. Hence it is interesting to study this class organic compounds.

Nomenclature of alkynes, according to common system and IUPAC System is given below :

Value of n	Formula of alkynes	Strueture of alkynes	Common name of alkynes	IUPAC name of alkynes
2	C_2H_2	HC ≡ CH	Acetylene	Ethyne
3	C_3H_4	H_3C–C ≡ C–H	Methylacetylene	Propyne
4	C_4H_6	CH_3CH_2–C ≡ C–H	Ethylacetylene	But-1-yne
4	C_4H_6	CH_3– C ≡ C–CH_3	Dimethylacetylexne	But-2-yne

5.2 Preparations of Alkynes

5.2.1 From Calcium Carbide

On industrial scale, ethyne/Acetylene is prepared by treating calcium carbide with water. Calcium carbide is prepared by heating quick lime with coke. Quick lime can be formed by heating lime stone as shown in the following reactions :

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$CaO + 3C \longrightarrow \underset{\text{Calcium Carbide}}{CaC_2} + CO$$

$$CaC_2 + 2H_2O \longrightarrow \underset{\text{Acetylene}}{HC \equiv CH} + Ca(OH)_2$$

The heat in the first step is generally nearly 2000°C and done in electric furnace.

5.2.2 Action of acetylides on alkyl halides

The metallic acetylides yield higher alkynes by reacting with alkyl halides. It is a very good method for converting lower alkynes to higher alkynes. For example :

$$\underset{\text{Sodium acetylide}}{CH \equiv C^{-}Na^{+}} + CH_3I \longrightarrow \underset{\text{Methyl acetylene}}{HC \equiv C - CH_3} + NaI$$

Acetylides used in the reaction are mainly obtained from alkynes with terminal triple bond (-C=C-H) by the action of sodium or sodium amide ($NaNH_2$) in liq.NH_3

$$-C \equiv C - H + Na \longrightarrow -C \equiv \bar{C}\,Na^{+} + \frac{1}{2}H_2$$

How-will bring about the following conversion ?

$$CH_3C \equiv CH \longrightarrow CH_3 - C \equiv C - CH_3$$

Answer:

$$CH_3C\equiv C-H \xrightarrow[NH_3]{liq.} CH_3C\equiv CNa$$

$$CH_3C\equiv C-Na+CH_3Br \longrightarrow H_3C-C\equiv C-CH_3+NaBr$$

The reaction meehanism follows S_N^2 type,

$$R-C\equiv C-H+\begin{cases}NaNH_2\\ or\\ Na\end{cases} \longrightarrow R-C\equiv \overset{\ominus}{C}\overset{\oplus}{N}a+\begin{cases}NH_3\\ +\\ \frac{1}{2}H_2\end{cases}$$

$$R-C\equiv \overset{\ominus}{C}+R'-CH_2-X \longrightarrow R-C\equiv C-CH_2-R'+X^-$$

[SN^2 Meehaism]

Note: R-X should be primary alkyl halide, since higher i.e, 2° and 3° alkyl halides give mainly alkene.

There is a fair amount of possibility for various product formation using this method. Acetylene itself may alkylated either once to make a terminal alkyne or twice to make an internal alkyne.

$$HC\equiv CH+NaNH_2 \xrightarrow[-33^\circ C]{\frac{liq}{NH_3}} HC\equiv C\overset{+}{N}a \xrightarrow{{}^nC_4H_9Br} \underset{1-hexyne}{CH_3(CH_2)_3C\equiv CH}$$

$$HC\equiv CH+\xrightarrow[liq.\,NH_3]{2NaNH_2} \overset{\oplus}{N}aC\equiv C\overset{\oplus}{N}a \xrightarrow{2\,{}^nC_3H_7Br} \underset{4-octyne}{CH_3CH_2CH_2C\equiv C\,CH_2CH_2CH_3}$$

Since acetylide ions are highly basic, competing elimination is a common side reaction.

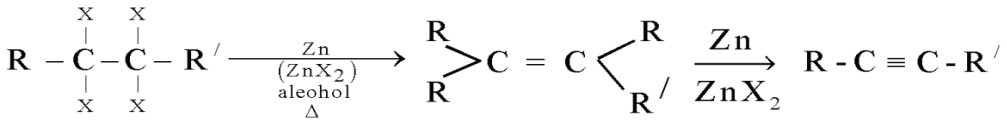
The product of such an elimination reaction are an alkene (from the alkyl halide) and alkyne.

$$R-C\equiv C^{(-)}+H-CH_2-\overset{Br}{\overset{|}{C}}H-R \longrightarrow CH_2=CHR+Br^{(-)}+RC\equiv C-H$$

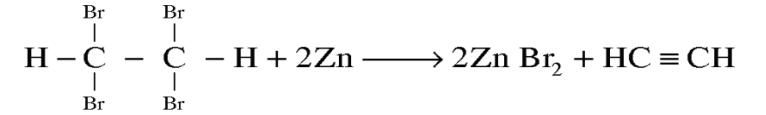
In practice the alkylation of acetylene or another terminal alkyne is only a good method for the synthesis of alkynes when applied to 1° i.e. primary halides that do not have branches close to the reaction centre. With secondary halides and even with primary halides that have branches close to the reaction centre, elimination usually the major reactions.

5.2.3 By Dehalogenation of tetra halides

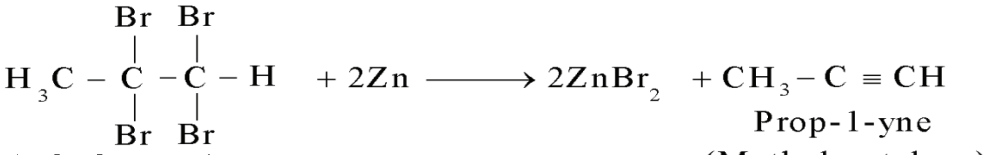
Dehalogenation of tetra halides (1,1,2,2-tetra haloalkanes) are carried out by passing their vapours over heated zine and it result in the formation of alkynes.



For example,

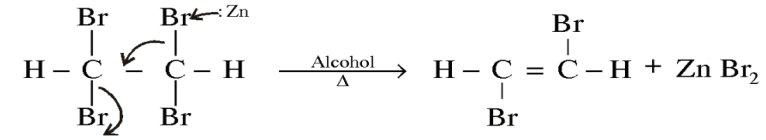


(1, 1, 2, 2 - tetra bromo ethane) (Aectylene)



(1, 1, 2, 2-tetra bromo propane) Prop-1-yne (Methylacetylene)

Mechanism for dehalogenation of Tetra-halides



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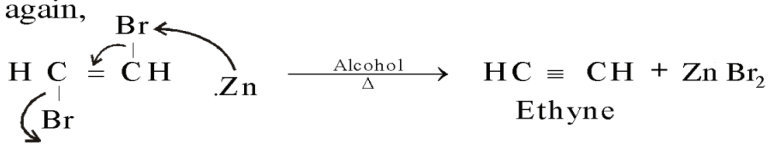
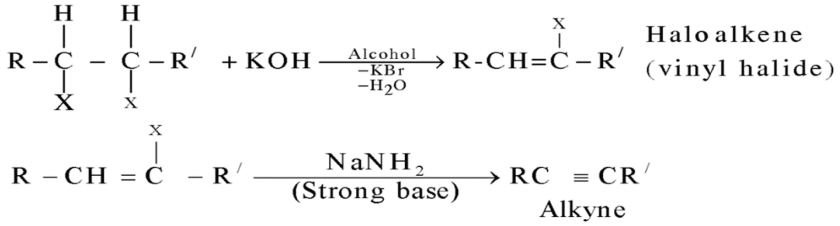


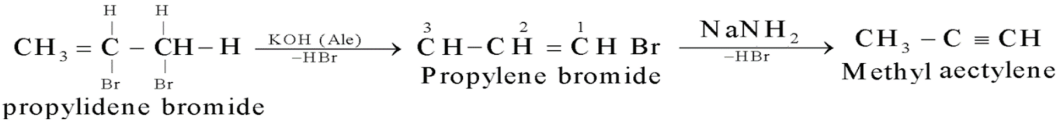
5.2.4 Dehydrohalogenation of vicinal dihalides

When 1,2-dihaloalkane is heated with alcoholic potassium hydroxide, it undergoes dehydrohalogenation, yielding an alkyne. Here one molecule of hydrogen halide is eliminated to form alkenyl halide which on treatment with sodamide give alkyne. [The second stage of reaction generally requires a stronger base (Sodium amide)]



[X = –Cl, Br, or I, R, R′ may be H or alkyl group]

For example,

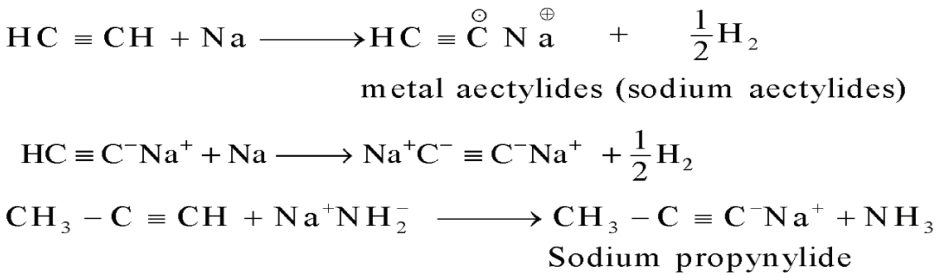


5.3 Reactions of Alkynes

5.3.1 Formation of metal acetylides (Acidic Character of alkyne)

Due to the maximum percentage of s character (50%), the sp hybridized orbitals of carbon atoms in ethyne molecules have highest electro negativity; hence, these attract the shared electron pair of the C-H bond of ethene to a greater extent than that of the sp2 hybridised orbital of carbon in ethene and the sp3 hybridised orbitals of carbon in ethene. Thus sp hybridised C-H bond are more acidic than sp2 and sp3 hybridised C-H bond.

Because of the greater acidity of sp hybrid orbital, terminal alkynes are readily deprotonated in they react with terminal alkynes (ethyne etc) to form sodium acetylide with the liberation of dihydrogen gas.



5.3.2 Formation of heavy metal acetylides

Acetylenic hydrogens of alkynes can also be replaced by heavy metal ions such as Ag+ and Cu^+ ions. For example, when treated with ammonical silver nitrate solution (Tollen's reagent), alkynes form a white precipitate of silver acetylides.

$$CH \equiv CH + 2\left[Ag(NH_2)_2\right]^+ OH^- \longrightarrow AgC \equiv CAg + 2H_2O + 4NH_3$$

Ethyne

$$R-C\equiv CH \;+\; \left[Ag(NH_3)_2\right]^+ OH^- \longrightarrow R-C\equiv C-Ag\downarrow + H_2O + 4NH_3$$

Terminal alkyne Tollen's reagent Silver alkynide (White ppt)

Similarly with ammoniacal cuprous chloride solution, terminal alkynes form red ppt of copper acetylides,

$$HC\equiv CH \;+\; 2\left[Cu(NH_3)_2\right]^+ OH^- \longrightarrow CuC\equiv CCu \;+2H_2O+4NH_3$$

$$R-C\equiv C-H \;+\left[Cu(NH_3)_2\right]^+ OH^- \longrightarrow R-C\equiv C-Cu\downarrow + H_2O + 2NH_3$$

Monocopper alkynide (Red ppt)

Unlike alkali metal acetylides are not decomposed by water they can however, be decomposed with dilute mineral acids to regenerate the original synthesis :

$$Ag\ C\equiv C\ Ag + 2NHO_3 \longrightarrow HC\equiv\ CH + 2AgNO_3$$

(Disilver acetylide)

$$Cu\ C\equiv C\ Cu + 2HCl \longrightarrow HC\equiv CH + 2CuCl$$

(Dicopper acetylide)

5.3.3 Addition to Bromine

The addition of halogens to an alkynes proceeds in the same manner as halogen addition to alkenes. The Bromine atoms add to an alkyne molecule in a stepwise fashion, leading to die formation of die corresponding alkene, which undergoes further reaction to a tetra bromo alkane.

$$R-C\equiv C-R \xrightarrow{Br_2\,/\,CCl_4} R-\underset{\displaystyle Br}{\overset{\displaystyle Br}{\underset{|}{\overset{|}{C}}}}=\underset{\displaystyle Br}{\overset{\displaystyle Br}{\underset{|}{\overset{|}{C}}}}-R \xrightarrow{Br_2\,/\,CCl_4} R-\underset{\displaystyle Br}{\overset{\displaystyle Br}{\underset{|}{\overset{|}{C}}}}-\underset{\displaystyle Br}{\overset{\displaystyle Br}{\underset{|}{\overset{|}{C}}}}-R$$

~ Unlike most halogenation, It is possible to stop this reaction at the alkene stage by running it at temperature slightly below 0°C. for an example

$$CH_3-C\equiv C-H \xrightarrow[CCl_4]{Br_2} \begin{matrix} Br \\ \diagup \\ H_3C \end{matrix}\!\!>C=C<\!\!\begin{matrix} H \\ \diagdown \\ Br \end{matrix} \xrightarrow{Br_2} H_3C-\underset{\displaystyle Br}{\overset{\displaystyle Br}{\underset{|}{\overset{|}{C}}}}-\underset{\displaystyle Br}{\overset{\displaystyle Br}{\underset{|}{\overset{|}{C}}}}-H$$

(1, 1, 2, 2-Tetra bromo propane)

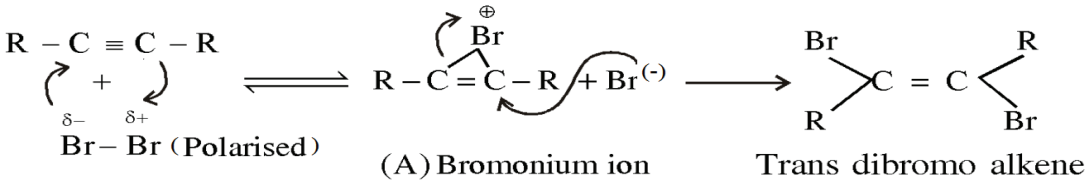
$$CH_3-C\equiv C-H \xrightarrow[CCl_4\ 0°C]{Br_2} \begin{matrix} Br \\ \diagup \\ H_3C \end{matrix}\!\!>C=C<\!\!\begin{matrix} H \\ \diagdown \\ Br \end{matrix}$$

Trans-1, 2-dibromo propane

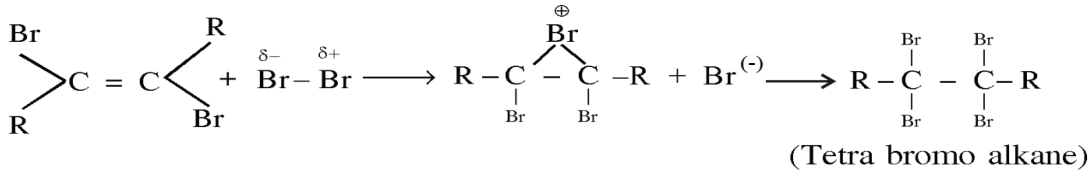
Mechanism

The mechanism of the reaction involves electrophilic addition. It takes place in two steps. This is known as halonium ion mechanism of addition. Bromine (or any halogen) gets polarised under influence of n electrons. Bromonium ion (Br+) adds first forming a bridged bond, followed by the attachment of bromide ion.

First Step

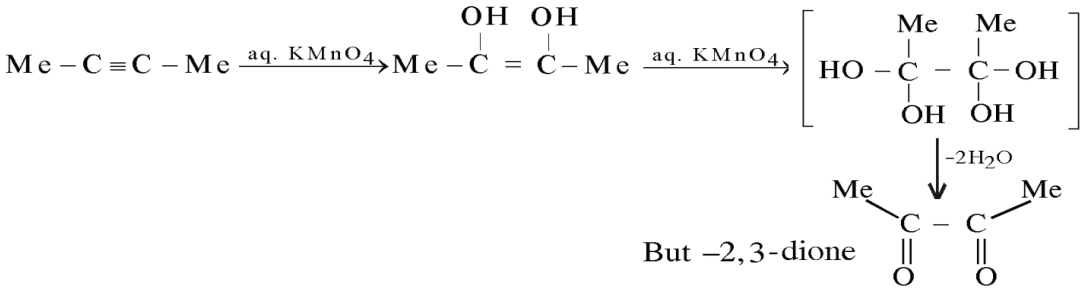


2nd Step

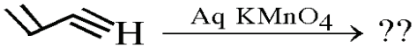


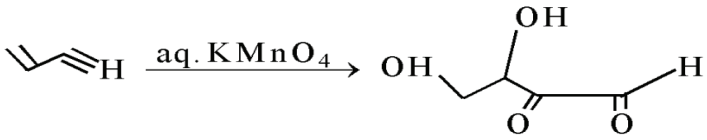
5.3.4 Hydroxylation of Alkynes and Oxidation with KMn04.

Hydroxylation of alkyne with aqueous and neutral $KMnO_4$ Solution (Baeyer's reagent) (test for unsaturation). Pink colour of $KMnO_4$ is discharged and brown black precipitated of MnO_2 is obtained. This reaction converts alkynes first to enediols and then further gives tetraols, which being unstable lose H_2O to give diketones. For example :



Q. Write down the product of the following reaction?

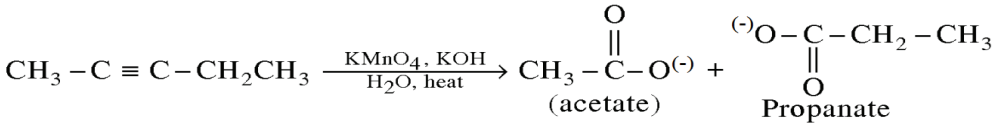




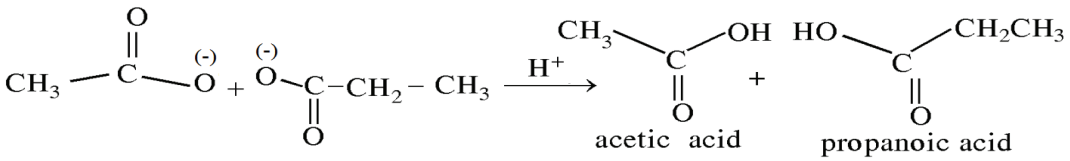
Answer:

However, basic condition cleave the triple bond leading to carboxylate salt and acidification generates the corresponding carboxylic acids.

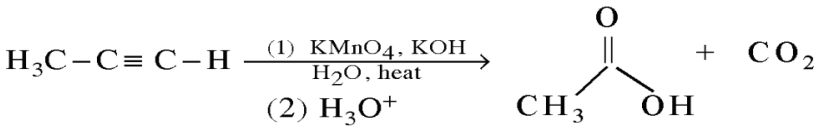
If the alkyne is unsymmetrical, two products will be formed, e.g.: CH_3-C = C-CH_2CH_3 is an unsymmetrical alkyne so under given condition it will give two products.



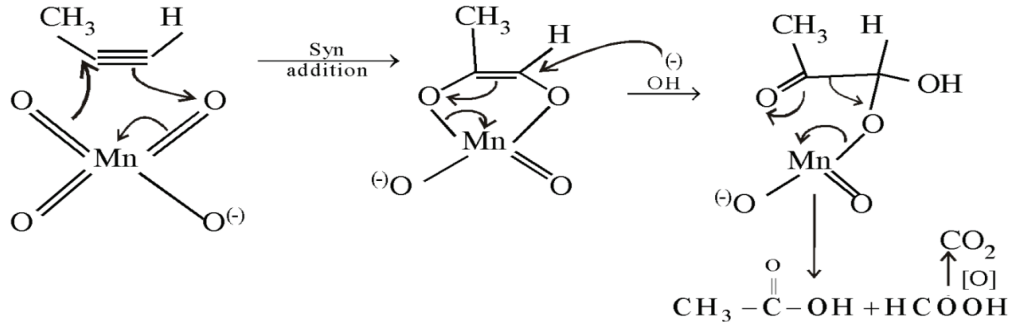
Acidification :



Terminal alkynes will give a carboxylic acid and CO_2



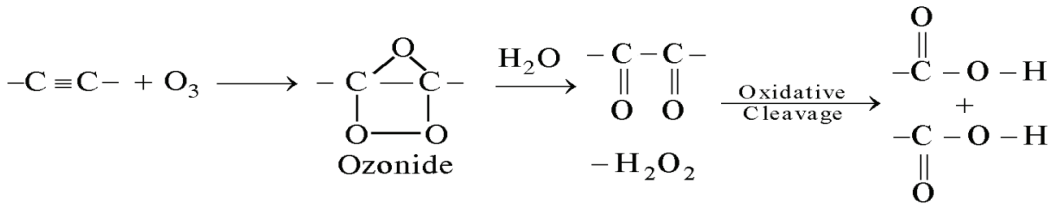
Mechanism:



5.3.5 Ozonolysis

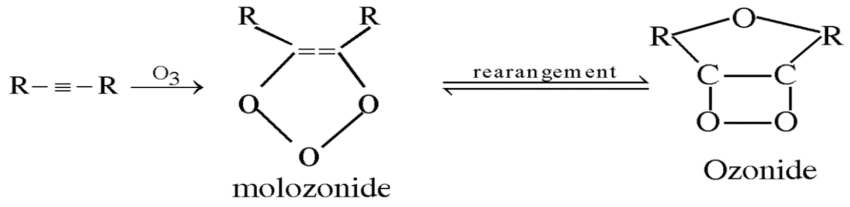
This is an example of 1, 3-dipolar addition. Alkynes add on ozone to form ozonides. The ozonides are hydrolysed by water to form dicarbonyl compounds (1, 2-di ketones) which undergo oxidative cleavage by H209 to form acids. The identification of the acids formed helps to locate the position to triple bond in the original alkyne. Thus, ozonolysis followed by

oxidative cleavage can be used or an unambiguous method for locating the position of triple bond in the original alkyne.

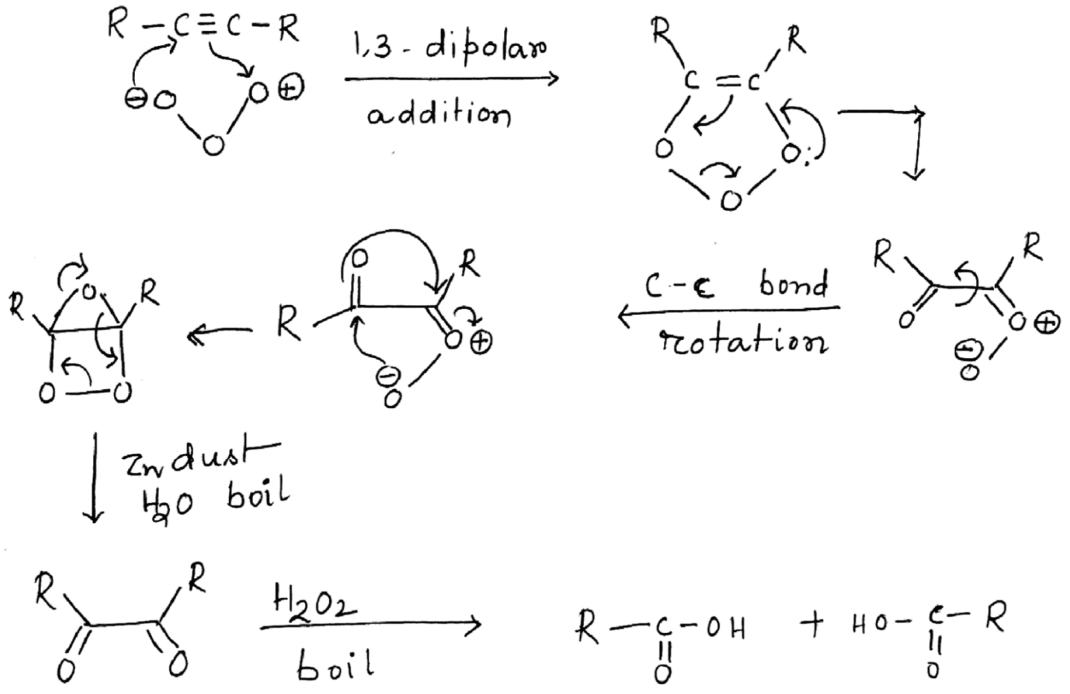


Mechanism

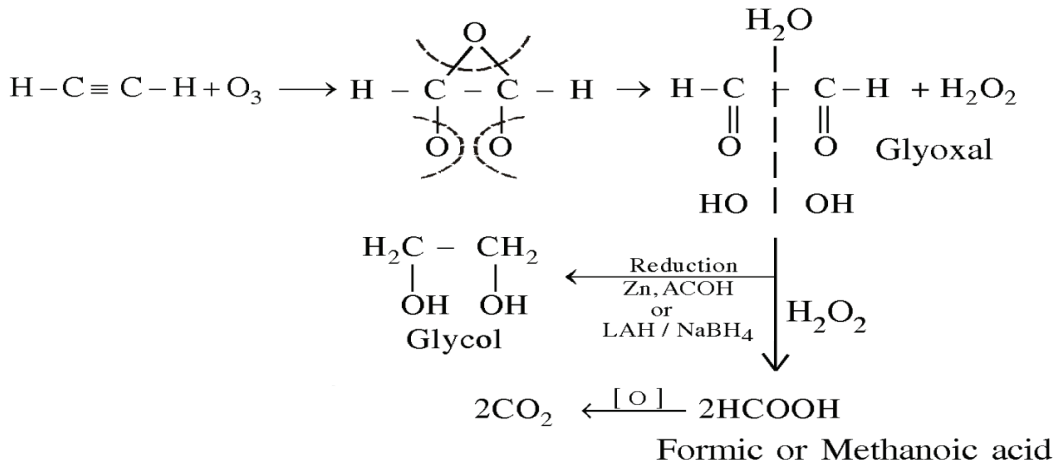
Although a large amount of work has been done on ozonation reaction, the actual mechanism is yet unknown the basic mechanism of ozonation war proposed by Criegee. The first step is the 1, 3-dipolar addition of ozone to the double/triple bond forming molozonide, which than rearranges to give ozonide.



Mechanism :



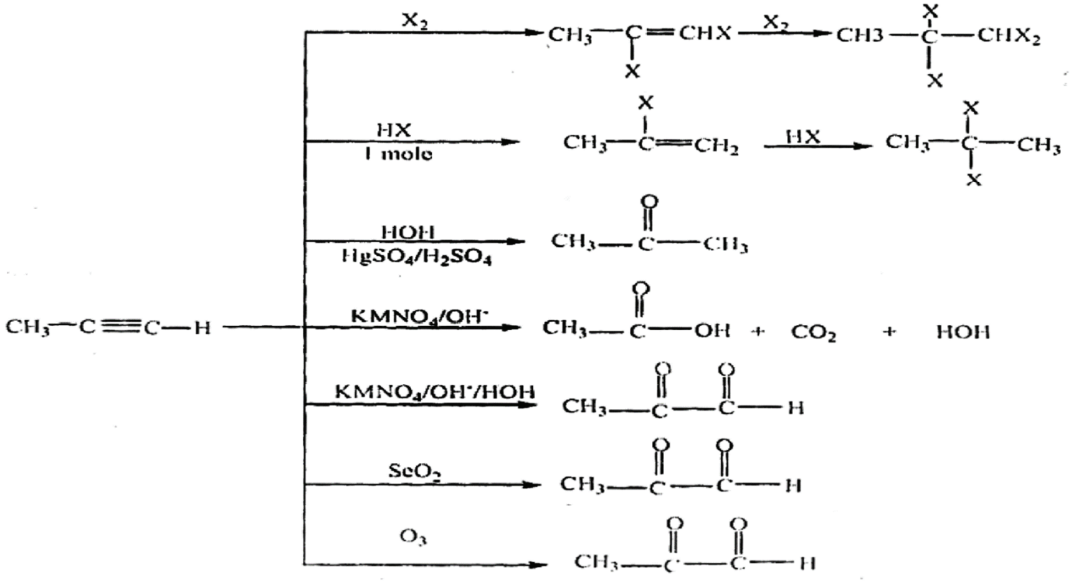
Alkyne form ozonides with O_3 and are then decomposed by H_2O to give diketones, which are then oxidised by H_2O_2 or KMnO4 or peracids and on reduction with metal / acid, LAH or $NaBH_4$ give diols.



5.4 Summary

Alkynes contain the doubly unsaturated C = C functional group. Due to their acidic nature, alkynes form metallic salts called alkynides. Terminal alkynes, RC = C-H, are also quite acidic hydrocarbons and can be deprotonated to form carbanion that can also then be alkylated. Like alkenes (C = C), the alkyne C = C undergoes a variety of addition reactions.

Alkynes give electrophile addition reactions similar to alkenes. Summary of the Key reaction of Alkynes are shown below :



5.5 Solved Problems

Q.1 How will you differentiate propyne from 2-butyne.

The compounds will be treated with ammoniacal cuprous chloride and ammoniacal silver nitrate separately. Propyne gives a red precipitate with ammoniacal silver nitrate. While 2-butyne does not give any precipitate with these reagents.

$$2CH_3CH_2 \equiv CH + Cu_2Cl_2 + 2NH_4OH \rightarrow \underset{\text{(red ppt)}}{2CH_3CH_2C.Cu} + 2NH_4Cl + 2H_2O$$

$$CH_3CH_2 \equiv CH + 2NH_4OH + 2AgNO_3 \rightarrow \underset{\text{(white ppt)}}{2CH_3CH_2 \equiv C.Ag} + 2NH_4NO_3 + 2H_2O$$

$$CH_3.C \equiv C.CH_3 + Cu_2Cl_2 + 2NH_4OH \rightarrow \text{No. rxn.}$$

$$CH_3.C \equiv C.CH_3 + 2NH_4OH + 2AgNO_3 \rightarrow \text{No. rxn.}$$

Q.2 How will you synthesise acetone from propene?

Answer:

$$CH_3CH=CH_2 \xrightarrow{Br_2} CH_3-\underset{Br}{CH}-\underset{Br}{CH_2} \xrightarrow{NaNH_2} CH_3\ C\equiv CH \xrightarrow[H_2SO_4/HgSO_4]{H_2O} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

Q.3 Complete the following reaction with proper mechanism.

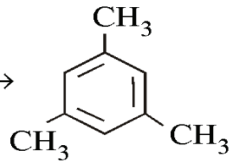
$$CH \equiv CH \xrightarrow{?} HCOOH$$

Answer:

$$CH \equiv CH \xrightarrow[CHCl_3]{O_3} HC\underset{O}{\overset{O}{\diagup\diagdown}}CH \xrightarrow[\text{Hydrolysis}]{H_2O} H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H + H_2O_2 \xrightarrow{[o]} 2\,HCOOH$$

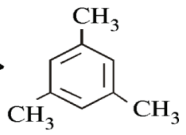
Q.4 Complete the following reaction with proper reagents.

$$HC \equiv CH \xrightarrow{?}$$



Answer:

$$HC \equiv CH \xrightarrow[Liq\ NH_3]{NaNH_2\ (1mol)} HC \equiv \overset{(-)}{C}\,Na^{\oplus} \xrightarrow{CH_3I} HC \equiv CCH_3 \xrightarrow[600^\circ C]{\text{Hot Cu tube}}$$



Q.5 Identify A, B, C in the following reactions.

$$C_2H_2 \xrightarrow[dil\ H_2SO_4]{Hg^{2+}} A \xrightarrow[Ni]{A} B \xrightarrow[NaOH]{Cl_2} B + C$$

Answer: A= CH_3CHO, B= $CHCl_3$, C= HCOONa

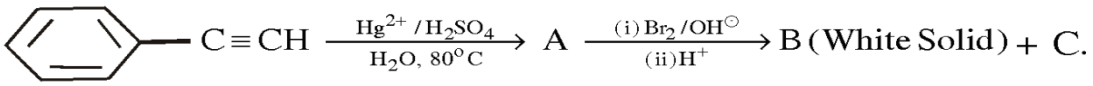
Q.6 Identify A, B, C, D in the following reactions.

$$A \xrightarrow[liq\ NH_3]{Na} B \xrightarrow{CH_3I} C \xrightarrow[Pd-BrSO_4]{H_2} D \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3} CH_3CHO + HCHO$$

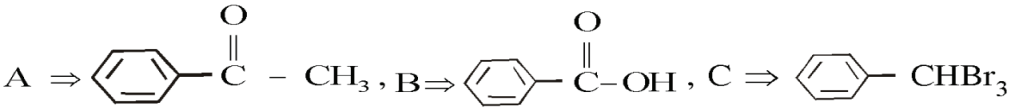
Answer:

$A \Rightarrow H-C\equiv C-H, B \Rightarrow H-C\equiv C\,Na, C \Rightarrow H_2C=CH-CH_3, D \Rightarrow H_2C=CH-CH_3$

Q.7 Identify A, B, C in the following reactions.



Answer:



5.6 Exercises

Mark-1

(1) Write down the general formula of Alkynes.

(2) What is Lindlar's catalyst?

(3) Convert Acetylene into Oxalic acid.

(4) **Complete the following reactions**

$$3\,HC\equiv CH \xrightarrow{500^oC} ?$$

$$HC\equiv CH + H_2O \xrightarrow{H_2SO_4} ?$$

$$HC\equiv CH + HBr \xrightarrow{HgSO_4} ?$$

$$CH_3C\equiv CH \xrightarrow{?} CH_3C\equiv CCH_3$$

Marks - 2

(1) What is anti-Markovnikov product

(2) Differentiate Ethylene and Acetylene.

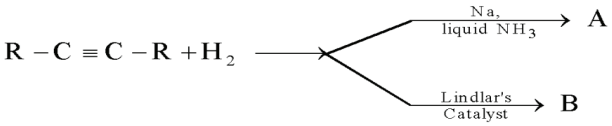
(3) What is Ozonolaysis.

(4) Ethyne forms metallic salt but 'ethane' does not. why?

(5) Discuss the orbital structure of acetylene.

(6) Explain why are alkynes less reactive than alkenes towards electrophilic addition reaction?

(7) Find A and B in the following reactions.



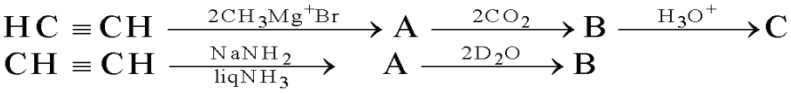
Marks – 5

Q1. Alkynes do not exhibit geometrical isomerism-Explain.

Q2. Explain the acidic nature of acetylenic proton.

Q3. Compare the acidic strength of acetylene, ethylene, and ethane.

Q4. Identify A, B, C in the following reactions



Q5. Convert acetylene to acetone.

Unit 6: Aromatic hydrocarbons

6.0 Objectives

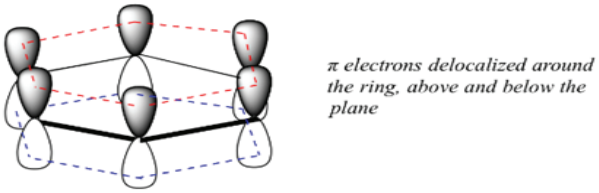
By the end of the unit learners should be able to know about:

- Aromatic nucleus and side chain Structure of benzene. Various methods of preparation of benzene derivatives.
- Aromatic electrophilic substitution
- Activating and deactivating substituent and ortho / Para & Meta orientation of substituent in benzene derivatives
- General pattern of nitration, halogenations& sulphonation & Friedel-Crafts reactions.
- Reduction of benzene (Birch reduction)
- Activating and deactivating substituent, Orientation and ortho / Para ratio.

6.1 Introduction

Benzene is die most straight forward aromatic compound. It is a planar symmetrical hexagon with six trigonal (sp2 hybridised) carbon atoms, each having one hydrogen atom in the plane of the ring. The special stability of benzene [aromaticity] is due to delocalization of π electrons [$(4n+2)\pi$ electrons, here n=2; Huckel's Rule] in the six molecular orbitals formed by the overlap of the six atomic p-orbitals on the carbon atoms.

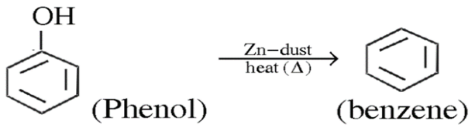
Benzene [C_6H_6] is the resonance hybrid of the following two equivalent Kekule structures (I & II) :



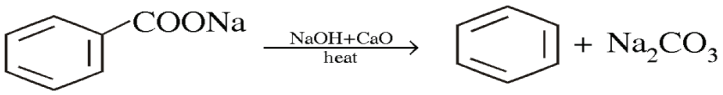
π Molecular orbitals of benzene

6.2 Preparation of Benzene

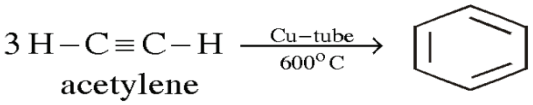
1. From phenol : When phenol is refluxed with zine dust or phenol vapour passed over zinc dust, then benzene is fanned.



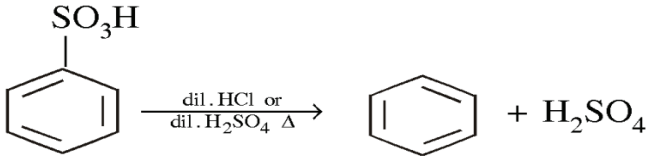
2. From sodium benzoate by decarboxylation : Benzene is formed when anhydrous sodium benzoate is heated in presence of sodalime (NaOH+CaO).



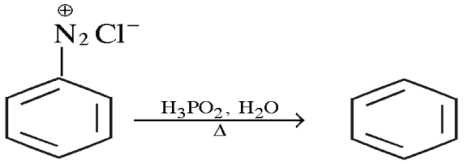
3. From acetylene : Benzene is formed when acetylene gas is passed over red hot copper tube (600°C)



4. From benzenesulfonic acid : When benzene sulfonic acid is treated with aqueous HCl or H_2SO_4, These benzene is formed (desulfonation)



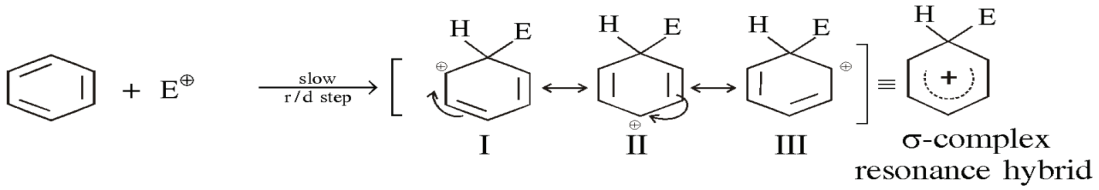
5. From diazonium salt : When benzene diazonium salts are heated with hypo-phosphorous acid (H_3PO_4), benzene is formed.



6.3 Chemical reactions of benzene

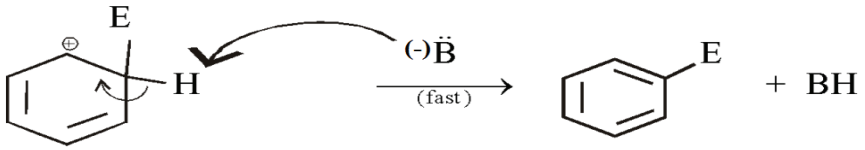
Being an aromatic compound benzene gives substitution and not addition products. When aromatic compounds react with electrophiles they generally do so by electrophilic aromatic substitution (ArS_E). The most common electrophilic substitutions of benzene are nitration, halogenation, sulfonation, Friedel Crafts reaction etc. General mechanism of electrophilic substitution—

Step-I



The carbocation resulting from the attack on the electrophile (E+) by the benzene ring π-electron-cloud is stabilized by resonance. The resonance hybrid of the structure I, II & III is called σ-complex [Wheland Intermediate], As the aromatic character of the benzene ring is lost, so it is the slowest step and hence the rate-determining step (r/d step) in the whole reaction sequence.

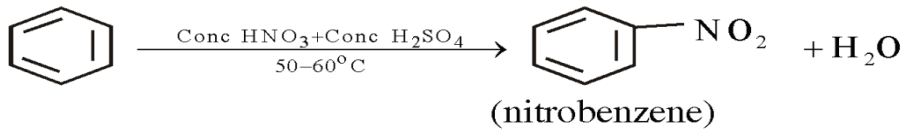
Step-II : To retain the aromatic stability, the σ-complex give up a proton (H+) [from the carbon bonded to the electrophile] to yield the substituted benzene.



$B^{(-)}$ refers to any basic compound present within the reaction mixture. Hie mechanistic pathway is 'bimolecular electrophilic aromatic substitution (ArS_E2)' since, both the substrate (benzene) & reagent (electrophile) are present in the r/d step.

6.3.1 Nitration of benzene : In this process the hydrogen atom of the benzene ring is substituted by nitro (-NO_3) group.

Reagent : Mix acid [ConC HNO_3 + ConC H_2SO_4] is the most common nitrating agent.



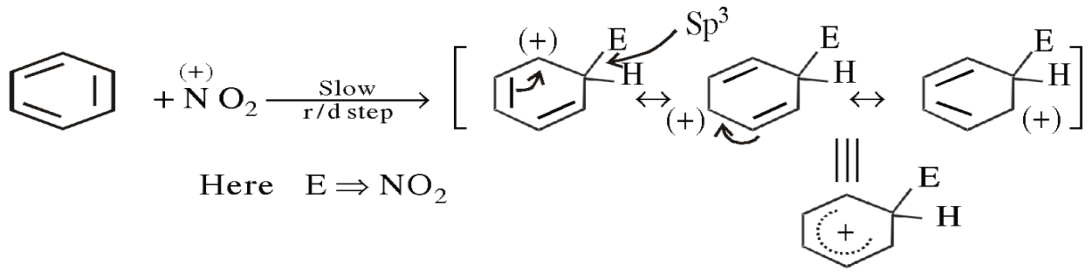
(nitrobenzene)

Mechanism :

In this ArS_E, reaction the reacting electrophile is nitronium ion (NO_2^+) which is formed from reaction of cone. HNO_3 with cone. H_2SO_4

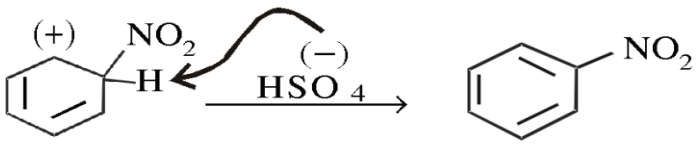
$$HNO_3 + 2H_2SO_4 \rightleftharpoons \overset{\oplus}{N}O_2 + H_3O^{\oplus} + 2HSO_4^{(-)}$$

Step-I : Carbocation σ-complex formation

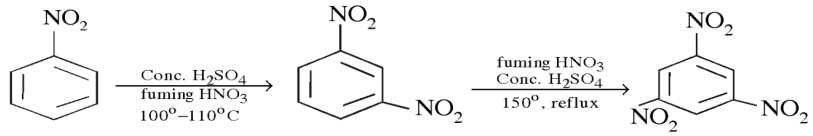


(Resonance hybrid)

Step-2 : Expel out of proton

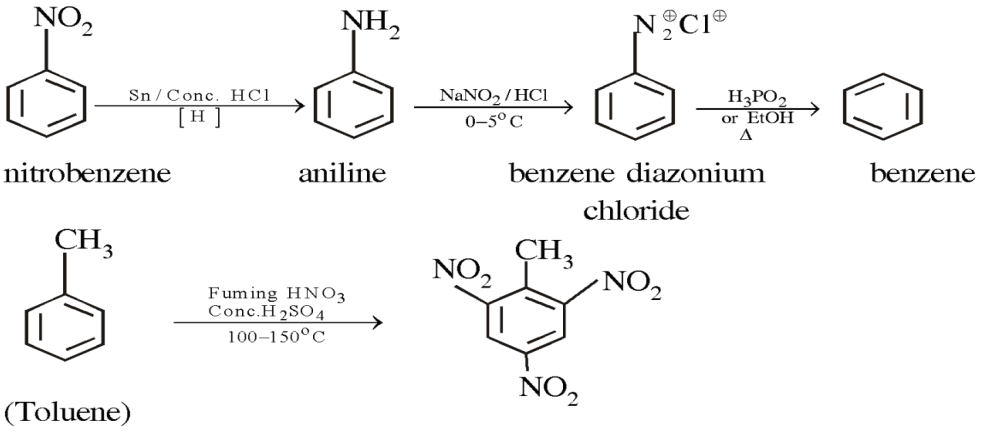


Sine, nitro group (-NQ_2) is very powerful electron withdrawing group, it decreases the π-electron density of the ring very effectively. Thus, introduction of second or third –NO_2 group to a mono-substituted nitro benzene is difficult & we have to use more drastic condition for successive nitration. A, -NO_2 group is an electron-with drawing group (EWG) and hence meta-directing the new upcoming NQ_2^+ electrophile is introduced in the meta-position w.r to the NO_2 group that already present in the nucleus.



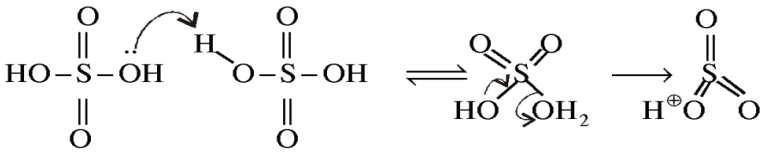
nitrobenzene m-dinitrobenzene 1,3,5-trinitrobenzene (TNB)

NO_2 group can be removed from the benzene ring by the following reaction sequence—

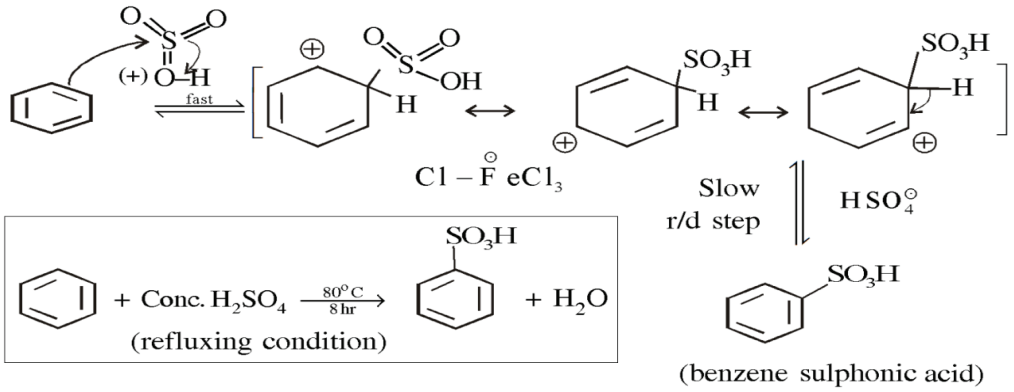


6.3.2 Sulfonation of benzene :

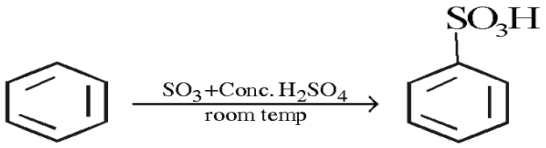
hi this process the hydrogen atom (s) on the benzene ting is/are substituted by sulfonic acid group(s) [-SO_3H]. Benzene reacts slowly with cone. H_2SO_4 alone to give benzene sulfonic acid. One molecule of H_2SO_4 protonates another and loses a molecule of water to form die reactive electrophile (HSO_3^+).



The cation produced is very reactive and attacks benzene by the same mechanism we have seen for nitration -slow addition of HSO_3^+ to the π system followed by rapid loss of a proton to regenerate aromaticity. The sulfonation of benzene is a reversible process.

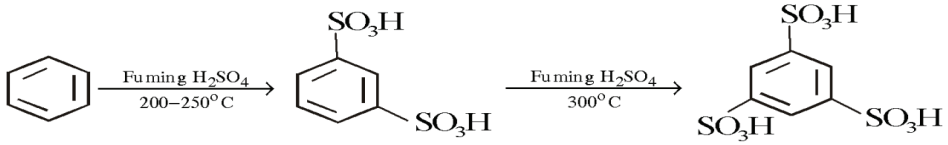


However, by using fuming H_2SO_4 [mixture of SO_3 & cone. H_2SO_4 or oleum ($H_2S_2O_7$)] sulfonation can be carried out in room temperature.



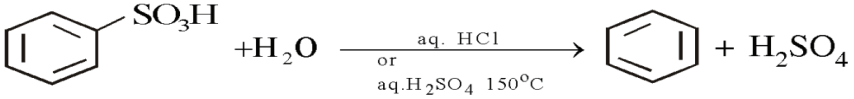
(benzene sulfonic acid)

When, benzene is treated with fuming H_2SO_4 at 200-250°C then benzene-m-disulfonic acid is obtained and when heated at about 300°C then 1,3,5-benzene-trisulfonic acid is obtained.



benzene benzene-m-disulfonic acid 1,3,5-benzene-trisulfonic acid

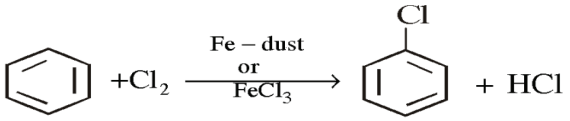
Being an EWG, -SO_3H group in the ring directs die upcoming E^+ to the meta position. De-sulfonation (removal of -SO_3H group from the ring) is carried out by treatment of dil. HC1 or dil. H_2SO_4 on the benzene sulfonic acid.



6.3.3 Halogenation of benzene :

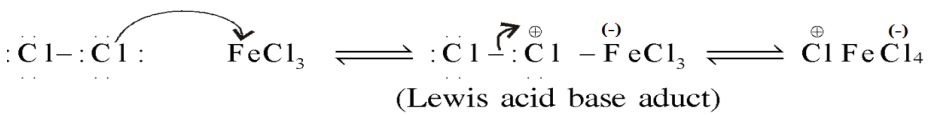
In this process the H atom(s) in the benzene ring is/are substituted by halogen atom [Cl, Br & I],

Chlorination : In presence of diffused sunlight, or halogen carrier (like Fe grain, $FeCl_3$, A1C13) benzene reacts with chlorine gas under room temp. To give chlorobenzene. In absence of halogen carrier [Lewis acid] chlorination doesn't occur.

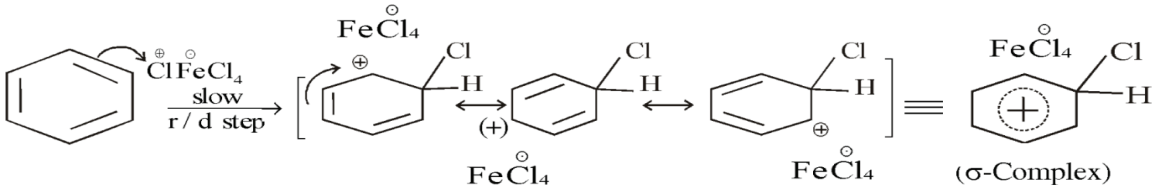


Chlorobenzene

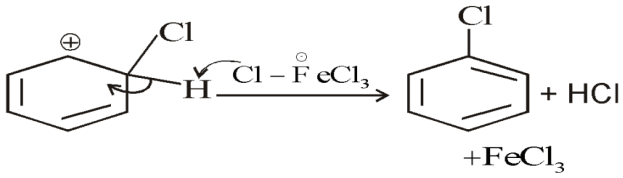
Mechanism : The reacting electrophile is Cl^+ ion formed by the reaction of $FeCl_3$ & Cl_2



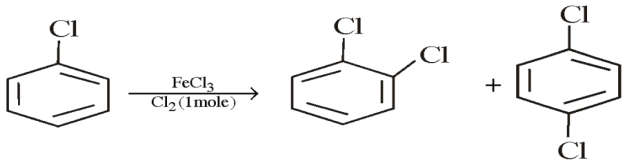
Step-1 : Carbocation (σ-complex) formation



Step-II : Removal of proton

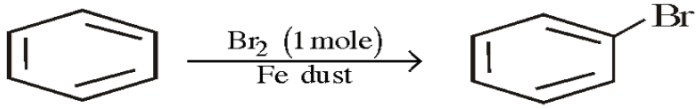


Halogens are ring deactivator but ortho para directing so the upcoming E+ will undergo to the ortho or para position.



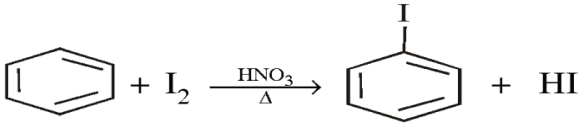
ortho-dichlordoenzene para-dichloro benzene

Bromination : Like Cl_2, Br_2 also react with benzene ring in presence of Lewis acid catalyst as halogen carrier, to produce bromobenzene.

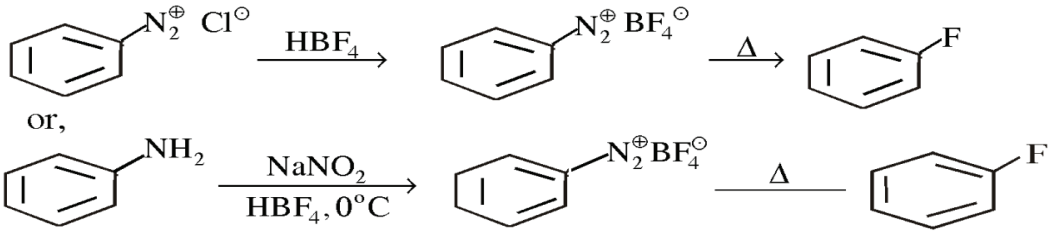


The mechanism is similar to that of chlorination.

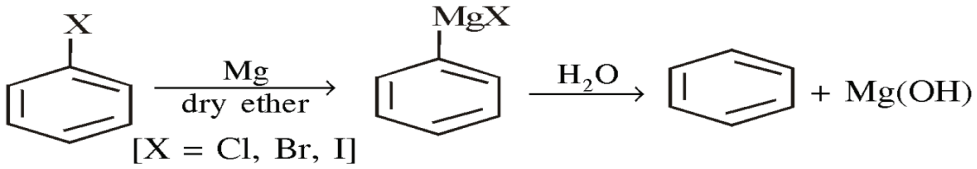
Iodination : The mechanism for iodination is slightly different : I_2 is treated with an oxidizing agent such as nitric acid to obtain the electrophilic iodine (I^+, probably $IONO_2$).



Fluorine can be introduced in the benzene ring by an indirect manner.



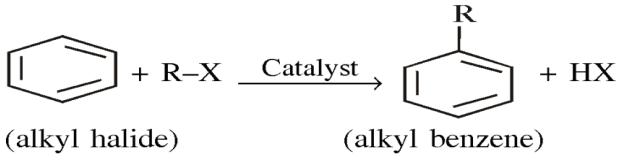
The halogen can be removed from die ring by means of Grignard reagent formation.



6.3.4 Friedel-Crafts reaction :

Introduction of an alkyl or acyl group into an aromatic nucleus in the presence of a Lewis acid or a protonic acid as catalyst is known as Friedel-Crafts reaction.

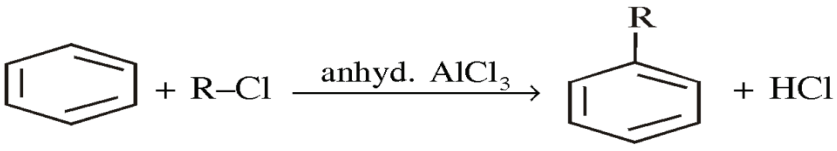
6.3.4.1 Friedel-Crafts alkylation : Introduction of R group to the ring.



(i) Alkylating agents : allyl or benzyl halide, tertiary, secondary or primary alkyl halide. Instead of alkyl halide, alcohols may also be used as alkylating agents in convenient way. Some times alkenes are also used.

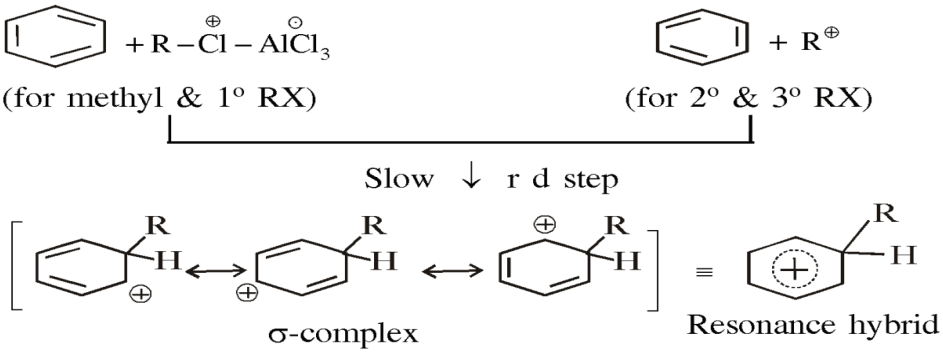
(ii) Catalyst : Anhyd. $A1C1_3$ is particularly useful as catalyst for F-C reactions. Other Lewis acid catalysts are BF_3, $SbCl_5$, $FeCl_3$, $SnCl_4$, $ZnCl_2$, etc. For alcohols as alkylating agent HF, H_2SO_4, BF_3, H_3PO_4 can be used. For alkene as alkylating agent anhyd. $A1C1_3$ & trace amount of HC1 is very effective catalyst.

(iii) Solvent : Either CS_2 or nitrobenzene can be used as solvent for F.C. reaction.



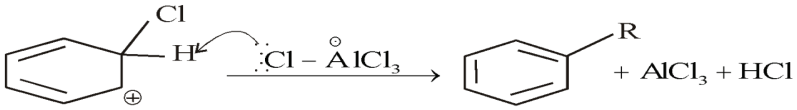
Mechanism In this reaction the reacting electrophile is a carbocation (R+)

Step-I : Formation of σ-complex

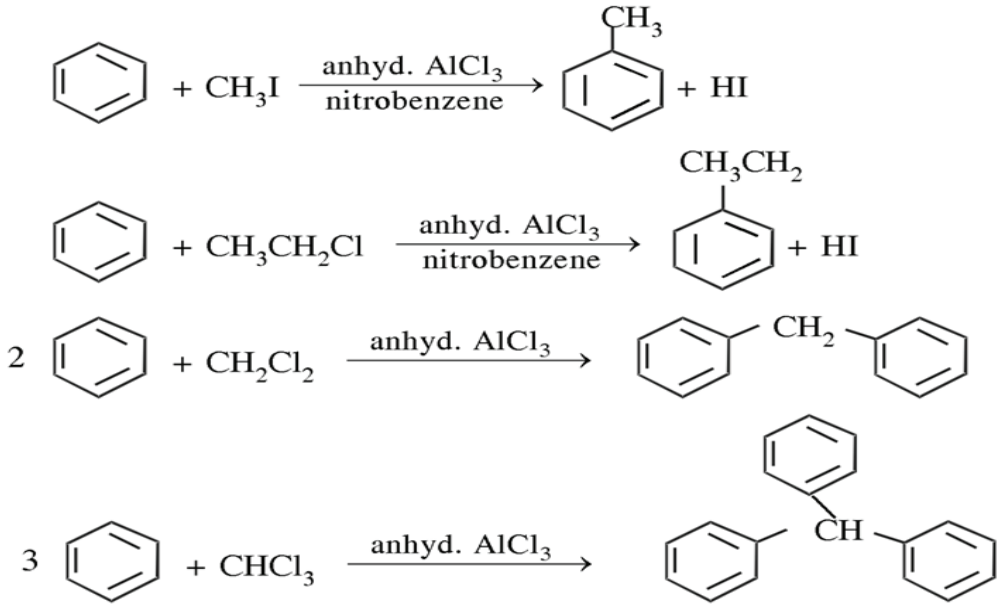


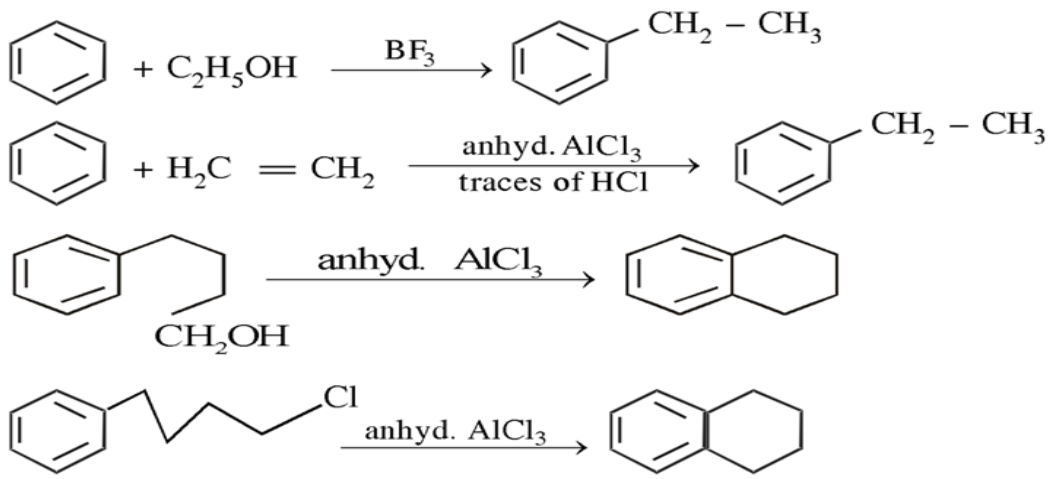
This is the slowest & hence rate determing step.

Step-II : Removal of proton & regeneration of aromaticity.



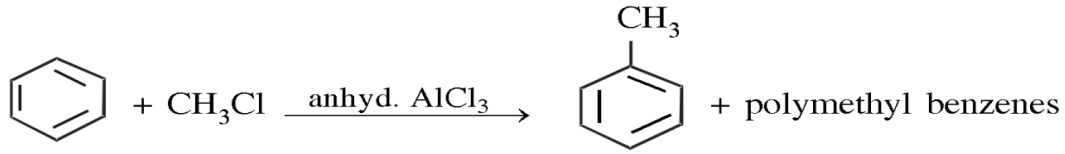
Since the catalyst is regenerated in the last step so only catalytic amount of anhyd. $A1Cl_3$ is needed to carry out the reaction. Example :



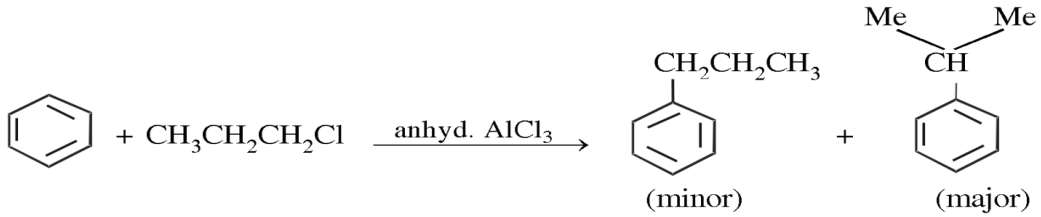


Limitation :

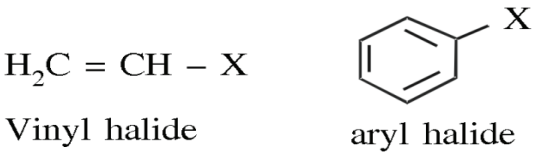
1. It is difficult to stop the reaction at the mono-alkylated stage, because, the introduction of the alkyl group tends to activate the ring towards a second substitution. Ultimately a poly alkylated product is obtained.



2. Another serious problem with F-C alkylation is that the alkyl cations (when 1 or 2°) often rearranged to give more stable cations.



3. Vinyl halide & halobenzenes cann't be used as alkylating agent.



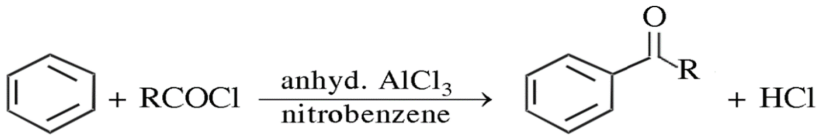
6.3.4.2 Friedel-Craft's acylation reaction :

Introduction of RCO-group to the ring.

(i) Reagents (acylating agents) :

Acyl halides (usually chlorides); cyclic & acyclic acid anhydrides ; carboxylic acid.

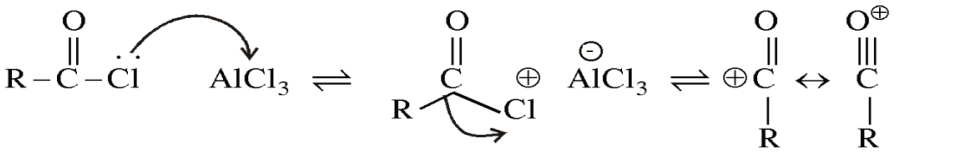
(ii) Catalyst : Anhydrous $A1C1_3$ is superior choice. H_3PO_4 or Polyphosphoric acid (PPA) used for carboxylic acid as acylating agent. Either CS_2 or nitrobenzene is employed as solvent.



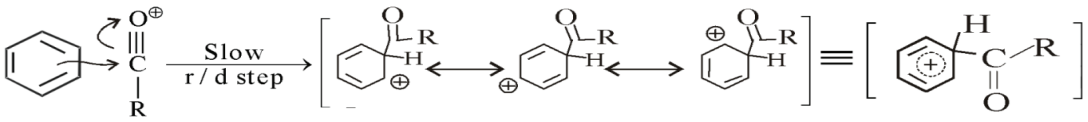
acyl benzene

Mechanism : The acylium cation is the reactive electrophile here.

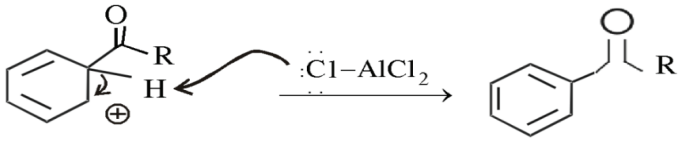
Step-I :



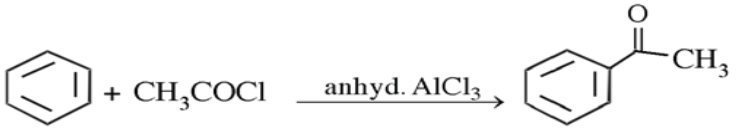
Step-II : Formation of σ-Complex

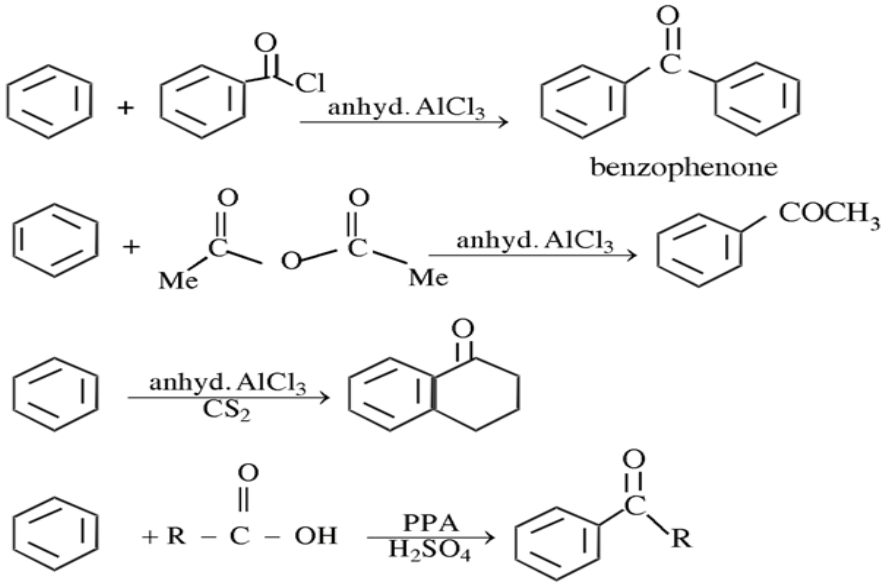


Step - III : Removal of proton



Example :

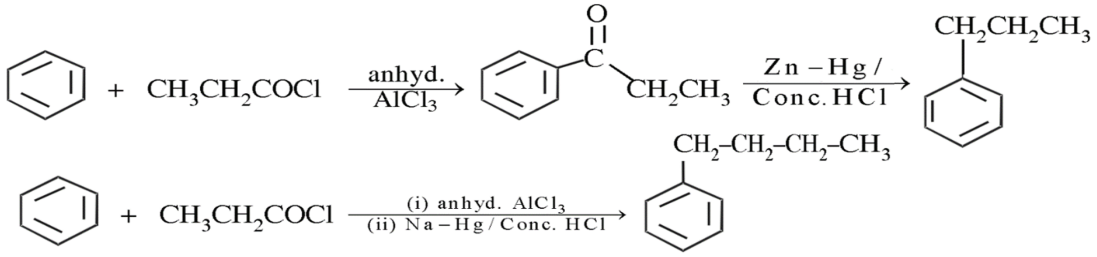




The F - C acylation is more reliable and advantageous than alkylation reaction—

(i) Unlike F - C alkylation, polyacylation does not occur. The acyl group in the product withdraws electrons from the ring nucleus, making poly-substitution harder. Thus pure mono-substituted aromatic ketones can be synthesized.

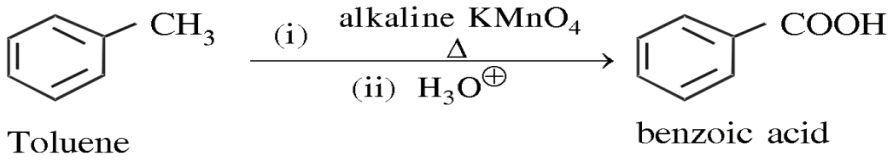
(ii) Unlike alkylation, acylation does not give rearranged product because an acylium cation is well stabilized by resonance. Because of these advantages acylation reaction is used for synthesis of alkyl benzene having 3 or more carbon atoms in the alkyl chain.



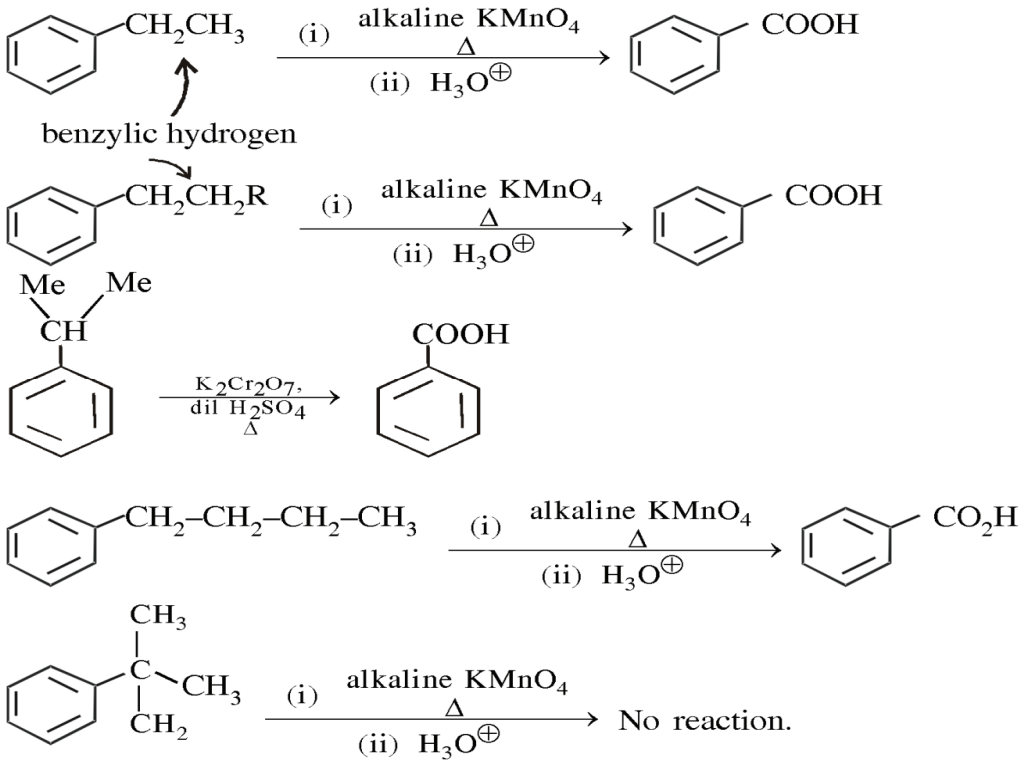
6.3.5 Side Chain Oxidation of aromatic Compounds :

As benzene ring nucleus is aromatic stabilized, so oxidation of aromatic hydrocarbons results only in the oxidation of the side chain leaving the ring intact.

Oxidizing agents : dil. HNO_3, alkaline solution of $KMnO_4$, acidified $K_2Cr_2O_7$ etc. are used as convenient oxidizing agents.



In this side chain oxidation of aromatic hydrocarbon the side chain containing benzylic hydrogen ultimately oxidized to carbonyl (-COOH) group.



Since, there is no benzylic hydrogen in the tert-butyl benzene, its side chain is not oxidized to $-CO_2H$ when treated with alkaline $KMnO_4$

6.4 Summary

- Aromatic hydrocarbons are known as arenes. In arenes, Benzene is most important compound.
- Stability of benzene depends on the resonating structures. By resonance we can easily define the stability of benzene.
- Benzene aromaticity causes it to undergo electrophilic aromatic substitution reactions.
- Electron rich substituents (may consist loan pair of electron) present in aromatic ring direct incoming second substituent group primarily to ortho and para position and it is known as o, p director. These are ring activator (except, halogen family due to -I effect), E. g. -OH, -

NH_2, -R_2N, -OR, alky), -F, -Cl, -Br, -I.

- Electron deficient substituents present in aromatic ring direct incoming second substituent group primarily to meta position and it is known as meta director, meta directors are also ring deactivator. E.g. NO_2, - COOH, - CHO, -SO_3H, $CONH_2$, -CN, -NR_3 etc.
- The electrophilic addition reactions characteristic of alkenes and dienes would lead to much less stable nonaromatic addition products. The most common electrophilic aromatic substitution reactions are halogenation, nitration, sulfonation, and Friedel-Crafts acylation and alkylation.
- Bromination or chlorination requires a Lewis acid catalyst; iodination requires an oxidizing agent.
- Nitration with nitric acid requires sulfuric acid as a catalyst. Either an acyl halide or an acid anhydride can be used for Friedel-Crafts acylation, a reaction that places an acyl group on a benzene ring. If the carbocation formed from the alkyl halide used in a Friedel-Crafts alkylation reaction can rearrange, the major product will be the product with the rearranged alkyl group.

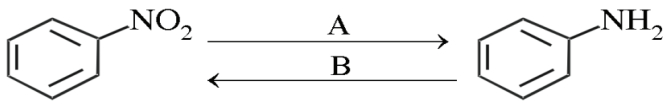
6.5 Solved Problems

F.M. - 1

1. What is the C-C bond length in benzene?

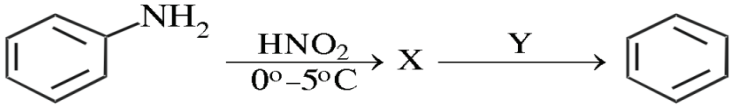
Ans. All the C - C bond length are same in benzene and the value is $1.39A^0$

2. Write the proper reagent for the following conversion.

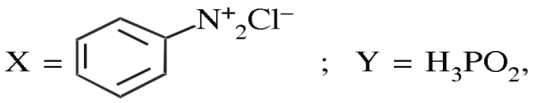


Ans. A : Sn / HC1 ; B : CF_3CO_3H

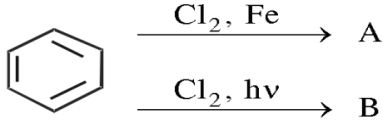
3. Identify X, Y in the following conversion.



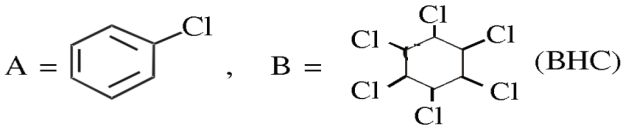
Ans:



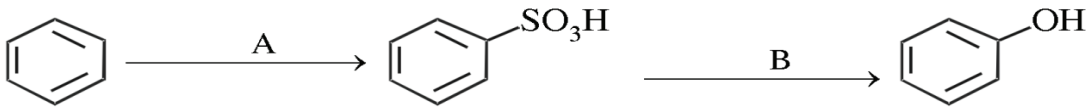
4. Identify A, B in the following conversion.



Ans:

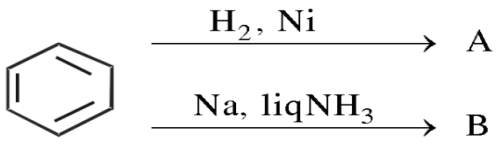


5. Identify A, B in the following conversion.

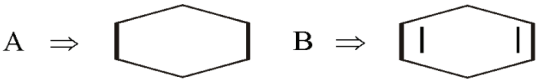


Ans: A = Cone. H_2SO_4, heat, B = fused NaOH

6. Identify A, B in the following conversion.



Ans:

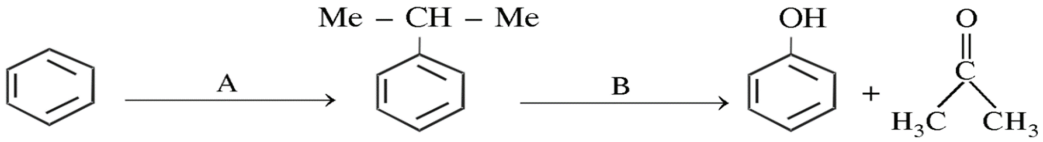


7. Find the value of 'n' for benzene if it satisfies Huckel's (4n+2) π electron rule.

Ans. n = 1

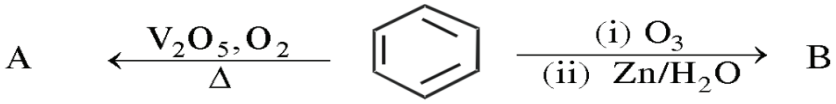
F.M. – 2

1. Identify A, B in the following conversion.

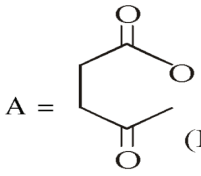


Ans. A = $CH_3CH{=}CHO$, H_3PO_4 B = (i) O_2, (ii) H_3O^+ or, $CH_3CH_2CH_2C1$, anhyd. $A1C1_3$, heat

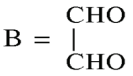
2. Identify A, B in the following conversion.



Ans:



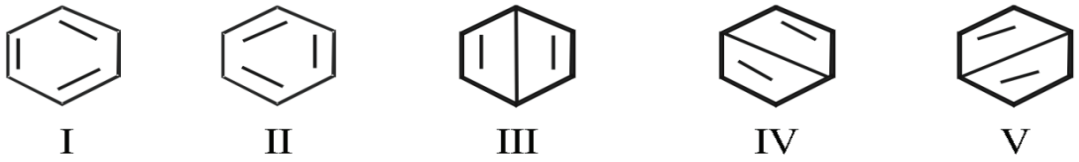
(Maleic anhydride)



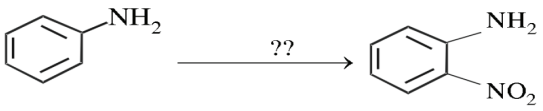
(3 moles)

3. Draw the Kekule & Dewar structures of benzene. Among these which are the resonance structure of benzene and which are not?

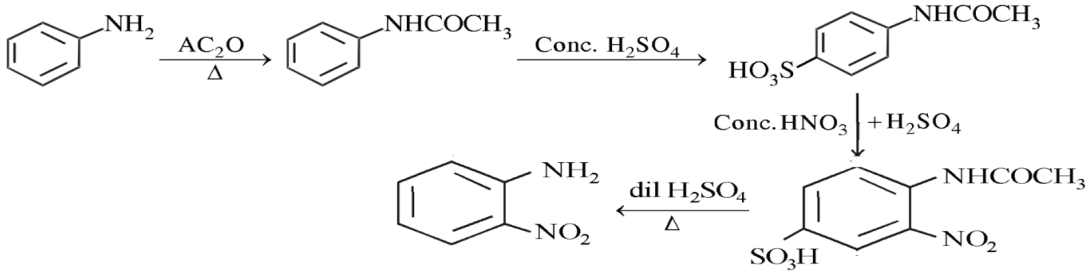
Ans: Kekule structure : I & II, Dewar structure : III, IV, V Only Kekule structure i.e., I & II are resonance structures of benzene white Dewar structures are not.



4. Complete the following conversion with proper reagents.



Ans:



6.6 Exercises

1. Why nitrobenzene is used as solvent for Friedel-Craft reaction?

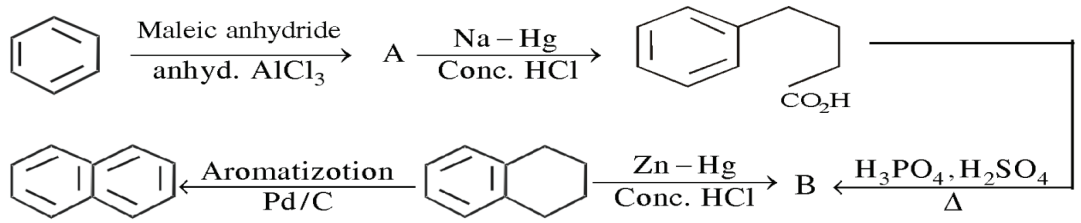
2. Why aniline does not take part in F - C reaction?

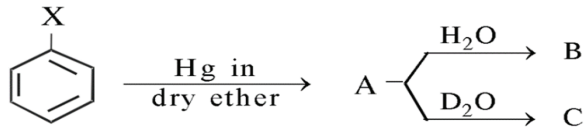
3. Why aniline can't be nitrated directly?

4. Halogens are deactivator but still ortho/para directing Explain.

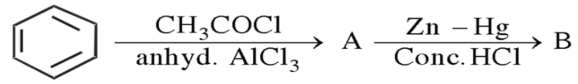
5. Give two advantages of F-C acylation over F-C alkylation.

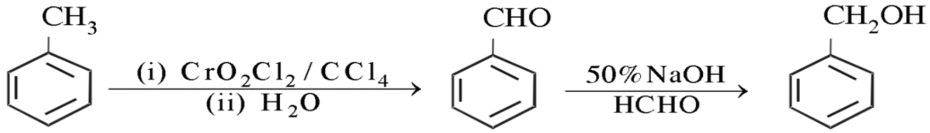
6. Identify A & B in the following conversion.


Maleic anhydride
anhyd. AlCl3
A
Na – Hg
Conc. HCl
CO2H
Aromatizotion
Pd/C
Zn – Hg
Conc. HCl
B
H3PO4, H2SO4
Δ

7. 
X
Hg in
dry ether
A
H2O
B
D2O
C

8. 
CH3Cl
anhyd. AlCl3
A
(i) alkaline KMnO4
dil. HCl
B
NH3, Δ
C
Br2/KOH
NH2

9. 
CH3COCl
anhyd. AlCl3
A
Zn – Hg
Conc. HCl
B

10. 
CH3
(i) CrO2Cl2 / CCl4
(ii) H2O
CHO
50% NaOH
HCHO
CH2OH

Unit 7: Alkyl and Aryl Halides

7.0 Objectives

By the end of the unit learners should be able to know about:

- The various methods of preparation of alkyl halide (haloalkanes) and Aryl Halides.
- The different reactions involving alkyl halide and Aryl Halides.
- The Williamson's ether synthesis of alkyl halide
- The aromatic nucleophilic substitution and effect of substituent.
- The mechanism of the reaction involving Benzyne intermediate.

7.1 Introduction

The Compounds which are formed from the replacement of one or more hydrogen atom of aliphatic and aromatic hydrocarbon by a halogen atom, are called alkyl halides and aryl halides.

7.2 Alkyl Halides or Halo alkanes

In alkyl halides, the halogen atom remains attached with the sp3 hybridised C-atom of alkyl group. e.g CH_3-Cl (Methyl Chloride)

7.2.1 Preparation of alkyl halide

(A) From alkenes :

(i) By the addition of halo acids : Halo alkanes are prepared by reaction by haloacids with alkenes. The reactivity order of the haloacids is HI > HBr > HC1 > HF

$$CH_3CH = CHCH_3 + HBr \rightarrow CH_3 - CH_2 - \underset{\underset{Br}{|}}{CH} - CH_3$$

but-2-ene — 2-bromobutane

$$CH_3 - CH = CH_2 + HBr \rightarrow CH_3 - \underset{\underset{Br}{|}}{CH} - CH_3 + CH_3 - CH_2 - CH_2 - Br$$

1-bromopropane (10%)

$$CH_3 - CH = CH_2 + HBr \xrightarrow{H_2O_2} CH_3 - CH_2 - CH_2 - Br$$

1-bromopropane (Main Product)

(ii) By Allylic halogenation: When alkene (except ethylene) is heated with chlorine or bromine at high temperature, the allylic hydrogen is replaced by halogen atom and haloalkane is formed, e.g.

$$CH_2 = CHCH_3 + Cl_2 \xrightarrow{500^oC} CH_2 = CH - CH_2 - Cl + HCl$$

3-Chloroprop-1-ene

$$CH_2 = CHCH_3 + Br_2 \xrightarrow{500^oC} CH_2 = CH–CH_2–Br + HBr$$

3-bromoprop-1-ene

B) From alcohols :

(i) by addition of haloacid

$$R - OH + HX \rightarrow R - X + H_2O$$

For a particular alcohol, the order of reactivity of haloacids is HI > HBr > HCl. for a particular haloacid, the order of reactivity of different types of alcohol is 3° alcohol > 2° alcohol > 1° alcohol

(ii) Grove's process :

$$1^o \text{ or } 2^o \text{ alcohol} \xrightarrow[\Delta]{\text{Anhydrous } ZnCl_2} 1^o \text{ or } 2^o \text{ Alkyl Chloride} + H_2O$$

$$\text{e.g} \rightarrow CH_3CH_2OH + HCl \xrightarrow[\Delta]{\text{Anhydrous } ZnCl_2} CH_3CH_2Cl + H_2O$$

$$CH_3 - \underset{\underset{OH}{|}}{CH} - CH + HCl \xrightarrow[\Delta]{\text{Anhydrous } ZnCl_2} CH_3 - \underset{\underset{Cl}{|}}{CH} - CH_3 + H_2O$$

Here $ZnCl_2$ acts as a Lewis acid

$$R - \ddot{\underset{\ddot{}}{O}}H + ZnCl_2 \rightleftharpoons R - \overset{+}{\underset{\underset{H}{|}}{O}} - \overset{-}{Z}nCl_2 \xrightarrow[Cl^-]{S_N2} R - Cl + [Zn(OH)Cl_2]^-$$

(iii) by reaction with phosphorous halide-

$$CH_3CH_2OH + PCl_5 \rightarrow CH_3CH_2Cl + POCl_3 + HCl$$

$$CH_3 - \underset{\underset{OH}{|}}{C}H - CH_3 + PCl_3 \rightarrow CH_3 - \underset{\underset{Cl}{|}}{C}H - CH_3 + H_3PO_3$$

(iv) Reaction with Thionyl Chloride ($SOCl_2$)

$$CH_3CH_2OH + SOCl_2 \xrightarrow{\text{Pyridine}} CH_3CH_2Cl + SO_2 \uparrow + HCl$$

7.2.2 Reactions of alkyl halide :

(1) Hydrolysis :

Hydrolysis of haloalkanes in presence of aqueous alkali (KOH or NaOH) or Ag_2O/H_2O or AgOH, gives alcohol.

$$CH_3CH_2Br + KOH \xrightarrow[\Delta]{H_2O} CH_3CH_2OH + KBr$$

$$CH_3I + AgOH \xrightarrow[\Delta]{H_2O} CH_3OH + AgI \downarrow$$

(2) Nitrite and Nitro formation :

Reaction of haloalkane with silver nitrite ($AgNO_2$) in presence of aq. alcohol gives alkyl nitrite.

$$R - X + AgNO_2 \xrightarrow{H_2O/\text{Ethanol}} \underset{\text{Alkylnitrite}}{R{-}ONO} + AgX\downarrow$$

$$\begin{matrix} H_3C \\ H_3C \end{matrix}\!\!>\!CH\text{-}Br + AgNO_2 \xrightarrow{H_2O/\text{Ethanol}} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH - O - N = O + AgBr\downarrow$$

Isopropyl nitrite

Reaction of haloalkanes (1° or 2°) with sodium or potassium nitrite gives nitro alkane.

$$R - X + KNO_2 \rightarrow R - NO_2 + KX$$

$$\text{e.g.} \rightarrow CH_3CH_2Br + KNO_2 \rightarrow \underset{\text{Nitroethane}}{CH_3CH_2NO_2} + KBr$$

(3) Nitrile and isonitrile formation :

$$R{-}X + KCN \xrightarrow{\text{Ethanol, }\Delta} \underset{\text{Alkyl cyanide } \textit{or} \text{ Alkanenitrile}}{R - CN + KX}$$

$$\text{e.g.} \rightarrow CH_3CH_2I + KCN \xrightarrow[\Delta]{\text{Ethanol,}} \underset{\text{Propane nitrile}}{CH_3CH_2CN} + KI$$

$$R{-}X + AgCN \xrightarrow[\Delta]{H_2O/\text{Ethanol}} \underset{\text{Alkyl isocyanide } \textit{or} \text{ Alkyl isonitrile}}{R{-}NC} + AgX\downarrow$$

$$\text{e.g.} \rightarrow CH_3CH_2Br + AgCN \xrightarrow[\Delta]{H_2O/\text{Ethanol}} \underset{\text{Ethyl isonitrile}}{CH_3CH_2{-}NC} + AgBr\downarrow$$

(4) Williamson's ether synthesis :

Haloalkanes give ether on reaction with alcoholic sodium or potassium alkoxide.

$$R - X + NaOR' \xrightarrow[\Delta]{\text{alcohol}} R{-}O{-}R' + NaX$$

e.g.→

$$CH_3CH_2Br + NaOC_2H_5 \xrightarrow[\Delta]{\text{alcohol}} CH_3CH_2 - O - C_2H_5 + NaBr$$

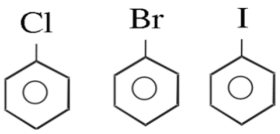
Bromo ethane sodium ethoxide ethoxy ethane

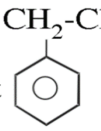
$$CH_3I + NaOC_2H_5 \xrightarrow[\Delta]{\text{alcohol}} CH_3OC_2H_5 + NaI$$

This reaction is known as Williamson's ether Synthesis.

7.3 Aryl Halides or Haloarenes

In haloarenes, halogen atom is directly attached with the sp2 hybridised C-atom of aryl group.



are called haloarenes. but 

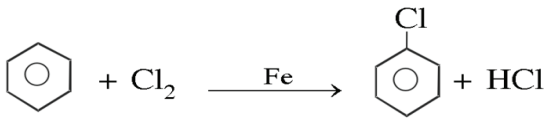
is not a aryl halide.

Aryl halides are less reactive than alkyl halide. Due to resonance, C-Cl bond gets double bond character, bond energy becomes very high so aryl halides are less reactive.

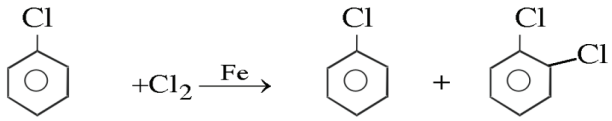
7.3.1 Preparation of aryl halides :

(i) halogenation :

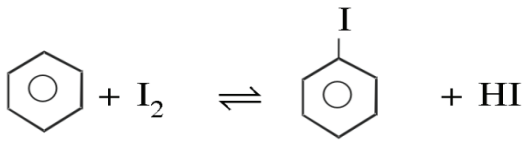
Chloroarenes and bromoarenes are prepared by reaction of halogens (Chlorine and bromine) with benzene derivative in presence of Lewis acids e.g. Fe, $FeCl_3$, $A1C1_3$ etc.



If halogen is used in large quantity, ortho and para isomers are formed because halogen is an ortho and para - directing group.

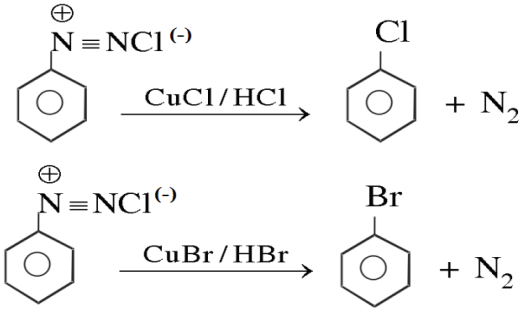


If we use I_2 instead of Cl_2 or Br_2, the reaction becomes reversible because HI produced during the reaction is a good reducing agent and converts aryl iodide back to the aromatic hydrocarbon.

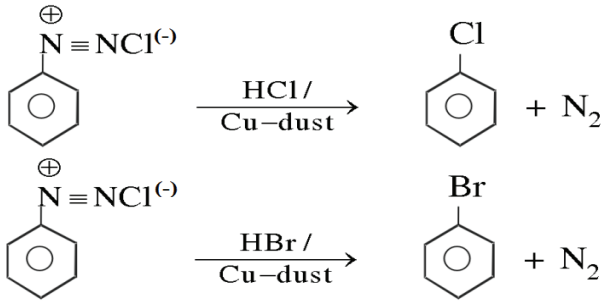


To Shift the equilibrium in forward, some oxidising agents like HNO_3, HIO_3, HIO_4 and HgO are used.

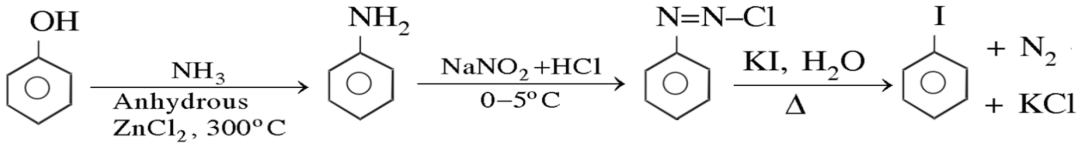
(2) Sandmyer reaction :



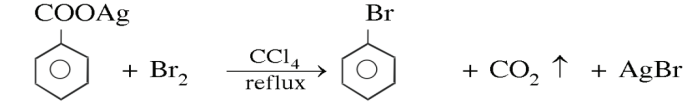
(3) Gattermann reaction :



(4) from phenol :

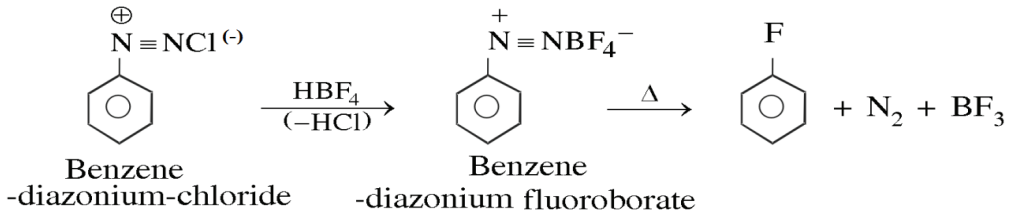


(5) Hunsdiecker reaction :



Silver benzoate

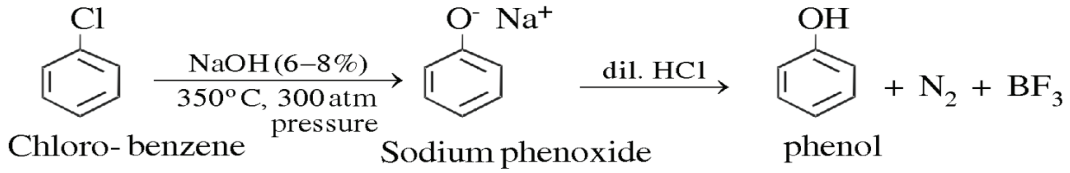
(6) Schiemann reaction :



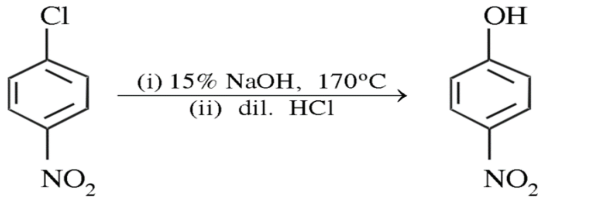
7.3.2 : Reactions of aryl halides :

(a) Aromatic nucleophilic substitution reaction by -OH group.

When chlorobenzene is re-fluxed with sodium hydroxide, it gives sodium phenoxide or phenol. As Chlorobenzene is less reactive, the reaction occurs under very drastic condition.



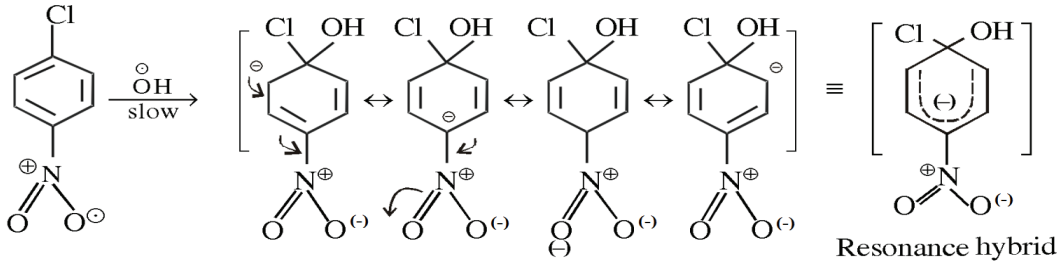
But when electron withdrawing group like $–NO_2$ group is present at ortho and para position with respect to Cl-atom, the nucleophilic substitution reaction becomes much easier.



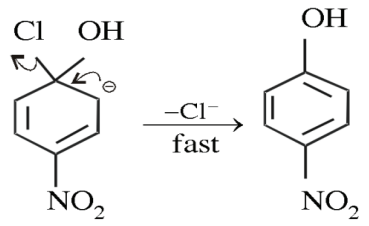
due to -R effect of $–NO_2$ group, die electron density of the benzene ring decreases, as a result nucleophilic attack becomes faster.

Mechanism: The reaction occurs in two steps—

Step-I

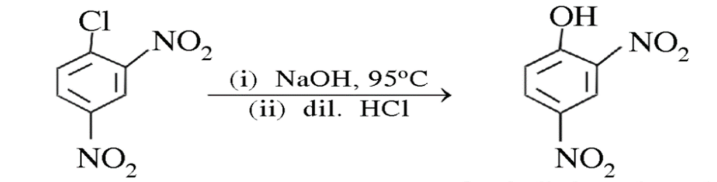


Step – 2

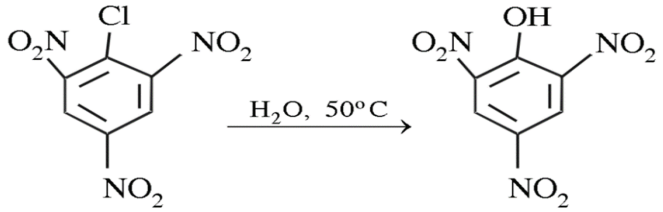


p-nitrophenol

like p-chloronitrobenzene, the reaction occurs through the same mechanism in o-chloronitrobenzene.

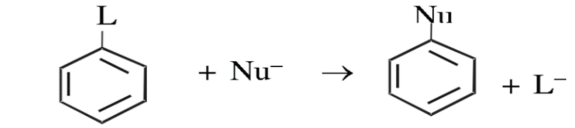


2, 4-dinitrophenol



2, 4, 6-trinitrophenol

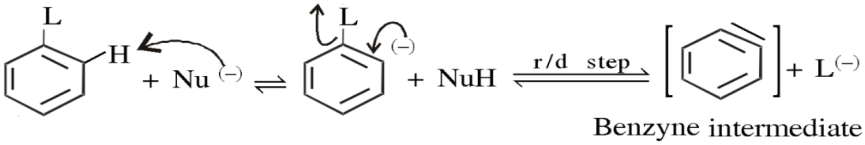
(b) Benzyne Mechanism : Elimination - addition Mechanism



where, L = Leaving group Nu^- = Nucleophile

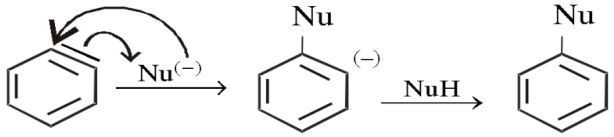
Mechanism :

Step - I : Elimination Step

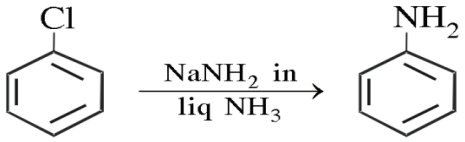


Benzyne intermediate

Step - II : Attack of Nu^-

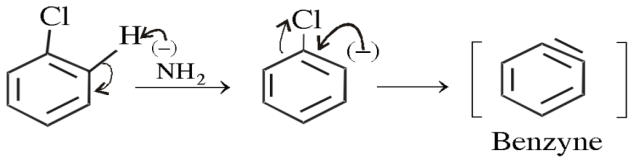


This is addition step. Benzyne formation is the r/d step. E.g.

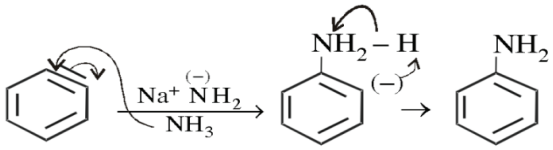


Mechanism :

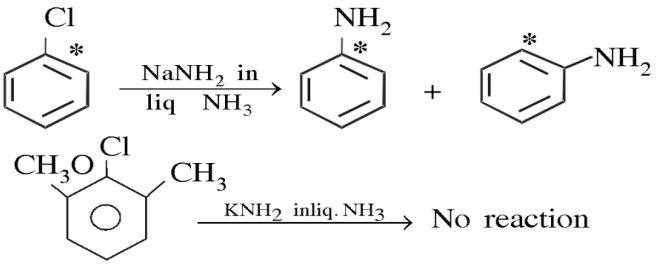
Step – I



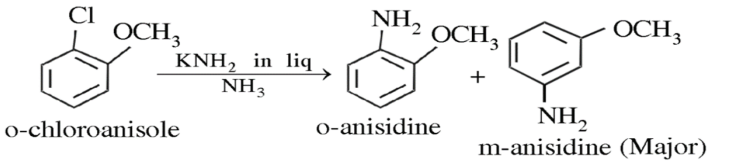
Step-II

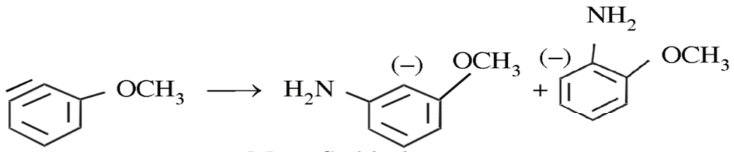


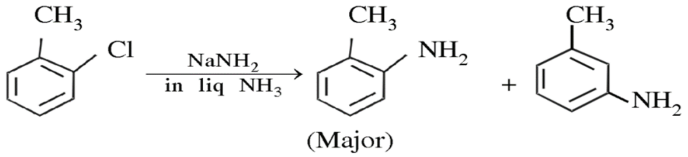
Evidence in favour of benzyne mechanism :



due to lack of ortho hydrogens no benzyne intermediate is formed. So no reaction takes place.







7.4 Reactivity and relative bond strength

Bond strength : C - F > C - Cl > C - Br > C - I

C - F 484 KJ moF1

C - Cl 338 KJ moF1

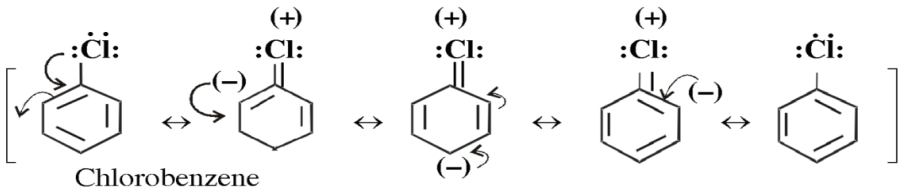
C - Br 276 KJ moF1

C - I 238 KJ mol"1

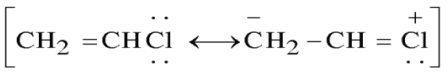
bond reactivity : C-F < C - Cl < C - Br < C - I

Stronger bonds are more difficult to break, making them less reactive. In addition, the reactivity can also be determined by the stability of the corresponding anion formed. A large electron density on F atom makes the F^- anion very less stable, so C-F bond is very less reactive. But iodine is large in size so I^- is very stable. Thus C-I bond is very reactive.

Aryl and Vinyl halides :



Chlorobenzene



Vinyl Chloride

due to resonance C-Cl bond gets partial double bond character bond energy becomes high, difficult to break. Thus less reactive.

7.5 Summary

- Alkyl halides are prepared by the free radical halogenation of alkanes, addition of halogen acids to alkenes, replacement of-OH group of alcohols with halogens using phosphorus halides, thionyl chloride or halogen acids.
- The boiling points of organohalogen compounds are comparatively higher than the corresponding hydrocarbons because of strong dipole-dipole and van der Waals forces of attraction.
- Aryl halide having electron withdrawing halogen substituents is ortho- and para-directing.
- Aryl halides can undergo many electrophilic aromatic substitution reactions similar to benzene like nitration, sulfonation, further halogenation and Friedel Crafts alkylation or acylation reactions.
- In the nucleophilic substitution reactions, alkyl halides undergo (3-elimination reaction. The halogen is removed from one carbon and a proton is removed from an adjacent carbon. A double bond is formed between the two carbons from which the atoms are eliminated. Therefore, the product of an elimination reaction is an alkene. Removal of a proton and a halide ion is called dehydrohalogenation.
- Nucleophilic substitution reactions in aromatic compounds proceed through a resonance stabilized anionic intermediate resulting from a nucleophilic attack of the aromatic ring. With the loss of halide ion from intermediate substituent product is formed.
- Elimination addition mechanism via benzyne mechanism is followed when the nucleophile is an exceptionally strong base (e.g. amide ion, NH_2^-) and the absence of the strong electron withdrawing groups.

7.6 Solved Problems

1. Convert the following compounds with proper reagents.

i) Benzyl Chloride → Benzyl alcohol

ii) Methyl magnesium bromide → 2-methyl propan–2–ol

iii) Propene → Propan-2-ol

iv) Ethyl magnesium Chloride → propan -1-ol

Answer:

i) 

ii) $CH_3-\underset{\underset{O}{\|}}{C}-CH_3+CH_3MgBr \xrightarrow{\text{dry ether}} H_3C-\underset{\underset{OMgBr}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow{H^+/H_2O} H_2C-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

iii) $CH_3-CH=CH_2 \xrightarrow{HBr} CH_3-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow{\text{aq. KOH}} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$

iv) $CH_3CH_2MgCl + HCHO \xrightarrow{\text{dry ether}} CH_3CH_2CH_2OMgCl \xrightarrow{H^+/H_2O} CH_3-CH_2-CH_2-OH$

2. Explain the following conversion with reason.

$$CH_2 = CH–CH_2–C \equiv CH + Br_2 \rightarrow \underset{Br}{\underset{|}{CH_2}}–\underset{Br}{\underset{|}{CH}}–CH_2–C \equiv CH$$

Hint : double bonds are more reactive than triple bond.

3. Write down the products :

(a) $CH_3 - Br + KCN \rightarrow ?$

(b) $C_2H_5 - Cl + aq.KOH \rightarrow ?$

Answer: a) CH_3CN, b) C_2H_5OH

4. R-Br, on reaction with AgCN, gives R-NC (alkyl iso-cyanide) while on reaction with NaCN or KCN. it gives R-CN (alkyl cyanide) - Explain.

Ans. CN- is a ambient nucleophile, as it has two donor centre. In presence of AgCN, the reaction takes place by SN1 mechanism. Ag+ ion, breaks the C-Br bond, precipitates as AgBr and forms the carbocation. Then, CN- attacks the carbocation via its more electronegative and electron-rich N-atom and as a result alkyl-isocyanide (R-NC) is formed.

$$\left[:\overset{(-)}{C} \equiv N: \longleftrightarrow :C = \overset{(-)}{\underset{..}{N}}: \right]$$

$$R - Br + Ag^{+}[CN]^{-} \rightleftharpoons \left[R - Br......\overset{+}{Ag} \right] [CN]^{-} \xrightarrow{Slow} R^{+} + AgBr \downarrow + [CN]^{-}$$

$$:C = \overset{(-)}{N}: + R^{+} \xrightarrow{fast} R - \ddot{N} = C:$$

Alkyl isocyanide

On the other hand, in presence of NaCN the reaction takes place by SN2 mechanism, as Na+ ion can not break the C-Br bond like Ag+ ion. In this case, the more polarisable and more nucleophilic C-atom of CN“ ion attacks R-Br Thus alkyl cyanide (R-CN) is formed.

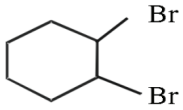
5. aq. KOH gives alcohol on reaction with alkyl chloride (R-Cl) but alcoholic KOH gives alkene - Why?

Answer: Strong bases and less polar solvents gives alkene by E2 elimination reaction alcohol is less polar than water and OEt- present in alcoholic KOH, is stronger base than OH- . So reaction of alcoholic KOH with alkyl chloride forms alkene. On the other hand, relatively less strong bases and more polar solvents responds to substitution reaction. OH- is weaker base than OEt- and water is more polar than alcohol so aqueous KOH, on reaction with alkyl chloride gives alcohol.

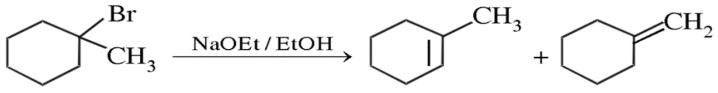
6. Write down the major products :

(a) 1-bromo-1-methyl cyclohexane $\xrightarrow{NaOEt/EtOH}$?

(b) 2-Chloro 2-methyl butane $\longrightarrow$?

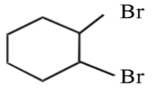
(c)  $\xrightarrow[196K]{NaNH_2/liq.\ NH_3}$

Answer:

(a) 

Major Pdt. (More substituted) Minor Pdt.

(b) $H_3C-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_3 \xrightarrow{NaOEt/EtOH} \underset{(Major)}{H_3C-\overset{\overset{CH_3}{|}}{C}=CH-CH_3} + \underset{(Minor)}{H_2C=\overset{\overset{CH_3}{|}}{C}-CH_2-CH_3}$

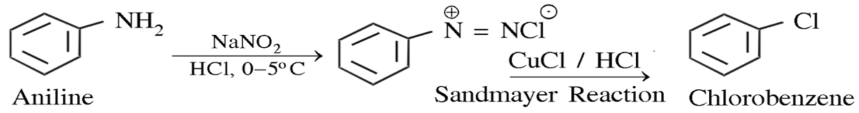
(c)  $\xrightarrow[196K]{NaNH_2/liq.\ NH_3}$ 

Cyclohexa-1,3–diene

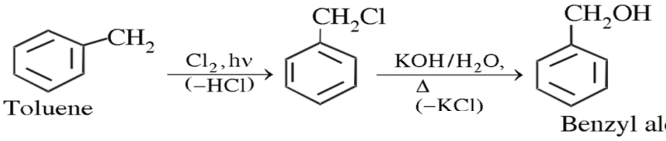
7. Convert the following

(a) Aniline → Chlorobenzene.
(b) Toluene → Benzyl alcohol
(c) Chlorobenzene → p-nitrophenol
(d) Benzene → Biphenyl.

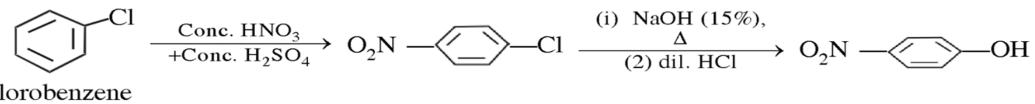
Answer:

(a) 

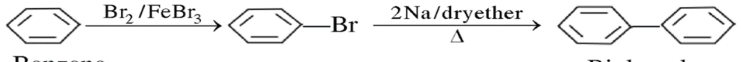
Aniline Sandmayer Reaction Chlorobenzene

(b) 

Toluene Benzyl alcohol

(c) 

Chlorobenzene

(d) 

Benzene Biphenyl

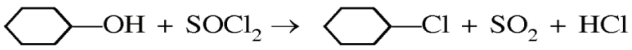
7.7 Exercises

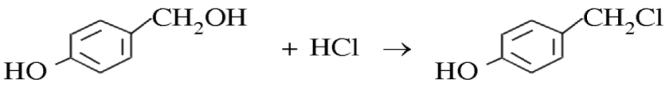
1. Predict the mechanism of the following reactions:

i) $CH_3CH_2CH = CH_2 + HBr \xrightarrow{\text{Peroxide}} CH_3CH_2CH_2 - CH_2 - Br$

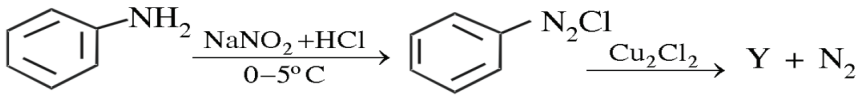
ii) $C_6H_5N_2Cl + KI \longrightarrow C_6H_5I + N_2 + KCl$

iii) $\begin{matrix} H & & H \\ & \diagdown & \diagup \\ & C=C & \\ & \diagup & \diagdown \\ H & & H \end{matrix} + Br_2 \xrightarrow{CCl_4} \begin{matrix} CH_2 - CH_2 \\ | \quad\quad | \\ Br \quad\quad Br \end{matrix}$

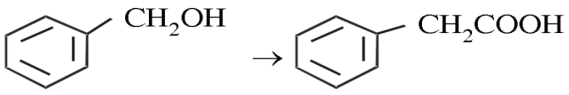
iv) 

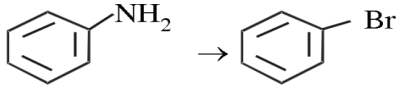
v) 

2. Identify 'Y' in the following reaction.



3. Convert the following

(a) 

(b) 

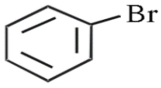
4. CH_3Cl hydrolyses readily than that of C_6H_5C1 - Why?

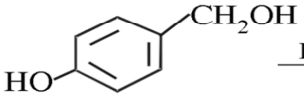
5. Why haloarenes are less reactive than haloalkanes?

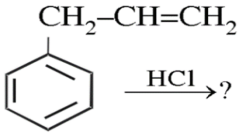
6. Write down the major products of the following reactions :

(a) 3-bromo -2, 2, 3-trimethylpentane $\xrightarrow{NaOEt / EtOH}$?

(b) $(CH_3)_3$ CBr + KOH $\xrightarrow{EtOH / \Delta}$?

(c)  $\xrightarrow{NaSH}$?

(d)  $\xrightarrow[\Delta]{HCl}$?

(e)  $\xrightarrow{HCl}$?

Unit 8: Alcohols

8.0 Objectives

By the end of the unit learners should be able to know about:

- The classification of alcohol on the basis of number of -OH groups present like monohydric alcohol, dihydric and polyhydric alcohols. Classification on the basis of nature of carbon attached with –OH group like primary, secondary and tertiary alcohols.
- Different methods of preparation of 1°, 2° and 3° alcohols using Grignard reagent. Ester hydrolysis, Reduction of carbonyl compounds.
- Chemical reactions of alcohols like reaction with sodium, Lucas test, esterification reaction, different oxidation methods, Oppeneauer oxidation Diols.
- Pinacol-Pinacolone rearrangement of diols.

8.1 Introduction

Alcohols are formed when a hydrogen atoms is aliphatic hydrocarbon is replaced by hydroxyl group. Alcohols are a versatile and important class of organic compounds that play a significant role in both daily life and various industrial applications. Characterized by the presence of one or more hydroxyl (-OH) groups attached to a carbon atom. Ethanol, perhaps the most well-known alcohol, is widely used in beverages, antiseptics, and as a biofuel. In addition to their practical uses, alcohols exhibit interesting chemical behaviour, undergoing reactions such as

oxidation, esterification, and dehydration. This chapter delves into the structure, classification as well as their synthesis and reactions.

8.2 Classification of alcohols

(i) According to number of hydroxyl group :

(a) Monohydric Alcohol : Contains only one -OH group. For example : Methanol (CH_3OH), Ethanol (CH_3CH_2OH) etc.

(b) Dihydric Alcohol : When an alcohol molecule conations two –OH groups, then they are called dihydric alcohol. For example : ethylene glycol ($HOH_2C\text{-}CH_2OH$)

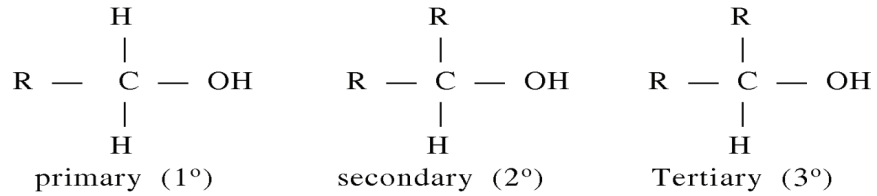
(c) Trihydric Alcohol : When an alcohol molecule contains three -OH group, then they are called trihydric alcohol. For example : Glycerol [$HOH_2C\text{-}CH(OH)\text{-}CH_2OH$]

(d) Polyhydric Alcohol : When an alcohol molecule contains more than three -OH group, e.g., sorbitol [$HOH_2C\text{-}(CHOH)_4\text{-}CH_2OH$]

(ii) According to the nature of hybridisation of the C-atom attached with the hydroxyl group :

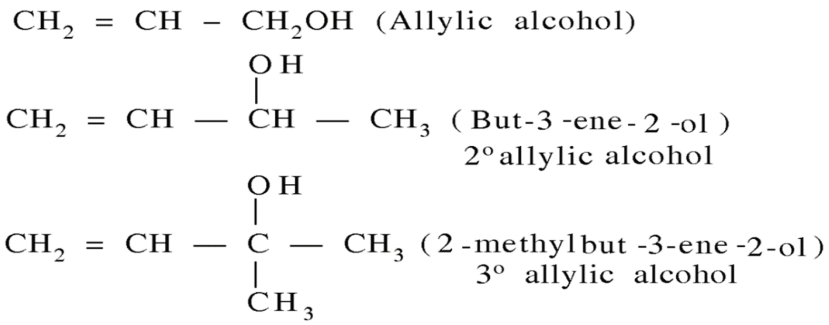
(A) Compounds containing Csp3-OH bond :

1. Primary (1°), Secondary (2°) and tertiary (3°) alcohol : When the -OH group of the alcohol is attached with primary, secondary and tertiary carbon atom then they are called primary (1°), Secondary (2°)and tertiary (3°) alcohol respectively.

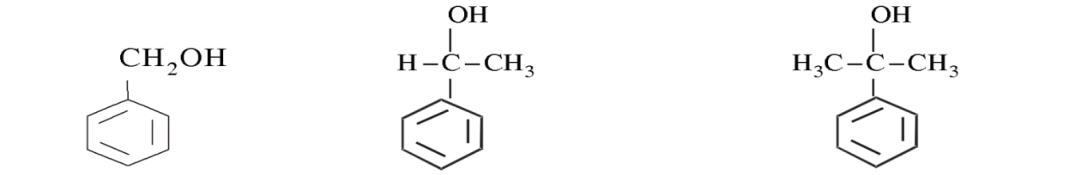


From the above structures it is cleared that the functional groups attached with primary (1°), secondary (2°) and tertiary (3°) alcohol are $–CH_2OH$, $(Me_3)_2CHOH$, and $(Me_3)_3COH$ respectively.

2. Allylic Alcohol : In these alcohols the -OH group is attached with a allylic carbon, (sp3 hybridised carbon which is directly attached with C = C) For example :



3. Benzylic alcohol : In this type of alcohol the carbon atom with which the -OH group is attached is directly linked with an aromatic ring , e.g.,

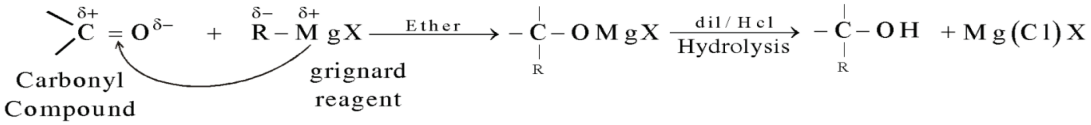


Benzylic alcohol (1°) 1-phenyl ethanol (2°) 2-phenyl-2-propanol (3°)

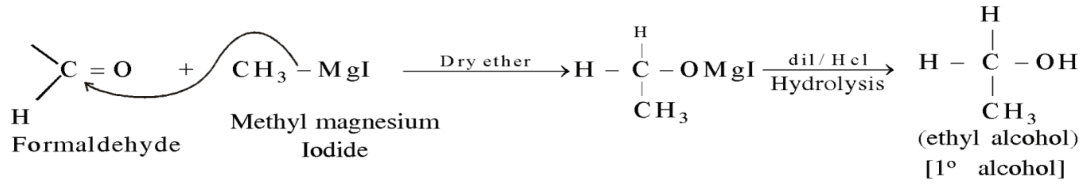
8.3 Preparation of Alcohols

8.3.1 Using Grignard reagent: (R-Mgx)

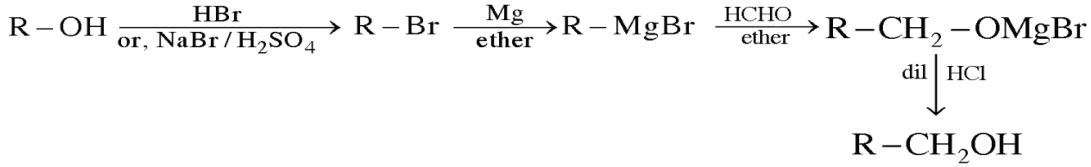
Grignard reagent by reacting with aldehyde or ketone produce primary, secondary and tertiary alcohol.



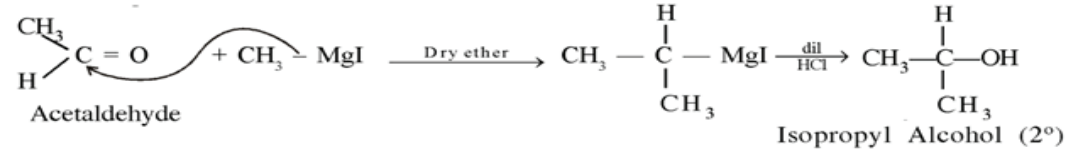
Preparation of 1° alcohol : Primary (1°) alcohol can be prepared by reacting Grignard reagent with formaldehyde (HCHO).

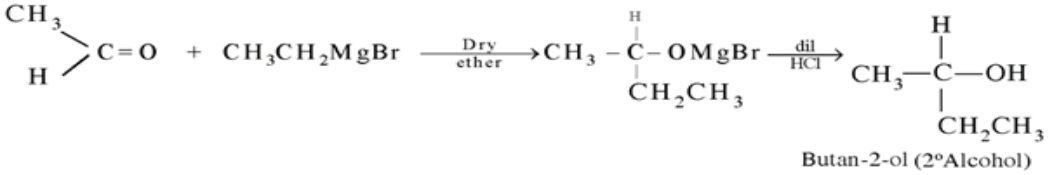


By using the above reaction lower alcohols can be converted to higher alcohol. For example :

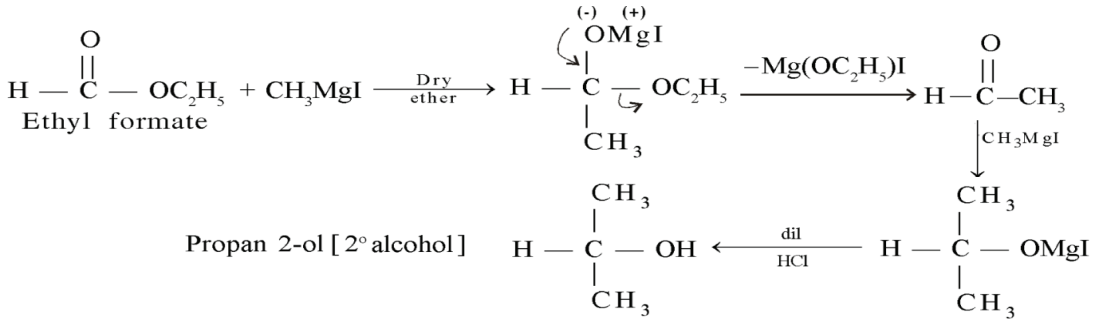


Preparation of 2° alcohol by Grignard reagent : Grignard reagent produce 2° alcohol by reacting with all the aldehydes except formaldehyde.

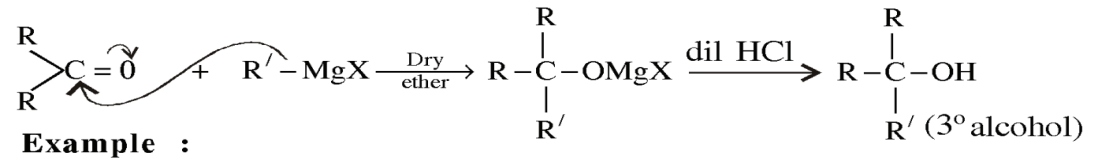




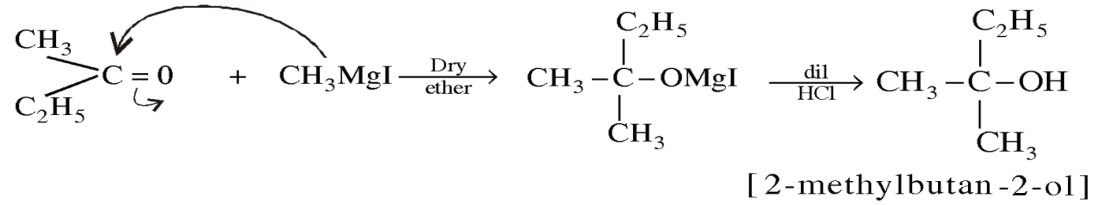
[*] Secondary alcohol can also be prepared by reaction with 1 mole of ethylformate and 2 mol of Grignard reagent.



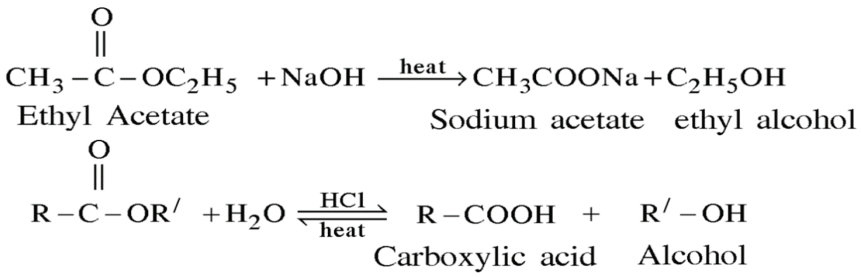
Preparation of 3° alcohol by using Grignard reagent : Grignard reagent in reaction with ketone forms tertiary (3°) alcohol For example :



Example :



8.3.2 By hydrolysis of ester : (Saponification reaction)



8.3.3 By reduction of aldehydes and Ketones :

$$\text{Aldehyde} \xrightarrow{\text{Reduction}} 1^{o}\ \text{alcohol}$$

$$\text{Ketone} \xrightarrow{\text{Reduction}} 2^{o}\ \text{alcohol}$$

Reducing agents : H_2 / Ni or Pt or Pd, Na / EtOH, $LiAlH_4$, NaBH4, Aluminium isopropoxide is isopropanol solution.

Example :

$$R-CHO \xrightarrow[\text{or, } Na / C_2H_5OH \text{ or, } LiAlH_4 \text{ or,} NaBH_4]{H_2/Ni \text{ or Pt or Pd}} R-CH_2OH\ (1^{o}\text{alcohol})$$

$$R-\overset{\overset{O}{\|}}{C}-R \xrightarrow[\text{or, } Na / C_2H_5OH \text{ or, } LiAlH_4 \text{ or,} NaBH_4]{H_2/Ni \text{ or Pt or Pd}} R-\overset{\overset{OH}{|}}{CH}-R\ (2^{o}\text{alcohol})$$

Meerwein Pondorf-Verley reduction :

$$R-\overset{\overset{O}{\|}}{C}-R + CH_3-\overset{\overset{OH}{|}}{CH}-CH_3 \xrightarrow[(\text{Aluminium isopropoxide})]{[(CH_3)_2CHO]_3Al} CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + R-\overset{\overset{OH}{|}}{CH}-R$$

isopropanol

$$* CH_3CHO \xrightarrow[\text{or } LiAlH_4 \text{ or } NaBH_4]{Na/EtOH \text{ or } H_2/Ni} CH_3CH_2OH$$

$$* CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\text{or } LiAlH_4 \text{ or } NaBH_4]{Na/EtOH \text{ or } H_2/Ni} CH_3-\overset{\overset{OH}{|}}{CH}-CH_3$$

(Propan−2−ol)

8.3.4 Reduction of Carboxylic acid :

Carboxylic acids on reduction with $LiAlH_4$ (lithium aluminium hydride) in dry ether medium produce primary alcohol. The -COOH group first converts to -CHO group and then to $-CH_2OH$ group.

$$R-COOH \xrightarrow[(ii)\ H_3O^{+}]{(i)\ LiAlH_4/\text{ether}} R-CH_2OH\ (1^{o}\text{alcohol})$$

$$CH_3-COOH \xrightarrow[(ii)\ H_3O^{+}]{(i)\ LiAlH_4/\text{ether}} CH_3CH_2OH\ (\text{ethanol})$$

8.3.5 By reduction of ester :

$$R-\overset{\overset{O}{\|}}{C}-OR' \xrightarrow[\text{or, } H_2/Ni \text{ or Pt or Pd}\ 175^oC,340\ atm]{Na\,/\,C_2H_5OH \text{ or, } LiAlH_4} R-CH_2OH \quad +R'-OH$$

1^o Alcohol $\quad 1^o, 2^o$ or 3^o alcohol

8.4 Reactions of Alcohol

8.4.1 Reaction with active metals like Na, K, A1 etc.

Alcohols are attacked by strongly electropositive metals e.g., Na, K etc; hydrogen is liberated and the alkoxide is formed : For

$$2C_2H_5OH + 2Na \longrightarrow 2C_2H_5ONa + H_2$$

The order of case of formation of an alkoxide with sodium or potassium is primary alcohol > secondary alcohol > tertiary alcohol.

8.4.2 Esterification reaction :

Alcohols react with carboxylic acid to form ester in presence of concentrated H_2SO_4, which is known as esterification reaction.

$$\underset{\text{carboxylic acid}}{R-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{alcohol}}{H-OR^1} \xrightarrow[H_2SO_4]{\text{Conc.}} \underset{\text{Ester}}{R-\overset{\overset{O}{\|}}{C}-OR'}$$

Rate of esterification of alcohol depends upon the size of the alkyl group of the carboxylic acid or alcohol. With increase in size of the alkyl group the rate of esterification decreases due to steric hindrance. The rate of esterification for alcohols follows the following order.

$CH_3OH > C_2H_3OH > (CH_3)_2CHOH > (CH_3)_3COH$

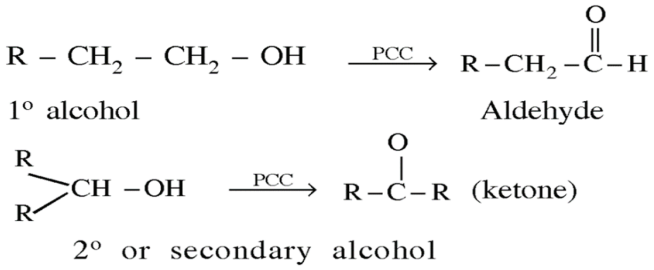
and for carboxylic acid the order is as follows :

$HCOOH > CH_3COOH > CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3C\text{-}COOH$

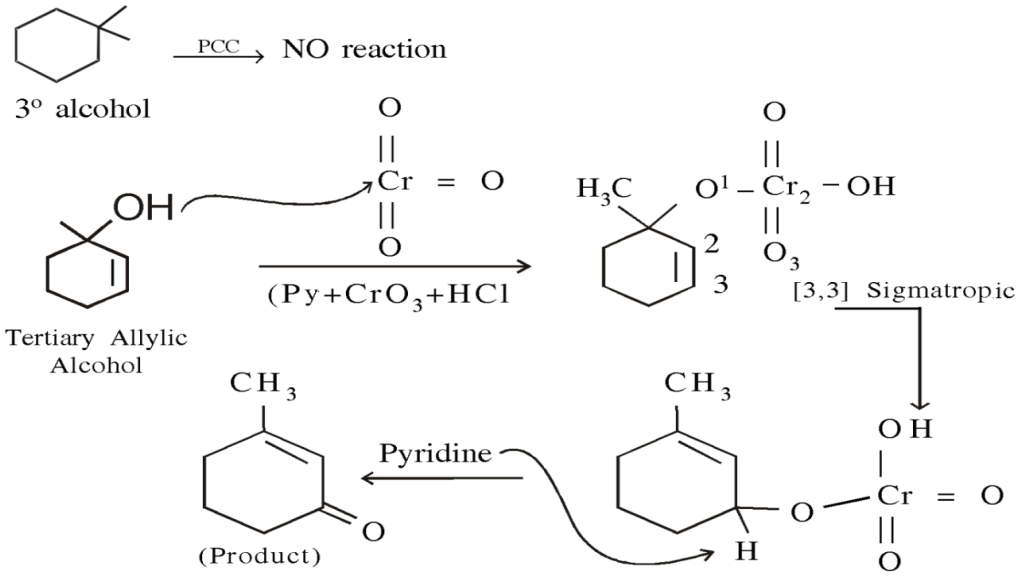
8.4.3 Oxidation of alcohols :

(i) Oxidation using pyridinium chlorochromate (PCC) :

PCC is the combination of three reagents (Pyridine + CrO_3 + HC1). CrO_3 is carcinogenic (cancer causing). It oxidised the alcohol into carbonyl compound. For example :



*** PCC does not oxidise tertiary alcohol (3° alcohol). But reacts with tertiary allylic alcohol.



Q. $CH_3CH=CH-CH_2OH \xrightarrow{PCC} ?$

Ans: $CH_3CH=CH-CH_2OH \xrightarrow{PCC} CH_3CH=CH-CHO$

Oxidation using acidic dichromate :

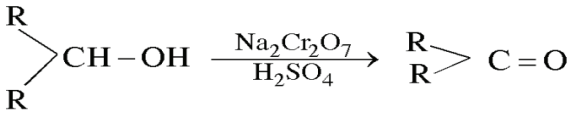
Primary alcohol on oxidation with sodium or potassium dichromate in H_2SO_4 gives, aldehyde which are further oxidised to carboxylic acid.

$$R-CH_2OH \xrightarrow{Na_2Cr_2O_7 \,/\, H_2SO_4} R-CHO \xrightarrow{Na_2Cr_2O_7 \,/\, H_2SO_4} R-COOH$$

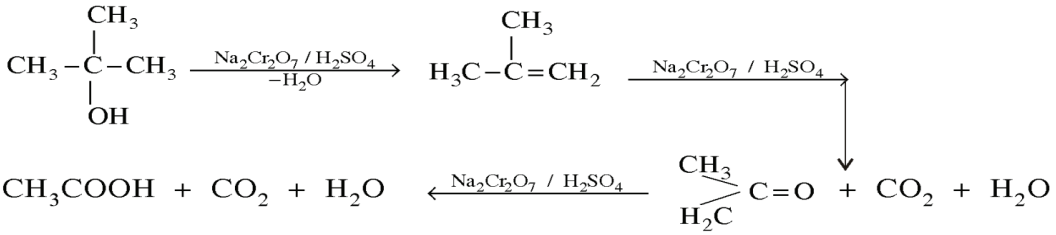
For Example :

$$CH_3CH_2OH \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} CH_3-CHO \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} CH_3-COOH$$

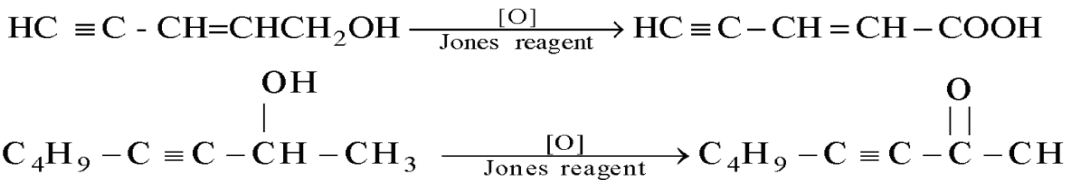
Secondary alcohols on the other hand give ketones which usually do not undergo further oxidation.



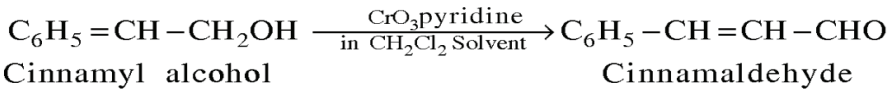
Tertiary alcohols have very less tendency to undergo oxidation. They are oxidised by strong oxidants in acidic condition by $K_7Cr_7O_7$ / H_2SO_4 or $KMnO_4$ / H_2SO_4. The tertiary alcohols first converts to alkene and there after the alkene is oxidised and form ketone with less number of carbon atoms which then further oxidised to form carboxylic acid with less number of carbon atoms. For example :



Jones reagent : (Combination of CrO_3, H_2SO_4 and acetone solvent) It is useful for the oxidation of alcohols which contains C - C double or triple bonds, allylic or benzylic C-H bonds and other sensitive groups. It is carried out at 0° - 20°C.

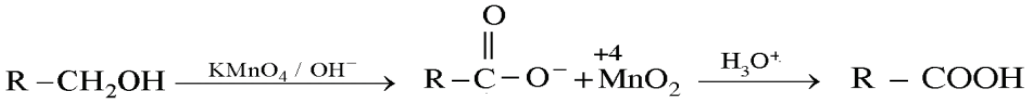


Collins reagent : Chromium trioxide-pyridine complex is known as Collins reagent and is useful for the oxidation of alcohol containing acid sensitive groups. Oxidations are generally carried out in CH_2C1_2 solution under anhydrous condition. For example :



(iii) Oxidation using alkaline $KMnO_4$:

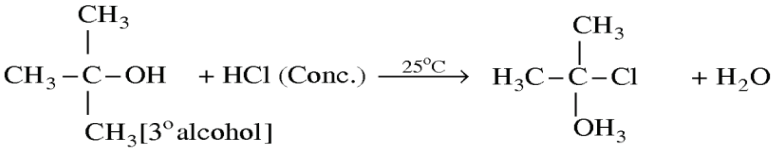
Another useful reagent for oxidising primary alcohols to carboxylic acids is potassium permanganate ($KMnO_4$) in basic solution.



Potassium permanganate is not used for the oxidation of secondary alcohols to ketones because many ketones react further with alkaline potassium permanganate..

8.4.4 Reactions of alcohols with hydrogen halides (HX) :

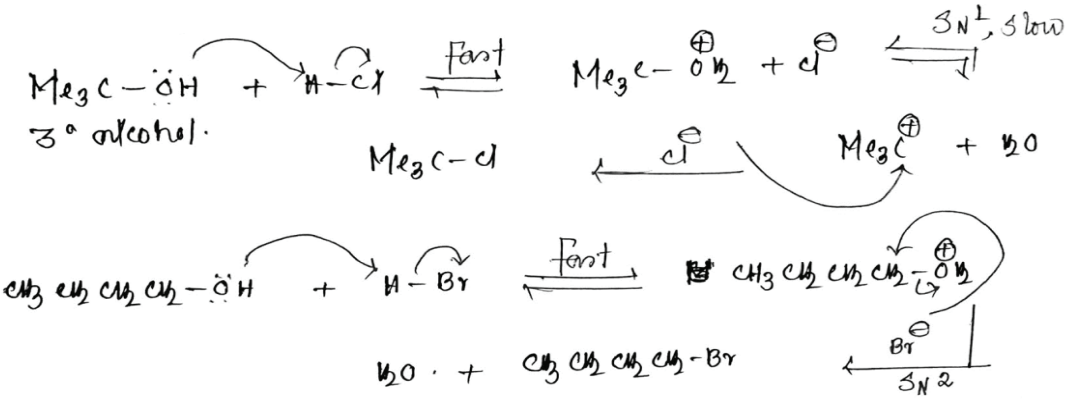
Alcohols react with hydrogen halides (HX. X = I. Br, Cl) to Form Haloalkane. For example :



$$CH_3CH_2CH_2CH_2OH + HBr\ (Conc.) \xrightarrow{reflux} CH_3CH_2CH_2CH_2Br + H_2O$$

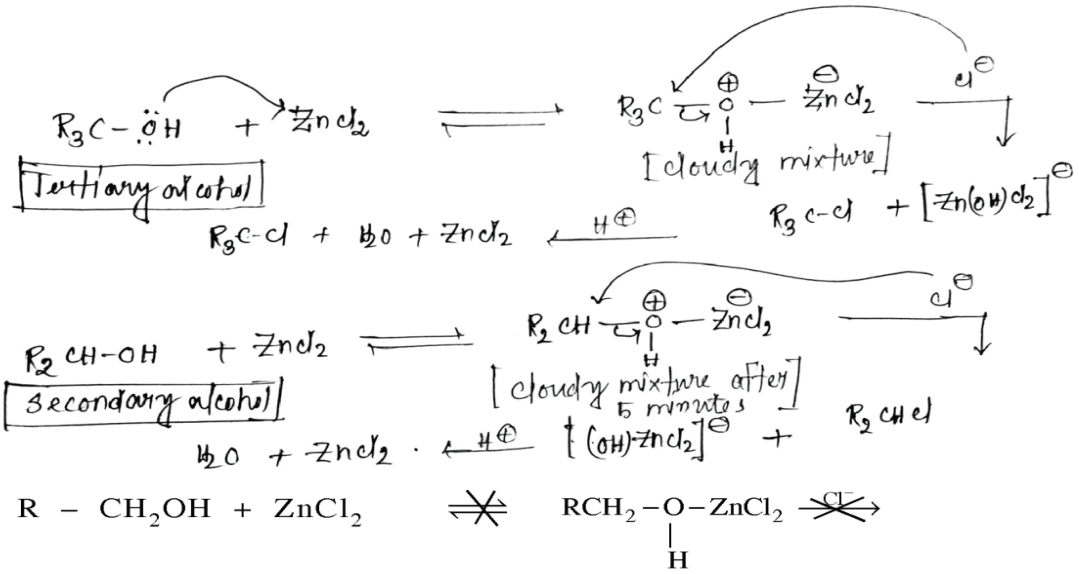
(1^o alcohol)

Mechanism : In case of tertiary alcohol the reaction proceeds through SN1 pathway and for primary or secondary alcohol the same reaction proceeds via SN2 pathway generally



The reaction of tertiary alcohols with hydrogen halides are much faster than the primary alcohols. Because the tertiary carbocation is more stable than primary or secondary carbocation. The reactivity order of the alcohols towards the halogen acids is 3° > 2° > 1°. On the other. the reactivity order of hydrogen halides (HI, HBr, HC1) is HI > HBr > HC1. This is because of the higher nucleophilicity of the I" ion. The nucleophilicity order of the hallides ions are I- > Br- > Cl- .

8.4.5 Lucas' Test : Lucas' reagent is a solution of anhydrous zine chloride ($ZnCl_2$) in concentrated hydrochloric acid. (HC1). Lucas' test tells us whether as alcohol is primary, secondary or tertiary. The given alcohol is mixed with anhydrous $ZnCl_2$ is concentrated HC1 solution. A tertiary alcohol reacts immediately and a cloudiness develops, forming tert-alkyl chloride. For secondary alcohols the cloudiness develops within five minutes, but a primary alcohol does not form cloudiness at all at room temperature. It was named after Howard Lucas.



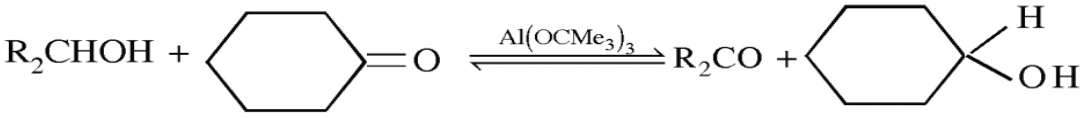
$$R - CH_2OH + ZnCl_2 \not\rightleftharpoons RCH_2-O(H)-ZnCl_2 \not\rightarrow$$

8.4.6 Oppeneaur Oxidation :

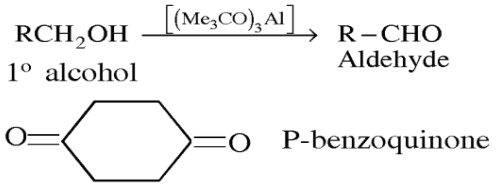
The reaction is the reverse of Meerwein-Ponndorf-verley reduction. The reaction involves the oxidation of a secondary alcohol with a ketone and a base to the corresponding ketone of the alcohol.

Commonly used ketones are acetone, methyl ethyl ketone and cyclohexanone. Commonly used bases are aluminium tert-butoxide, aluminium isopropoxide, potassium tert-butoxide etc. Thus when a secondary alcohol in acetone or cyclohexanone is refluxed with alumunium tert-butoxide in benzene or toluene solution, the secondary alcohol is dehydrogenated to a ketone and the hydrogens are transferred to acetone or cyclohexanone converting them to alcohols

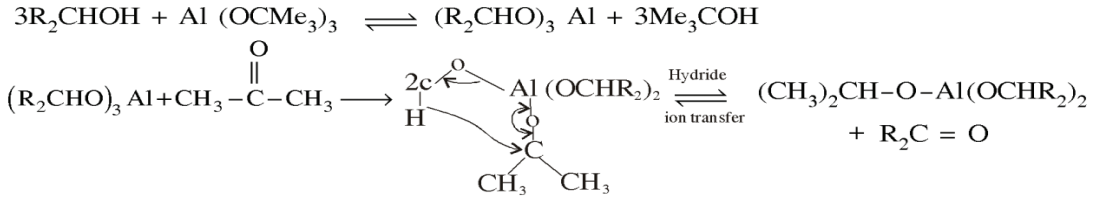
$$\underset{2^o\ \text{alcohol}}{R_2CHOH} + \underset{\text{Acetone}}{(CH_3)_2CO} \overset{Al(OCMe_3)_3}{\rightleftharpoons} \underset{\text{Ketone}}{R_2CO} + \underset{2^o\ \text{alcohol}}{CH_3CHOHCH_3}$$



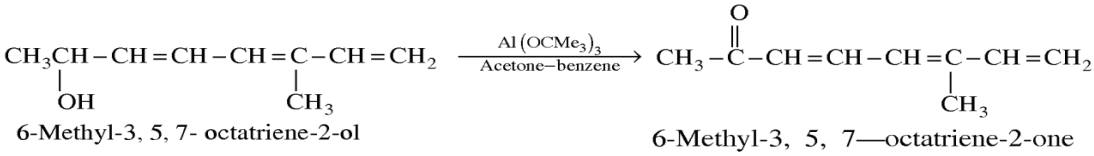
Primary alcohols may also be oxidized to aldehydes if acetone is replaced by a better H acceptor. e.g. benzoquinone. The equilibrium can be controlled by the amount of acetone, an excess of which favours the oxidation of the alcohol



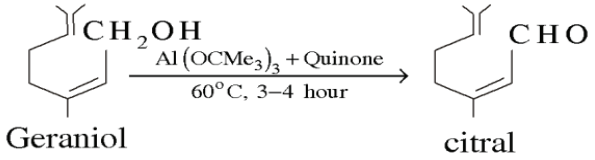
Mechanism : The mechanism is the reverse of MPV reaction. The alcohol and aluminium tert-butoxide react to form aluminium derivative of the 2° alcohol.



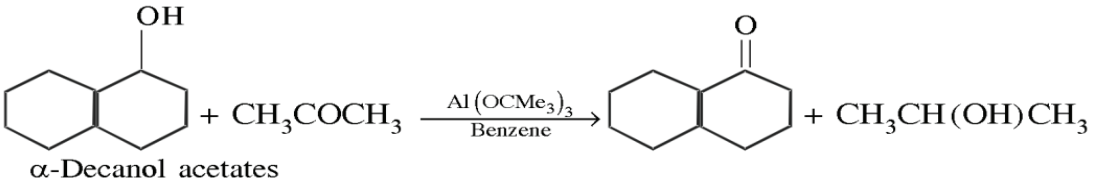
Application: 1. The reagent is particularly useful for oxidising unsaturated alcohols because it does not affect the double bonds.



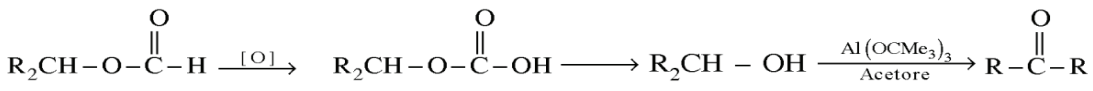
2. Primary unsaturated alcohols have been oxidized to aldehydes in the presence of good hydrogen acceptors e.g., p-benzoquinone. In some cases, acetaldehyde or cinnamaldehyde have been used.



3. Alicyclic alcohols have been oxidised to alicyclic ketones.



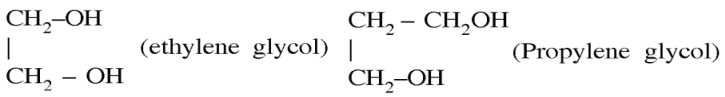
4. Formates (But not acetates or benzoates) have been oxidized to ketones



5. The (β, γ unsaturated alcohols undergo oxidation with migration of double bond to form α, β unsaturated ketones.

8.5 Diols or dihydric alcohols

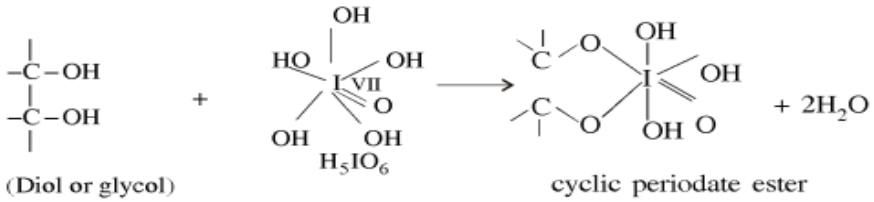
When an alcohol molecule contains two -OH groups, then they are called diols or dihydric alcohols. They are classified as α, β, γ ... glycols, according to their relative positions of the two hydroxyl groups, α is the 1, 2, glycol, β is 1, 3, glycol, γ is 1, 4 glycol etc. The commonest glycols are the α-glycols. For example :



8.6 Oxidation of diols

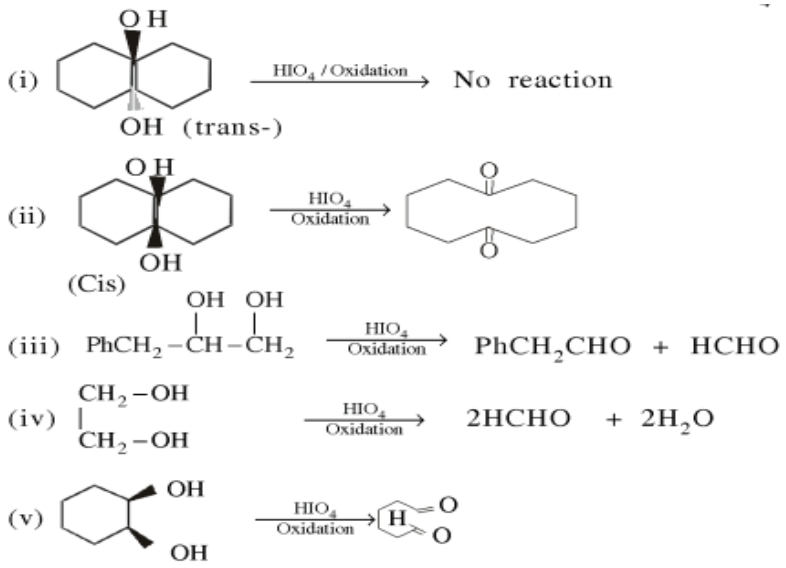
8.6.1 Oxidation of diols using periodic acid (H_5IO_6) :

Periodic acid is commercially available as $HIO_4.2H_2O$ often abbreviated as H_5IO_6. Periodic acid is a fairly strong acid (pKa = -1.6) The cleavage of diols with HIO_4 takes place through a cyclic periodate ester intermediate.



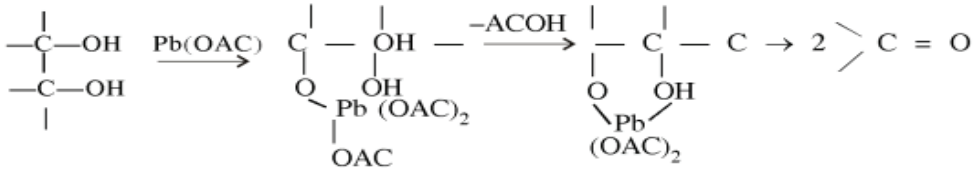
The cyclic periodate ester spontaneously breaks down forming two moles of carbonyl compound.

A glycol that cannot, form a cyclic ester intermediate is not cleaved by periodic acid. For this reason the trans diols are not oxidised by HIO_4. For example.

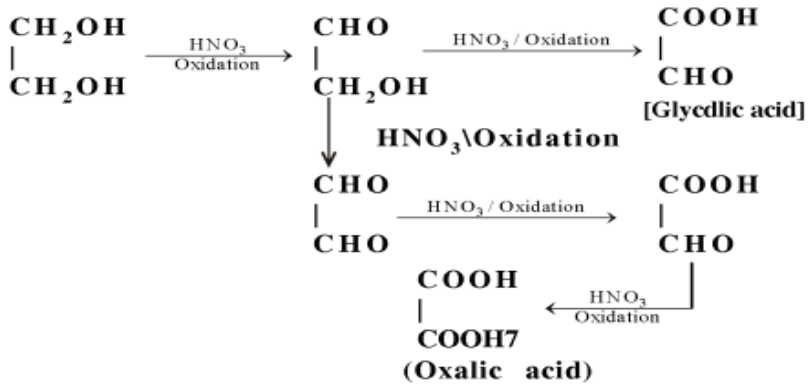


8.6.2 Oxidation of diols by using lead tetracetate [Pb(OAC)$_4$]

Oxidative clearage by lead tetracetate the same mechanism as the oxidation by HIO_4 ; i.e., the reaction takes place through the formation of a cyclic ester intermediate. Fead in $Pb(OAC)_4$ is in +IV oxidation state and after the oxidation of the diols itself gets reduced to +II state.

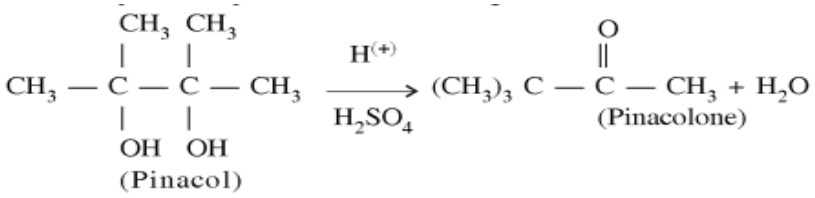


8.6.3 Oxidation of diols by using nitric acid (HNO_3):

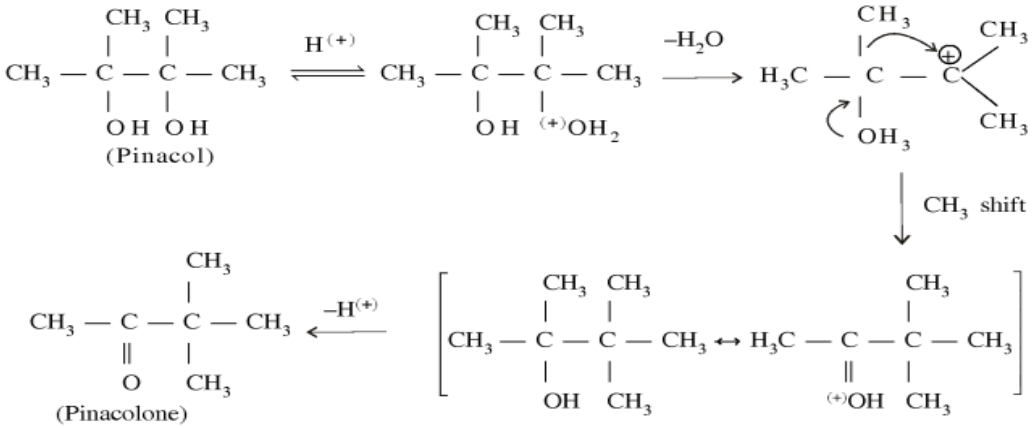


8.7 Pinacol-pinacolone rearrangement

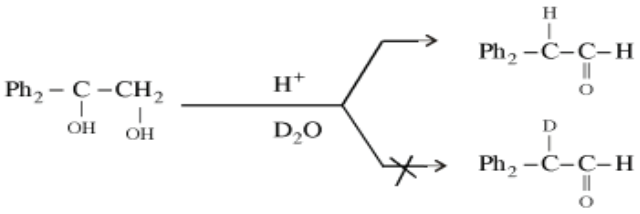
When 1, 2 or vicinal diol (glycols) are treated with acids. They undergo a facile dehydrative rearrangement to yield a ketone or aldehyde. This is known as pinacol pinacolone rearrangement.



Mechanism :-



It is an intramolecular rearrangement which is proved by a labelling experiment when the following pinacol rearrangement involving a hydride shift is carried out is D_2O, no deuterium is found to be incorporated in the final rearrangement product.

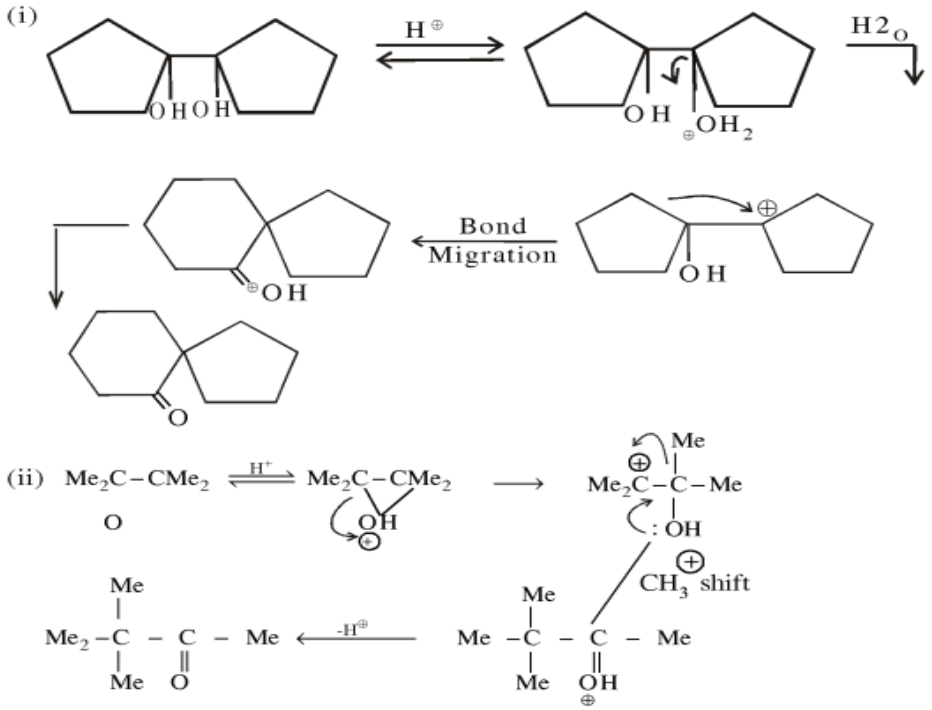


The relative migratory aptitude depends on the electron donating ability of the groups. Since the rearrangement involves movement of the migrating group with its bonding electrons to an electron deficient centre. The migrating tendency of a group may sometime depends on :

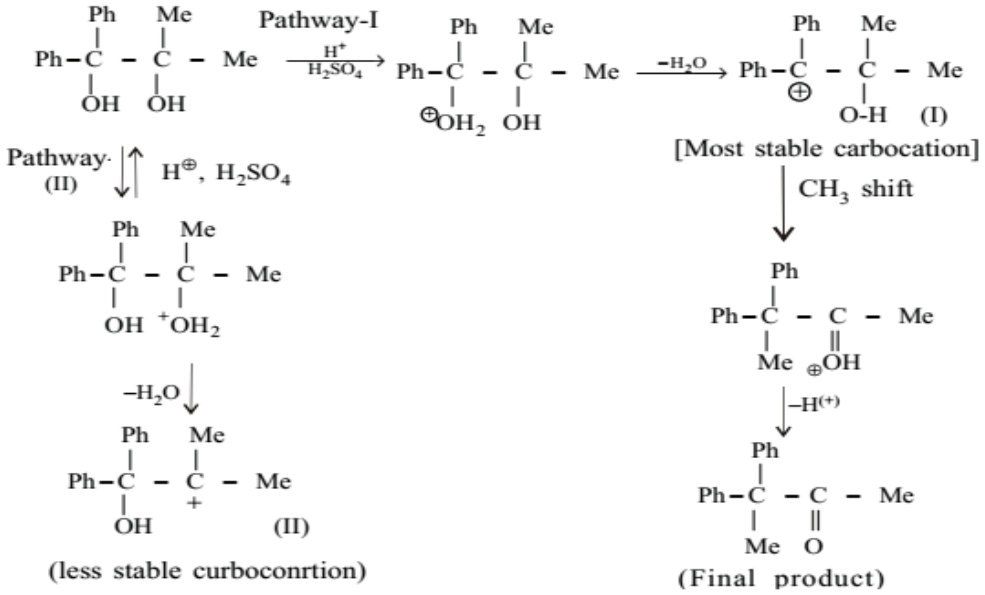
(i) Its position in the most stable conformation of the molecule.

(ii) Weather the group, that migrates produce the most stable conformation. In general the relative migratory order is found to be : p-$MeOC_6H_4$- > C_6H_5- > p-$C1C_6H_4$- > o-$MeOC_6H_4$ > H > R

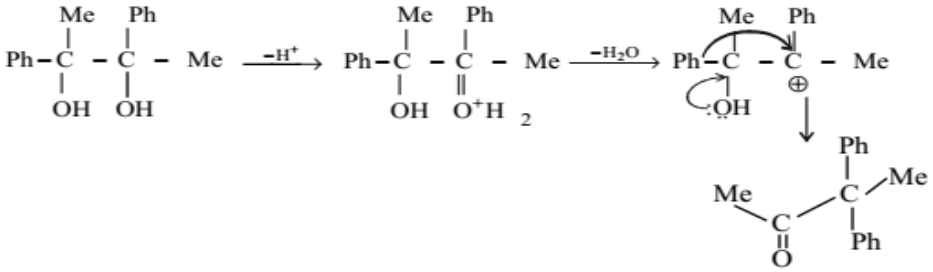
Some examples of pinacol-pinacolone rearrangement :



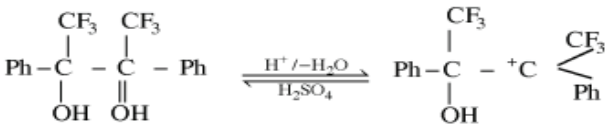
(iii) The isomeric pinacols (A) $PhOC(OH)C(OH)Me_2$ and (B) PhMeC(OH)C(OH)PhMe undergo rearrangement to give the common product.



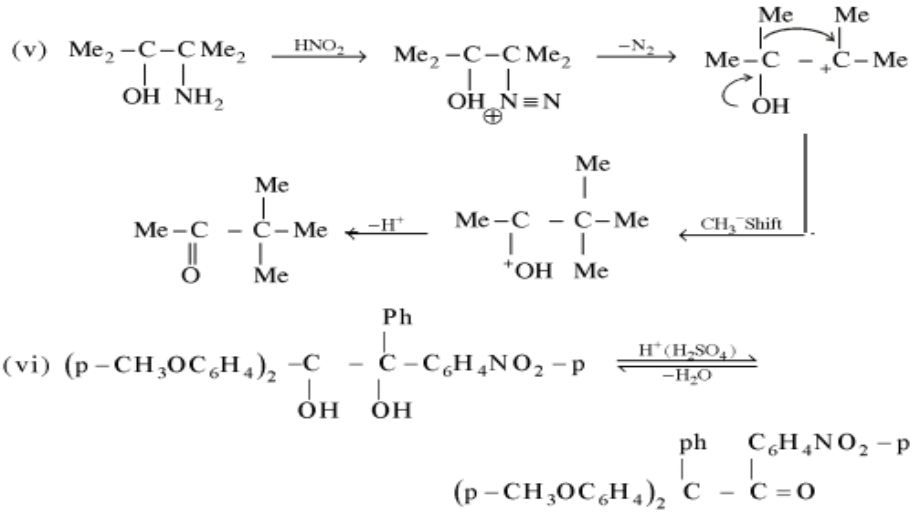
The reaction proceeds via the pathway I, which produce the more stable carbo cation. The carbocation (I) is more stable than (II) due to the delocalization of the (+)ve charge with the double bonds of phenyl rings.



(iv) The following pinacol is relatively unreactive under conditions which give pinacol-pinacolone rearrangement.



The carbocation produced is highly destablized by the strongly electron withdrawing -CF_3 group. So the reaction does not proceed.



The -OH group on C-1 than on C-2 migrates to from the more stable carbocation (resonance stabilized by two p-anisyl group) migrates is preference to p-nitrophenyl because migration leads to a more stable phenonium ion intermediate.

8.8 Summary

In this unit we have learnt that:

- Alcohols are compounds in which a hydrogen of alkane has been replaced by an-OH group and are classified as monohydric, dihydric, trihydric or polyliydric on the basis of-OH group present. The monohydric alcohols can be classified into 1°, 2° and 3° alcohols.
- The amphoteric nature of alcohols has also been described in this unit. As an acid, it ionizes to form an alkoxide ion (RO^-) and hydrogen ion (H^+) in the presence of a base, while in presence of an acid, the alcohol may function as a base and can accept a proton (H^+).
- Alcohols can be oxidized to aldehyde, ketones or carboxylic acids depending upon the strength of oxidizing agents. The alcohol, aldehyde and acid retain the same number of carbon atoms.
- Strong oxidizing agents such as hot alkaline $KMnO_4$ or CrO_3 in H_2SO_4 will oxidize primary alcohols to carboxylic acid. 2° alcohols oxidize to a ketone, which cannot be oxidized any further. In acidic solutions, 3° alcohols can be oxidized to give a mixture of ketone and acid, both with fewer carbon atoms than the alcohol.
- The order of the relative ease of dehydration of alcohols is 3°> 2°>1 .

8.9 Exercises

1. How will you differentiate between a primary, secondary and tertiary alcohol? 5

2. What product would you obtain when formaldehyde is treated with CH3MgI? 2

3. Give any two preparatory method of isopropyl alcohol. 2

4. Convert : 2 Propanol to 1 propanol. 2

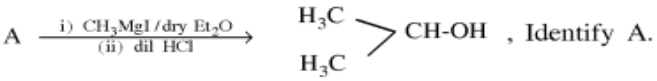
5. What is Lucas' reagent? Which type of alcohol does not react with Lucas' reagent at normal temperature? (1+1)

6. Which reagent is used in Oppenauer oxidation? 1

7. How will you prepare primary and tertiary alcohol by using Grignard reagent?

8. Write a short note on Oppenauer oxidation. 2

9. What is PCC? What product is obtained when is treated with ethyl alcohol. (1+1)

10.  , Identify A.

Unit 9: Phenols

9.0 Objectives

By the end of the unit learners should be able to know about :

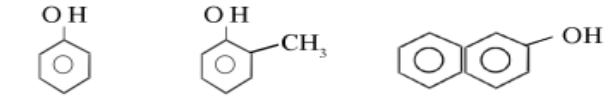
- The structure and bonding of phenol.
- To study physical and chemical properties of phenols, their acidic characters.
- General methods of preparation of phenols.
- Various chemical reactions, characteristic electrophilic substitution reactions and some name reactions involving phenols.

9.1 Introduction

Aromatic compounds that contain one or more hydroxyl groups (-OH) bonded directly to benzene or benzenoid ring such as napthalene are called phenols. They are classified as monohydric, dihydric, trihydric etc phenols, as they contain one, two, three etc hydroxy groups attached to the aromatic ring.

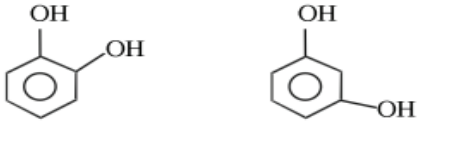
Examples of each kinds are given below.

Monohydric phenols



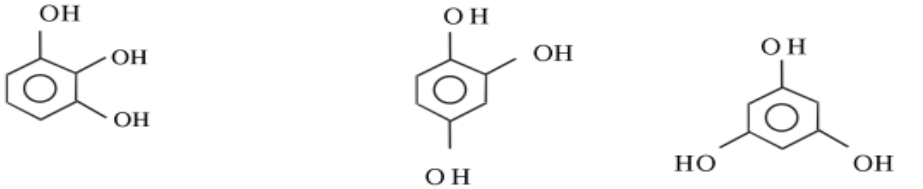
Benzene (Phenol) | 2Methylphenol (O–Cresol) | 2-Napthol (β-Napthol)

Dihydric Phenols :



Benzene-1, 2-diol (Catechol) | Benzene-1, 3-diol (Resorcinol) | Benzene-1, 4-diol (Hydroquinone or quinol)

Trihydric phenols :



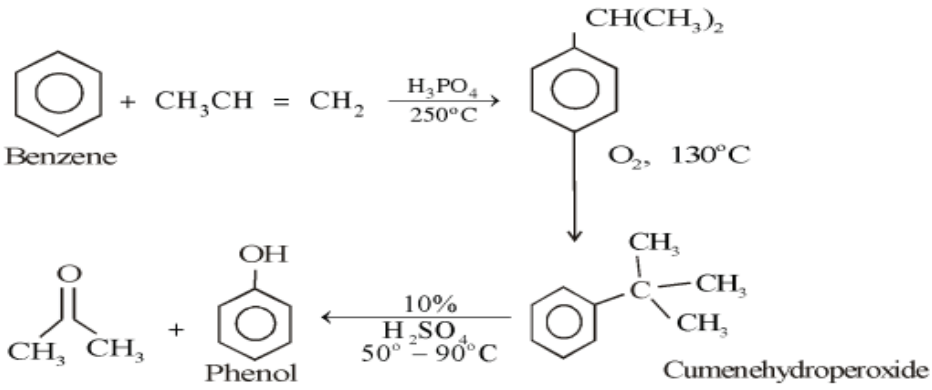
Benzene-1,2, 3-triol (Pyrogallol) | Benzene-1, 2, 4-triol (Hydroxyquinol) | Benzene-1, 3, 5-triol (Phloroglucinol)

Phenol was first isolated by Runge in 1834 from coal tar. He named it carbolic acid (Carbo = coal ; oleum = 0:1). Its systematic name should be benzenol but it is often called phenol because phene is an old name of benzene. It has now become an accepted systematic name.

9.2 Preparation of Phenol

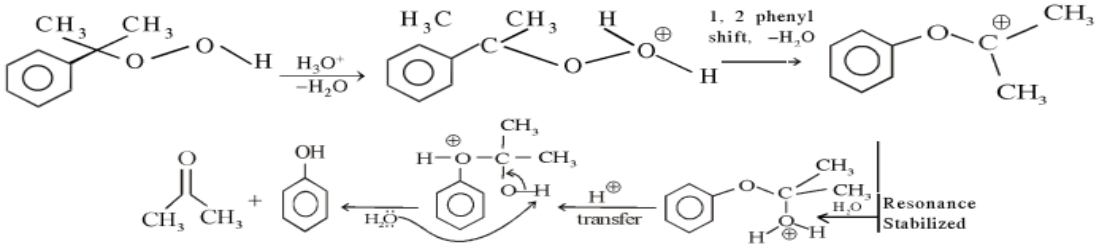
9.2.1 The Cumene Process

The synthesis begins with Fridel-Crafts alkylation of benzene with propene in the gas phase in the presence of phosphoric acid on an inert solid as catalyst at 250°C under pressure, to produce isopropylbenzene, often called cumene. Cumene is then oxidised to cumene hydroperoxide by passing air through the hot liquid. Cumene hydro-peroxide is then treated with the hot dilute sulphuric acid (10%) to produce phenol and acetone. The reaction involves acid-catalysed hydrolysis involving rearrangement. Most of the worldwide production of phenol is now based on this method.



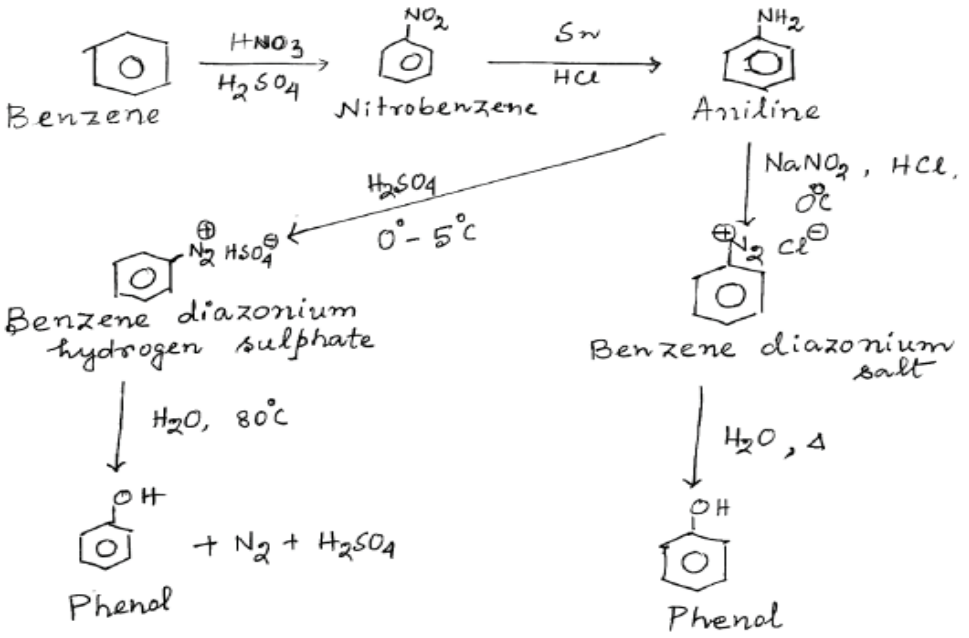
Mechanism

The acid catalysed conversion of cumene hydroperoxide to phenol and acetone occurs by the following mechanism.



9.2.2 Diazoiiium Salt

When we treat an aromatic primary amine with nitrous ($NaNO_2$+HCl) acid at 273-278K, we can easily obtain diazonium salts. These diazonium salts are highly reactive in nature. Upon warming with water, these diazonium salts finally hydrolyse to phenols. We can also obtain phenols from diazonium salts by treating it with dilute acids.



9.3 Nitration Reaction

Substitution of a hydrogen atom in an aromatic nucleus by a -NO_2 group is known as nitration reaction. Aromatic nitration reaction is irreversible and kinetically controlled. Several nitration agents for the reaction are given below :

(a) Concentrated glacial acetic acid + concentrated HNO_3

(b) Dilute nitric acid.

(c) (Concentrated HNO_3 + Concentrated H_2SO_4) in mixed acid (M.A) in 1:1 ratio.

(d) Fuming HNO_3 + Concentrated H_2SO_4

(e) Fuming HNO_3+ Fuming H_2SO_4

(f) Fuming HNO_3 in acetic anhydride.

Among these nitrating agents, mixed acid (Concentrated HNO_3 + Concentrated H_2SO_4) is the most common nitrating agent, while the others are used depending on varying substrate.

Mechanism of nitration reaction

(a) With concentrated HNO_3 as a nitrating agent one mole of acid acts as an acid and another as a base.

$$HNO_3 \rightleftharpoons H^+ + NO_3^-$$

$$H^+ + HNO_3 \rightleftharpoons H_2O + \overset{\oplus}{N}O_2$$

$$2HNO_3 \rightleftharpoons \overset{\odot}{N}O_3 + H_2O + \overset{\oplus}{N}O_2$$

(b) With mixed acid (Conc HNO_3 + Conc. H_2SO_4) an acid-base reaction in found. Here H_2SO_4 acts as an acid and HNO_3 acts as a base.

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

$$HNO_3 + H^+ \rightleftharpoons H_2O + NO_2$$

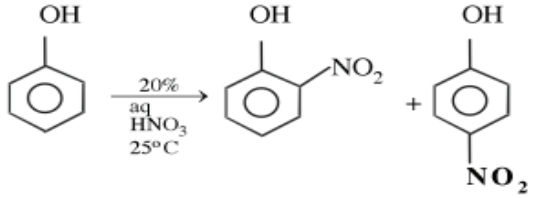
$$H_2O + H_2SO_4 \rightleftharpoons H_2O^+ + HSO_4^-$$

$$HNO_3 + 2H_2SO_4 \rightleftharpoons H_3O^+ + N^+O_2 + 2HSO_4^-$$

Nitration :

(i) With dilute HNO_3

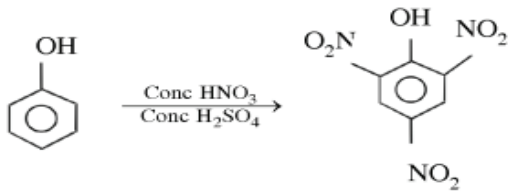
Phenol being very reactive can be nitrated with dilute aqueous nitric acid at room temp to yield a mixture of O-nitrophenol (major) and p-nitrophenol (minor). The yield is low because a considerable amount of phenol undergoes oxidation at the ring to yield tarry products. Yet the reaction is useful because from the product mixture the components can be separated by steam distillation.



N-Nitrophenol (30-40%) p-Nitrophenol (15%)

(ii) With Concentrated HNO_3

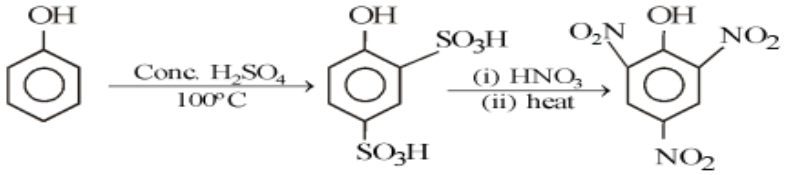
When phenol is treated with a mixture of concentrated HNO_3 and concentrated H_2SO_4 2, 4, 6-trinitro-phenol (picric acid) is formed. The yield is low due to oxidation of a large amount of phenol by nitric acid into undesirable tarry products.



2, 4, 6 Trinitrophenol (Picric acid)

Picric acid can be prepared by the following two methods :

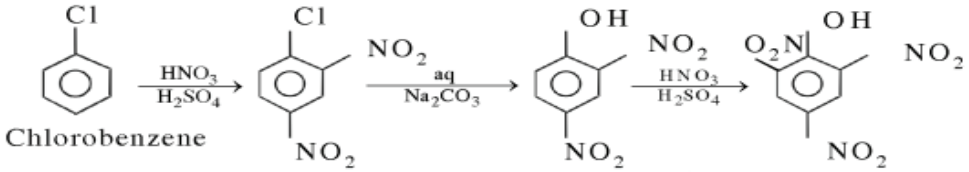
Method 1



Picric acid
(90%)

At higher temperature -SO_3H groups are replaced by -NO_2 group (ipso substitution)

Method 2



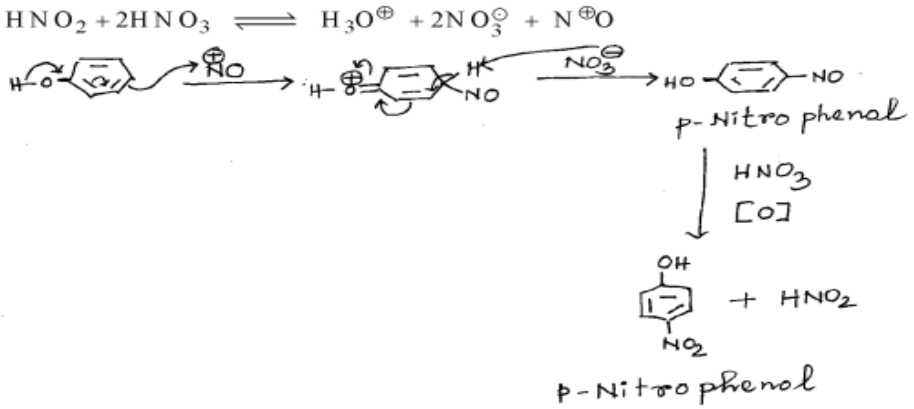
Chlorobenzene

2,4-Dinitrochloro-benzene

2,4-Dinitrophenol

Picricacid

Mechanism :



9.4 Aromatic halogenation reaction

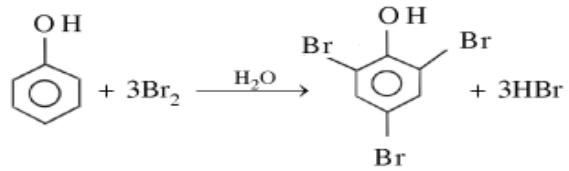
Replacement or substitution of a hydrogen atom from an aromatic nucleus by a halogen atom is called aromatic halogenation reaction.

Fluorination and iodination processes differ from those of chlorination and bromination.

Aromatic chlorination and bromination may be carried out at ordinary temperature by allowing the compound to reaction with molecular chlorine (Cl_2) on bromine (Br_2) in presence of Fe or a Lewis acid like $A1C1_3$, $AlBr_3$, $SbCl_5$, $SbBr_5$ etc. $HOCl / Cl^-$ or $HOBr / Br^-$ may also be used. Activated aromatic compounds like phenols, amines etc. react with molecular Br_2 or Cl_2 even in the absence of Lewis acid. Interhalogens like ICl, IBr etc and I_2 itself can act as a halogen carrier.

Halogenation

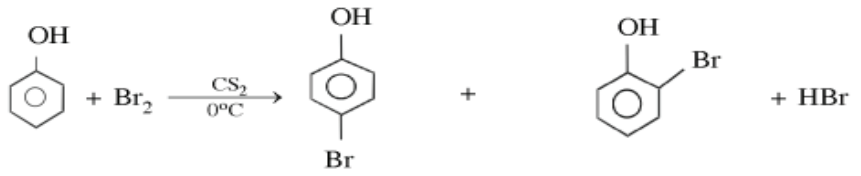
(i) In aqueous medium : Phenol on being treated with an excess of aqueous solution of bromine (bromine water) at room temperature forms 2, 4, 6- tribromophenol as a white precipitate in quantitative yield. This reaction may be used to estimate phenol quantitatively. It is also useful as a test of phenol. Reaction with chlorine water gives similar result.



Phenol 2, 4, 6-Tribromophenol

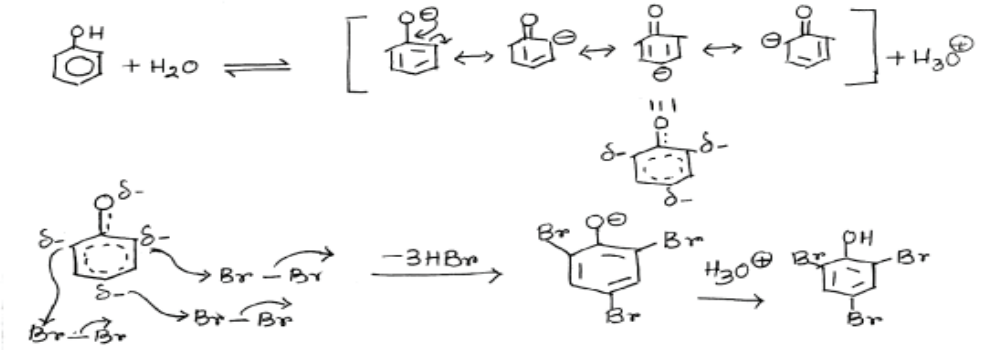
In aqueous medium, phenol ionises to form a small amount of phenoxide ion. The phenoxide ion being a stronger nucleophile than phenol, reacts with bromine to give the above tribromo product.

ii) In nonpolar medium: When phenol is treated with Br_2 (one mole) of in a solvent of low polarity such as carbon disulphide, chloroform or carbon tetrachloride at 0°C, P-bromophenol is formed as the main product.

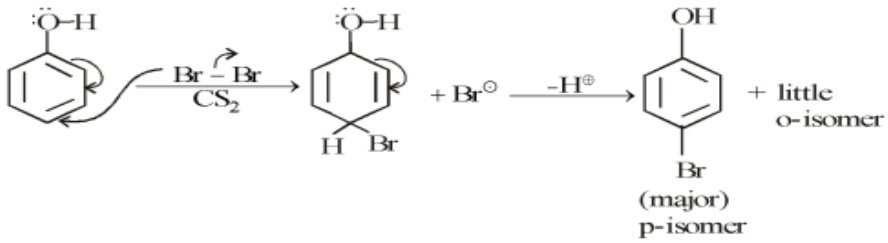


p-Bromophenol (major pdt) o-Bromophenol (minor pdt)

Mechanism :



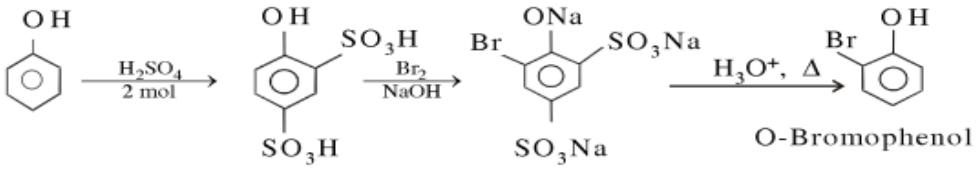
In carbon disulphide (CS_2) medium phenol forms p-bromophenol (major) with little amount of o-bromophenol.



(major)
p-isomer

Formation of o-Bromophenol

o-Bromophenol may be prepared by protecting one ortho position and para position by sulphonation followed by bromination and desulphonation.



O-Bromophenol

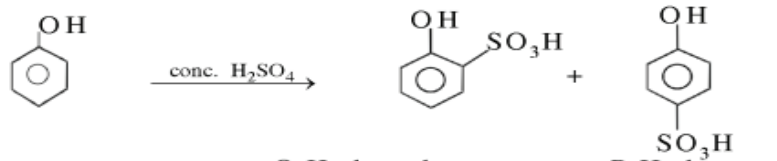
9.5 Sulphonation reaction

The process of introducing a $-SO_3H$ group into an aromatic nucleus by the action of concentrated H_2SO_4 or fuming H_2SO_4 [oleum $H_2S_2O_7$ — Sulphur trioxide in H_2SO_4] or $-SO_3$

in organic solvent (nitromethane, pyridine etc) or chlorosulphonic acid in CCl_4 (carbon tetrachloride) is known as aromatic sulphonation reaction.

When phenol is treated with cone H_2SO_4 at room temp (20° - 25°C), nearly equal amounts of o - and p-hydroxybenzene sulphonic acids are formed.

When phenol is sulphonated below this temperature, o-hydroxy benzene sulphonic acid is formed as the major product and when the reaction is carried out at 100° - 110°C p-hydroxybenzene sulphonic acid is formed as the major product.



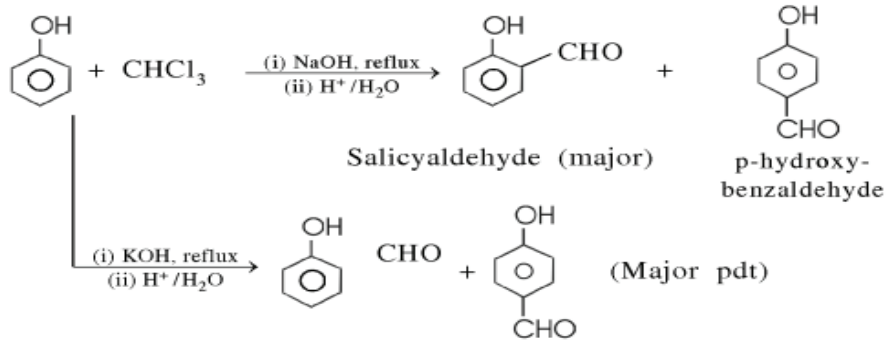
O-Hydroxybenzene sulphonic acid

P-Hydroxy-benzene Sulphonic acid

Reaction temp 20°C	49%	51%
Reaction temp 80°C	10%	90%

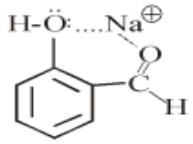
9.6 Riemer - Tiemann Reaction

This is a method of formylation of phenol in general. When phenol is treated with chloroform ($CHCl_3$) in strong alkali solution at 70°C and the product is acidified, o-hydroxybenzeldehyde (salicyaldehyde) is formed as the major product together with a small amount of p-hydroxybenzaldehyde. The reaction is known as the ReimeaTiemann reaction.



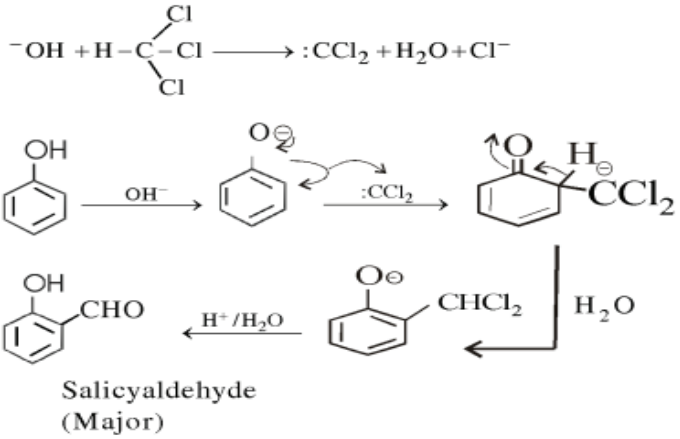
From the mixture of o-and p-hydroxybenzeldehydes the components can be separated by steam distillation because o-hydroxybenzeldehyde is steam volatile due to intramolecular hydroxgen bonding (chelation) where as p-hydroxybenzaldehyde is not steam volatile due to intramolecular hydrogen bonding.

The reaction gives mainly o-aldehyde because the phenolic oxygen from a stable six membered complex with Na+ and carbonyl oxygen of the -CHO group as follows :



When KOH is used instead of NaOH the major product is p-hydroxybenzaldehyde. This is due to the fact that larger size of K+ prevents the formation of intramolecular chelate and thus, most of the electrophilic attack takes place at the sterically more free para position.

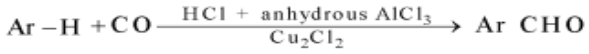
Mechanism



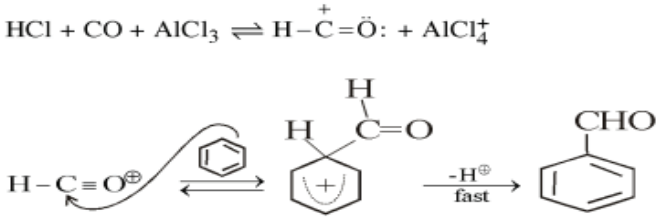
Salicyaldehyde
(Major)

9.7 Gattermann Koch formylation

The formyl group (-CHO) may be introduced into aromatic nucleus by treatment of the aromatic compound with CO and concentrated HC1 in presence of a Lewis acid like anhydrous A1C1$_3$. The reaction is carried out either under pressure or in presence of Cu+ ion (generally Cu_2Cl_2).



Mechanism :



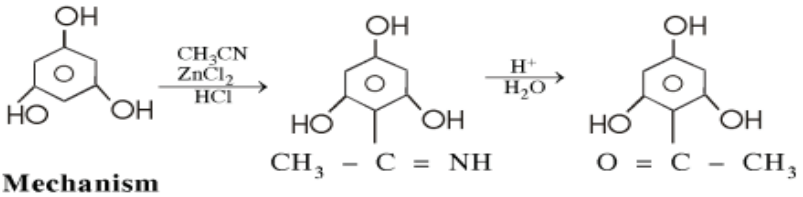
The role of Cu_2Cl_2 may be to aid the reaction between CO and HC1 via complex which it forms with CO.

Application and Scope

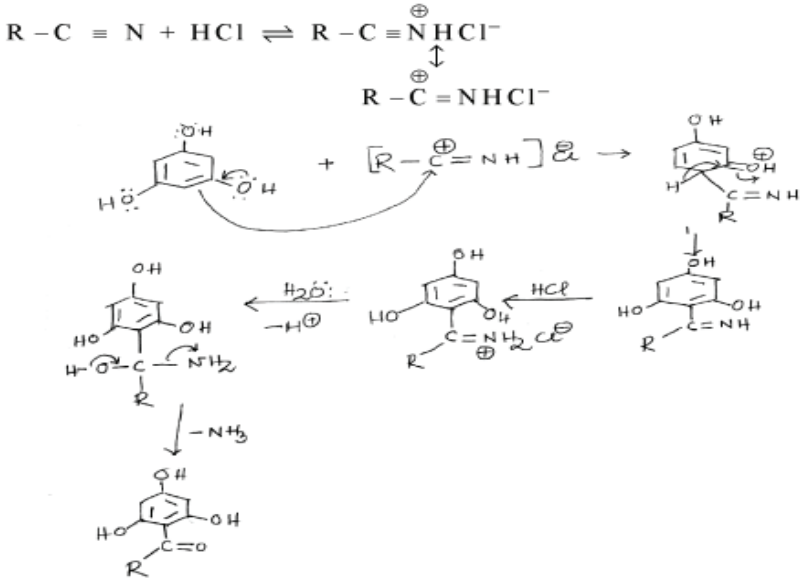
Gatteraiann-koch formylation can not be applied to compounds of lower reactivity than halobenzenes. Nitrobenzene is inert and it can be used as a solvent for this reaction. It is also unsuccessful with phenols and phenolic ethers because the Lewis acid used for this reaction form complex with the phenolic oxygen.

9.8 Houben-Hoesch Reaction

The Houben reaction or Houben-Hoesch reaction is an organic reaction in which a nitrile reacts with an arene compound to form an aryl ketone. The reaction is a type of Friedel crafts acylation with hydrogen chloride and a Lewis acid catalyst.



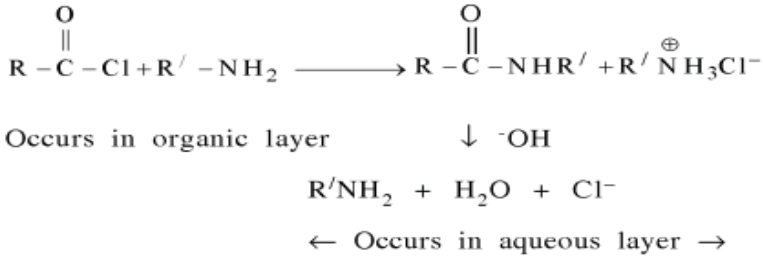
Mechanism



9.9 Schotten-Baumann reaction

The Scliotten-Baumann reaction is a method to synthesis amides from amines and acid chlorides.

The reaction involves an acid chloride in a separate layer (either alone on in a solvent) over an aqueous solution of sodium hydrodxide Hydrolysis of the acid chloride by sodium hydroxide is avoided as acid chloride are typically insoluble in water and therefore can not come in direct contact with the water soluble hydroxide ions.



9.10 Summary

- Commercially phenol can be synthesised from cumene, which in turn is prepared from petroleum by oxidising at 130°C in presence of metal catalyst.
- Unlike alcohols (which also contain an -OH group) phenol is a strong acid. Phenols turn blue litmus reel and react with metals liberating hydrogen.
- Phenol having electron withdrawing OH substituents is ortho- and para- directing.
- Phenol can undergo many electrophilic aromatic substitution reactions similar to benzene like nitration, sulfonation, halogenation and Reimer- Tiemann Reaction.
- Introduction of-CHO group ortho to -OH group by treating phenol with HCN, HCl and $ZnCl_2$ catalyst is known as Gattermann Koch reaction,
- Process of formylation of phenols with chloroform in alkaline solution is known as Reimer-Tiemann reaction.
- Reactive polyhydric phenols in which -OH groups are meta to another may be acylated by treating with alkyl cyanides in the presence of ZnCl? and HC1. This reaction is known as Houben-Hoesch reaction. The product of the reaction is phenolic ketone.

9.11 Exercises

Multiple - Choice Questions

(1) Phenol is treated with excess of bromine water at room temperature.

The product formula is.

(a) 4 - bromophenol, (b) 2, 4-dibromophenol, (c) a mixture of 2- and 4- bromophenols

(d) 2, 4, 6 - tribromophenol.

2. Phenol on treatment with dilute HNO_3 at room temperature yields—

(a) 2, 4, 6 - trinitrophenol (b) 2 – nitrophenol, (c) 4 - nitrophenol, (d) a mixture of 2 - and 4 - nitrophenol.

3. Phenol is prepared industrially by heating chlorobenzene with aqueous NaOH at 360°C under high pressure.

$$C_6H_5Cl + NaOH \xrightarrow[(ii)\ H_3O^+]{(i)\ 360^oC,\ pressure} C_6H_5OH$$

The reaction involves—

(a) SN1 mechanism

(b) SN2 mechanism

(c) benzyne mechanism

(d) addition - elimination mechanism.

4. Benzendiazonium chloride on heating with water yields mainly—

(a) Phenol, (b) Chlorobenzene

(c) benzyl alcohol (d) benzene

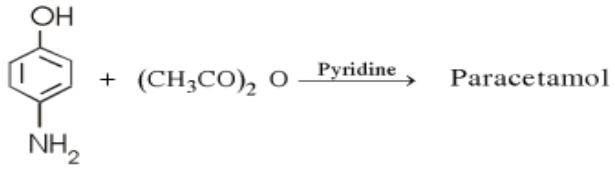
5. Sodium benzene sulphonate is fused with solid NaOH and then acidified with dilute H_2SO_4- The product is—

(a) 3-hydroxybenzenesulphonic acid.

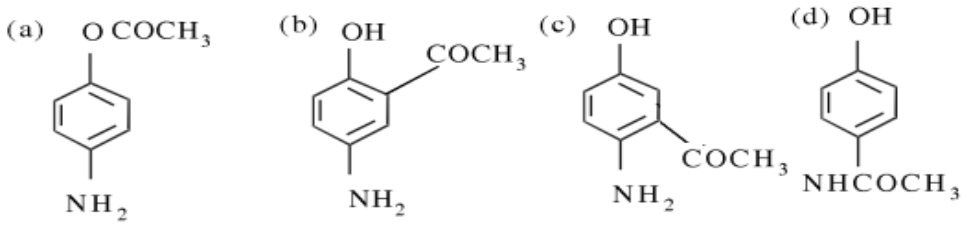
(b) Phenol

(c) Thiophenol

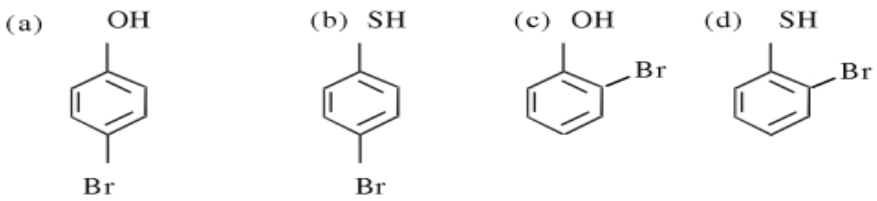
(d) benzene

6. 

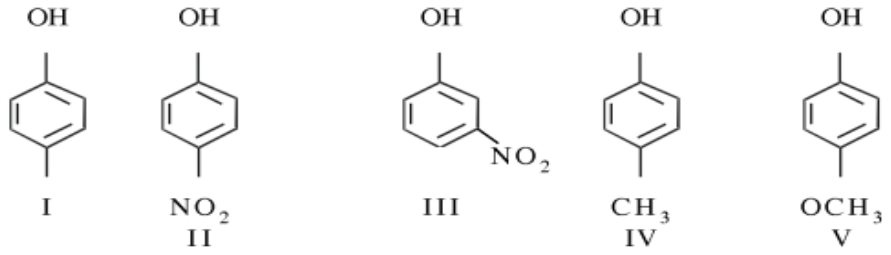
The Structure of Paracetamol is-



7. When Phenol is treated with a solution of Br_2, in CS_2 at 0°C, the major product is-



8. Among the Compounds-



The order of acidity is NO_2

(a) III > II > V > IV > I

(b) II > III > I > IV > V

(c) II > V > III > IV > I

(d) II > III > V > IV > I

9. Which of the following does not possess a carboxy group?

(a) Salicylic acid (b) Anthranilic acid (c) Picric acid (d) O-Toluric acid

10. When phenol is treated with chloroform and aqueous NaOH and subsequently acidified, the major product formed is—

(a) p-hydroxybenzaldehyde

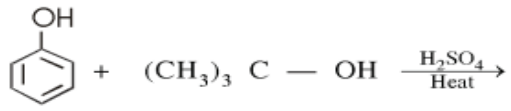
(b) Salicylaldehyde

(c) Salicylic acid

(d) Benzaldehyde

11. Phenol is heated with phthalic anhydride in the presence of concentrated H0S04, The Product formed is—

(a) Salicylic acid (b) P-hydroxy benzen sulphonic acid (c) Phenolphthalein (d) florescein.

12. 

The major Product formed is —

13. Sodium phenoxide is heated with CO_2 under pressure. The resulting product is acidified with dilute HC1. The final product formed is mainly—

(a) Salicylic acid (b) Salicyaldehyde, (c) 4-hydroxybenzoic acid, (d) 4-hydroxy benzaldehyde.

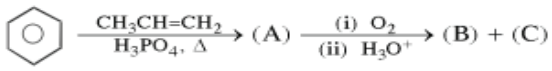
14. Aspirin, an analgesic drag is obtained by acetylation of —

(a) 2-aminobenzoic acid

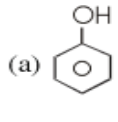
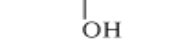
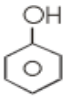
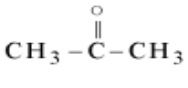
(b) 2-hydroxy benzoic acid

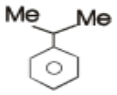
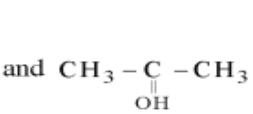
(c) 2-hydroxybenzene sulphonic acid

(d) 2-aminobenzene sulphonic acid.

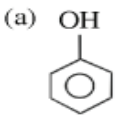
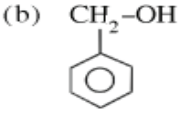
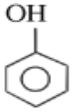
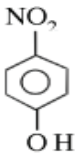
15. 

The products (B) and (C) are—

(a)  and  (b)  and 

(c)  and  (d)  and 

16. Which of the following reacts with both $NaHCO_3$ and NaOH?

(a)  (b)  (c)  (d) 

17. Which of the following reagent is not able to distinguish between phenol and ethanol?

(a) Aqueous NaOH (b) Aqueous FeCl3 (c) Metallic Na (d) Aqueous Br,

18. Bakelite is condensation copolymer of—

(a) Phenol and acetaldehyde

(b) Urea and formaldehyde

(c) Phenol and formaldehyde

(d) Aniline and benzaldehyde

19. A mixture of o and p-nitrophenols the components are usually separated by—

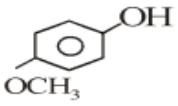
(a) Fractional crystallisation

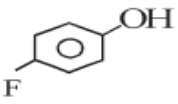
(b) Chromatography

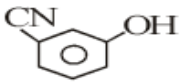
(c) Fractional distillation

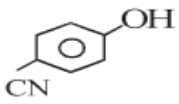
(d) Steam distillation.

20. Which of the following is the most acidic?

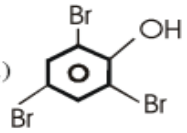
(a) 

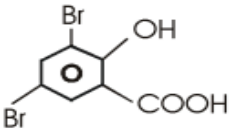
(b) 

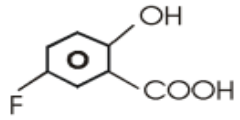
(c) 

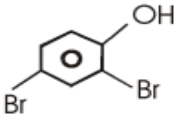
(d) 

21. Salicylic acid is treated with excess of bromine water. The product formed is

(a) 

(b) 

(c) 

(d) 

Answer to Multiple-Choice Questions :

l-(d) 2.(d) 3-(c) 4-(a) 5.(b) 6.(d) 7.(a) 8 (b) 9-(c) 10.(b) 11.(c) 12.(c) 13.(a) 14.(b) 15.(b) 16.(d) 17-(c) IB.(c) 19.(d) 20.(d) 21.(a)

22. How will you accomplish the following transformation?

(a) Benzene to phenol

(b) Acetophenol to phenol

(c) Phenol to Aspirin

(d) Phenol to Salicyaldehyde

(e) Phenol to o-hydroxyacetophenone

(f) Phenol to o-nitrophenol

(g) Phenol to catechol

(h) Phenol to p-bromophenol

(i) Phenol to Picric acid

(j) Phenol to allyl phenyl ether

(k) Aniline to Anisole

(l) p-Cresol to p-hydroxy benzoic acid

(m) Phenol to o-bromophenol

(n) Phenol to p-nitrophenol

(o) Phenol to Phenoxyacetic acid.

Unit 10: Ethers

10.0 Objectives

The objectives of this unit are to make aware the learners about.

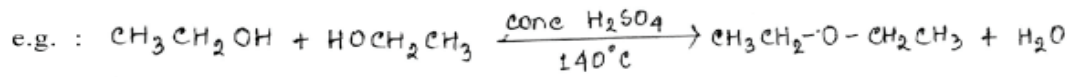
- The structure and physical properties of ether.
- The different methods to preparation of ethers.
- Various chemical reactions of ethers including electrophilic substitution of aromatic ethers.
- Cleavage of ether bond with HI

10.1 Introduction

C— O— C Linkage is called ether linkage. Compounds containing ether linkage are called ethers. Depending on the nature of the hydrocarbon groups, the ether may be classified as dialkyl ethers, alkylaryl ether, Diaryl ether etc.

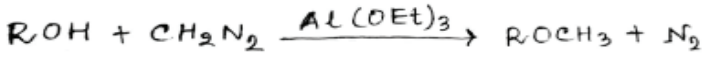
10.2 Preparation of Ether

By dehydration of alcohol : Ether can be produced by dehydration of alcohol in presence of conc H_2SO_4 or H_3PO_4



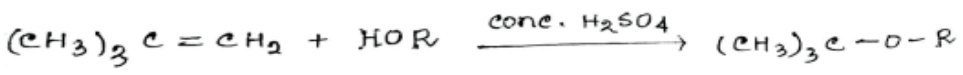
By treating alcohol with diazomethane :

When alcohols are treated with diazomethane in the presence of Lewis acid e.g., $Al(OEt)_3$ or BF_3, a methyl ether forms.



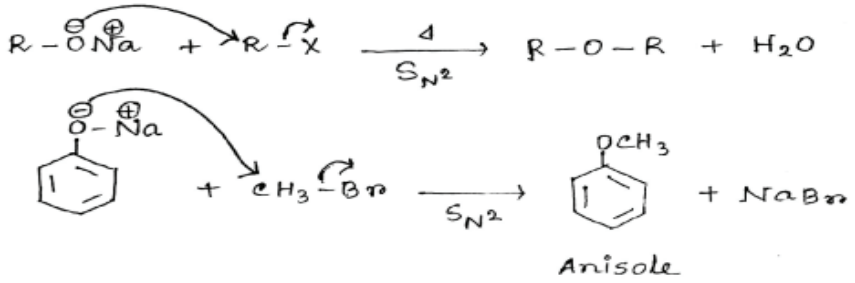
By treating alkene with alcohol :

In presence of acid catalyst alkene reacts with alcohol to give ether



Williamson synthesis

This is the best method of preparing on symmetrical and unsymmetrical dialkyl and arylalkyl ethers. This involves the treatment of alkyl halide with sodium alkoxide or phenoxide respectively.

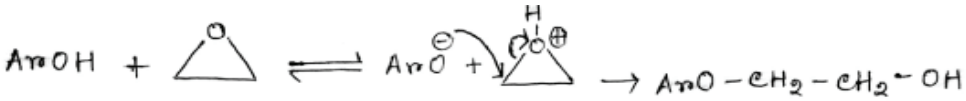


By treating alkyl halide with silver oxide :

Dry silver oxide and alkyl halide gives ether on heating

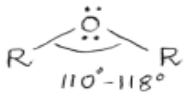
Conversion of an epoxide to a p-hydroxy ether :

Alcohols and phenols can be converted to hydroxy ethers by their reaction with epoxides

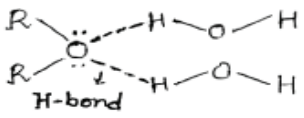


10.3 Structures and physical properties of ether

Ether linkages, have angular shapes. The bond angles are usually 110 degree to 118 degree. The O atom holds 2 lone pairs of electrons



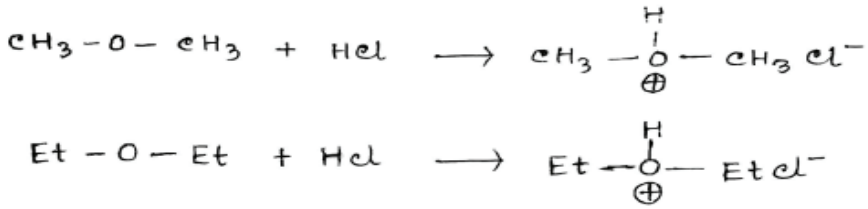
Ethers can form H-bond with water molecules and for this reason lower members are slightly soluble in water; The solubility decreases with the increasing molecular weight.



10.4 Chemical reactions

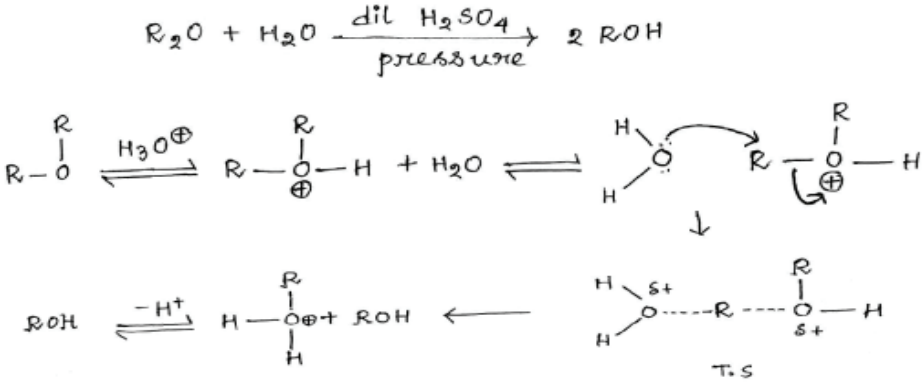
Formation of Oxonium salts :

Ethers are basic. They form salt with protonic and Lewis acids at a low temperature. If a solution of hydrogen chloride in dry diethyl ether is cooled to allow temperature, a crystalline oxonium salt is obtained.



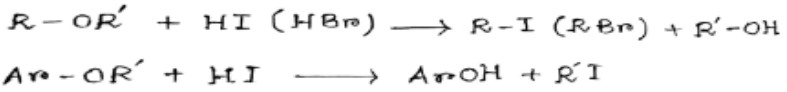
Reaction with dilute sulfuric acid :.

When ethers are heated with dilute sulphuric acid under pressure, alcohols are formed.



Reaction of hydrohaloacids :

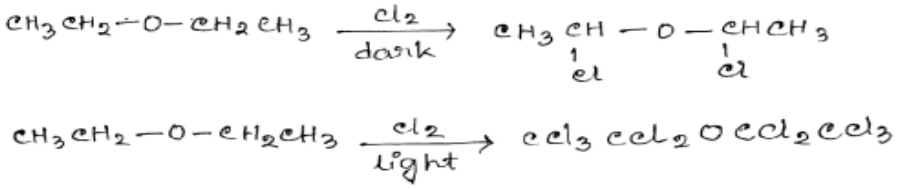
When ethers are treated with hydroiodic acid or hydrobromic acid in cold, an alcohol and an alkyl halide are formed.



Usually methyl iodide forms, when one of the hydrocarbon groups is methyl. However, if there is a 3 degree alkyl group, a 3 degree alkyl iodide and methyl alcohol are formed. In this condition, it is important to note that HI is more reactive than HBr.

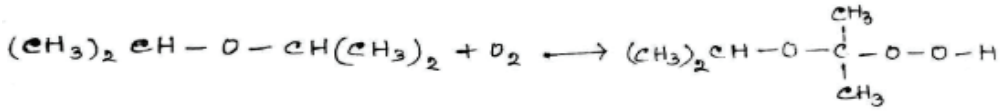
Reaction with halogens :

Chlorine and bromine react with ethers to form chloro or bromo derivatives. When ethyl ether is treated with chlorine in the dark, dichloro derivatives is obtained. On the other hand, in the presence of light perchloro or decachlorodiethyl ether formed.



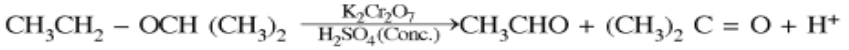
Auto oxidation :

When an ether is left exposed to air oxygen of the air reacts with it and forms hydroperoxide. Thus, i-propyl ether form di-i-propyl hydro peroxide. The a-H atoms are involved in the auto oxidation.



Oxidation

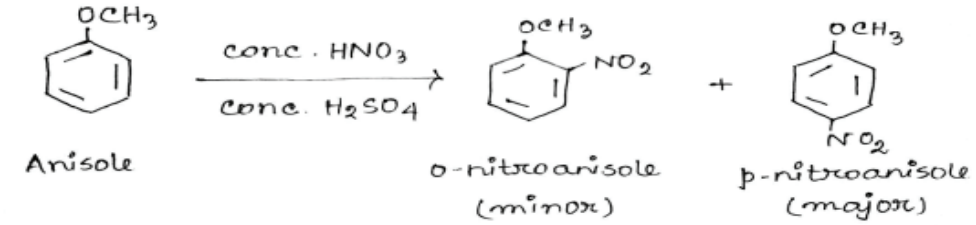
Strong oxidising agents like potassium permanganate and sulfuric acid or dichromate and sulphuric, acid oxidise an ether to a carbonyl compound. The alkyl groups present in the ether determine the nature of the carbonyl group to be formed.



10.5 Electrophilic substitution or Aromatic ethers

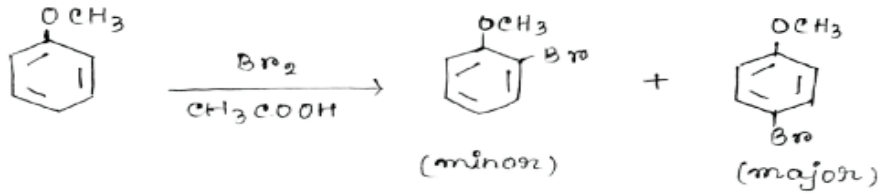
Nitration reaction :

Anisole reacts with cone. HNO_3 and cone. H_2SO_4 mixture to give o- and p-nitroanisole



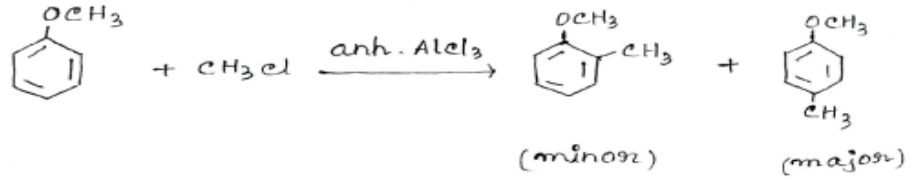
Bromination reaction :

Anisole gives o- and p-bromoanisole with acetic acid



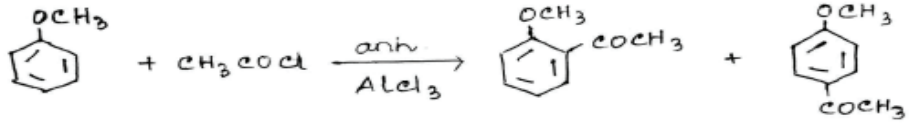
Friedel craft alkalization :

In presence of A1C1$_3$ anisole reacts with CH_3C1 and give o-and p-methyl anisole.



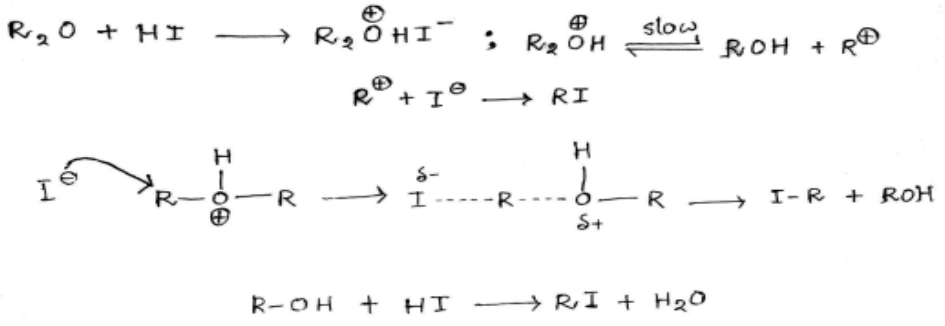
Friedel craft acylation :

Anisole gives 2-and 4-methoxyacetophenone with Acetyl chloride in presence of anh. A1C1$_3$



Cleavage of ether with HI :

When ethers are heated with HI, two moles of alkyl iodide are obtained. At first an alcohol and an alkyl iodide form and then the alcohol changes to the alkyl iodide again either by the by the SN 1 or by the SN 2 pathway.



10.6 Summary

In this unit we learn that :

- Ethers possess the structure : R - O - R and are compounds having the general formula $C_nH_{2n+2}O$.
- Ethers are isomeric with the aliphatic monohydric alcohols with the general formula $C_nH_{2n+1}OH$.
- epoxides are the three membered cyclic ethers.
- symmetrical or simple ethers have R and R' being identical while unsymmetrical or mixed ethers have different R and R' groups.
- alcohols, ethers are fairly unreactive except to very strong acids such as HI or HBr. This low reactivity makes them useful as solvents, e.g. diethyl ether. $(C_2H_5)_2O$ and

tetrahydrofuran (THF), C_4H_8O.

10.7 Exercises

1. Which of the following is correct IUPAC name of ally1 isopropyl ether?

A. 3-(l-Methylethoxy) propene.

B. 2-(2-Propenyloxy) propane.

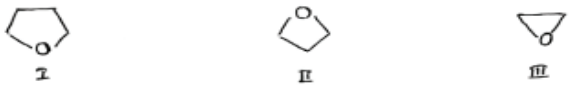
C. l-(l-Methylethoxy) prop-2-ene

D. 1-Isopropoxypropene.

2. Ethyl alcohol excess is heated with concentrated sulphuric acid at 140 degrees Celsius. The major product formed is—

A. Ethene, B. Ethoxyethane, C. Ethyl hydrogen sulphate. D. Diethyl sulphate

3. Name the following ethers



A. Oxirane, oxetane and oxolane

B. Oxolane, oxirane and oxetane

C. Oxolane, oxetane and oxirane

D. Oxetane, oxolaiie and oxirane

4. The total number of constitutionally isomeric ethers of molecular formula $C_5H_{12}O$ is.

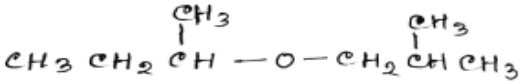
A. Three

B. Four

C. Five

D. Six

5. The IUPAC name of the sec-butyl isobutyl ether



A. 1-methyl- l-(2-methylpropoxy) propane

B. 2-(2-methylpropoxy) butane

C. 1-(1-methylpropoxy)-2-metylpropane

D. l-butoxy-2-methylpropane

6. The Ether 18-crown-6 contains.

A. 12 carbons and six oxygens

B. 18 carbons and 6 oxygens

C. 6 carbons and 12 oxygens

D. 6 carbons and 18 oxygens

7. Which of the following reactions would give the best yield of butyl methyl ether?

(a) $(CH_3)_3C - Cl + CH_3OH \rightarrow$

(b) $(CH_3)_3COK + CH_3Br \rightarrow$

(c) $(CH_3)_3C - I + CH_3OK \rightarrow$

(d) $(CH_3)_3COK + CH_3I \rightarrow$

8. Which of the following sequences of reaction should be chosen to accomplish the following conversion?

(a) $(CH_3)_2CHCH=CH_2 \xrightarrow{H_3O^+} \xrightarrow{Na} \xrightarrow{CH_3I}$

(b) $(CH_3)_2CHCH=CH_2 \xrightarrow[2.\ H_2O_2,\ \bar{O}H]{1.\ BH_3} \xrightarrow{Na} \xrightarrow{CH_3I}$

(c) $(CH_3)_2CHCH=CH_2 \xrightarrow[CH_3OH]{(CH_3COO)_2Hg} \xrightarrow[\bar{O}H]{NaBH_4}$

(d) $(CH_3)_2CHCH=CH_2 \xrightarrow{HBr} \xrightarrow{CH_3ONa}$

9. Which of the following reaction would not yield methoxybenzene (anisole)?

(a) $C_6H_5OH + CH_2N_2 \rightarrow$

(b) $C_6H_5ONa + CH_3I \rightarrow$

(c) $C_6H_5OH + (CH_3)_2SO_4 \xrightarrow{NaOH}$

(d) $C_6H_5OH + CH_3MgI \rightarrow$

10. Which of the following reaction should be carried out to prepare t-butyl phenyl ether?

(a) $C_6H_5Br + (CH_3)_3COK \rightarrow$

(b) $C_6H_5ONa + (CH_3)_3C\ Br \rightarrow$

(c) $C_6H_5ONa + (CH_3)_3Cl \rightarrow$

(d) $(CH_3)_2C = CH_2 \xrightarrow[2.\ NaBH_4,\ \bar{O}H]{1.\ Hg(OAC)_2,\ C_6H_5OH}$

ETHERS

Problems

1. Write the structural formula of all the isomeric compounds that can be represented by the molecular formula. Write their IUPAC names. [North Bengal University 1999]

2. Write notes on Williamson's synthesis. [Punjab University 1998, Baroda University 1999]

3. Write step by step mechanism for the reaction of diethyl ether with hot concentrated HI.

[Madras University 1998]

4. n-Butyl alcohol has a much higher boiling point than its isomer, diethyl ether. [Delhi University 1999]

5. Explain why the boiling point of ethyl alcohol is higher than that of diethyl ether though they add of the same molecular weight.

6. How will you distinguish between diethyl ether and ethyl alcohol?

Hints : (i) Ethyl alcohol responds to iodoform test.

$CH_3 - CH_2OH + I_2 / NaOH \rightarrow CH_3{-}CHO \rightarrow CHI_3$

Ethanol Iodoform

(ii) Ethyl alcohol reacts with sodium metal to produce hydrogen gas.

$2CH_3 - CH_2 - OH + Na \rightarrow 2\ CH_3 - CH_2\ ONa + H_2\uparrow$

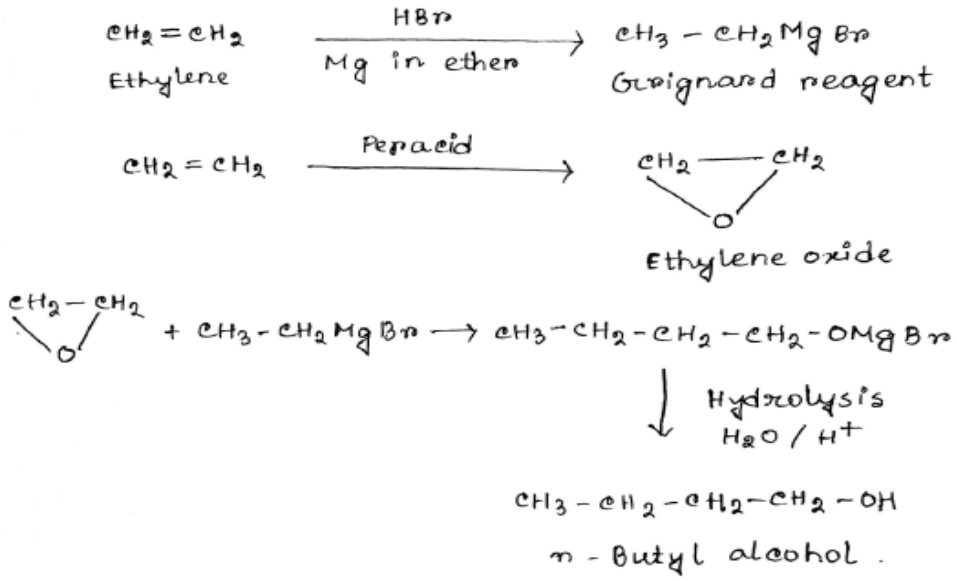
Diethyl ether fails to respond above two reactions.

7. How will you synthesise diethyl ether from ethanol? How will you purify it?

Hints : Excess of ethyl alcohol taken in distilling apparatus is heated with cone. H_2SO_4 at temperature of 140°C. The ether vapour coming out through a condenser is collected in a receiver immersed in ice. Ether obtained above contains ethyl alcohol and sulphuric acid as impurities. It is shaken with dilute NaOH to remove sulphuric acid. The organic layer is collected and repeatedly treated with to remove ethyl alcohol and water.

8. How will you prepare n-butyl alcohol from ethylene?

Hints :


CH2 = CH2
Ethylene
HBr
Mg in ether
CH3 – CH2 Mg Br
Grignard reagent
CH2 = CH2
Peracid
CH2 — CH2
O
Ethylene oxide
CH2 – CH2
O
+ CH3 – CH2 Mg Br
CH3 – CH2 – CH2 – CH2 – OMg Br
Hydrolysis
H2O / H+
CH3 – CH2 – CH2 – CH2 – OH
n - Butyl alcohol .

Unit 11: Carbonyl compounds

11.0 Objectives

By the end of the course learners should be able to know about:

- Preparation of aldehyde and ketone from acid chlorides and from nitriles.
- Reactivity of carbonyl group, i.e. nucleophilicity of carbonyl group.
- Reaction of carbonyl group with HCN, ROM, $NaHSO_3$
- Addition elimination of carbonyl group to form NH-G derivatives.
- Different types of name reactions involving carbonyl group namely Iodoform test. Aldol Condensation. Cannizzaro's reaction. Wittig reaction. Benzoin condensation. Clemensen reduction, Wolff Kishner reduction and Meerwein-Pondorff Verley reduction.

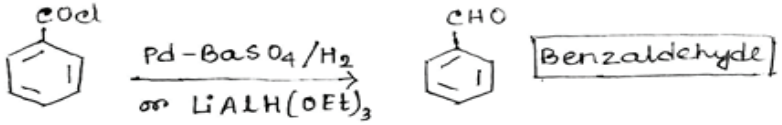
11.1 Introduction

Carbonyl compounds are two types formyl (-CHO) and keto (>C = O). Compounds containing formyl group are called aldehydes whereas keto group containing compounds are called ketones. The simplest member of the aldehydes is formaldehyde. And acetone is the simplest ketone.

HCHO	CH_3CHO	CH_3COCH_3	PhCHO
Formaldehyde	Acetaldehyde	Acetone	Benzaldehyde

11.2 Preparations of Aldehydes

By the Rosenmund reduction (From acid chlorides) : Aliphatic, alicyclic and aromatic acid halides on reduction with Pd/H2 in barium sulphate suspension containing sulphur as poison give aldehydes.



By the Stephen's reaction (From nitriles) : When alkyl or aryl cyanides are reduced with stannous chloride and hydrochloric acid in ethereal solution and then the products are hydrolysed with water, the corresponding aldehydes are obtained and the reaction is known as the Stephen's reaction.

$$CH_3CN \xrightarrow[2.\ H_2O]{.\ SnCl_2/HCl} CH_3CHO$$

11.3 Preparations of Ketones

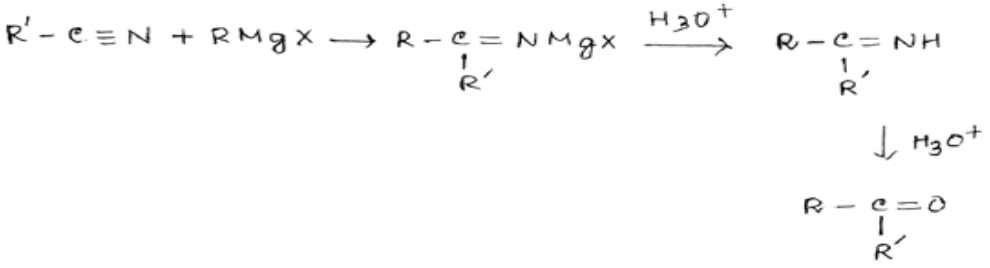
From acid chloride : The ketones may also be prepared from the Grignard reagents by converting them to organocadmium compounds and then treating the latter with acid halides.

$$R'_2MgX + CdCl_2 \rightarrow R'_2Cd + MgXCl$$

$$2RCOCl + R'_2Cd \rightarrow 2RCOR' + CdCl_2$$

$$2ArCOCl + R'_2Cd \rightarrow 2ArCOR' + CdCl_2$$

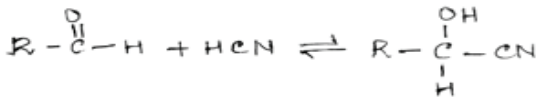
From nitriles :Ketones can also be prepare from Grignard reagent, upon treatment with nitriles.

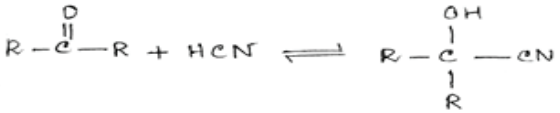


11.4 Chemical Reactions

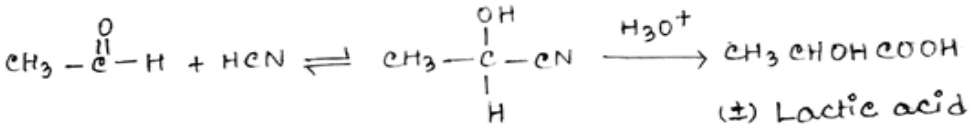
11.4.1 Reactions with HCN :

In a slightly acidic medium hydrogen cyanide adds to aldehydes and ketones to yield a-hydroxynitriles, called aldehyde and ketone cyahohydrins.



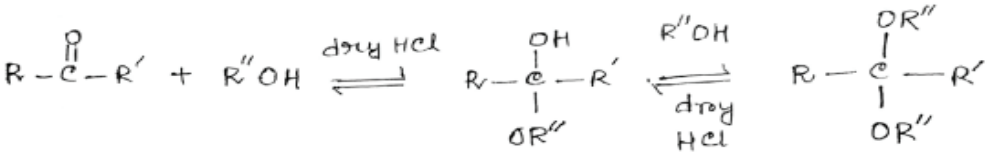


The reaction gives appreciable yield with aldehydes and aliphatic and alicyclic ketones; but it gives poor yield with ArCOR and doesn't occur with ArCOAr. However the reaction has some preparative value. α-Hydroxy acids can be prepared from aldehydes ad ketones via cyanohydrin.

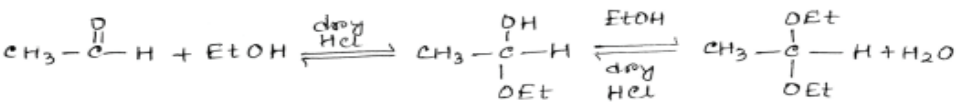


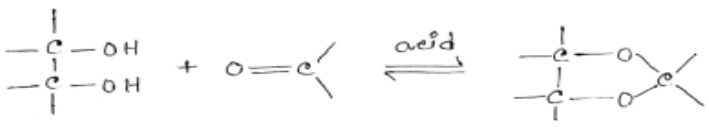
11.4.2 Reactions with alcohols :

Alcohols add to aldehydes and ketones in the presence of specific acid catalysis to yield acetals via hemiacetals. Acetals are 1, 1-diethers and hemiacetals are a-hydroxy-ethers, i.e., half acetals.



R & R′ = H or alkyl group.

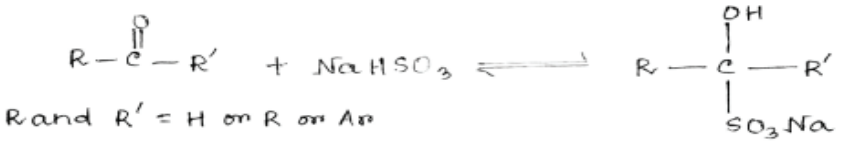


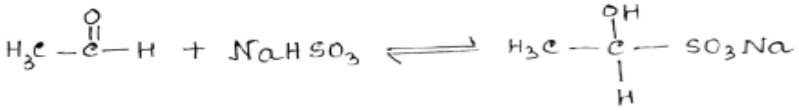


11.4.3 Addition of Sodium Bisulphite :

When aldehydes and ketones are shaken with an aqueous solution of sodium bisulphite (Saturated), slightly soluble bisulphite addition compounds, called aldehyde bisulphite and

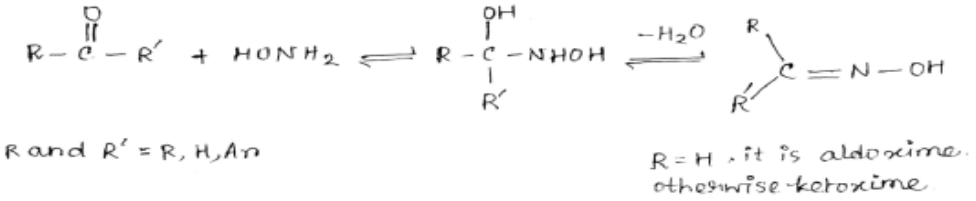
ketone bisulphite, are formed ; here hydrogen adds to the oxygen and sodium sulphonate to the carbonyl carbon. The reaction is reversible one.

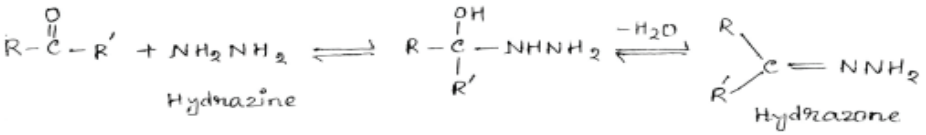


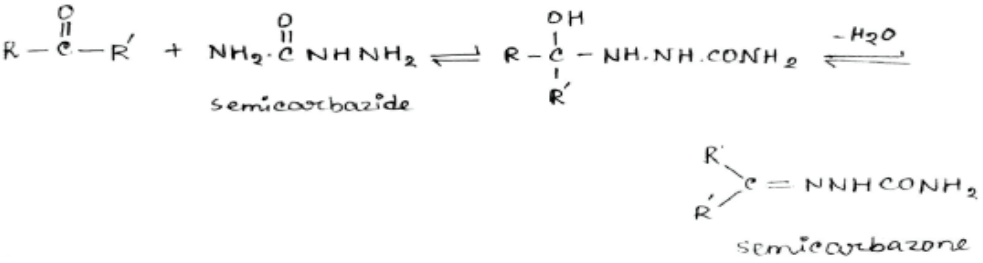


11.4.4 Addition-Elimination Reactions :

Certain derivatives of ammonia undergo addition reaction with aldehydes and ketones to yield a-hydroxy derivatives. These, in their turn, undergo water elimination reaction to give compounds containing C-N double bond.







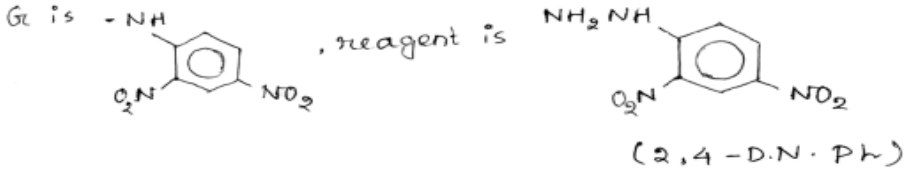
The addition-elimination reactions involve derivatives of ammonia which may be represented in general as : GNH_2. When,

G is – OH, reagent is NH_2OH (hydroxylamine)

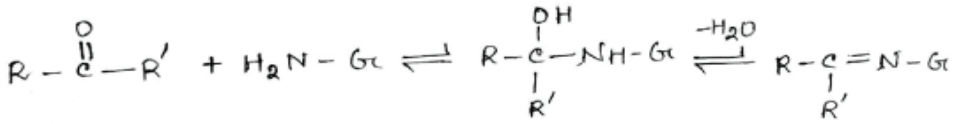
G is $-NH_2$, reagent is NH_2NH_2 (hydrazine)

G is – NHPh, reagent is NH_2NHPh (Phenylhydrazine)

G is $-NHCONH_2$, reagent is $NH_2NHCONH_2$ (Semicarbazide)

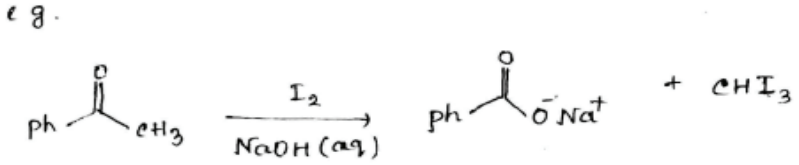


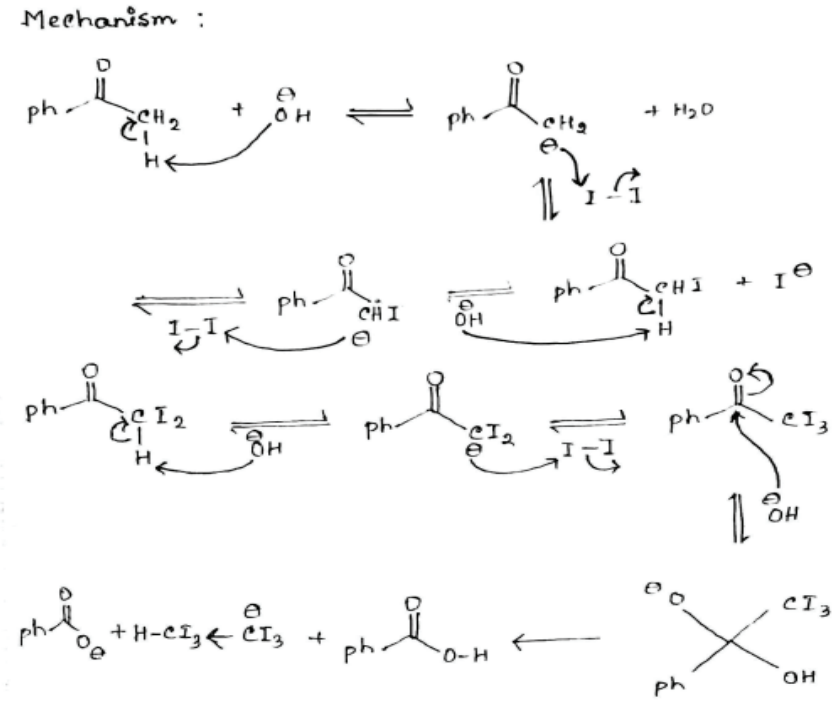
Thus the general equation of this class of reaction may be represented as :



11.4.5 Iodoform Test (Haloform Reaction) :

The iodoform reaction is the reaction of a methyl ketone with iodine in the presence of hydroxide ions to give a carboxylate ion and a iodoform. There is one aldehyde that undergoes the iodoform reaction, which is acetaldehyde. When Cl or Br is used it is called Haloform. This reaction is very important because it is used to identify methyl ketones because iodoform is a yellow solid with a characteristic odour.



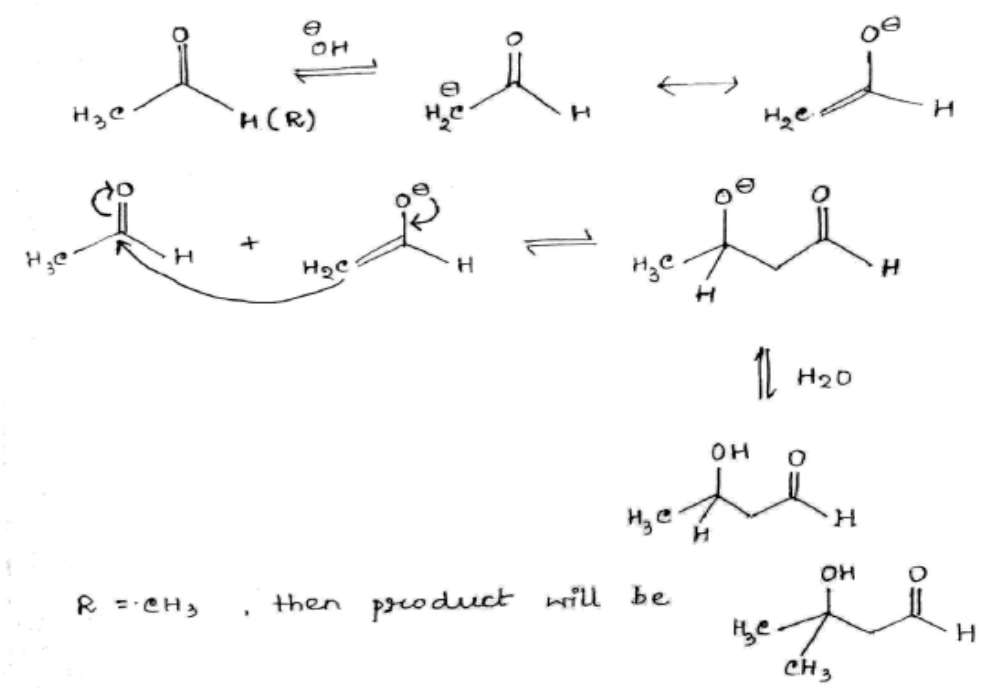


11.4.6 Aldol Condensation :

An aldol condensation is a condensation reaction in organic chemistry in which an enol or an enolate ion reacts with a carbonyl compound to form a β-hydroxy aldehyde or β-hydroxy ketone, followed by dehydration to give a conjugated enone.

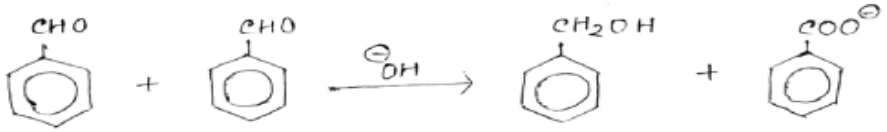
$$2CH_3CHO \rightleftharpoons^{^-OH} CH_3.CHOH.CH_2CHO$$

Mechanism :



11.4.7 Cannizzaro Reaction :

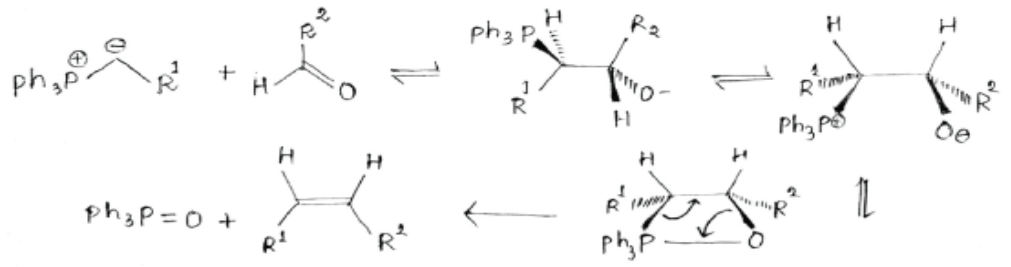
When aldehydes, which do not posses a-H atom, are treated with strong bases (usually 50% aqueous or ethanolic NaOH). they undergo self oxidation reduction in which one molecule of the aldehyde acts as an oxidising agent and gets reduced to the corresponding alcohol while another molecule gets oxidised to the corresponding carboxylate ion and the reaction is known as the cannizzaro reaction.



11.4.8 wittig Reaction :

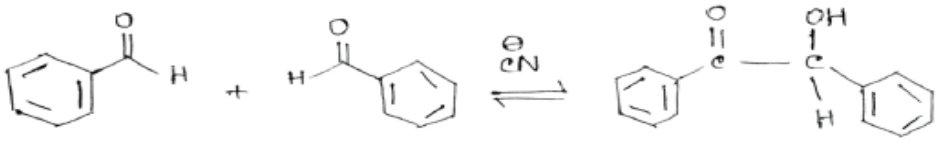
The wittig reaction is a chemical reaction of an aldehyde or ketone with a triphenyl phosphonium ylide (Often called witting reagent) to give an alkene and triphenylphosphine oxide.

Mechanism :

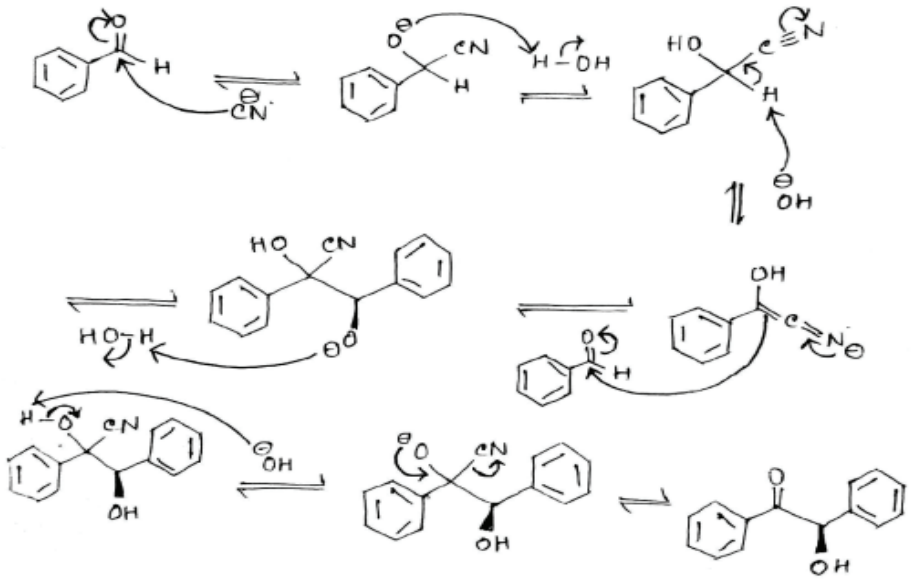


11.4.9 Benzoin Condensation :

The self-condensation reaction of an aromatic aldehyde specifically catalysed by cyanide ion is usually referred to as benzoin condensation. An α-hydroxy ketone, a dimer known as benzoin, is formed by this reaction. Thus benzaldehyde on benzoin condensation gives benzoin. This condensation is carried out by boiling the alcoholic solution of the aldehyde containing a small amount of NaCN or KCN.

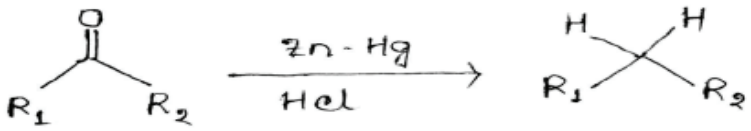


Mechanism :



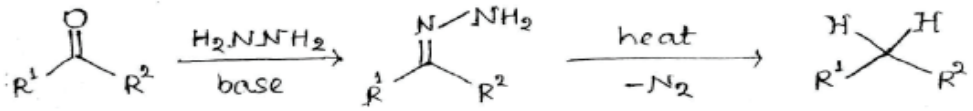
11.4.10 Clemmensen Reduction :

Clemmensen reduction is a chemical reaction described as a reduction of aldehydes or ketones to alkanes using zinc amalgam and concentrated hydrochloric acid. This reaction is named after Erik Christian Clemmensen, a Danish chemist.



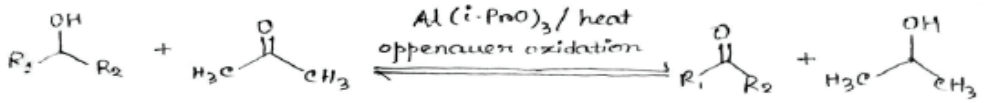
11.4.11 Wolff-Kishner reduction :

The Wolff-Kishner reduction is a reaction used in organic chemistry to convert carbonyl functionalities into alkanes. In the context of complex molecule synthesis it is most frequently employed to remove a carbonyl group after it has served its synthetic purpose of activating an intermediate in a preceding step.

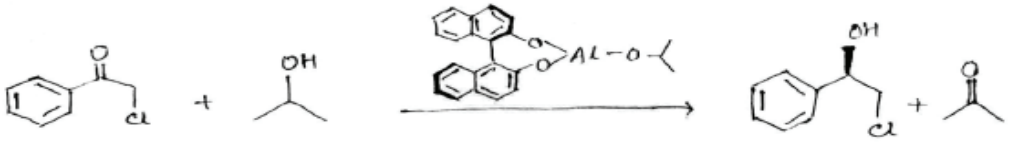


11.4.12 Meerwein-Ponndorf-Verley Reduction :

The Meerwein-Ponndorf-Varley (MPV) reduction in organic chemistry is the reduction of ketones and aldehydes to their corresponding alcohols utilizing aluminium alkoxide catalysis in the presence of a sacrificial alcohol. The advantages of the MPV reduction lie in its high chemo selectivity, and its use of a cheap environmentally friendly metal catalyst.



MPV reaction with chiral ligand



11.5 Summary

- Carbonyl compound contain Oxo (Carbonyl) group >C=0.
- Aldehydes undergo nucleophillic addition reactions due to polarity of carbonyl group.
- Reactivity of carbonyl group towards nucleophillic addition reactions decreases as steric hindrance and +I effect of attached alkyl group increases.
- In nucleophillic addition reactions ketones are less reactive than corresponding aliphatic aldehydes

- Mild oxidizing agents like Tollen' s reagent or Fehling' s solution do not oxidize ketones. Reagents like $LiAlH_4$, $NaBH_4$ etc, can reduce ketones.
- Aldehydes and ketones give a series of condensation reactions and alpha hydrogen substitution reactions as per their structural constitution.
- Aromatic ketones show nucleophillic addition reactions. Positive part of adding reagent always goes to carbonyl oxygen while negative part to carbonyl carbon.

11.6 Exercises

1. Phenylglyoxal, C_6H_5COCHO on heating with concentrated sodium hydroxide yields-

(a) C_6H_5COONa and CH_3OH

(b) $C_6H_5CHOHCOONa$

(c) $C_6H_5CH_2OH$ and $HCOONa$

(d) C_6H_5COONa and $HCOONa$

2. To accomplish the conversion -

$CH_3CH = CHCHO \rightarrow CH_3CH = CHCOOH$

Which of the following reagents sshould be employed?

(a) $K_2Cr_2O_7$, H_2SO_4 (b) $KMNO_4$, H_2SO_4

(c)  (d) $AgNO_3$, NaOH, subsequently H_3O^+

3. Benzaldehyde is heated with alcoholic KCN, The product formed is—

(a) $C_6H_5CHOHCN$ (b) $C_6H_5COCHOHC_6H_5$

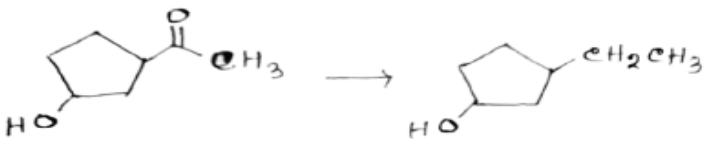
(c) $C_6H_5COCOC_6H_5$ (d) C_6H_5COCN

4. The reagent that can distinguish between benzaldehyde and propionaldehyde is—

(a) Tollens reagent (b) 2, 4-dinitrophenyltiydrazine

(c) sodium hydrogen sulphite (d) Fehling's solution

5. To achieve the conversion—

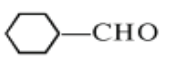


The reagent that should be employed is :

(a) Zn–Hg, conc. HCl, heat (b) NH_2 NH_2, KOH, heat

(c) $LiAlH_4$ (d) $NaBH_4$

6. Cannizzaro reaction does not take place with_

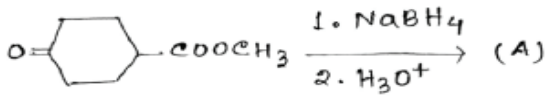
(a) $(CH_3)_3CCHO$, (b) C_6H_5CHO, (c)  (d) CH_3CHO

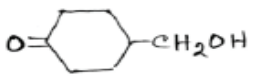
7. Ethanal is allowed to react with ethanol (excess) in presence of dry HCl gas. The product formmed is.

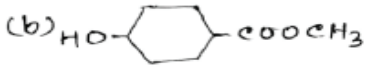
(a) ethoxyethane (b) 1, 2-diethoxyethane

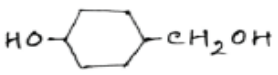
(c) 1, 1 diethoxyethane (d) 1-ethoxyethanol.

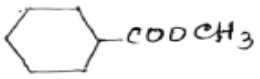
8. The following reaction is carried out—



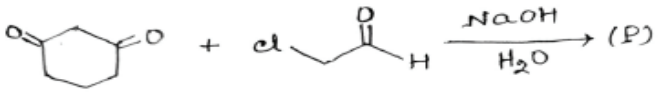
(a) 

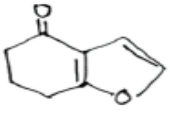
(b) 

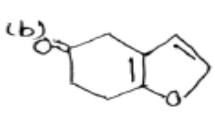
(c) 

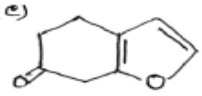
(d) 

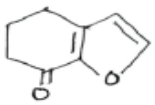
9. Identity the major product (P) in the following reaction



(a) 

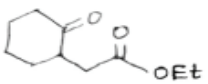
(b) 

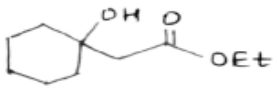
(c) 

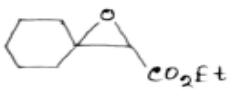
(d) 

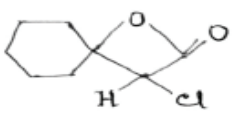
10. Consider the following reaction.

The product (P) is—

(a) 

(b) 

(c) 

(d) 

11. Consider the following sequence of reactions

$$PhCHO \xrightarrow{NH_2OH} (A) \xrightarrow[heat]{P_2O_5} (B)$$

The final product (B) is

(a) PhNC (b) PhCN (c) $PhCONH_2$ (d) PhNCHO

12, The reagent that may be used to separate cyclohexxane and 2, 6-dimethylcyclohexanone is—

(a) $NaHSO_3$, (b) $NaHSO_4$ (c) $NaHCO_3$ (d) $C_6H_5NHNH_2$

13. The most suitable reagent for the conversion RCH_2OH — RCHO is

(a) $KMnO_4$, H_2SO_4 (b) $K_2Cr_2O_7$, H_2SO_4

(c) CrO_3, H_2SO_4 (d) 

14. Consider the following sequence of reactions.

$$C_6H_5CHO + CH_3CHO \xrightarrow[heat]{NaOH} (A) \xrightarrow{NaBH_4} (B)$$

The final product (B) is—

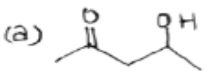
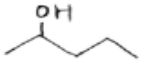
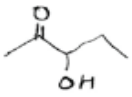
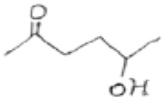
(a) $C_6H_5CHCHOHCH_2CH_2OH$

(b) $C_6H_5CH_2CH_2CH_2OH$

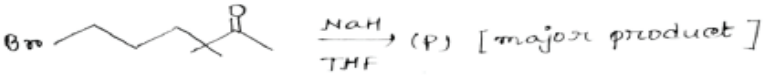
(c) $C_6H_5CH = CHCH_2OH$

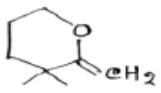
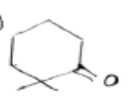
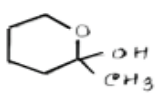
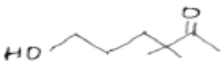
(d) $C_6H_5CH_2CH_2CHO$

15. Which of the following will be dehydratedmost readily in acidic conditions?

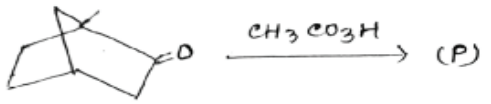
(a)  (b)  (c)  (d) 

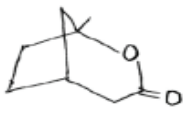
16. For the reaction

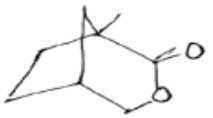


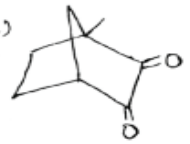
(a)  (b)  (c)  (d) 

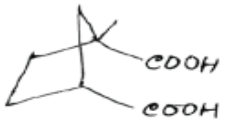
17. Identify the major product (P) of the following reaction



(a) 

(b) 

(c) 

(d) 

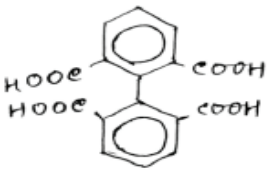
18. 

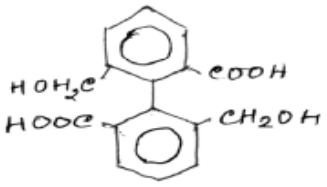
Which of the following reagents is suitable?

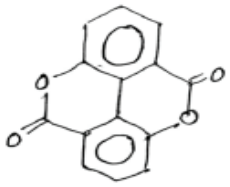
(a) NH_2NH_2, KOH, DMSO (b) $NaBH_4$

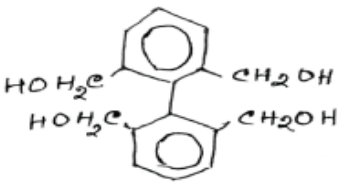
(c) Zn – Mg, Conc. HCl (d) Di AlH_4

19. Which is the major producte (X) obtained in the following reaction?

(a) 

(b) 

(c) 

(d) 

Ans. (1) b (2) d (3) 6 (4) d (5) b (6) d (7) c
(8) b (9) a (10) c (11) b (12) a (13) d (14) a
(15) a (16) b (17) a (18) a (19) b

ALKEHYDES AND KETONES

PROBLEMS

1. Explain :
   (i) Boiling of acetone is 56°C but propanol boils at 49°C.
   (ii) n-butyl alchol has higher boiling point than n-butyraldehyde.
2. Arrange the following in order of decreasing acidity :

   $CH_3 - CHO$, $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$, $Cl - CH_2 - CHO$

3. What happens when
   (a) acetaldehyde is treated with NaOH?
   (b) formaldehyde is treated with NaOH solution?
   (c) acetone is heated with barium hydroxide?
   (d) calcium acetate is heated?
4. Explain why acetaldehyde is more reactive than acetone towards nucleophilic addition reaction.
5. Addition to certain nucleophilic reagents to carbonyl compounds is catalysed by acid. Explain.
6. Acid catalyses the addition of semi carbazide to acetone but too much acidity is harmful.
7. Identify (A), (B) and (C)

   $$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{LiAlH_4} (A) \xrightarrow{SOCl_2} (B) \xrightarrow{\text{alc. KOH}} (C)$$

8. How will you synthesize acetaldehyde grom formaldehyde?
9. How will you synthesize acetone from acetaldehyde?
10. Explain :
    (a) Aldehydes are more active than ketone towards nucleophilic addition.

Unit 12: Carboxylic acid derivatives

12.0 Objectives

The aim of this unit is to make learners aware about the following:

- Preparation of carboxylic acid derivatives by different methods of acidic and alkaline hydrolysis of esters, acid chlorides, anhydrides, esters
- the methods for the conversion of carboxylic acids into acid chlorides, esters and amides.
- To study the properties and reaction of.carboxylic acids including the reduction of carboxylic acid

12.1 Introduction

Carboxylic acids are aliphatic or aromatic compounds which contain at least one carboxyl group (-COOH) in the molecule. The word " carboxyl" " is derived from the names of two functional groups i.e. carbonyl and hydroxyl. Carboxylic acids are classified as mono, di, tri, or polycarboxylic acids according to the number of carboxyl groups present in the molecule. For example, the one -COOH group containing hydrocarbons such as formic acid, acetic acid, propionic acid, lactic acid, malic acid, benzoic acid etc. are called monocarboxylic acids whereas the two -COOH groups containing compounds such as oxalic acid, succinic acid, adipic acid, fumeric acid, malic acid, tartaric acid phthalic acid etc. are called dicarboxylic acids similarly like citric acid contains three -COOH group and termed as tri-carboxylic acid. The long chain monocarboxylic acids are also known as fatty acids such as stearic acid, palmitic acid, oleic acid etc. Now we will learn about the preparation and reactivity of these compounds.

12.2 Acidic and Alkaline hydrolysis of esters

Hydrolysis of esters may be carried out by refluxing them either with dilute acid or with dilute alkali.

$$R^1OH + RCOO^- \underset{}{\overset{^-OH/H_2O}{\rightleftharpoons}} R-\overset{O}{\overset{\|}{C}}-OR^1 \overset{H^+/H_2O}{\rightleftharpoons} RCOOH + R^1OH$$

OR^1 is a poor leaving group compared to anhydrides (OCOR) or halide & thus, water can not alone hydrolyse most esters. When bases catalyse the reaction, the attacking species is " OH, a more Powerful nucleophile than water. This reaction is called saponification & gives salts of acids. Acid catalyses the reaction by making the carbonyl carbon more positive and therefore more susceptible to attack by the nucleophile.

Ingold classified the acid & base catalysed hydrolysis of esters into eight possible mechanisms depending on the following criteria—

(1) Acid or base catalysed (2) Unimolecular or bimolecular, (3) Acyl cleavage or alkyl cleavage.

Type of mechanism	Hydrolysis
$B_{AC}1$	—
$B_{AC}2$	Very Common
$A_{AC}1$	Special Cases
$A_{AC}2$	Very Common
$B_{AL}1$	Special Cases
$B_{AL}2$	rare
$A_{AL}1$	Very Common
$A_{AL}2$	—

All the eight of these are S_N1 or S_N2 or tetrahedral mechanisms. The acid catalysed mechanisms are reversible as well as symmetrical i.e. the mechanisms for the ester formations are exactly the same as for the hydrolysis. Here A & B refers to the acidic or basic medium, the subscripts AC & AL, respectively denote acyl & alkyl oxygen bond cleavage and the number 1 & 2 represents the molecularity of the rate determining step.

1) B_{AC} 1 Mechanism (Base Catalysed acyl oxygen fission unimolecular)

This mode of hydrolysis is not observed.

2) B_{AC} 2 Mechanism (Base Catalysed acyl oxygen fission bimolecular)

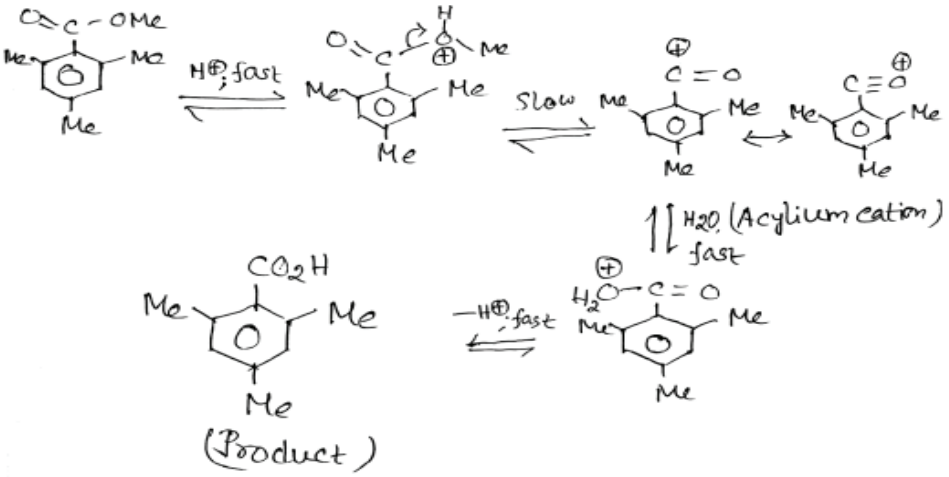
B_{AC} 2 follows tetrahedral mechanism.

$$CH_3-\overset{O}{\overset{\|}{C}}-OEt + \overset{\ominus}{O}H \overset{Slow}{\rightleftharpoons} CH_3-\overset{O^\ominus}{\underset{OH}{C}}-OEt \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}-OH + \overset{\ominus}{O}Et$$

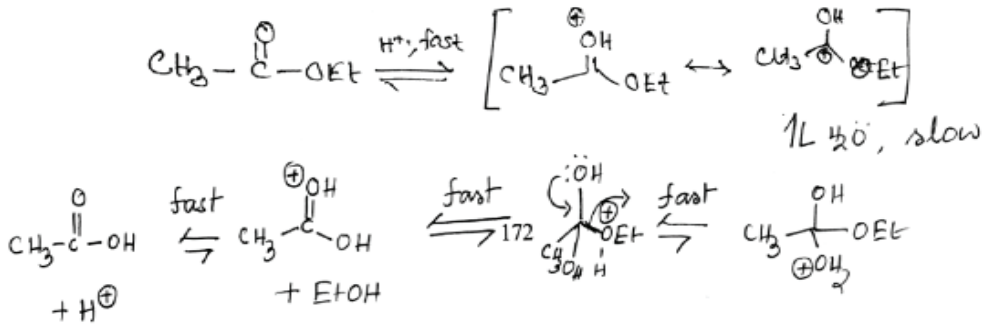
$$\downarrow$$

$$CH_3-C\overset{\ominus}{O}O + EtOH$$

3) $A_{AC}1$ Mechanism (Acid catalysed acyl oxygen fission, unimolecular) $A_{AC}1$ mechanism follows S_N1 pathway. Some special esters having high steric strain, such as esters of mesitoic acid undergo this type of hydrolysis.

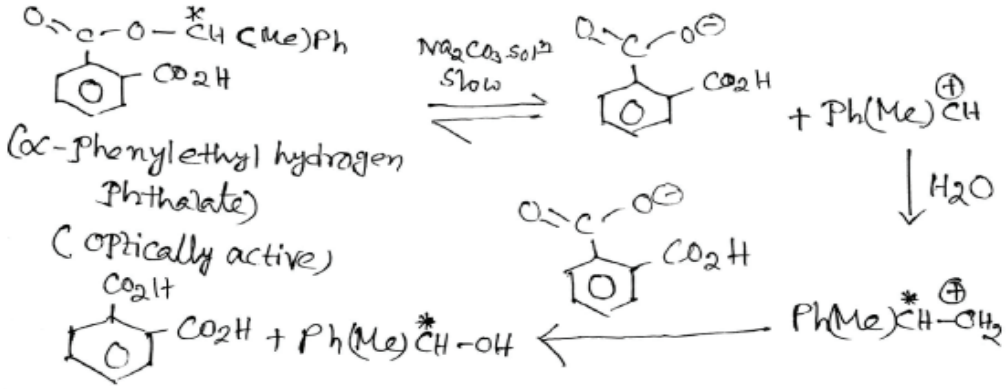


4) A_{AC} 2 mechanism (Acid Catalysed acyl oxygen fission, bimolecular) $A_{AC}2$ mechanism follows tetrahedral mechanism. It is the most general mechanism of acid catalysed hydrolysis of esters.



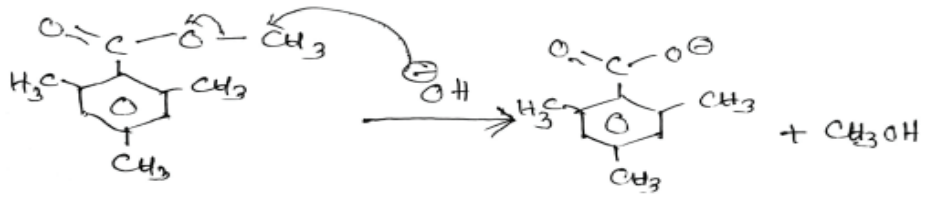
5) $B_{AL}1$ Mechanism (Base catalysed alkyl oxygen fission unimolecular)

$B_{AL}1$ mechanism follows S_N1 pathways. This mechanism has been shown to operate when the alkyl group of alcohol is capable of forming a relatively stable carbocation, the solvent has high ionizing power & the medium is weakly alkaline or neutral.



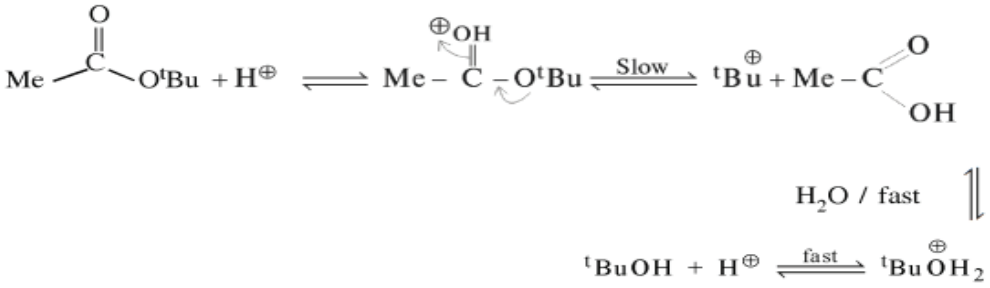
6) $B_{AL}2$ Mechanism (Base catalysed alkyl oxygen fission, bimolecular)

$B_{AL}2$ Mechanism follows S_N2 pathway, it is extremely uncommon & is observed only is special cases.

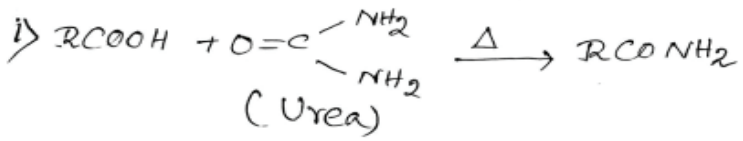


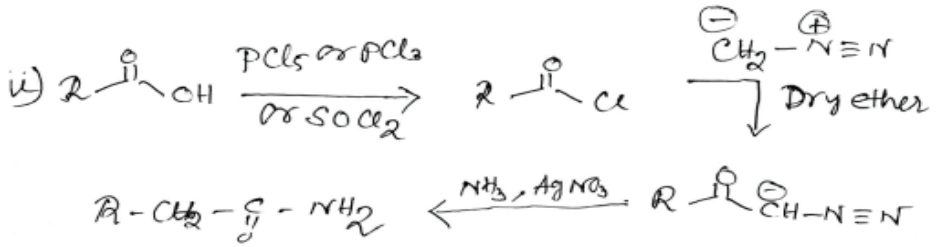
7) A_{AL} 1 Mechanism (Acid catalysed alkyl oxygen fission Unimolecular)

$A_{AL}1$ mechanism follows S_N1 Pathway. Esters, (RCO_2R^1) where the alkyl group R^1 can form a relatively stable carbocation follows this mechanism.



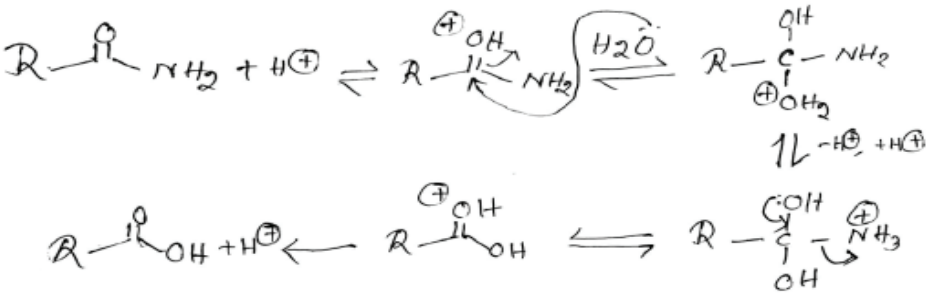
12.3 Synthesis of amide derivative from carboxylic acid



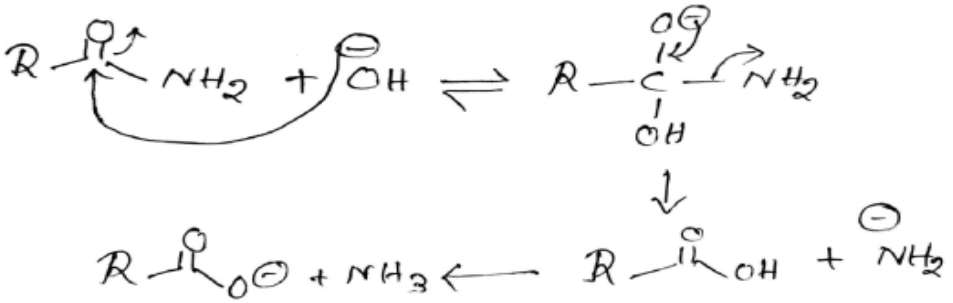


12.4 Synthesis of Carboxylic acid from amide derivative

a) In acidic medium :



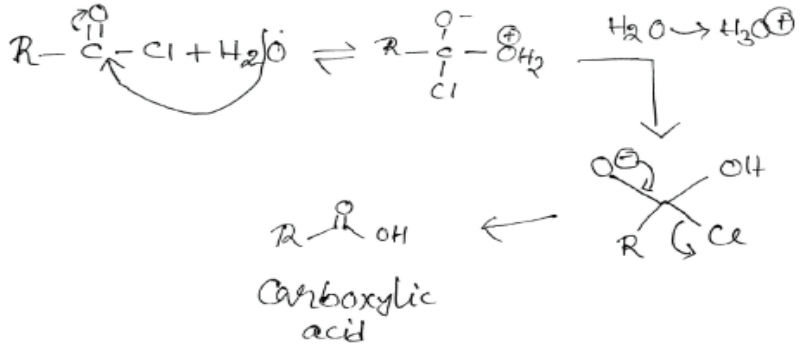
b) In basic medium :



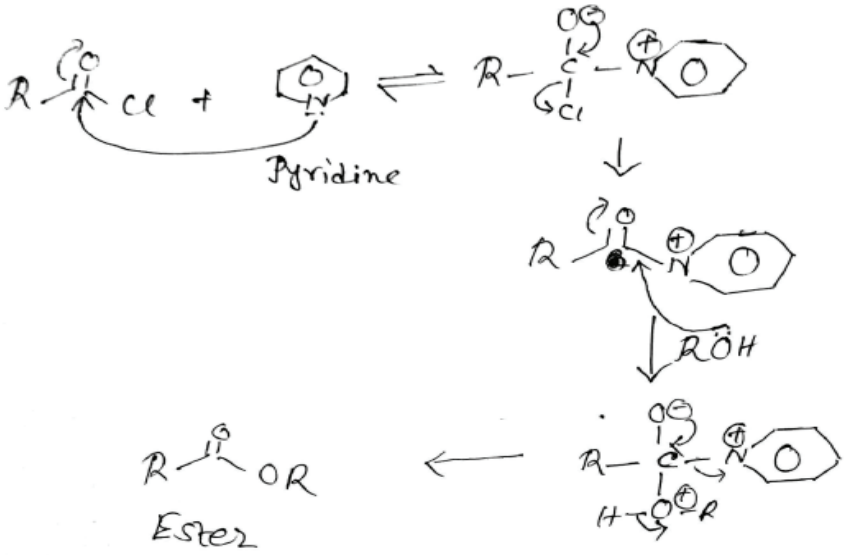
12.5 Hydrolysis of Acid Chloride

Hydrolysis of acid chloride produce carboxylic acid. The reaction follows tetrahedral intermediate.

e.g.



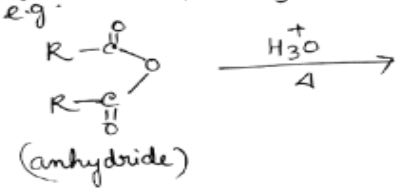
b)



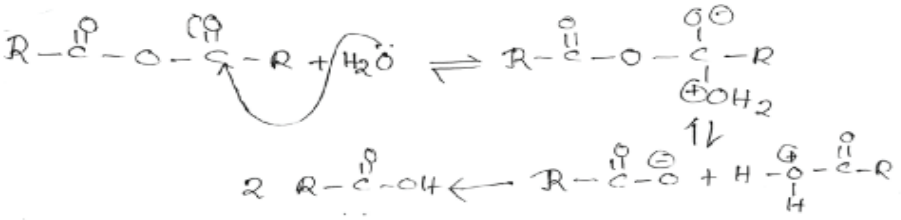
12.6 Hydrolysis of Acid anhydride

Hydrolysis of anhydride produces carboxylic acids.

e.g.



carboxylic acid



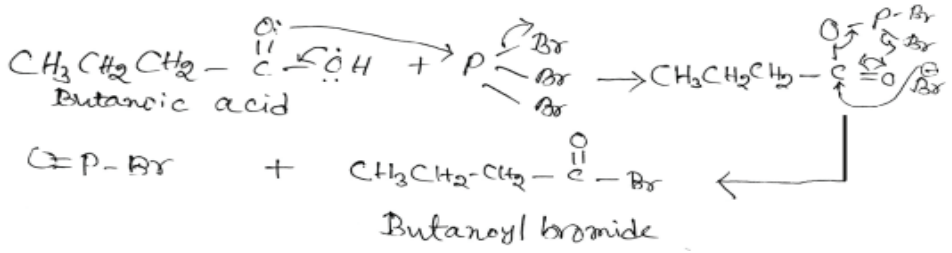
12.7 Hell-Volhard-Zelinsky reaction

α–bromocarboxylic acids can be prepared by treating carboxylic acids having α–hydrogen with bromine & phosphorus tribromide or the equivalent mixture of phosphorus & bromine followed by water to hydrolyse the intermediate α–bromo acyl bromide, α–chloro carboxylic acids may be prepared similarly but the reaction is less specific due to some free radical chlorination. This reaction is known as Hell Volhard-Zelinsky reaction or more simply, as HVZ reaction.

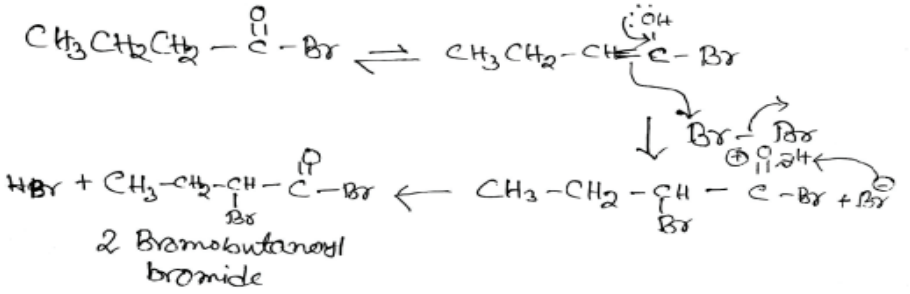
Mechanism :

First Stage : Formation of 2-bromobutonoyl bromide from butanoic acid.

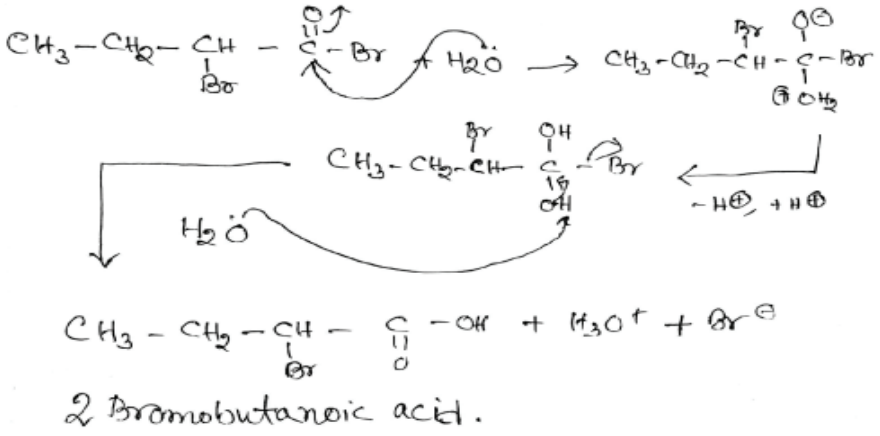
Step-I : Butanoic acid reacts with PBr_3 to give butanoyl bromide.



Step-II : The resulting butanoyl bromide undergoes enolization & the enol being nucleophilic attacks bromine to give 2-bromobutanoyl bromide.



Second stage : Hydrolysis of 2-bromobutanoyl bromide gives 2-bromobutanoic acid.

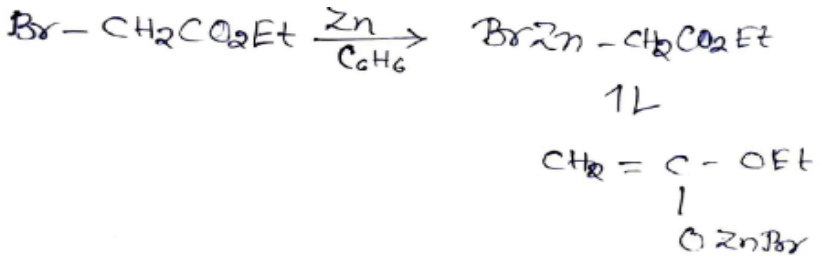


12.8 Reformatsky reaction

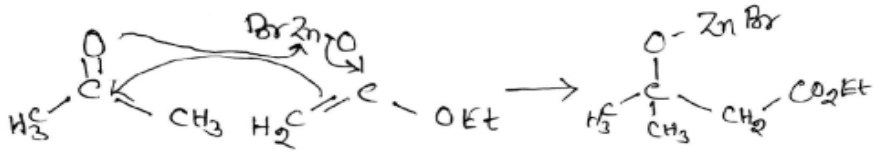
The Reformatsky reaction condenses aldehydes or Ketones with a-halo esters using metallic zinc to form β-hydroxy-esters.

Mechanism :

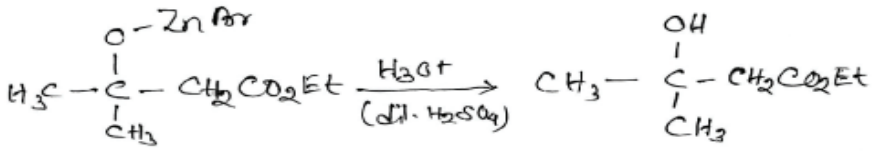
Step-I : α-bromoester reacts with zinc.



Step-II : The zinc bromide enolate adds to the carbonyl group by a cyclic mechanism to form a zinc alkoxide.



Step-III: The alkoxide on hydrolysis with dilute mineral acid produce β-hydroxy ester.

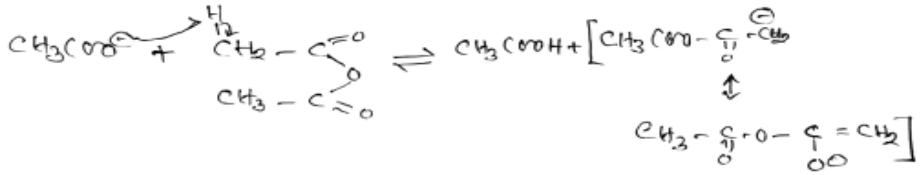


12.9 Perkin reaction

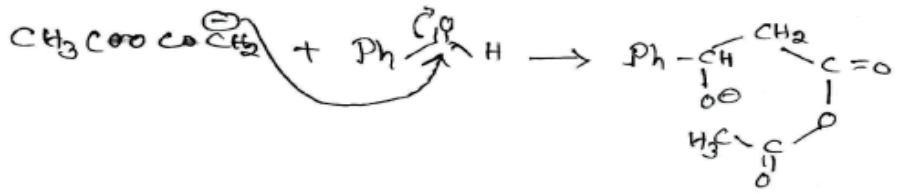
The condensation of an aromatic aldehyde with an acid anhydride in the presence of sodium or potassium salt of the acid corresponding to the anhydride (Which acts as a base) to form an α,β- unsaturated acid, is known as Perkin reaction.

Mechanism :

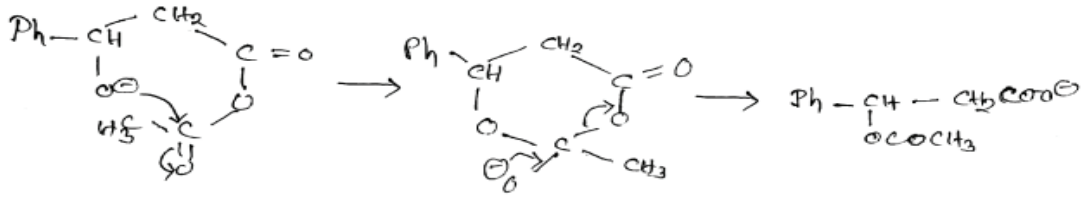
Step-I : Abstraction of an α-H atom from the anhydride molecule by the base CH_3COO^- to form a resonance stabilized carbanion.



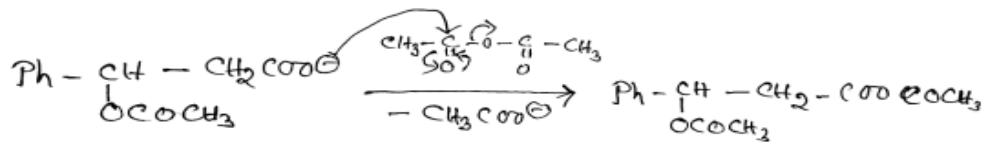
Step-II : Nucleophilic addition of the carbanion to the carbonyl carbon of the aldehyde to form a tetrahedral alkoxide ion intermediate.



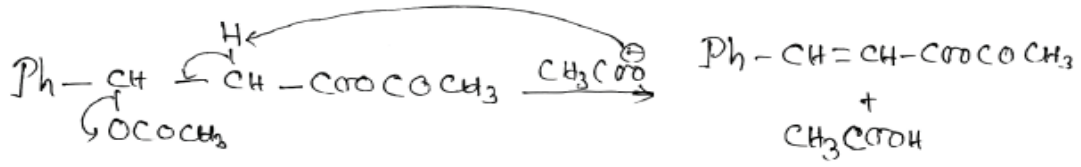
Step-III : Internal transfer of the acetyl group from the carbonyl oxygen atom to the alkoxy oxygen atom via a cyclic intermediate.



Step-IV : Acetylation of the resulting carboxylate ion by Ac_2O.



Step-V : Elimination of acetic acid by the base to form an unsaturated mixed anhydride.

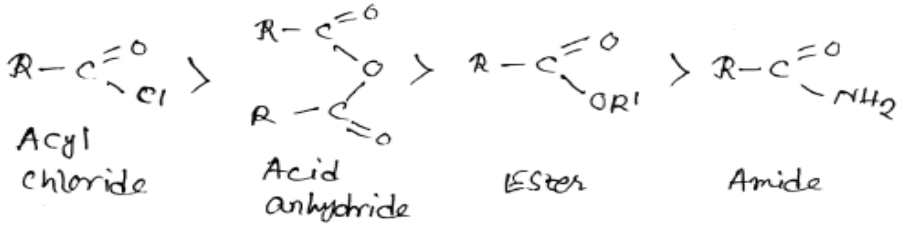


Step-VI : Hydrolysis of the mixed anhydride to form the constituent acids.

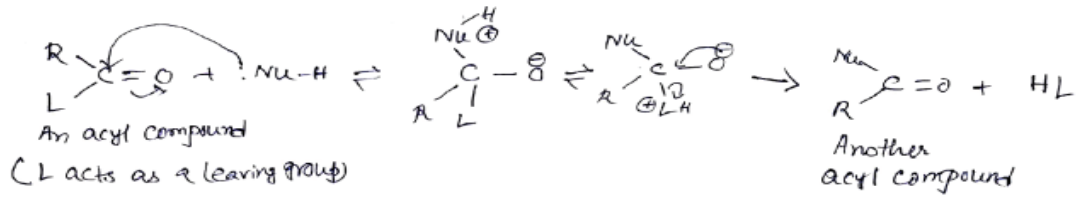
$$Ph-CH=CH-COOCOCH_2 \xrightarrow{H_2O} \underset{\text{Cinnamic acid}}{Ph-CH=CHCOOH} + CH_3COOH$$

12.10 Relative Reactivity of Acyl Compounds

Among the acid derivatives, acyl chlorides are the most reactive toward nucleophilic addition-elimination, & amides are the least reactive. In general, the overall order of reactivity is—



Mechanism of the reaction :



- The initial step in an acyl substitution reaction is nucleophilic addition at the carbonyl carbon. This step is facilitated by the relative steric openness of the carbonyl carbon atom & the ability of the carbonyl oxygen atom to accommodate an electron pair of the carbon-oxygen double bond.
- In the second step the tetrahedral intermediate eliminates a leaving group, this elimination leads to regeneration of the carbon-oxygen double bond & to a substitution product.
- The general order of reactivity of acid derivatives can be explained by taking into account the basicity of the leaving group.

12.11 Summary

The unit can be summarized as:

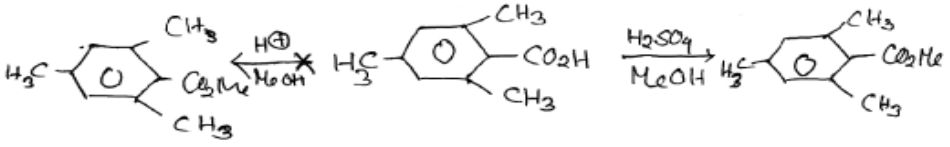
- The carboxylic acids are known as mono, di, tri, or polycarboxylic acids according to number of carboxyl groups present in the molecule.
- Long chain monocarboxylic acids are also known as fatty acids such as stearic acid, palmitic acid, oleic acid etc.

- Carboxylic acids have higher boiling points than other hydrocarbons such as alcohols, ethers, aldehydes, or ketones of comparable molecular weight.
- The carboxylic acids are weak acids, their acidic strength decreases with increase in molecular weight. Electron withdrawing groups enhance the acid strength and the electron releasing groups reduce the acidity of carboxylic acids.
- The carboxylic acids (pKa 4-5) are stronger acids than alcohols (pKa 16-18) because of delocalization of the negative charge of the carboxylate anion through resonance and the electron withdrawing inductive effect of the carbonyl group.
- The carboxylic acids can be prepared, by various methods.
- by the oxidation of primary alcohols and aldehydes with acidic $KMnO_4$ or acidic $K_2Cr_2O_7$.
- By the hydrolysis of esters and other functional derivatives either in acidic or alkaline medium.
- The carboxylic acids undergo halogenations with chlorine or bromine, are reduced to alcohol with a suitable reducing agent like lithium aluminium hydride ($LiAlH_4$ can be decarboxylated, undergo Kolbe' s electrolysis, release hydrogen gas while reacting with active metals such as K, Ca, Mg.
- The carboxylic acids react with alkalis like sodium hydroxide to form salts and water.

12.12 Exercises

Q.l : 2, 4, 6-Trimethyl benzoic acid (mesitoic acid) does not undergo esterification under ordinary acid-catalysed conditions ($A_{AC}2$ mode) , whereas in concentrated sulphuric acid it undergo quantitative esterification— Why?

Ans. :



Under normal acid, catalysed conditions mesitoic acid undergoes protonation on the carbonyl oxygen of the -COOH group. The bulky O-Me group force the planar protonated carboxyl group out of the plane of the benzene ring & as a result, the p orbital on the adjacent ring carbon atom. Overlap between them thus can't take place & because of this steric inhibition of delocalisation, die protonated carbonyl group becomes unstable. Again, die attacking nucleophile, MeOH has to attack die positive carbon from a direction at right angles to the plane hi which the protonated carboxyl group is lying. But, as both the directions are blocked by bulky o-Me groups, the approach of the nucleophile is inhibited. For these reasons, esterification does not take place under normal acid-catalysed conditions.

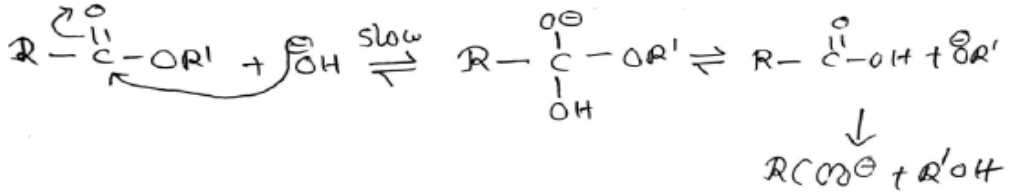
In cone. H_2SO_4 abnormal protonation on the hydroxyl oxygen atom allows formation of an acylium ion. The p orbital on the positive carbon is no longer prevented from being parallel with the p orbital on the ring carbon atom & so it is stabilised by delocalisation of its positive charge over the n orbital system of the benzene ring. Again sine the acylium ion is linear, the approach of die nucleophile from directions at right angles to the plane of the molecule is no longer inhibited & so it undergoes nucleophilic attack by MeOH from that directions to give an ester.

Q. 2. : 2. 3, 4, 5-Trimethyl benzoic acid undergoes ready esterification by the normal $A_{AC}2$ mode - explain.

Ans. : This acid undergoes esterification by the normal Aac2 mode because p/p orbital overlap is no longer sterically inhibited in the simple protonated species & delocalisation of the '+ve' charge, with consequent stabilisation, takes place. Also the approach of the nucleophile is no longer inhibited from the directions at right angles to the plane of the molecule. For these reasons, 3,4,5-tri methyl benzoic acid undergoes esterification by the normal $A_{AC}2$ mechanism.

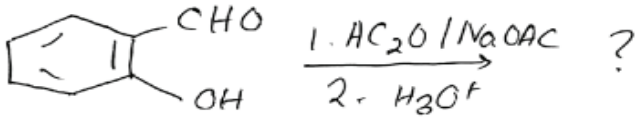
Q.3. Methyl Chloroacetate ($ClCH_2COOCH_3$) Undergoes alkaline hydrolysis ($A_{AC}2$) at a much faster rate than methyl acetate (CH_3COOCH_3). Explain

Ans. The mechanism of alkaline hydrolysis ($B_{AC}2$) of an ester may be given as follows :

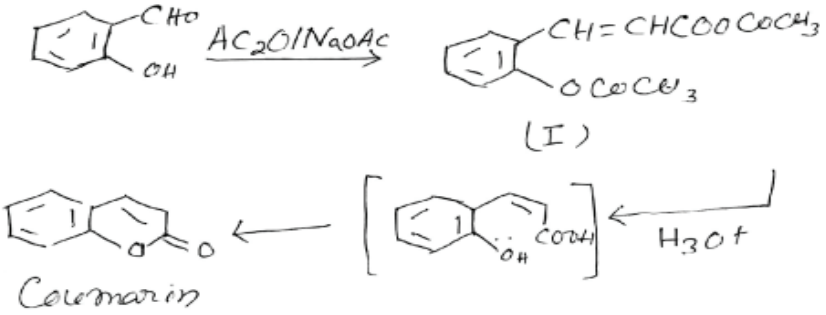


Electron withdrawing substituents in either the acyl or alkyl part of the ester make the carbonyl carbon more positive & thereby facilitates the attack by OH- on it. This results in increase in reaction rate because it is the r/d step of the reaction. In $ClCH_2COOCH_3$, Cl atom exerts its -I effect & as a consequence, the carbonyl carbon becomes relatively more positive than that of methyl acetate. Since, in $ClCH_2COOCH_3$, Cl atom exerts its-I effect & as a consequence, the carbonyl carbon becomes relatively more positive than that of methyl acetate. Because of this $ClCH_2COOCH_3$ undergoes hydrolysis at a much faster rate than CH_3COOCH_3.

Q4. Predict the product of the following reaction & explain its formation:

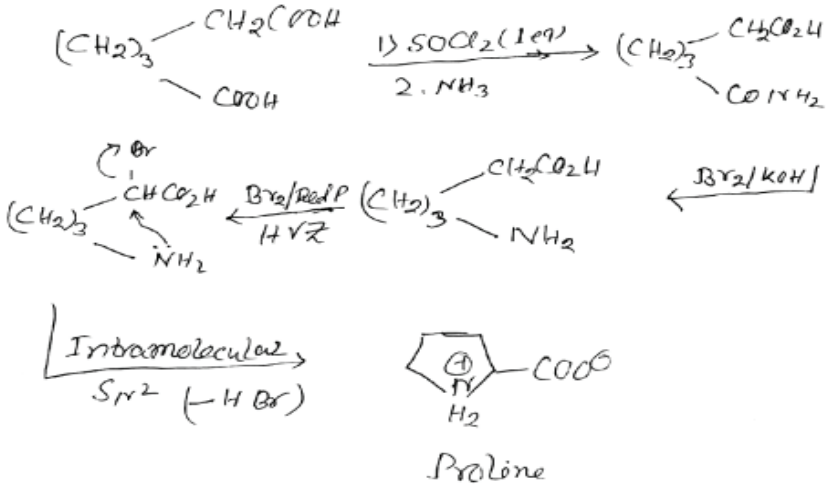


Ans. o-Hydroxybenzeldehyde undergoes perkin reaction & acetylation to give the compound (I). This when treated with dil. acid, undergoes hydrolysis by ring closure to give coumarin.



5. How can proline be synthesized from adipic acid using HVZ reaction in one of the step?

Ans. Proline can be synthesized from adipic acid as follows :



Questions

1. Ethyl 2-methylpropanoate undergoes alkaline hydrolysis at a much slower rate than ethyl acetate - explain.

2. The rate of hydrolysis of phenyl acetate is increased about 150-fold at neutral pH by the presence of a carboxylate ion in the ortho position.

4. Explain why the base NaOEt or NaOH can' t be used in the Perkin reaction.

Unit 13: Amines and Diazonium Salts

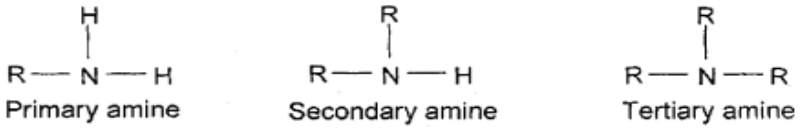
13.0 Objectives

By the end the unit learners should be able to know about;

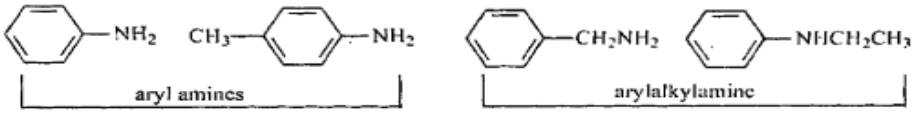
- the organic compounds containing nitrogen particularly the aliphatic and aromatic amine and diazonium compounds,
- Preparation of aliphatic and aromatic amines.
- Saytzeff rule and Hofmann rule for elimination reaction of amines.
- Hinsberg test for distinguish between primary, secondary and tertiary amine.
- Electrophilic substitution reaction of aniline including the conversion of aromatic amine to benzene, phenol and dyes.
- Preparation and reactions of diazonium Salts.

13.1 Introduction

Amines are aliphatic and aromatic derivatives of ammonia which are obtained by the replacement of one. two or all three hydrogen atoms of ammonia by alkyl or aryl groups. Amines are described as primary (1°). secondary (2") or tertiary (3") depending on how many alkyl or aryl substituents are attached to the nitrogen atom.



Aromatic amino compounds are of two types, aryl amines and arylalkyl amines. Aryl amines are those compounds in which the $-NH_2$ group is directly attached to the nucleus e.g., aniline, p-toluidine etc. whereas in arylalkyl amines the $-NH_2$ group is attached to a carbon atom of the side chain e.g., benzylamine, p-phenylethylaniine etc.



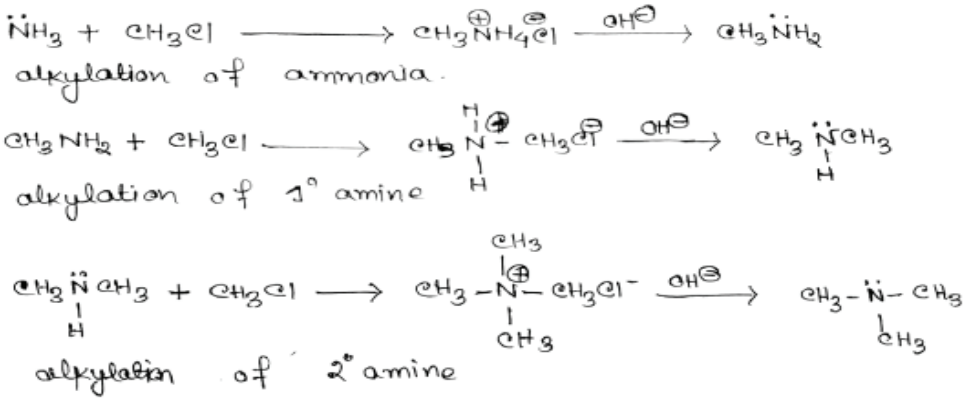
13.2 Amines

In organic chemistry, amines are compounds and functional group that contain a basic nitrogen atom with a lone pair. Amines are formally derivatives of ammonia, wherein one or more hydrogen atoms have been replaced by substituent such an alkyl or aryl group.

13.3 Preparation of Aliphatic amines

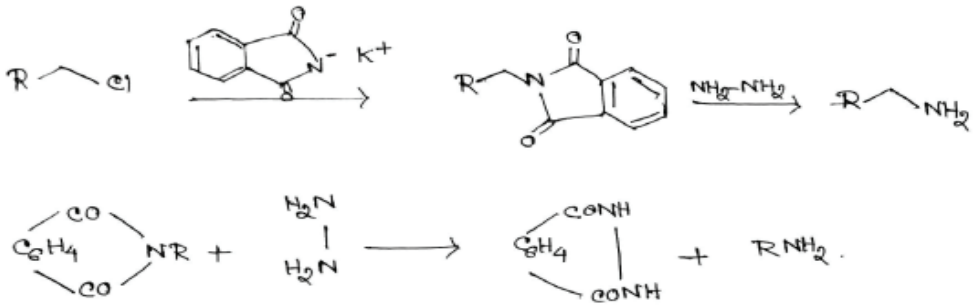
13.3.1 From alkyl halide :

The reaction of ammonia with an alkyl halide leads to die formation of a primary amine. The primary amine that is formed can also react with the alkyl halide, which leads to a di-substituted amine that can further react to form a tri-substituted amine. Therefore, die alkylation of ammonia leads to a mixture of products.



13.3.2 Gabriel's Phthalimide Synthesis :

The Gabriel synthesis is a chemical reaction that transforms primary alkyl halide into primary amines. The reaction used potassium phthalimide which is N-alkylated with primary alkyl halide to give the corresponding N-alkylphalimide. Upon workup by acidic hydrolysis the primary amine is liberated as the amine salt.



13.3.3 Hoffmann's Bromamide Reaction :

We can also prepare amines (only primary) by Hoffmann degradation. In this method, the amine will have one carbon atom less than the amide by removing CO_2. The reaction proceeds via formation of nitrene.

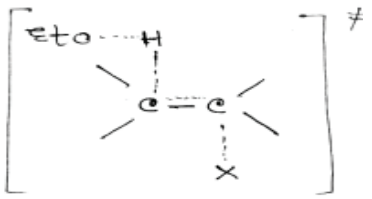
$$CH_3CH_2CH_2CONH_2 \xrightarrow[NaOH]{Br_2} CH_3CH_2CH_2NH_2$$

13.4 Saytzeff's rule

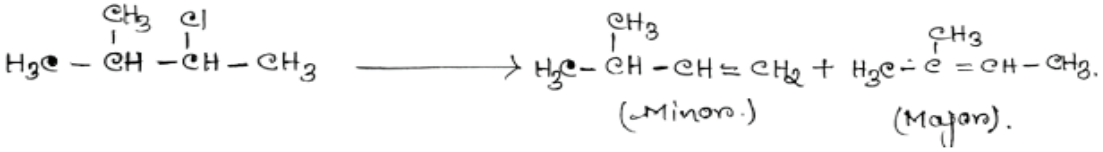
This rule is valid for neutral substrates like halide, alcohols etc.

Statement : More substituted alkene will be the major product.

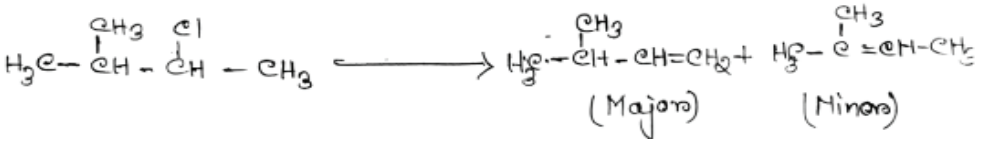
Justification : Neutral substrates except F, undergo ideal E_2 reaction in which both C-H and C-X bonds are being broken and C-C double bond is being formed simultaneously is possesses considerable double bond character.



Therefore, according to Hammond's postulate any effect that stabilizes the product alkene also stabilizes the TS because TS is product like. The TS leading to the formation of 2-bufene is greatly stabilized due to greater number of (6) hyper conjugative structure.



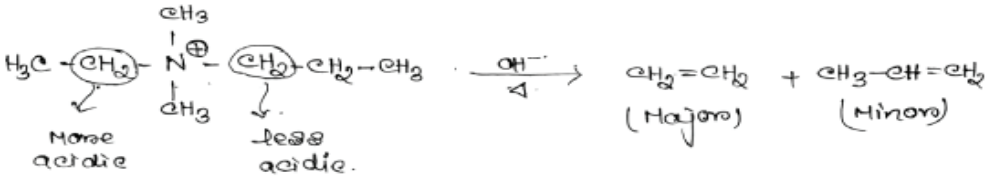
Exception of Saytzeff's rule:



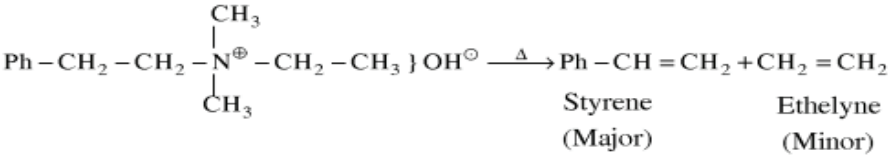
13.5 Hofmann rule

Valid for charged substrate like quaternary ammonium salts, sulphonium salts etc.

Statement : Less substituted alkene will be major



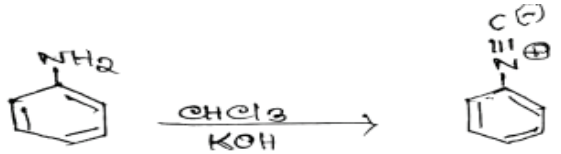
Explanation : Substrates containing charged leaving group (R_3N^+-) undergo E_2 elimination in which breaking of C-H bond starts well before the breaking of C-NR_3^+ bond, the TS of such a reaction possesses little alkene character but considerable carbaniovile character (E_1CB like E_2)



It is an exception of Hofmann's rule.

13.6 Carbylamine reaction of amines

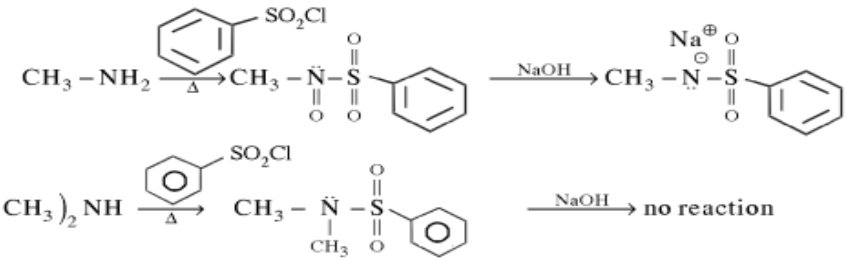
The Carbylamine reaction is a chemical test for detection of primary amines. In this reaction, the analyte is heated with alcoholic potassium hydroxide and chloroform. If a primary amine is present, the isocyanide is formed.



The carbylamine test does not give a positive reaction with 2° and 3° amines.

13.7 Hinsberg test

The Hinsberg test, which can distinguish primary, secondary and tertiary amines, is based upon sulfonamide formation. In this test an amine is reacted with benzene sulfonyl chloride. If a product forms, the amine is either a 1° or 2° amine, because 3° amine do not form stable sulfonamides If the sulfonamide that forms dissolves in aqueous sodium hydroxide solution it is a primary amine. If the sulfonamide is insoluble in aqueous sodium hydroxide, it is a secondary amine. The sulfonamide of a primary amine is soluble in an aqueous base because it still possesses an acidic, hydrogen on the nitrogen, which can be lost to form a sodium salt.

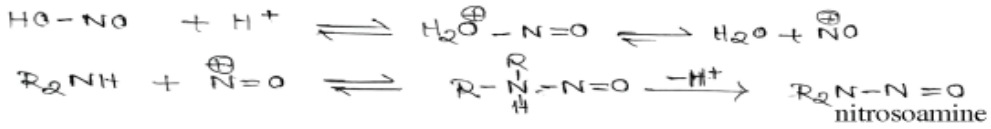


13.8 Action of HNO_2 on 1°, 2°, 3° amine

1° amine react with nitrous acid with the evolution of nitrogen.

$$RNH_2 + HNO_2 \rightarrow R\text{–}OH + N_2 + H_2O$$

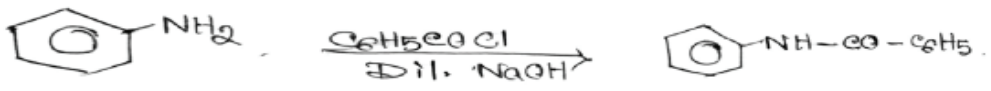
Whatever are the products by the action of HNO_2, on 1° amine N_2 always evolve? Thus this reaction is may be used as a test for 1° amine. 2° amine react with HNO2, to form insoluble oily nitrosoamine. Here N_2 is not evolved.



3° amine dissolve in cold HNO_2 to form - R_3NHNO_2 or $[R_3NH]^{(+)}\ NO^{(-)}$ nitrosoamine.

13.9 Schotten - Baumann reaction

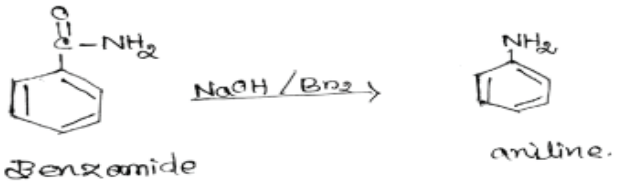
The Schotten - Baumann reaction is a method to synthesis amides from amines and acid chlorides. Sometimes die name for this reaction is used to indicate die reaction between an acid chloride and an alcohol to form an ester.



13.10 Preparation of Aromatic amines

13.10.1 Hoffmann degradation of amides :

Heating the amides with a mixture of bromine and KOH or NaOH. Amides will change to amines. It is used to shorten the chain by one carbon.



13.10.2 From aromatic hydrocarbon :

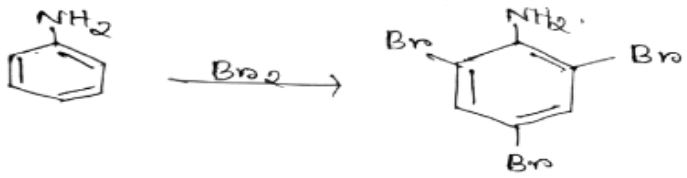
In presence of catalyst $FeCl_3$ and $A1C1_3$ aromatic hydrocarbon reacts with hydroxylamine to prepare aromatic amine.

$$ArH + HONH_2 \xrightarrow{FeCl_3 / AlCl_3} ArNH_2 + H_2O$$

13.11 Electrophilic substitution Reaction of Anilines

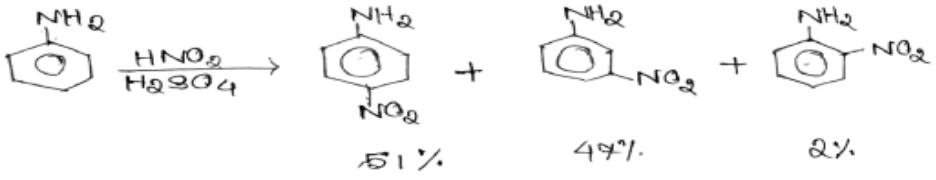
An electrophile refers to an electron seeking species. Thus electrophilic substitution reaction refers to the reaction in which an electrophile substitutes another electrophile in an organic compound (-NH2) group in aniline is electron donating group and hence is very activating towards the electrophilic substitution reaction.

Halogenation :



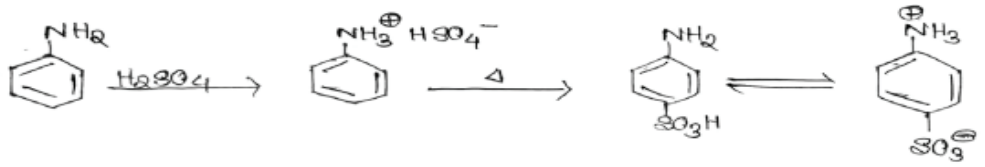
When aniline comes in the vicinity of bromine water, then the bromine molecule develops a polarity with in itself and bromine with a slightly positive charge acts as an electrophile and attacks the electron rich ortho and para position of aniline. A white coloured precipitate of 2, 4, 6 tribromoaniline is obtained at room temperature.

Nitration :



In this reaction, alongside para isomer, the meta isomer is also observed, It is because the aniline molecule gets protonated in acidic medium to become anilinium ion which is meta directing.

Sulfonation :



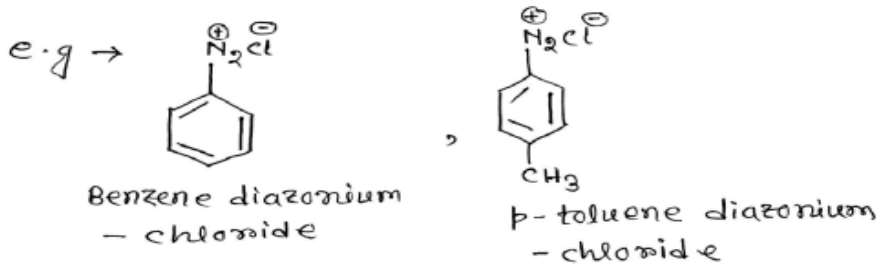
Sulphuric acid reacts vigorously with aniline to form anilinium hydrogen sulphate which on heating produces sulphanilic acid which in turn also has a resonating structure with zwitterion as shown in the above figure.

13.12 Diazonium Salts

Aromatic primary amines on reaction with nitrous acid in cold condition (0-5°C) gives diazonium salts.

These salts have general formula :

ArN_2X^-, Where, Ar = Aryl group, such as phenyl (C_6H_5 –), p-nitrophenyl (p–$NO_2C_6H_5$–) etc.



13.13 Preparation of diazonium salt

Diazonium salts are prepared by adding sodium nitrite in cold aqueous solution of aromatic amines in presence of dilute HC1.

At first, HC1 reacts with sodium nitrite to form nitrous acid then aromatic amines react with nitrous acid and HC1 and forms diazonium salt.

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$
Sodium-nitrite — nitrous acid

$$C_6H_5NH_2 + HNO_2 + HCl \longrightarrow C_6H_5\overset{+}{N}_2Cl^- + 2H_2O$$
(Aniline)

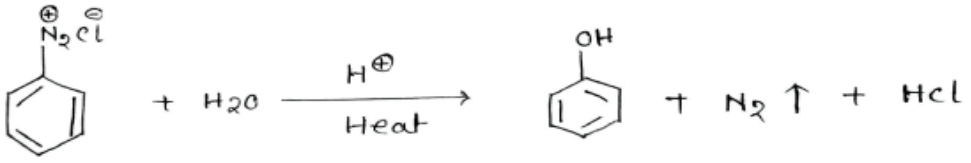
Over all reaction : $C_6H_5NH_2 + NaNO_2 + 2HCl \longrightarrow C_6H_5\overset{\oplus}{N}_2\overset{\ominus}{Cl} + NaCl + 2H_2O$

Benzene diazonium chloride

13.14 Reactions of diazonium salt

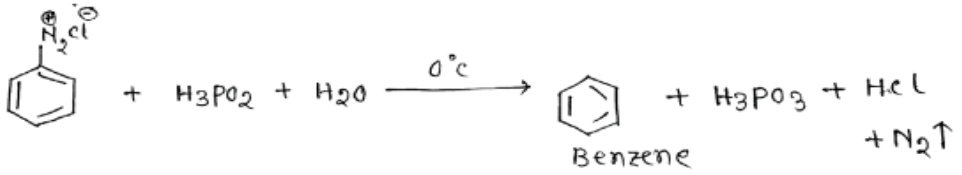
(1) Preparation of phenol from $C_6H_5N^+_2Cl^-$:

If dilute H_2SO_4 is added in the solution of benzene diazonium chloride and heated, the diazonium group $\left(N_2^{\oplus}X^{\ominus}\right)$ is replaced by hydroxyl group (–OH)

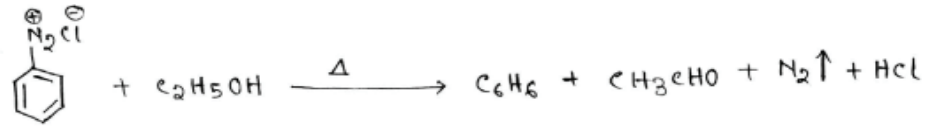


(2) Preparation of Benzene from $C_6H_5N^+_2Cl^-$:

(i) When hypophosphorous acid (H_3PO_2) is added in the soluton of diazonium salt, the diazonium salt is reduced and diazonium group $\left(^{\oplus}_{-N_2}X^{\ominus}\right)$ is replaced by Hydrogen.



(iii) If Benzene diazonium chloride is heated in presence of alcohol, it reduces to benzene.

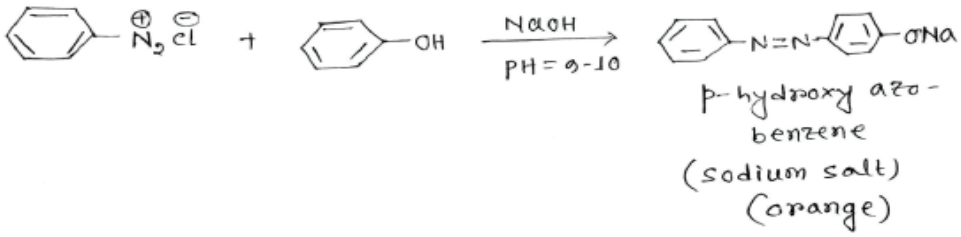


(3) Coupling Reaction (formation of azo-dye) :

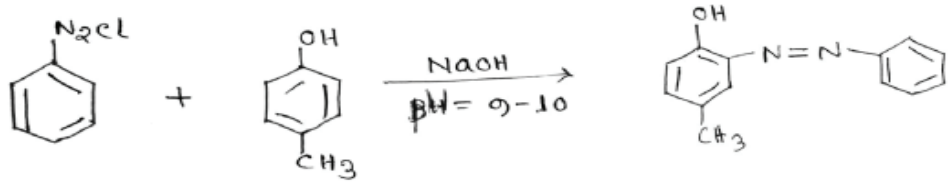
Diazonium salts reacts with phenols, naphthol or aromatic amines and gives colourful (orange, red or yellow) azo-compounds. In these compounds, two aromatic rings are attached by diazo group (- N = N-). These type of reactions are called **Coupling reaction**.

(a) Coupling with phenol :

When benzene diazonum chloride is added in die alkaline solution of phenol, coupling reaction occurs and orange coloured azo-dye, p-hydroxyazobenzene is formed.

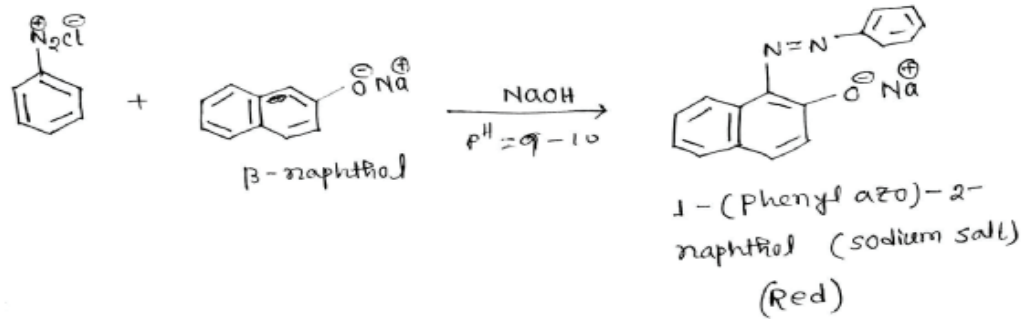


due to steric hindrance, die coupling reaction does not occurs at ortho position with respect to-OH group rather it takes place at para position. If the para position is blocked then the coupling occurs at -ortho position. If both ortho and para positions are blocked then coupling reaction does not happen



(b) Coupling with p-naphthol :

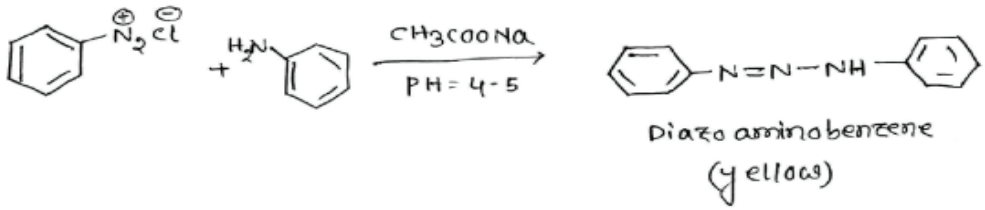
Benzene diazonium chloride forms red azo-dye when it reacts with alkaline solution of β-naphthol. It is a identification test of primary aromatic amine.



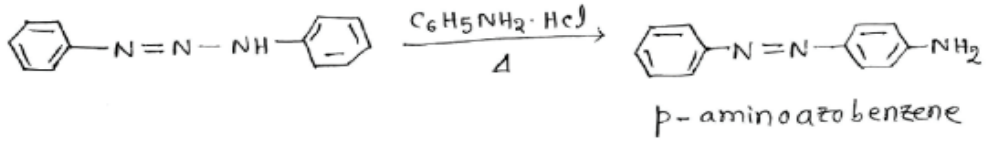
(c) Coupling with amines :

(i) With primary amines -

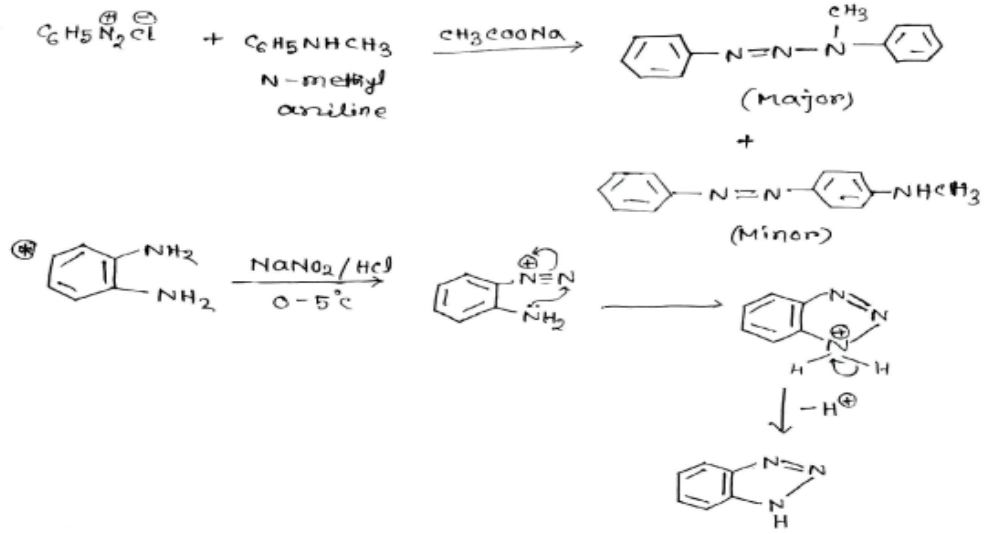
N-Coupling takes place with primary amines.



when diazonaminobenzene is heated with aniline hydrochloride it rearranges to -aminodiazobenzene. (C-Coupling)

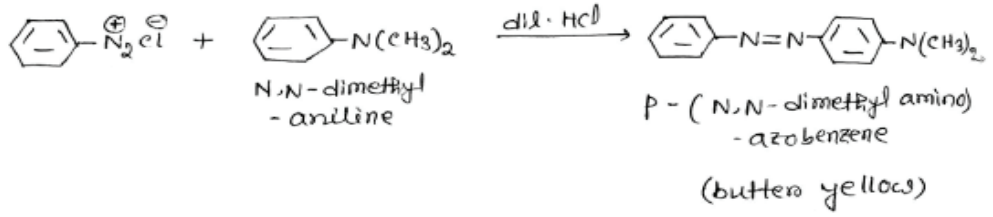


(ii) **With Secondary amines :**
Secondary amines also give N-Coupling reaction.



(iii) With tertiary amines :

In neutral or slightly acidic solution, benzene diazonium chloride reacts with N, N-dimethyl aniline and C-coupling occurs. N-coupling does not takes place due to lack of hydrogens at N-atom.



13.15 Summary

After studying this unit it can be summarized that this unit educate us about:

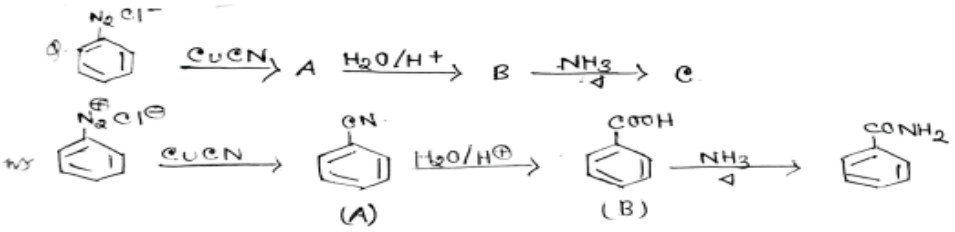
- Aliphatic and aromatic derivatives of ammonia known as amines and are obtained by the replacement of one, two or ah three hydrogen atoms of ammonia by alkyl or aryl groups.
- Classification of amines as primary, secondary and tertiary amines based on the number of hydrogens replaced by alkyl or aryl groups.
- We studied the physical and chemical properties of aliphatic and aromatic amines in detail.
- As amines posses basic character, this unit also tells us about basic characters pKb values

indicating the basic strength and stereochemistry of amines. ;

- We also studied various methods of preparation of primary, secondary and tertiary amines.
- The consolidated chemical reactions of aliphatic and aromatic reactions have also been described in this unit.
- Aromatic diazonium salts are normally prepared from arylamine, NaNCK and MCI ai temperature below 5°C.
- The reaction of diazonium salt with aromatic nuclei is known as coupling reaction. The overall reaction is a case of aromatic electrophilic substitution.

13.16 Exercises:

(1)



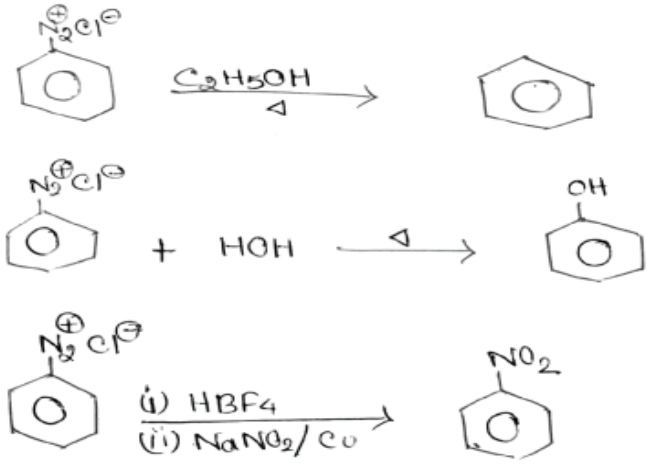
(2) Complete the following reactions :

(i) $C_6H_5N_2^+Cl^- \xrightarrow[\text{(Room temp)}]{H_2O}$

(ii) $C_6H_5N_2^+Cl^- + H_3PO_2 + H_2O \longrightarrow$

(iii) $C_6H_5N_2^+Cl^- \xrightarrow{CuCl/HCl}$

(3) How to prepare benzene, phenol, nitrobenzene, through $C_6H_5N_2^+Cl^-$



(4) Complete the following reaction :

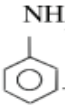
(i) $CH_3NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta}$

(ii) $C_2H_5NH_2 + CH_3I \xrightarrow{\Delta}$

(iii) $C_6H_5\overset{\oplus}{N}_2Cl^- + HBF_4 \longrightarrow A \xrightarrow{\Delta}$

(iv) $C_6H_5NH_2 + NaNO_2 + 2HCl \longrightarrow$

(v)  $\xrightarrow{CF_3CO_3H}$ C

(vi)  $\xrightarrow[NaOH]{COCl}$

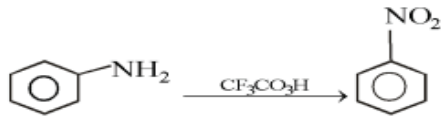
Ans.

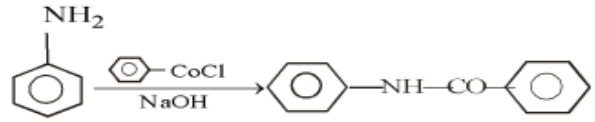
(i) $CH_3NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} CH_3NC + 3KCl + 3H_2O$

(ii) $C_2H_5NH_2 + CH_3I \xrightarrow{\Delta} \begin{matrix} C_2H_3 \\ CH_3 \end{matrix}\!\!>\!\!NH + HI$

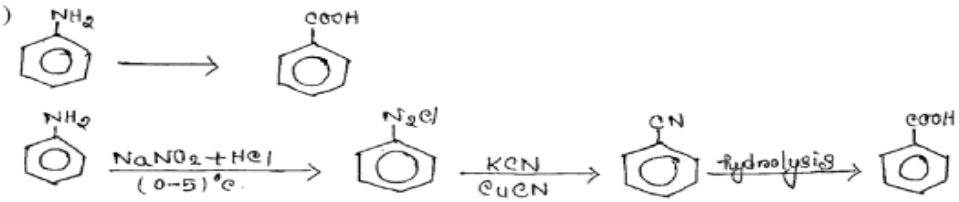
(iii) $C_6H_5\overset{\oplus}{N}_2Cl^{\ominus} + HBF_4 \longrightarrow C_6H_5N_2BF_4 \xrightarrow{\Delta} C_6H_5F + BF_3 + N_2$

(iv) $C_6H_5NH_2 + NaNO_2 \xrightarrow{HCl} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$

(v) 

(vi) 

Conversion

(1) 

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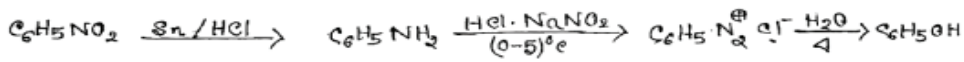
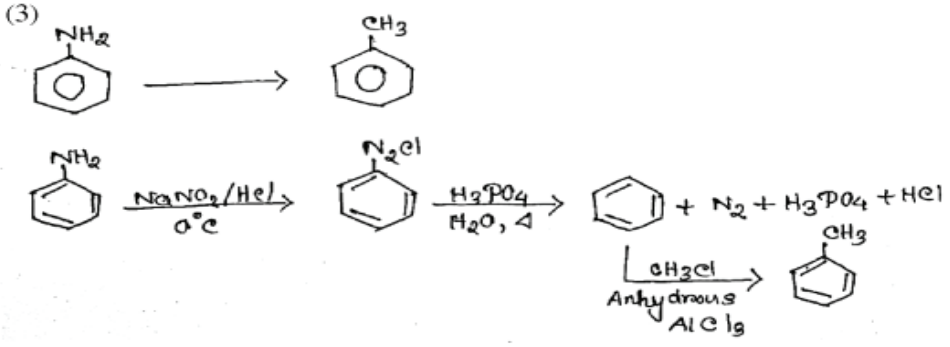
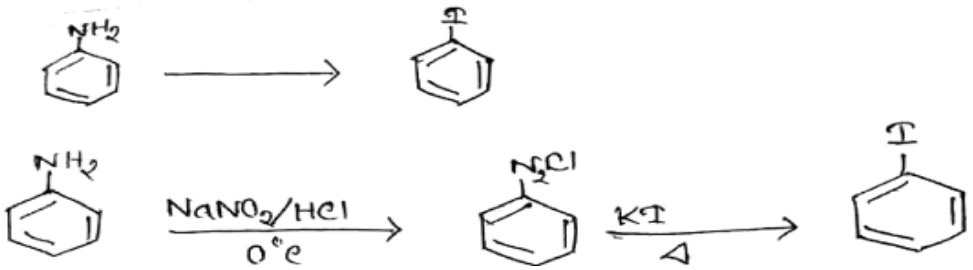
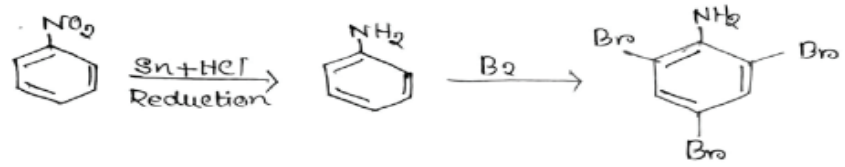


(3) 

(4) 

(5) Nitrobenzene ⟶ 2, 4, 6 tribromoaniline



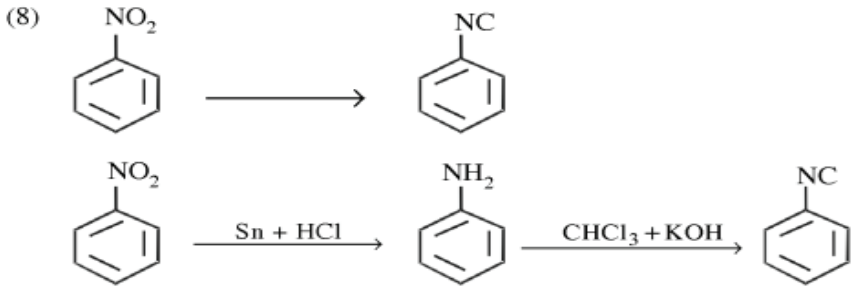
(6) $CH_3OH \longrightarrow CH_3CH_2NH_2$

$$CH_3OH \xrightarrow{SOCl_2} CH_3Cl \xrightarrow{NaCN} CH_3CN \xrightarrow{LiAlH_4} CH_3CH_2NH_2$$

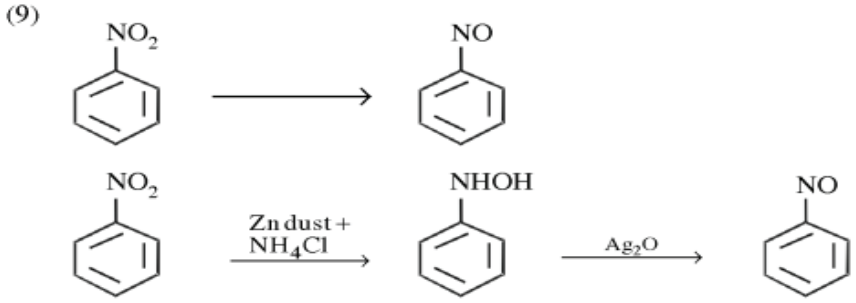
(7) $CH_3CN \longrightarrow CH_3NH_2$

$$CH_3CN + H_2O \xrightarrow{NaOH} NH_3CONH_2 \xrightarrow{Br_2/NaOH} CH_3NH_2$$

(8)



(9)



Unit 14 Carbohydrates

14.0 Objectives

By the end of the unit learners should be able to know about:

- The importance of carbohydrates especially monosaccharides
- Classification of carbohydrates
- Structure and properties of Monosaccharides such as glucose
- Step-up and step-down reaction in Monosaccharides
- Structure and properties of Disaccharides and Polysaccharides

14.1 Introduction

Carbohydrates are polyhydroxy aldehydes and ketones or compounds that can be hydrolysed to them. The general formula of carbohydrates is $C_x(H_2O)_y$, i.e. they appeal' to be 'hydrates of carbon'. e.g.- glucose, fructose, etc.

14.2 Classification

Carbohydrates are classified into three major categories.

(A) **Monosaccharide** : These carbohydrates contain single polyhydroxy aldehyde or ketone unit which cannot be further hydrolysed to give smaller carbohydrate unit. e.g.-glucose, fructose etc.

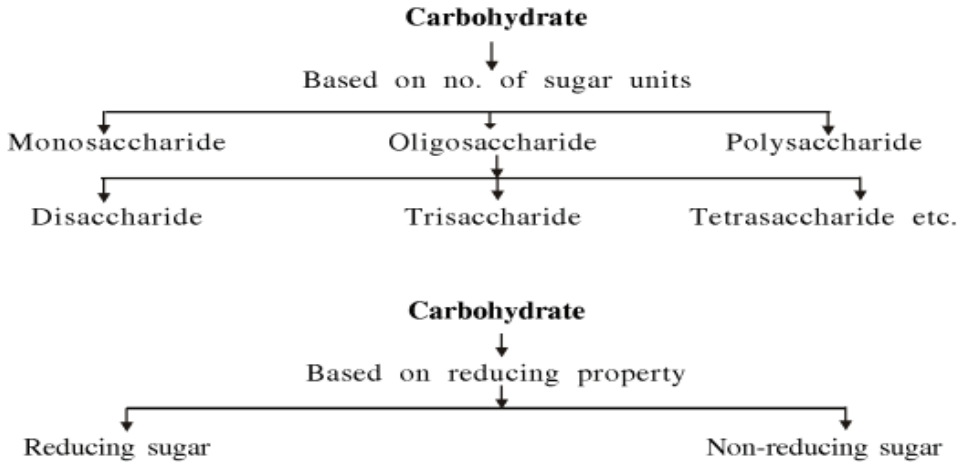
(B) **Oligosaccharide** : These carbohydrates give 2-10 monosaccharide units on hydrolysis.

e.g.- disaccharide – sucrose → glucose + fructose
trisaceharide – raffinose →glucose + fructose + galactose.
tetrasaccharide – stachyose → glucose + fructose + 2 galactose.

(C) **Polysaccharide** : These carbohydrates give a large number of monosaccharide units on hydrolysis, i.e. it is polymer of sugar that have molecular weight from a few thousand to several millions. e.g.-starch, cellulose, etc. Carbohydrates are classified into two categories on the basis of their reducing property.

(A) **Reducing sugar** : Sugars which reduce mild oxidising agents (Tollen's reagent, Fehling's solution) are called reducing sugars. e.g /-Monosaccharides (D-glucose, D-fructose), some oligosaccharides (Maltose, Lactose etc.) are reducing sugars. Sucrose is a non-reducing sugar.

(B) **Non-reducing sugar** : Sugars which do not reduce Fehling solution, Tollen's reagent etc. are called non-reducing sugars. e.g.-care sugar (sucrose).

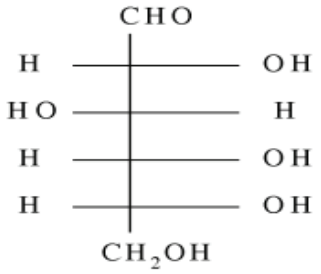


14.3 Monosaccharides

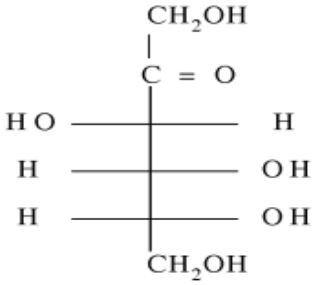
Monosaccharides are simplest carbohydrates. They may contain 3-7 carbon atoms. General formula $C_n(H_2O)_n$ [n = 3-7]

Classification : Monosaccharides are of two types based on the nature of carbonyl group.

(1) **Aldose** : Aldose are carbohydrates with an aldehyde as their most oxidised functional group, e.g. glucose.

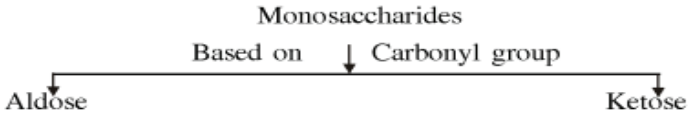


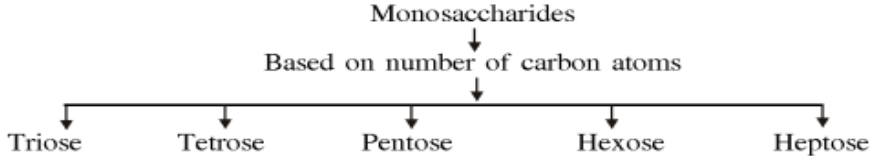
(2) Ketose : These are carbohydrates with a keto group as their most oxidised functional group, e.g. fructose



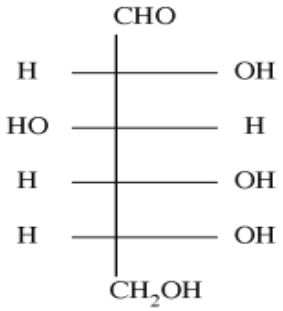
Monosaccharides are classified on the basis of no. of carbon atoms.

(1) Triose (3 carbon atoms)
(2) Tetrose (4 carbon atoms)
(3) Pentose (5 carbon atoms)
(4) Hexose (6 carbon atoms)
(5) Heptose (7 carbon atoms)

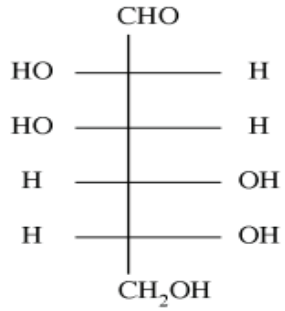




Epimer : Epimers are the stereoisomers which contain more than one chiral centre, but differ only in configuration at one chiral centre. These stereoisomers are diastereomers of each other



D-Glucose

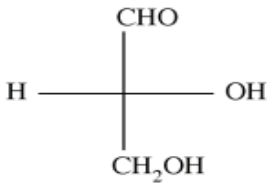


D-mannase

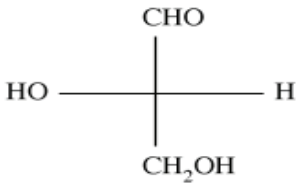
These are C_2 epimers

14.4 Configuration of monosaccharides

D-(+) glyceraldehyde and L-(-) glyceraldehyde have been chosen as configurational standards for all monosaccharides.

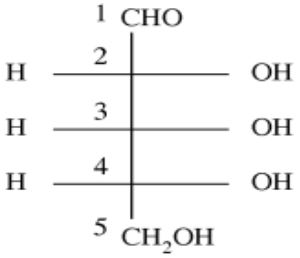


D – (+)-glyceraldehyde
(–OH group at right side)

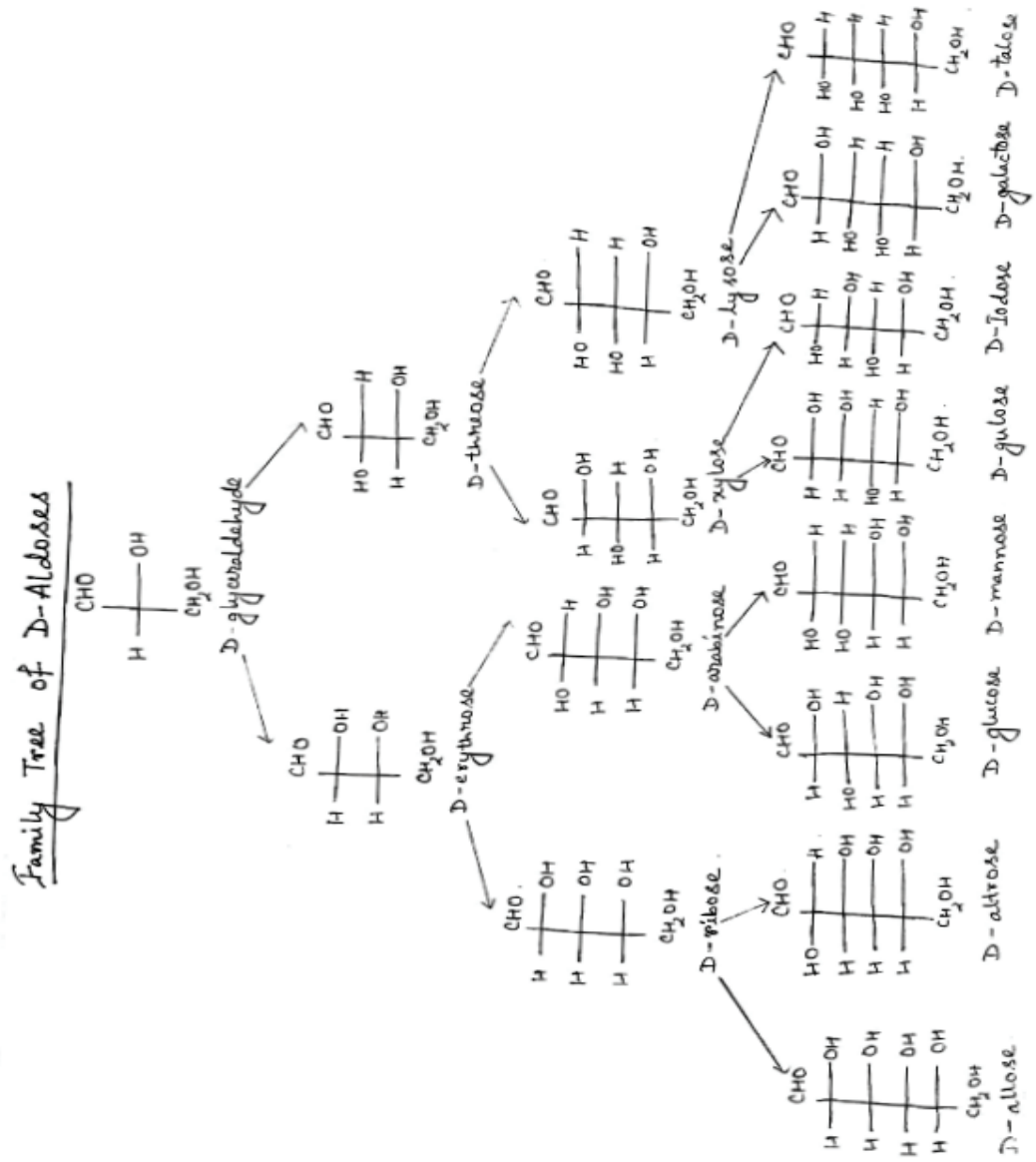


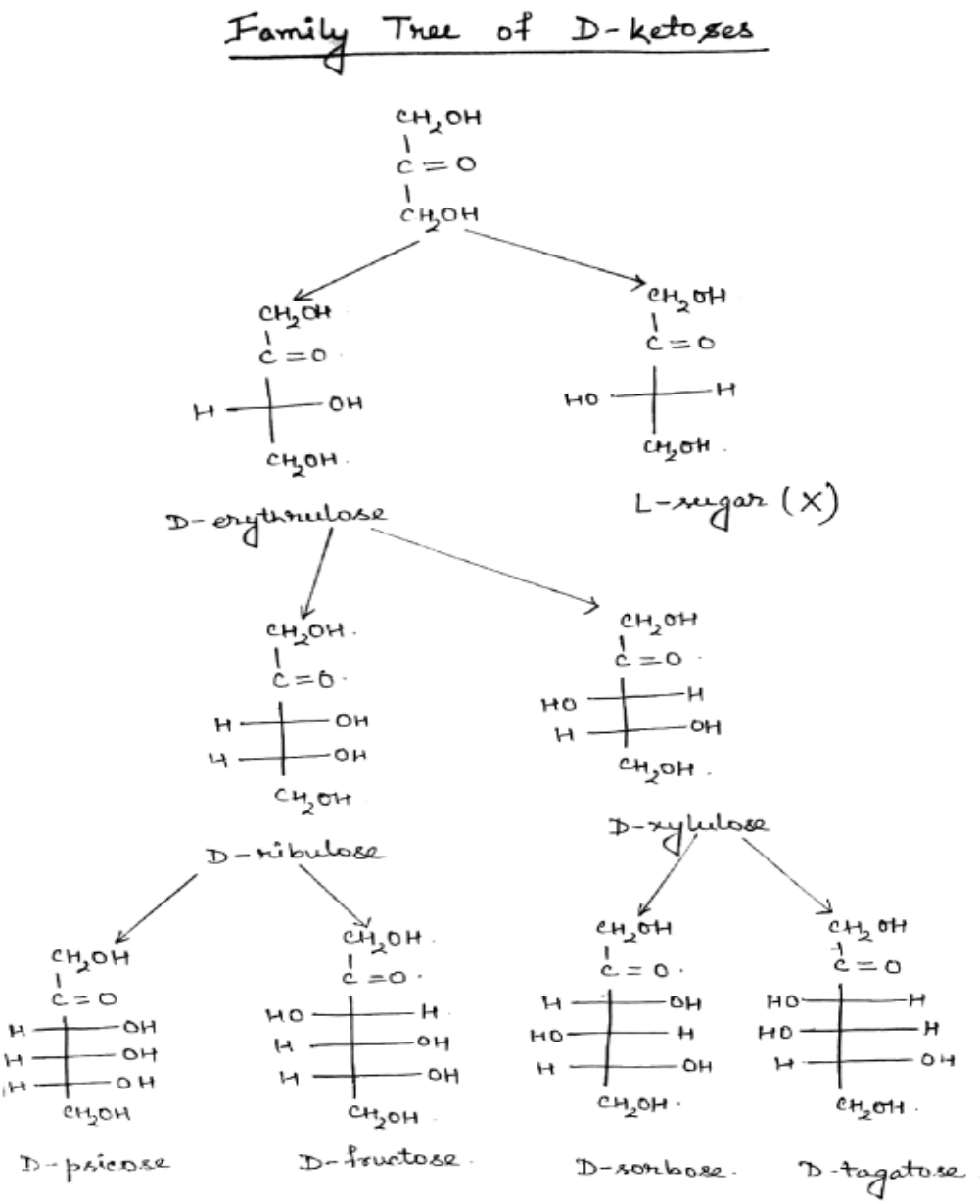
L–(–)–glyceraldehyde
(–OH group at left side)

Monosaccharides are designated as either D or L depending upon the configuration of the highest numbered chiral carbon atom, i.e. the bottom-most chiral carbon atom. A monosaccharide whose highest numbered chiral carbon atom has the same configuration as D - (+) - glyceraldehyde is designated as D-sugar and the one whose highest numbered chiral carbon atom has the same configuration as L-(-)-glyceraldehyde is designated as L-sugar.



The highest-numbered chiral carbon atom, C-4 has the -OH group at right side as in D-(+)-glyceraldehyde.


Family Tree of D-Aldoses
D-glyceraldehyde
D-threose
D-erythrose
D-ribose
D-arabinose
D-xylose
D-lyxose
D-allose
D-altrose
D-glucose
D-mannose
D-gulose
D-idose
D-galactose
D-talose



14.5 Structure of glucose

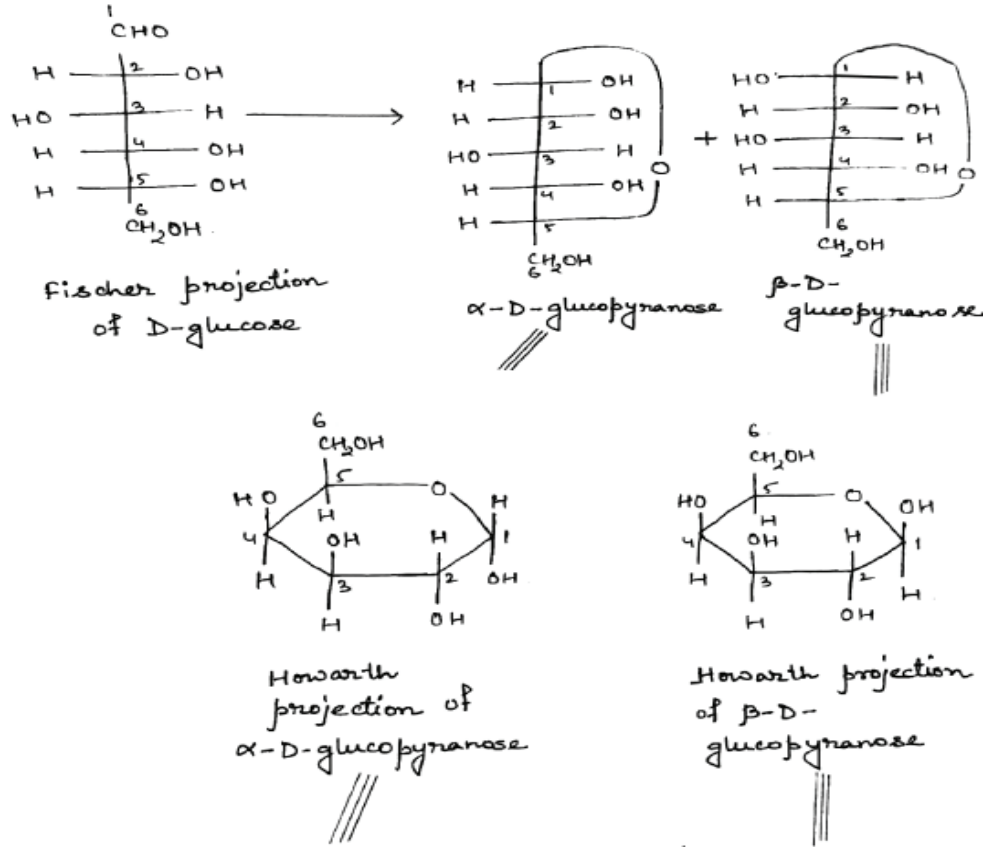
(1) **Open chair**: From the previous discussion it is clear that glucose molecule has one -CHO group, one primary alcoholic group (-CH_2OH) and four secondary alcoholic groups (-CHOH-) Open chain structure of glucose is—

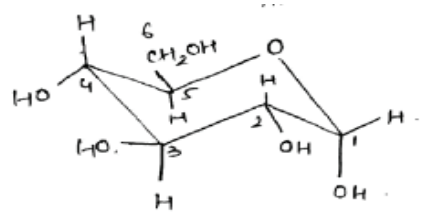
$$OHC-\overset{*}{C}HOH-\overset{*}{C}HOH-\overset{*}{C}HOH-CH_2OH$$

No. of chiral centres = 4

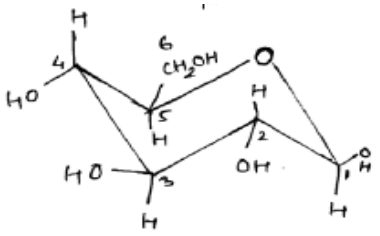
Total no. of stereoisomers = $2^4 = 16$

(2) **Cyclic structure** : Glucose has cyclic structure because aldehyde and alcohol are part of the same molecule and therefore they react easily to form a hemicetal. The fischer projection is first laid down on its right side. The groups that were on the right in Fischer projection are down in cyclic structure, and groups on the left are up. The -OH group on C-l can either be up or down the -OH group at down is called α-anomer while the other is called β-anomer. All ring substituents at equatorial in chair conformation is called β-anomer. The α-anomer in chair conformation has Cl -OH group at axial position.





Chair conformation of α-D-glucopyranose



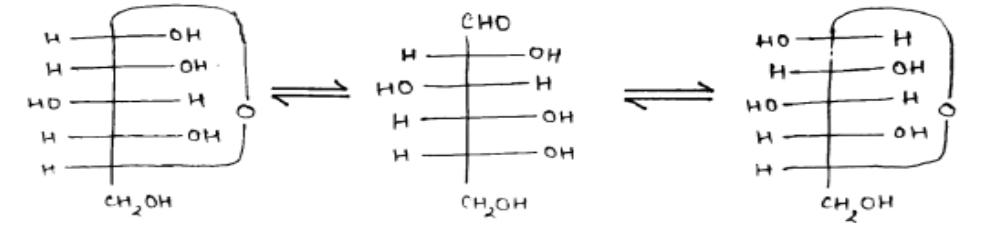
Chair conformation of β-D-glucopyranose

14.6 Mutarotation

Mutarotation is defined as the change in specific optical rotation representing the interconversion of α-and β-forms of D-glucose to an equilibrium mixture.

Pure α-D-glucose has specific rotation $[\alpha]_D = +112°$ and pure β-D-glucose has specific rotation $[\alpha]_D = +19°$. When either form is dissolved in an amphiprotic solvent the optical rotation of the solution gradually changes with time and at last becomes +52.5°.

This phenomena is known as mutarotation.

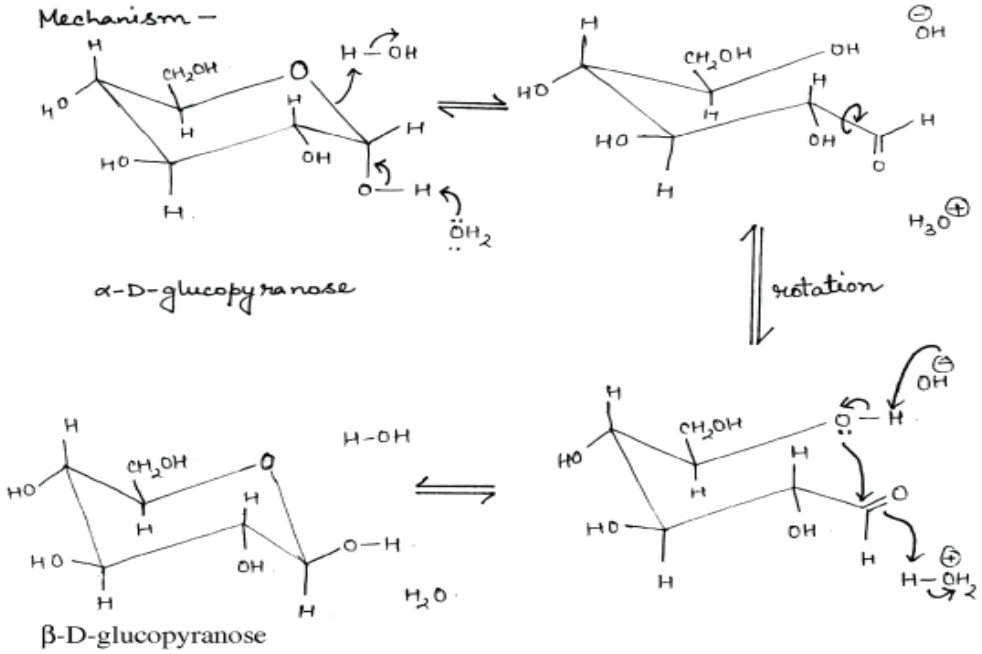


α-D-glucopyranose (36%) $[\alpha]_D = 112°$

Open chain form of D-glucose

β-D-glucopyranose (64%) $[\alpha]_D = 19°$

Mutarotation is catalysed by both acid and base. It even occurs in pure water in which an acid-base catalysed mechanism operates.



The opening of cyclic hemiacetal is a concerted process involving die simultaneous removal of a proton from acetal hydroxyl group and donation of a proton to ethereal oxygen atom.

Since water is an amphiprotic solvent (can act as both, acid and base), mutarotation proceeds most readily by this mechanism in aqueous solution.

14.7 Structure Determination of glucose

A tentative structure of glucose may be established on the basic of following observations.

(i) **Molecular formula** : Elemental analysis and molecular weight determination confirm that the molecular formula of glucose is $C_6H_{12}O_6$.

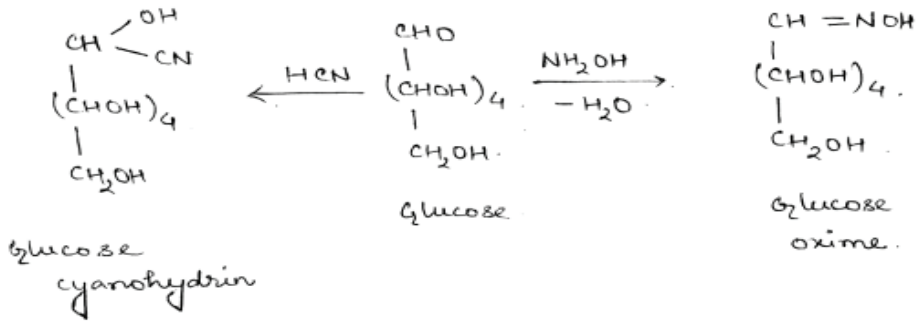
(ii) **Straight chain** : When reduced with hydroiodic acid and red phosphorus at 100°C, glucose gives a mixture of n-hexane and 2-iodohexane. This indicates that the six carbon atoms in glucose are in a straight chain.

$$C_6H_{12}O_6 \xrightarrow[100^\circ C]{HI+red\ P} CH_3-CH_2-CH_2-CH_2-CH_2-CH_3 + CH_3-\underset{\displaystyle I}{\underset{|}{C}}H-CH_2-CH_2-CH_2-CH_2$$

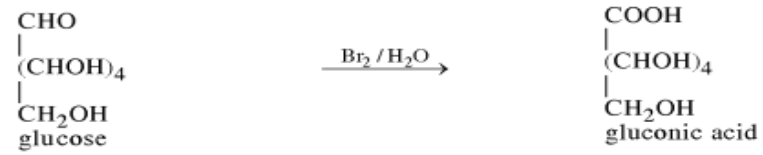
n-hexane 2-iodohexane

(iii**) Carbonyl group** :

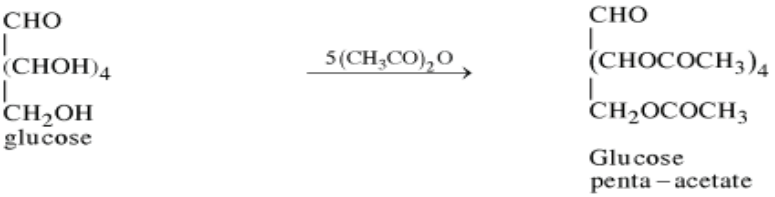
(a) Glucose forms an oxime and a cyanohydrin with hydroxylamine and hydrocyanic acid respectively. This indicates that glucose contains a carbonyl group either aldehyde or ketone.



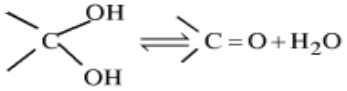
(b) Mild oxidising agent like bromine-water oxidises glucose in a pentahydroxy acid having same number of C-atoms, i.e. glucose has an aldehyde group and not ketone.



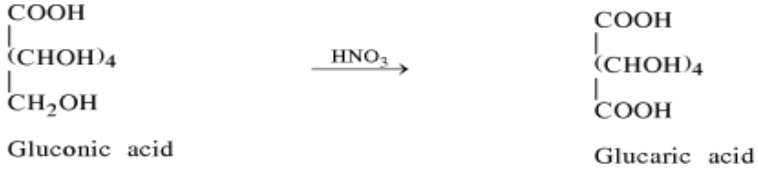
(iv) **5-hydroxyl groups** : When treated with acetic anhydride, forms penta-acetate. This indicates the presence of five hydroxyl glucose groups.



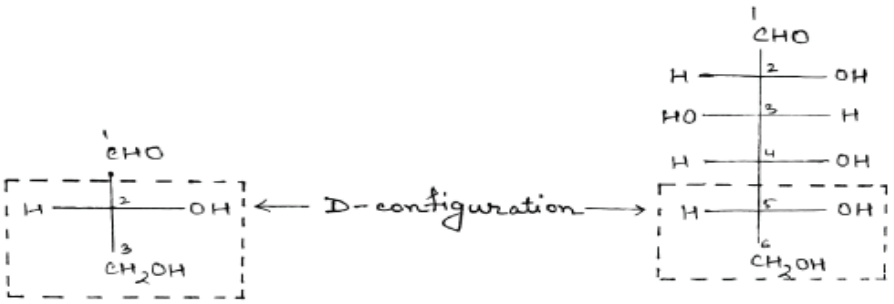
Organic compounds with two -OH groups attached to a single carbon atoms usually lose a molecule of water Glucose is a stable molecule and does not eliminate water on heating. This proves that 5-OH groups are attached at different C-atoms.



(v) **1° alcoholic group** : Oxidation of pentahydroxy acid with HNO_3 yields dicarboxylic acid. This indicates presence of 1° alcoholic group.

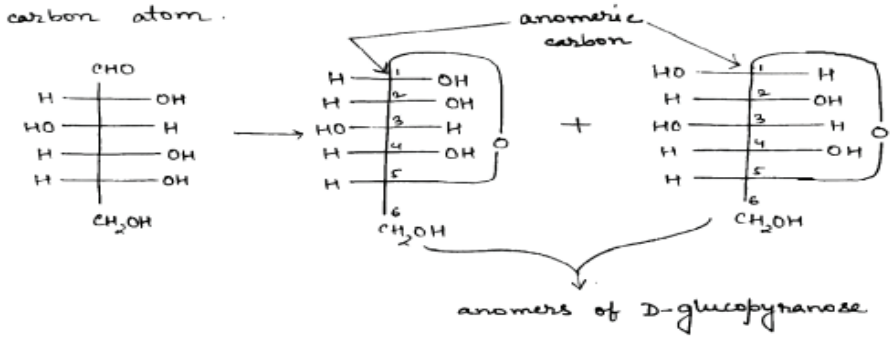


Absolute Configuration of Glucose : Glucose is an important aldohexose. The word 'Glucose' came from Greek word 'Glukas' (means sweet) Naturally occurring glucose is called D-glucose because its highest numbered chiral carbon atom (i.e C-5) has the configuration same as D-glyceraldehyde. The aqueous solution of this D-glucose rotates the plane polarised light in the clockwise direction. So, it is dextrorotatory (+). Hence, naturally occurring glucose is known as D-(+)-glucose.

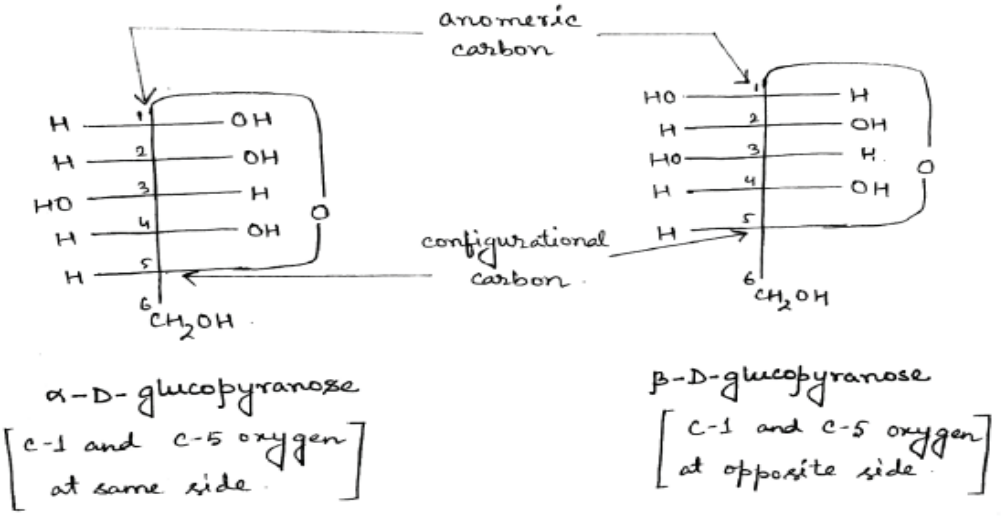


14.8 Anomers of glucose

When a pyranose or furanose ring closes, the hemiacetal carbon atom is converted from a flat carbonyl group to an asymmetric carbon. Depending on which face of the carbonyl group is attacked, the hemiacetal –OH group can be directed either up or down. In carbohydrates these diasteromers are called anomers. The hemiacetal carbon atom is called the anomeric carbon atom.



The anomer in which the hemiacetal -OH group is on the same side of Fischer projection as the oxygen at configurational carbon (highest numbered asymmetric carbon) is called α-anomer and the anomer in which hemiacetal -OH group is on the side of Fischer projection opposite to the oxygen at configurational carbon is called β-anomer.

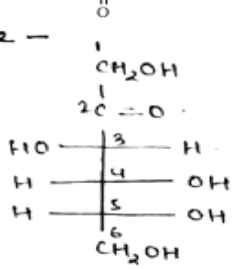


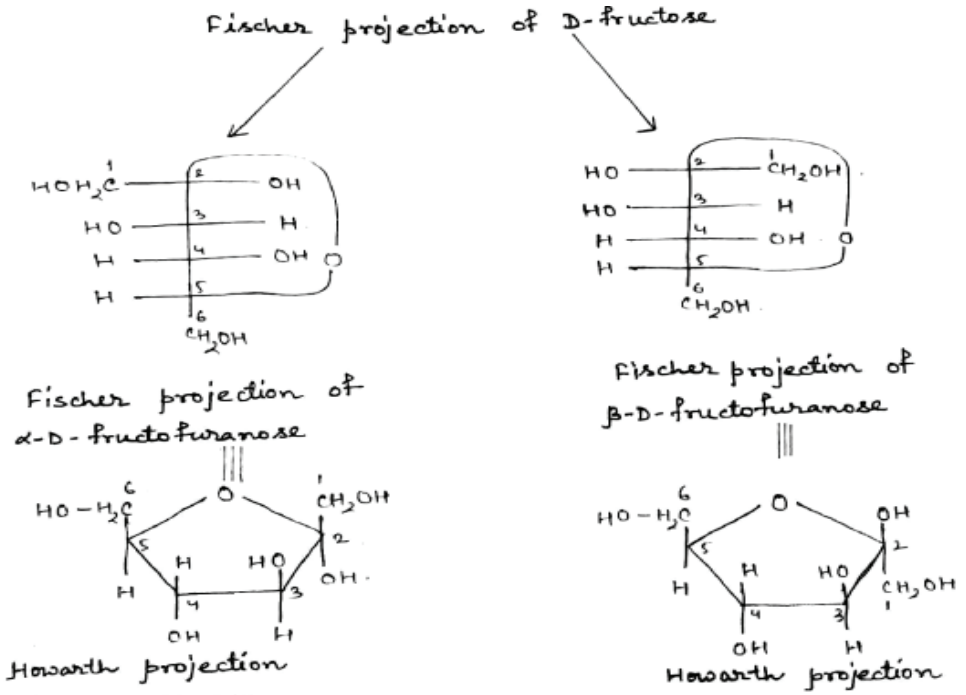
14.9 Structure of Fructose

(1**) Open chain** : A fructose molecule contains one (=C - O) keto group, two primary alcoholic groups (-CH_2OH) and three secondary alcoholic groups (=CHOH).

∴ The structure is, $CH_2OH-\underset{\underset{O}{\|}}{C}-CHOH-CHOH-CHOH-CH_2OH$

(2) Cyclic structure –





14.10 Step-up Reaction-Ascending in Monosaccharides

(1) Kiliani-Fischer Reaction—

The Kiliani-Fischer reaction is a chemical process used to synthesize higher-order monosaccharides (aldoses) from smaller aldoses by chain elongation. It is particularly useful in carbohydrate chemistry for extending the carbon chain of sugars.

Reaction Steps:

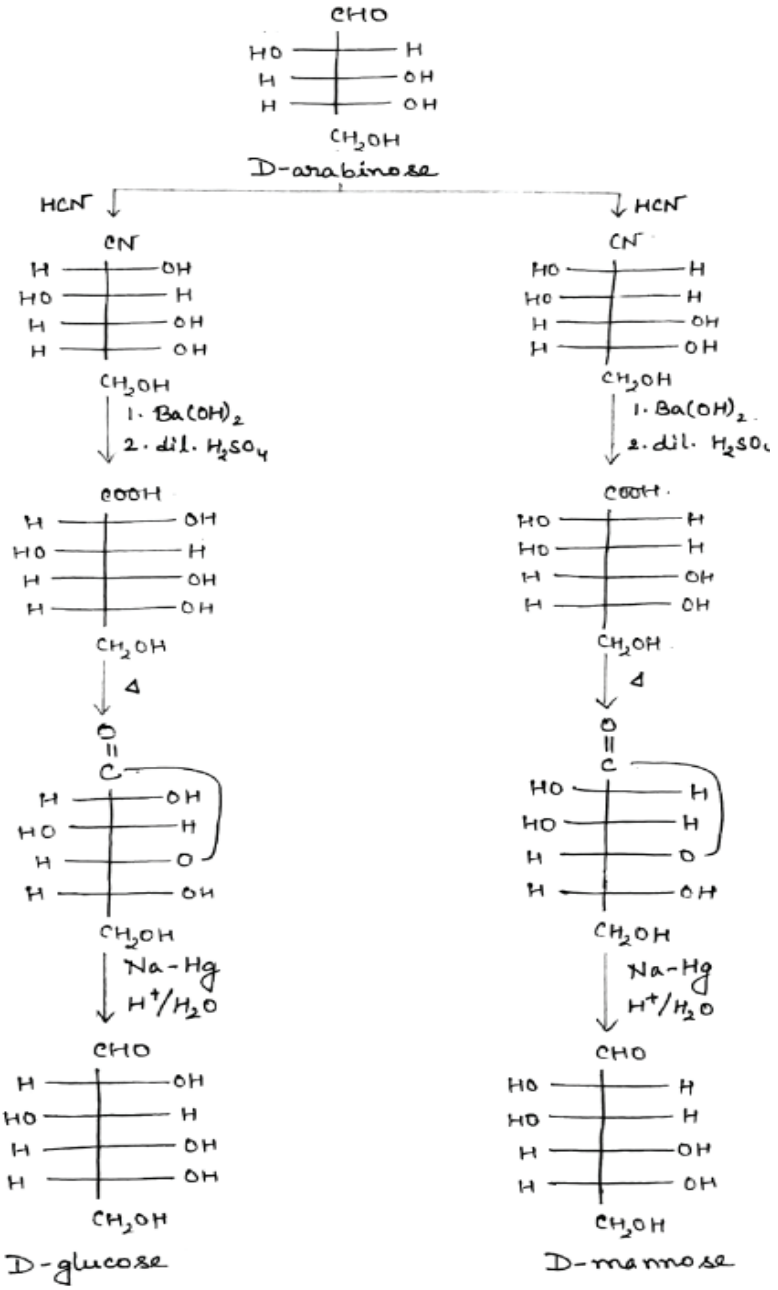
i) Cyanohydrin Formation: The aldose reacts with hydrogen cyanide (HCN) to form a cyanohydrin.

ii) Hydrolysis: The cyanohydrin undergoes acidic hydrolysis to yield an α-hydroxy carboxylic acid (aldonic acid).

iii) Reduction (Selective): The carboxyl group is selectively reduced (e.g., using sodium amalgam) to form a new aldose with an extra carbon.

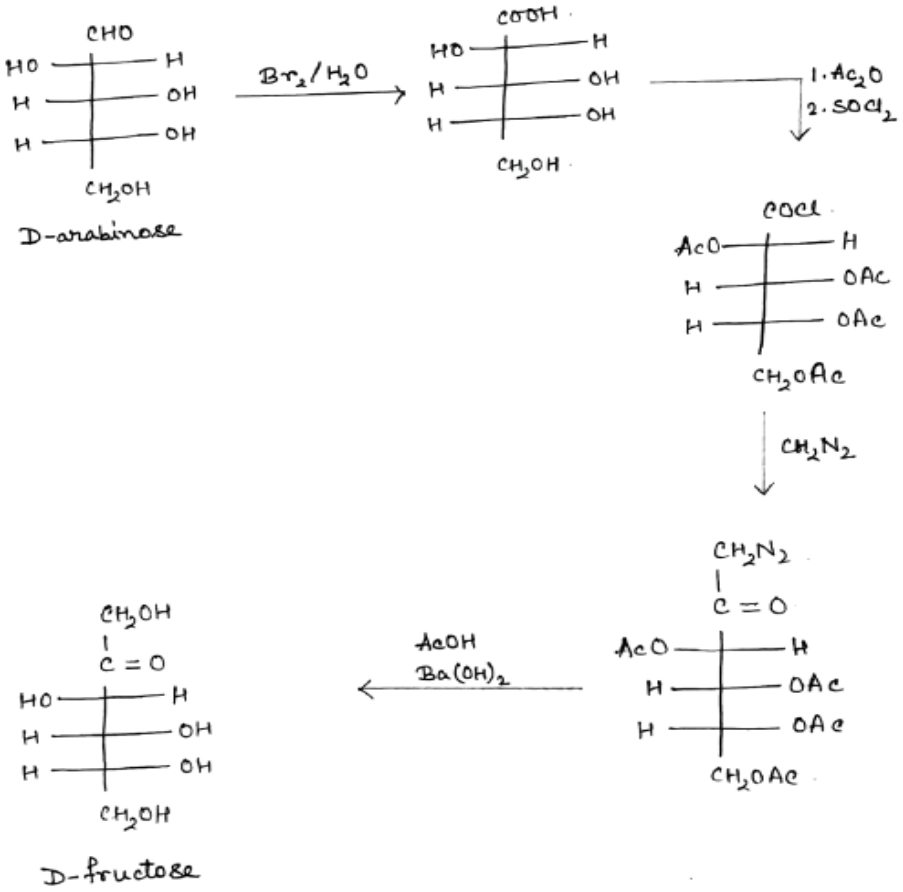
Example: Chain Elongation of D-Arabinose to D-Glucose and D-Mannose

The Kiliani-Fischer reaction applied to D-arabinose leads to the formation of D-glucose and D-mannose as a mixture due to the formation of two possible epimers at the new chiral center.



(2) Wolf Method—

It is a step-up reaction where we get ketose from an aldose containing one more carbon (ketose).



14.11 Step-down Reaction-Descending in Monosaccharides

(1) Ruff Degradation—

The Ruff Degradation is a chemical method used to shorten the carbon chain of aldoses by removing the C-1 carbon as carbon dioxide (CO_2). It is commonly used in carbohydrate chemistry for structural determination and sugar synthesis.

Reaction Steps:

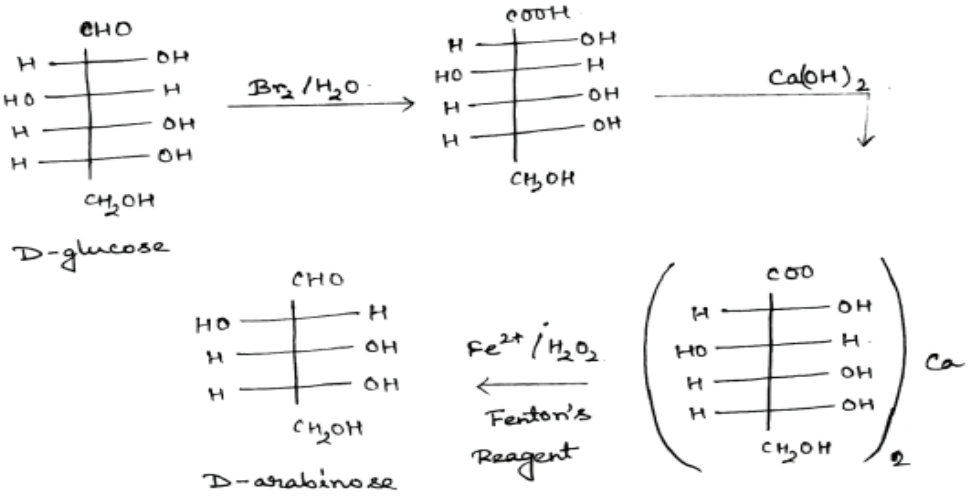
i) Oxidation to Aldonic Acid: The aldose is oxidized using bromine water (Br_2/H_2O) to form the corresponding aldonic acid.

Example: D-Glucose → D-Gluconic Acid

ii) Ferric Ion (Fe^{3+}) Catalyzed Decarboxylation: The aldonic acid is treated with hydrogen peroxide (H_2O_2) in the presence of Fe^{3+} (Ferric hydroxide, $Fe(OH)_3$).

This results in the loss of the C-1 carbon as CO_2, yielding a new aldose with one carbon less.

Example: D-Gluconic Acid → D-Arabinose



Here the C_2, of aldose is converted into a -CH= O aldehydic group. Because of this reason C_2 epimeric aldoses give the same aldopentose by this reaction.

(2) Wohl's Degradation—

The Wohl Degradation (Wohl Method) is a chemical reaction used to shorten the carbon chain of aldoses by one carbon. It is the reverse of the Kiliani-Fischer reaction, which elongates the sugar chain.

Reaction Steps in Wohl Degradation:

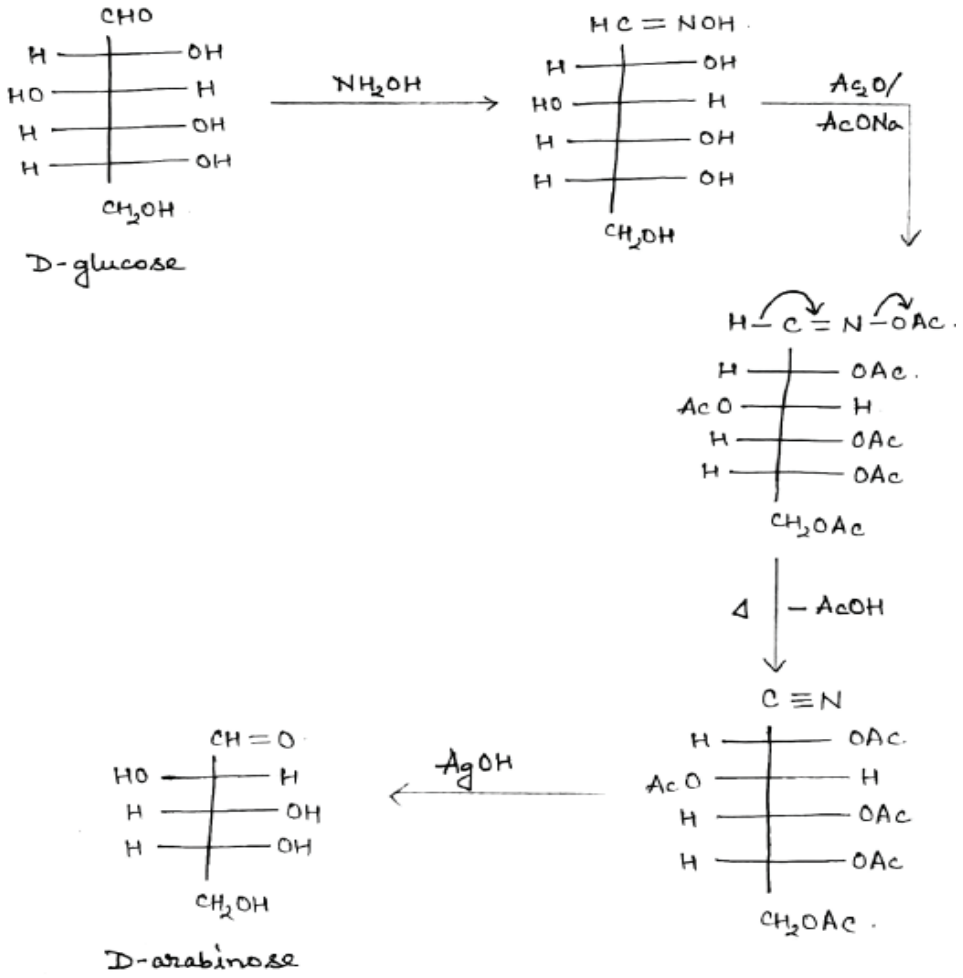
i) Formation of Oxime: The aldose is treated with hydroxylamine (NH_2OH) to form an oxime.

ii) Conversion to Cyano Compound: The oxime is reacted with acetic anhydride (Ac_2O), leading to the formation of a nitrile (-CN) group by elimination of water.

iii) Base-Catalyzed Removal of -CN: The nitrile undergoes basic hydrolysis (e.g., using NaOH), which removes the -CN group, resulting in a shorter aldose (one carbon less than the original sugar).

Example: Shortening of D-Glucose to D-Arabinose

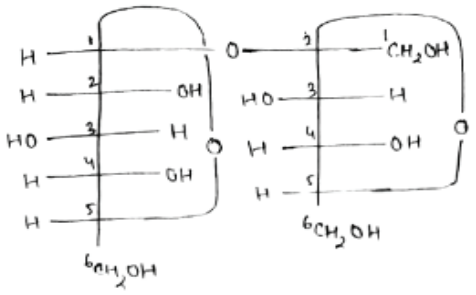
D-Glucose undergoes Wohl degradation to give D-Arabinose (a 5-carbon sugar).



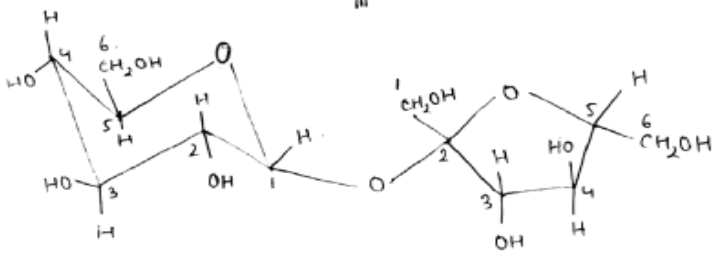
14.12 Disaccharides

A disaccharide is a glycoside in which die anomeric -OH group of one monosaccharide is bonded by an acetal linkage to any of the hydroxyl groups (anomeric -OH or alcoholic -OH) of a second monosaccharide. e.g.- cellobiose, maltose, lactose, sucrose etc.

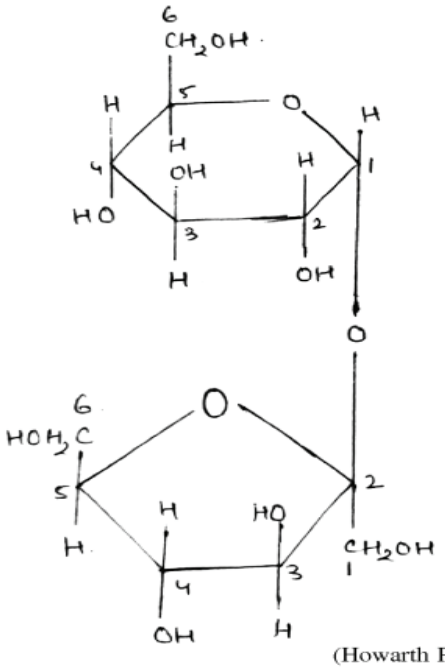
Sucrose (Cane Sugar), $C_{12}H_{22}O_{11}$: Sucrose is α-D-glucopyranosyl-β-D-fructofuranoside. It is hydrolysed by dilute acids or by invertase enzyme to an equimolar mixture of D-(+)- glucose and D-(-)-fructose where glucose is present in pyranose form and fructose in furanose form.



Fischer projection of sucrose



Chair conformation of glucose and Howarth projection of fructose



(Howarth Projection

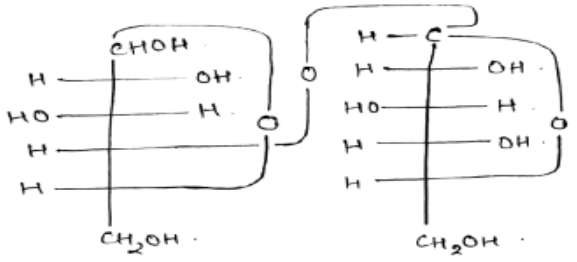
Sucrose is dextrorotatory and its specific rotation is +66.5°. On hydrolysis with dilute acid or invertase enzyme sucrose produce an equimolar mixture of D(+)-glucose ($[\alpha]_D$ = +52.7°) and D(-) - fructose ($[\alpha]_D$ = -92.4°)

Sucrose	⟶	Glucose	+	Fructose
$[\alpha]_D$=+66.5°		$[\alpha]_D$=52.7°		$[\alpha]_D$= –92.4°

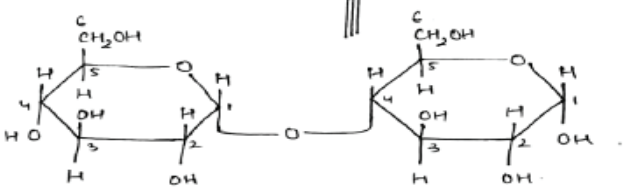
Since specific rotation of D (-) fructose is greater than that of D(+) glucose, the resulting mixture becomes laevorotatory. So, on hydrolysis of sucrose the optical nature changes from dextrorotatory to laevorotatory. This process is called inversion and the mixture is called invert sugar. Therefore, sucrose is also known as invert sugar.

Maltose (Malt Sugar), $C_{12}H_{22}O_{11}$ —

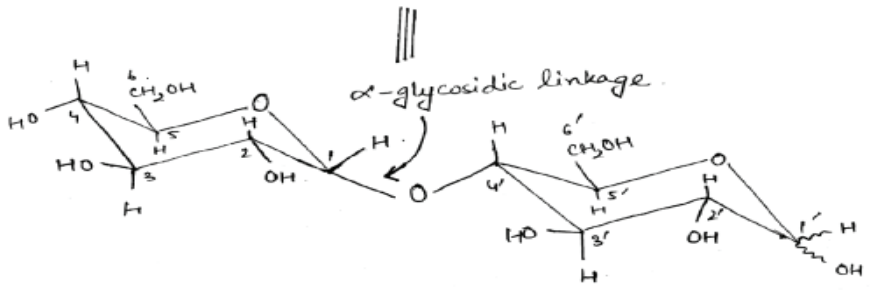
Maltose is 4-O-α-D-glucopyranosyl-D-Glucopyranose. It is hydrolysed by dilute acid or maltase enzyme to produce 2 moles D-glucose. It is a reducing sugar because one glucose unit is present as hemiacetal.



Fischer projection of maltose



Howarth projection of maltose

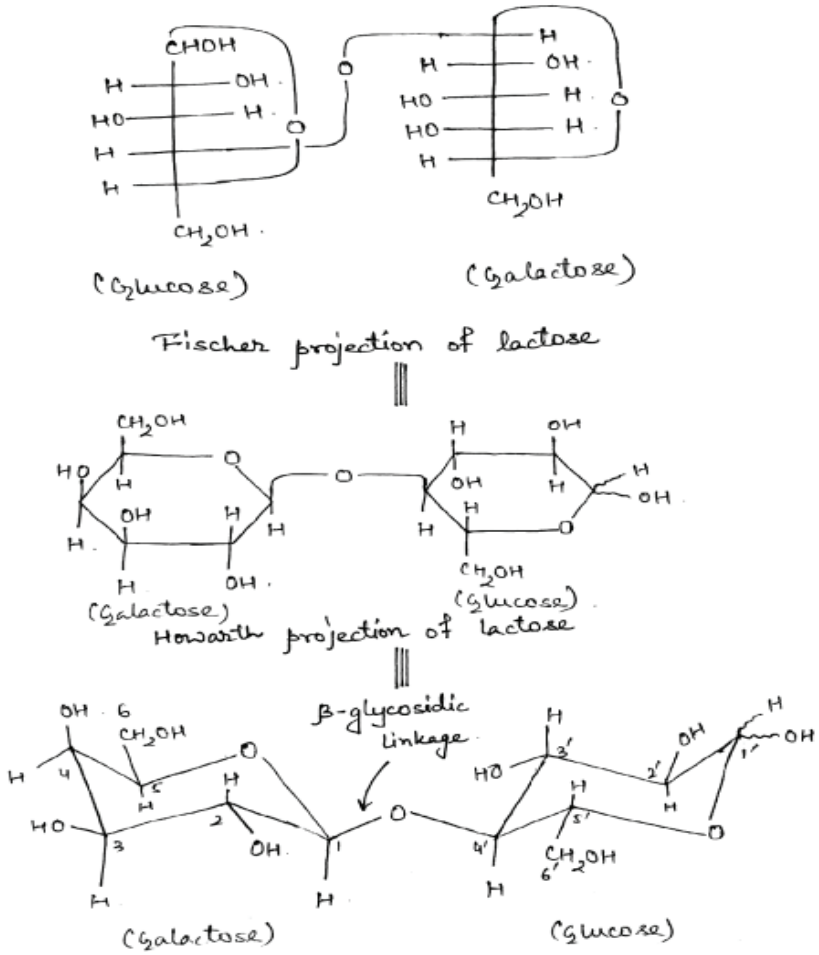


Chair conformation of maltose

It also shows mutarotation.

Lactose (Milk Sugar), $C_{12}H_{22}O_{11}$ —

Lactose is 4-O-β-D-galactopyranosyl -D-glucopyranose. On hydrolysis by dilute acids lactose produces equimolar mixture of D-glucose and D-galactose. Lactose has free hemiacetal ring and it is in equilibrium with its open-chain form. So, it is reducing sugar and exhibits mutarotation.



14.13 Polysaccharides

Polysaccharides are polymers of monomeric sugar and have molecular weight that may range from a few thousand to several millions. e.g.-starch, cellulose etc.

Starch—

Starch is a homopolymer composed of D-glucose units held by glycosidic bonds. It is one of the most important source of carbohydrates in human diet. Rice, wheat, potatoes and corn are the most forms of starch. Molecular formula of starch is $(C_6H_{10}O_5)_n$

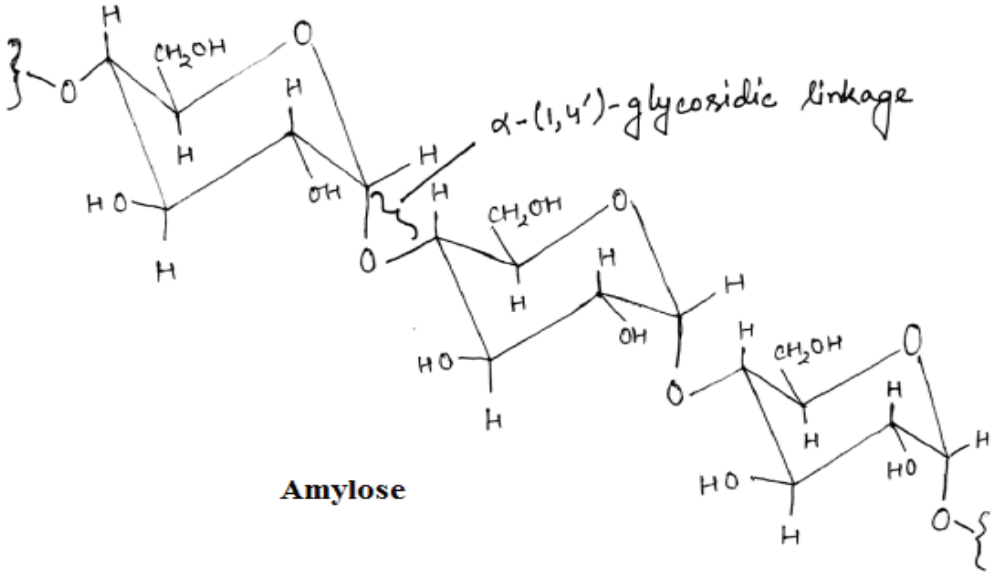
Starch consists of two polysaccharide components. These are amylose (20%) and amylopection (80%).

Amylose-

1. Insoluble in water.

2. A long unbranched chain like structure in which D-glucose units are held by α-(l, 4)-glycosidic linkage.

3. The solution of amylose gives blue colour with iodine.



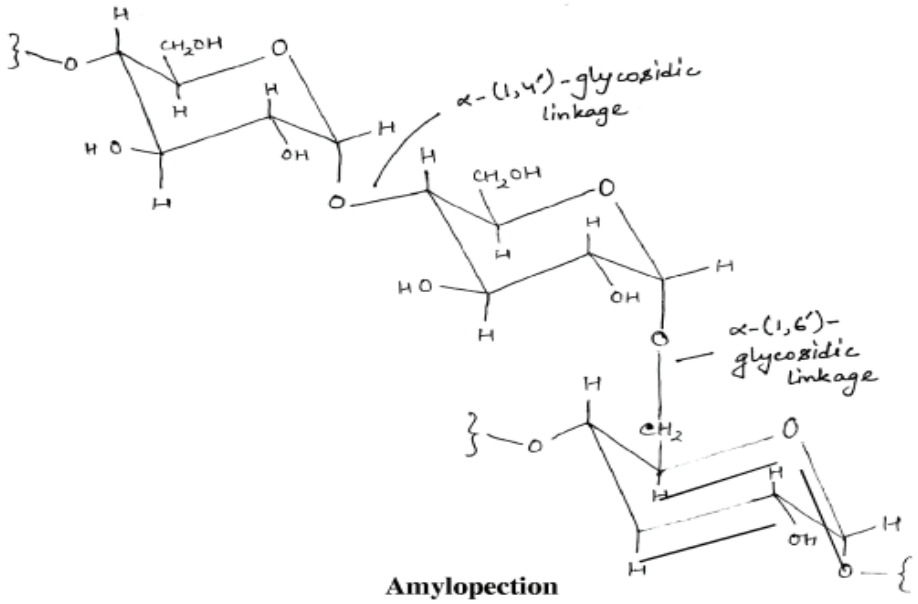
Amylose

Amylopectin –

1. Soluble in water.

2. It is a branched chain like structure in which glucose unite are joined together by α-(l, 4) glycosidic bond and α-(l, 6)-glycosidic bonds at branching points.

3. It gives violet colour with iodine.



Amylopection

* Starch is hydrolysed to D-glucose by dilute acids.

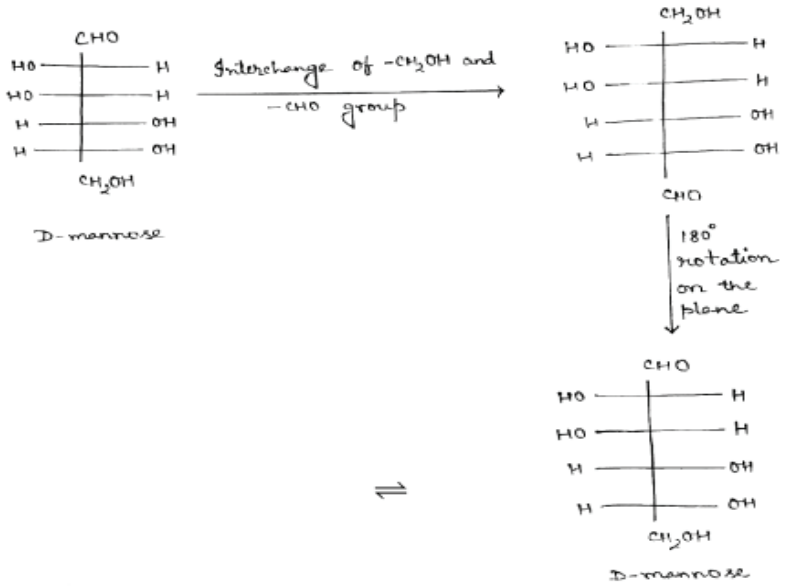
* Starch is hydrolysed to maltose by enzyme hydrolysis

14.14 Summary

- Carbohydrates are compounds that contain either an aldehyde or ketone group or two or more hydroxyl groups.
- Monosaccharides contain one or several chiral carbons due to which they can exist as stereoisomers.
- Monosaccharides form a cyclic structure due to formation of hemiacetal/hemiketal, which generates the α and β anomeric forms of sugars.
- Various chemical tests can be used to differentiate between aldoses and ketoses.
- Two monosaccharides joined together by a glycosidic bond generate a disaccharide.
- Oligosaccharides are short polymers of several monosaccharides joined by glycosidic bond

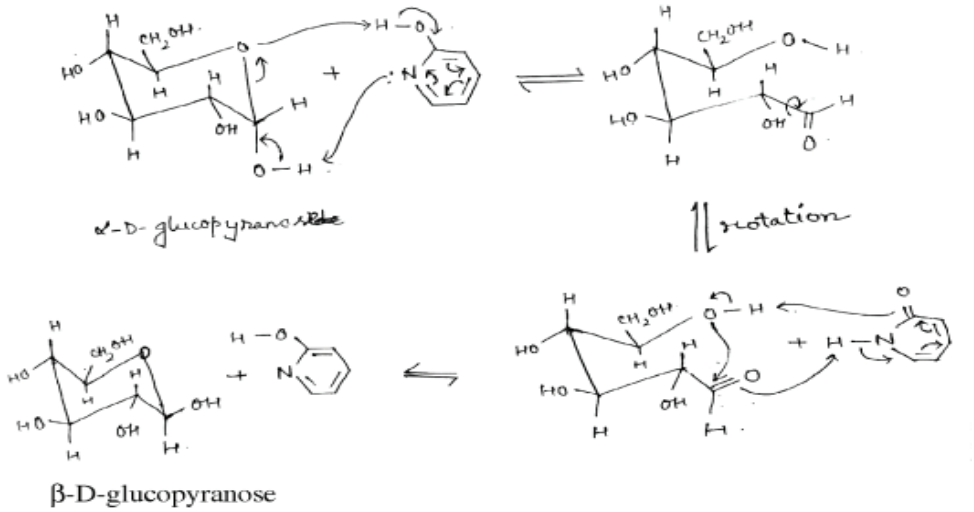
14.15 Exercise

1. Interchange of -CH_2OH and -CHO group in mannose occurs. Is it new hexose?



2. Explain why mutarotation occurs readily in the presence of 2-pyridinol.

Ans. Since 2-pyridinol is an acid-base catalyst that gives H^+ to the acetal O while removing H^+ from anomeric -OH in a synchronous manner, mutarotation occurs readily in the presence of 2-pyridinol.



3. The specific rotation of α-D-glucopyranose is +112°, while that of the β-anomer is +18.7° when either of the pure anomers is dissolved in water, the specific rotation gradually changes to +52.7°, Determine the percentages of the two anomers present at equilibrium.

Ans. Let, the mole fraction of α-anomer is a and the mole fraction of the β-anomer is b. since, the rotation of the mixture is +52.7°, we have

$$a(112°) + b\,(18.7°) = 52.7° \quad \text{(i)}$$

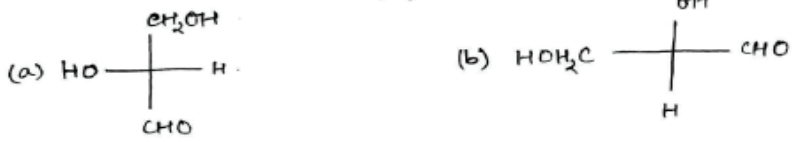
Again, $a + b = 1$

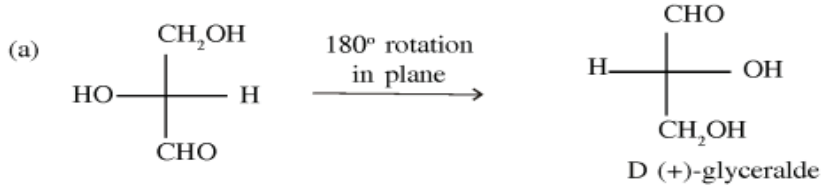
.-. b = 1-a
Therefore from eq. (i),
a x ll2° + (1-a) x 18.7° = 52.7°
=> 18.7° - 93.3° a = 62.7°
=> a = 0.36
b = 1-0.36 = 0.64

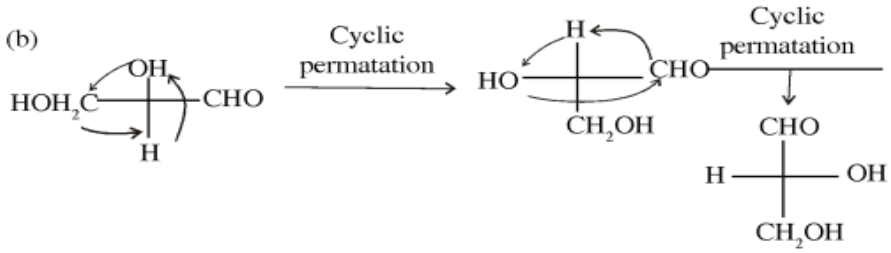
4. Identify each of the following Fischer projections as either D- or L-glyceraldehyde.

Ans.

either D- or L-glyceraldehyde.







Additional Problems :

1. What are carbohydrates?
2. Define with example - Epimers and Anomers.
3. Give cylclic structure of glucose and fructose.
4. Define mutarotation. Give mechanism.
5. Draw α and β form of glucose and fructose.
6. Interchange of $–CH_2OH$ and -CHO group is glucose occurs. Is it a new hexose?
7. What happens when glucose is treated with HNO_3?
8. Convert — (i) D-arabinose —> D-fructose.
(ii) D-arabinose —> D-glucose + D-mannose.
9. What products do you obtain when D-tallose and D-galactose undergo Ruff degradation reaction?
10. Give the structure and definition—
(i) Sucrose, (ii) Lactose.
11. Write a short note on starch.

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