

ORGANIC CHEMISTRY

Organic Chemistry is the subclass of chemistry that involves the study of carbon and its compounds. It is established fact now that carbon can form unlimited number of compounds. Thus the domain of organic chemistry is continuously growing with new 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 new students of organic chemistry require a great deal of study to understand the latest developments in the field. The study of organic chemistry seems intricate, however it is very interesting and in this course begins with concise details on the concepts on structure and bonding in organic compounds.

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UNIT 1: STRUCTURE AND BONDING

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1.1 OBJECTIVES

Objective of this chapter is to provide students with a concise and succinct detail on the basic fundamentals of the organic chemistry. Topics covered in this chapter such as hybridization, delocalized bonding and electronic effects are essential basics of the organic chemistry. The chapter is developed to stimulate interest of the reader into the organic chemistry and at the same time to build the deep understanding of the fundamental concepts of organic chemistry. To offer students an easy and interesting learning experience, each of the topics covered is depicted with lucid diagrams and figures also.

1.2 INTRODUCTION

Organic Chemistry is the subclass of chemistry that involves the study of carbon and its compounds. It is established fact now that carbon can form unlimited number of

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compounds. Thus the domain of organic chemistry is continuously growing with new 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 new students of organic chemistry require a great deal of study to understand the latest developments in the field. The study of organic chemistry seems intricate; however it is very interesting and in this course begins with concise details on the concepts on structure and bonding in organic compounds.

1.3 HYBRIDISATION

Concept of hybridization is given in valence bond theory to describe chemical bonding and molecular geometries. Hybridization is the mixing of atomic orbitals of different shape and energies to yield same number of new orbitals of identical energy. The shape of hybrid orbitals is different than the component orbitals. Mixing of spherical shaped s orbital with dumbbell shaped p orbitals results in hybrid orbitals those have one lobe of their dumbbell shape much larger than the other lobe. Usually, all hybrid orbitals form sigma bonds. Carbon atom forms four covalent bonds with other atoms for which one s and three p orbitals get hybridised in different three manners; namely, sp^3 , sp^2 and sp .

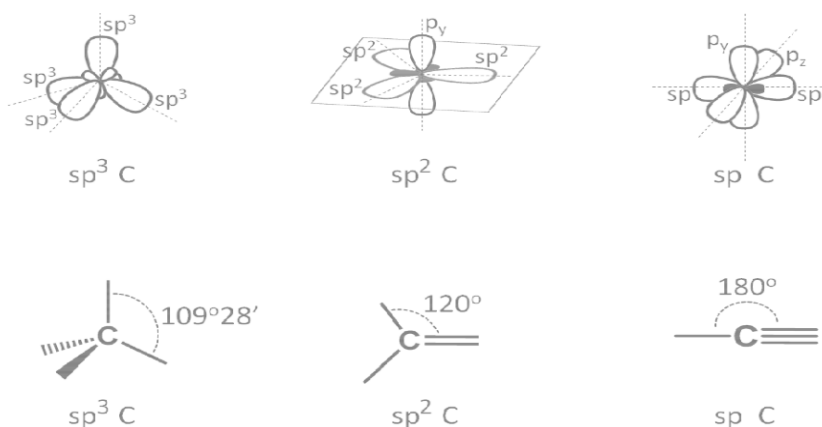


Figure 1. Orbital arrangements around carbon nuclei and the resulting geometry in case of sp^3 , sp^2 and sp hybridization.

An easy method to determine the hybridization of a carbon, oxygen or nitrogen atom in neutral organic molecules is to count the number of π bonds it forms. If there is no π bond,

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the atom is sp^3 hybridized. If there is one π bond, it indicates sp^2 hybridization and if there are two π bonds it means the atom is in sp hybridized state.

(i) sp^3 hybridization

The term sp^3 hybridization indicates mixing of one s and three p orbitals resulting in four hybrid orbitals of same size and energy as depicted in the **Figure 2**. Each sp^3 hybrid orbital has 25% s-character and 75% p-character. The four sp^3 hybrid orbitals of carbon atom remains directed at an angle of $109^\circ 28'$ from each other and thus impart tetrahedral geometry to the molecules where carbon is connected to four atoms or groups by four sigma bonds (**Figure 1**). For example the carbon atom in saturated organic molecules such as methane, ethane and ethyl alcohol.

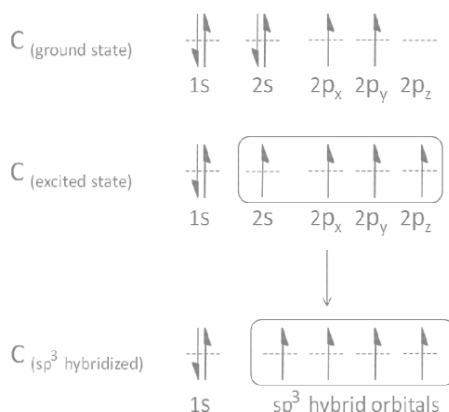


Figure 2. Hybridization theory explains how carbon can make four equivalent bonds in saturated organic compounds. Three p and one s orbital mix in the excited state carbon atom to give four sp^3 hybrid orbitals of equal energy.

(ii) sp^2 hybridization

The term sp^2 hybridization indicates mixing of one s and two p orbitals resulting in three hybrid orbitals of same size and energy as depicted in the **Figure 3**. Each sp^2 hybrid orbital has 33.33% s-character and 66.66% p-character. The three sp^2 hybrid orbitals of carbon atom remains directed at an angle of 120° from each other and thus impart trigonal planar geometry to the molecules where carbon is connected to three atoms or groups by three sigma bonds and one pi bond (**Figure 1**). For example the carbon atoms in ethylene and benzene are sp^2 hybridized.

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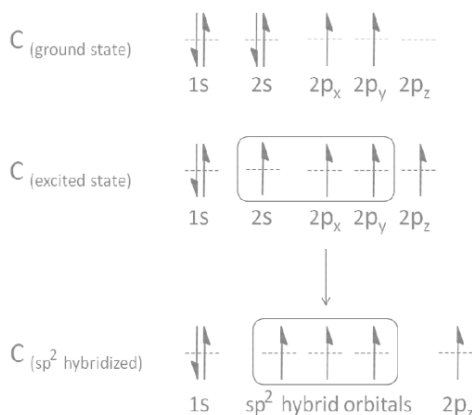


Figure 3. Hybridization theory explains how carbon can make three equivalent sigma bonds in unsaturated organic compounds. Two p and one s orbitals mix in the excited state carbon atom to give three sp² hybrid orbitals of equal energy. One p orbital remain unhybridized to participate in formation of pi bond.

(iii) sp hybridization

The term sp hybridization indicates mixing of one s and one p orbital resulting in two hybrid orbitals of same size and energy as depicted in the **Figure 4**. Each sp hybrid orbital has 50% s-character and 50% p-character. The two sp hybrid orbitals of carbon atom remains directed at an angle of 180° from each other and thus impart linear geometry to the molecules where carbon is connected to two atoms or groups by two sigma bonds and two pi bonds (**Figure 1**). For example the carbon atoms in acetylene molecule are sp hybridized.

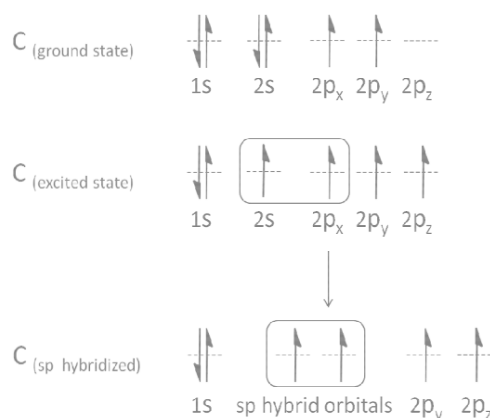


Figure 4. Hybridization theory explains how carbon can make two equivalent sigma bonds in unsaturated organic compounds. One p and one s orbitals mix in the excited state carbon atom to give two sp hybrid orbitals of equal energy. Two p orbitals remain unhybridised to participate in pi bonds.

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(iv) Effect of the type of hybridization on properties

It is important to note that different contribution of s and p orbitals in hybrid orbitals affect some properties of the hybrid orbitals. Important properties are the size of the hybrid orbital, bond distance and acidic character. Size of hybrid orbital decreases with increase in the % of s-character. Thus, sp hybrid orbital is smaller in size than sp² orbital which in turn is smaller than the sp³ hybrid orbital. Since bond distance depends on the size of the involved orbitals, therefore, CC triple bonds are shorter than CC double bonds which in turn are shorter than single bonds as these bonds involve sp, sp² and sp³ hybrid orbitals respectively. Higher contribution of s orbital in a hybrid orbital provides the bond with higher acidic nature. Therefore, terminal alkynes show higher acidic properties than alkenes and alkanes. These properties are tabulated in **Table 1**.

Table 1. Comparison of different properties of sp³, sp² and sp hybridization states

	sp ³ hybridization	sp ² hybridization	sp hybridization
Orbital size	Largest	Medium	Smallest
Bond distance	Largest	Medium	Smallest
Acidic character	Smallest	Medium	Largest

1.4 BOND LENGTH, BOND ANGLES AND BOND ENERGY

Bond length or bond distance is the average distance between nuclei of two bonded atoms in a molecule. It indicates the strength of the attractive force binding two atom nuclei. Thus, shorter bonds are much stronger. Generally, more electrons participating in the bond formation result in much shorter and stronger bonds. Thus, triple bonds are shorter than the double bonds which are further shorter than the single bonds formed between same nuclei. Common bond lengths encountered in organic chemistry are tabulated as **Table 2**.

Table 2: Common bond lengths observed in organic compounds

S.No.	Bond	Bond distance (pm)
1	CC (single bond, alkane)	154
2	CC (double bond, alkene)	133
3	CC (triple bond, alkyne)	120
4	CC (delocalized, benzene)	139
5	CH (organic compounds)	~109

Generally, bond lengths decrease along the periods in the periodic table and increase down a group. This trend is identical to the periodic trend of atomic radius. Some important properties of molecules depend on the bond lengths as depicted in **Figure 5**.

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$$\text{bond strength} \propto \frac{1}{\text{bond length}}$$
$$\text{bond energy} \propto \frac{1}{\text{bond length}}$$
$$\text{bond length} \propto \frac{1}{\% \text{ s-character}}$$

Figure 5. Relation of bond strength, bond energy and % s-character with bond length.

Bond angle determines the arrangement of orbitals around the central atom in a molecule. Therefore, bond angle helps to describe the geometry of a molecule. It is the average angle between the orbitals of the central atom in a molecule which shares the bonding electrons with the atoms being considered. The unit of bond angle is either degree or minute or second. It is noticeable that one degree is equal to 60 minutes and one minute is equal to the 60 seconds. Bond angles of sp^3 , sp^2 and sp hybrid carbon atoms are $109^{\circ}28'$, 120° and 180° respectively. So it can be deduced that the bond angle increases with increase in the % s-character.

Bond energy is the average value of bond dissociation energies for all bonds of the same type in a molecule. It can be defined as the amount of energy needed to break apart one mole of covalently bonded gases. Bond energy (E) is the measure of bond strength. Bond energy of C-H bonds of methane is 414 kJ/mol. Bond energies of some bonds frequently observed in Organic Chemistry are tabulated as **Table 3**.

Table 3: Bond energies of common bonds observed in organic compounds

Bond	Bond energy (kcal/mol)	Bond	Bond energy (kcal/mol)
H-H	104.2	C-O	85.5
C-C	83	C-Cl	81
H-C	99	C=C	146
H-N	93	C=O (carbonyl)	177
H-O	111	C \equiv C	200
C-N	73	C \equiv N	213

1.5 LOCALIZED AND DELOCALIZED CHEMICAL BOND

In organic compounds the bonding pair of electrons are not always associated with an atom or a bond. In many cases the bonding electrons show movement across the molecule. Such electronic situations can be distinguished by the concept of localized and delocalized chemical bonds.

A chemical bond is said to be localized if the bonding pair of electron is shared by two and only two atoms (**Figure 6**). However, a delocalized bond can be defined as a chemical bond where the bonding pair of electron is shared between more than two atoms (**Figure 6**). For example, bonding electrons in case of each of the four C-H bonds of methane molecules remains shared between only two atoms; namely, C and H atoms. Thus, all four bonds in methane molecules are localized covalent bonds. In case of benzene pi electron cloud of three pi bonds is equally spread over the six carbon atoms. Thus, each pair of pi bonding electrons is shared by more than two atoms. Thus, the pi-bonding system of benzene molecule is an example of delocalized bonding.

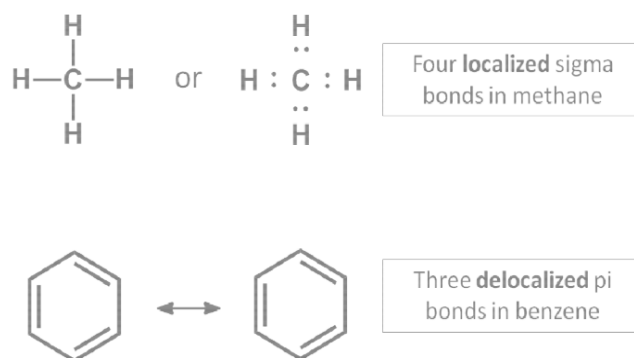


Figure 6: Localized and delocalized bonds in case of methane and benzene molecules.

1.6 VANDER WAAL INTERACTION

Neutral molecules have equal number of electrons and protons resulting in the charge neutrality. Since electrons continuously revolve around the nucleus, despite the charge neutrality of the overall system, instantaneous electric dipoles of very small magnitude come into being. These permanent dipoles of very small magnitude can induce creation of other dipoles in the molecules coming into their vicinity. van der Waal's forces are residual attractive or repulsive forces which are weaker than covalent and hydrogen bonds. They arise due to interaction between permanent dipoles and/or induced dipoles (**Figure 7**). van der Waal's forces play important role in biology and supramolecular chemistry. These forces also play important role in defining the boiling points of compounds such as hydrocarbons.

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For example, due to close packing of normal (straight chain) alkanes, more van der Waal's forces come into action holding the molecules more strongly. This leads to higher boiling points for straight chain alkanes than the branched chain alkanes where the operating van der Waal's forces are relatively weaker.

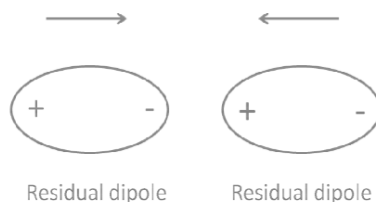


Figure 7. Schematic depiction of residual dipoles and van der Waal's forces in organic molecules.

1.7 INCLUSION COMPOUNDS, CLATHERATES, CHARGE TRANSFER COMPLEXES

(i) Inclusion compounds

Inclusion compounds are the adducts of two or more different molecules which are formed due to close geometrical fitting of one type of molecules termed as guests into the cavities formed by other type of molecules called as host (**Figure 8**). The prime forces that stabilize the structure are van der Waal's forces. For example, hydrocarbon molecules can be trapped in the cavities formed between urea molecules during crystallization which gives urea-hydrocarbon inclusion compound. Inclusion compounds can be synthesized by crystallizing host molecules in presence of guest molecules.

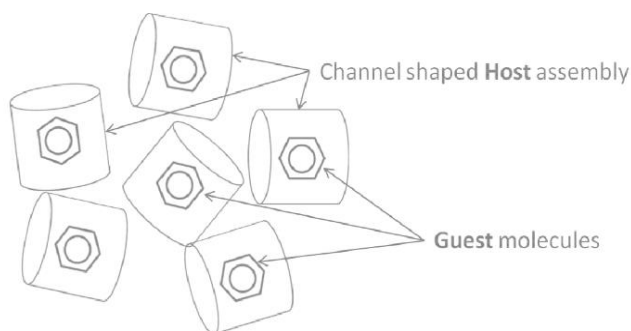


Figure 8. Schematic depiction of organic inclusion compounds.

(ii) Clathrate Compounds

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Clathrate compounds or simply clathrates represent subclass of inclusion compounds where adducts form by geometrical fitting of guest molecules into the cage shaped cavities formed by host molecules (**Figure 9**). Clathrate compounds are also stabilized by van der Waal's forces between guest and host molecules. Hydroquinone-H₂S clathrate is one of the oldest known clathrate compounds. Clathrate compounds can be synthesized by crystallizing host molecules in presence of suitable guest molecules.

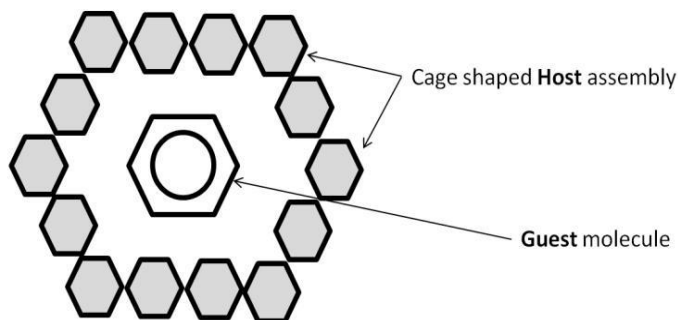


Figure 9. Schematic depiction of organic clathrate compounds.

(iii) Charge-transfer complex (CT complex)

When an electron rich and an electron deficient chemical species come geometrically closer to each other a fraction of electronic charge transfers between them. This charge transfer results in the formation of molecular complex due to electrostatic attraction between the donor (electron rich) and acceptor (electron deficient) molecules. The donor and acceptor chemical species could be two different molecules or two different parts of single molecule.

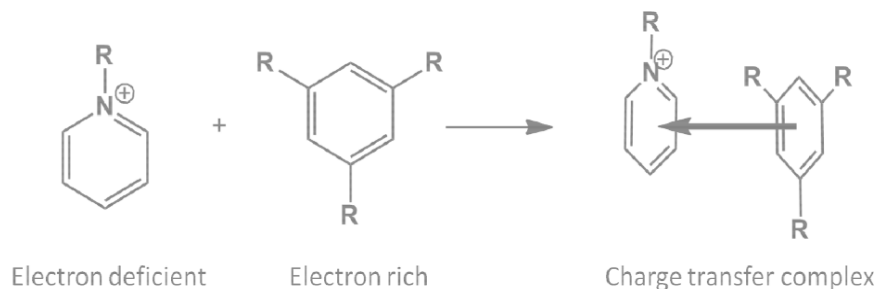


Figure 10. Schematic depiction of charge transfer (CT) complex formed between electron deficient pyridinium ion and electron rich trialkylbenzene.

In organic chemistry many compounds make charge transfer complexes. Electron deficient part is generally played by pyridinium ions or trinitroarenes whereas, trialkylarenes are convenient electron species (**Figure 10**). A well-known inorganic example is the blue coloured charge transfer complex formed by iodine and starch.

1.8 RESONANCE

Resonance is the hypothetical depiction of two or more structures for a given chemical species which differ only in the distribution of electrons (**Figure 11**). Each of such hypothetical resonating structures are called canonical structures. The actual structure is represented by hybrid of all the canonical forms and usually termed as resonance hybrid. For example, the two Kekule structures for benzene are its canonical forms whereas in the depiction of resonance hybrid, six delocalizing pi electrons are represented by a circle. Resonance is also called mesomeric effect.

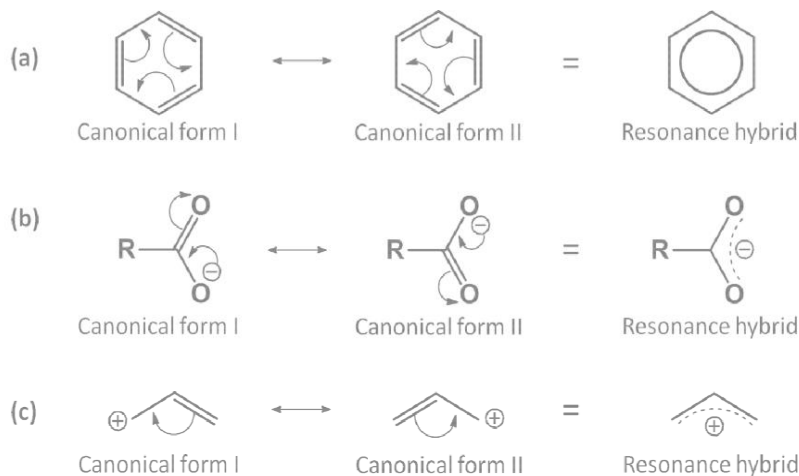


Figure 11. Resonance phenomenon depicted for benzene, carboxylate anion and allylic carbocation.

The phenomenon of resonance provides a molecule with additional stability which is indicated by resonance energy. The difference between the potential energy of the actual structure (resonance hybrid) and that of the canonical structure with the lowest potential energy is called the resonance energy. There are some general rules to identify the most significant canonical form as presented ahead:

Rule 1. The most significant canonical form possesses highest number of full octets.

Rule 2. The most significant canonical form has the greatest number of covalent bonds.

Rule 3. The most significant canonical form possesses fewest atoms with formal charges.

Rule 4. Aromatic canonical forms are more significant.

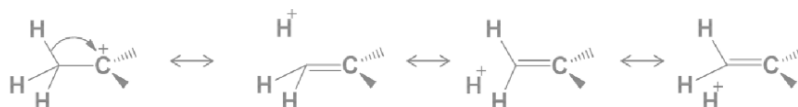
Rule 5. The most significant canonical form bears negative formal charges on the most electronegative and positive formal charges on the least electronegative atoms.

1.9 HYPERCONJUGATION

Hyperconjugation is the interaction of the sigma electrons with an adjacent empty or partially filled p-orbital or π bonds. Hyperconjugation is also called 'no-bond' resonance or Baker-Nathan effect. This interaction provides the structure with additional stability. Hyperconjugation phenomenon explains the stability order of carbocations, free radicals and that of alkenes.

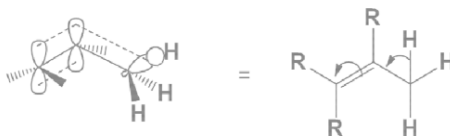


Depiction of interacting orbitals in carbocation having α hydrogen

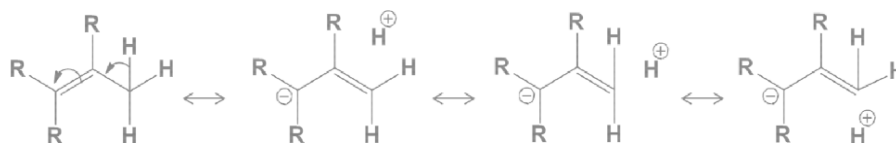


Hyperconjugation forms for a carbocation having three α hydrogen atoms

Figure 12. Hyperconjugation forms for a carbocation having α hydrogen.



Depiction of interacting orbital in alkene having α hydrogen



Hyperconjugation forms for alkene with three α hydrogen atoms

Figure 13: Hyperconjugation forms for a substituted alkene.

Figures 12 and 13 depicts that hyperconjugation allows representing alkenes or carbocations having α hydrogen by $(n+1)$ no-bond resonating structures, where n is the number of α hydrogen atoms. Therefore, hyperconjugation provides these structures additional stability. Free radicals also show hyperconjugation as shown by carbocations. The phenomenon of

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hyperconjugation affects several properties of alkenes, carbocations and free radicals which are discussed ahead.

Since due to hyperconjugation σ bonds acquire double bond character, therefore these C-C bond lengths decrease. For example, the C-C bond length in 1,3-butadiene is 1.46 Å which is shorter than standard value of 1.54 Å.

Since higher the number of α hydrogen atoms higher the number of hyperconjugation forms for a carbocation. Therefore carbocations with higher number of α hydrogen atoms show higher stability. Thus, stability order for carbocations is: $3^\circ > 2^\circ > 1^\circ > \text{methyl}$

Since higher the number of α hydrogen atoms higher the number of hyperconjugation forms for a free radical. Therefore free radicals with higher number of α hydrogen atoms show higher stability. Thus, stability order for free radicals is: $3^\circ > 2^\circ > 1^\circ > \text{methyl}$

Since higher the number of α hydrogen atoms higher the number of hyperconjugation forms for an alkene. Therefore alkenes with higher number of α hydrogen atom, *i.e.*, more substituted alkenes show higher stability.

1.10 AROMATICITY

The term aromaticity is used to describe a cyclic, planar molecule with complete conjugation that exhibits more stability than other geometric arrangements with the same set of atoms. Aromatic molecules are very stable and do not easily undergo chemical reactions. A compound must fulfill following criteria to be aromatic:

It must be a cyclic system

It must have complete conjugation *i.e.*, ring have alternate single and double bonds
It must be a planar structure

It must follow Huckel's rule, *i.e.*, it must possess $(4n+2)$ π electrons; where $n = 0, 1, 2, 3 \dots$

Benzene, pyridine, furan and naphthalene are few common examples of aromatic compounds (**Figure 14**). It is noteworthy that aromatic compounds usually don't give addition reactions. They undergo substitution reactions.

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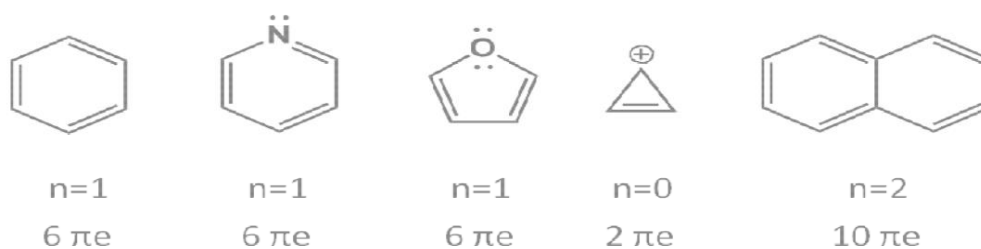


Figure 14: Some aromatic compounds with the value of n for which they satisfy Huckel's $(4n + 2)$ rule and the count of their π electrons.

1.11 STERIC EFFECT

Each atom occupies certain space therefore two different atoms cannot be brought too much closer to each other as it increases the electronic repulsion between them. This phenomenon of repulsion when two atoms come very close to each other is called steric effect. Steric hindrance is said to be operative when a molecule does not exhibit an obvious property or an obvious chemical reaction due to the presence of a large group in its structure.

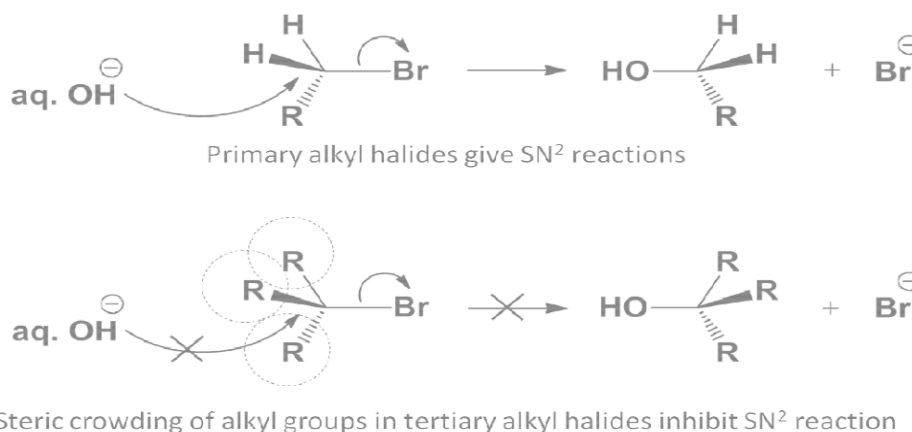


Figure 15: Demonstration of steric effects operative in S_N2 reactions of tertiary alkyl halides.

For example, a tertiary alkyl halide doesn't undergo S_N2 reactions as the three bulky alkyl groups sterically deny the nucleophile to reach the electron-deficient reaction center. Steric inhibition of resonance is present only in benzene rings. The presence of any group at the ortho position in benzoic acid will throw the carboxylic acid group out of the plane, and thus its mesomeric connection with the benzene ring vanishes. This means that ortho-substituted benzoic acids are stronger than meta- and para-substituted benzoic acids.

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1.11.1 INDUCTIVE, RESONANCE/MESOMERIC, ELECTROMERIC AND FIELD EFFECT

Inductive effect is the polarity produced in a molecule due to the difference in electronegativity of bonded atoms. It is an experimentally observable effect and transmits through the C-C chain in organic molecules. The electron cloud in a σ -bond is slightly pulled in by more electronegative atom. Thus more electronegative atom assumes partial negative charge (δ^-) and the less electronegative atom assumes partial positive charge (δ^+). This causes permanent polarization of the bond. Thus inductive effect is a permanent effect.

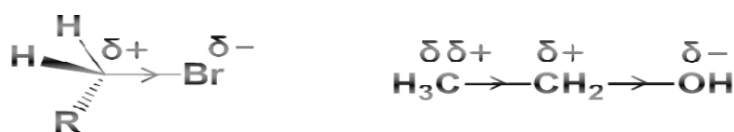
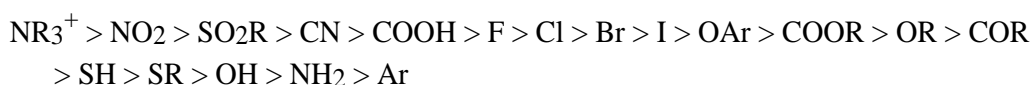


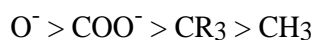
Figure 16: Demonstration of inductive effect operative in alkyl bromide and ethyl alcohol.

For example, bromine atom has higher electronegativity than carbon atom. Hence bromine atom in bromoalkane molecule slightly attracts the electron pair of C-Br bond and assumes δ^- -charge (**Figure 16**). As a result, adjacent carbon atom assumes a δ^+ charge. Practically inductive effect transmits up to two to three atoms across the C-C chain.

Inductive effect is classified as $-I$ and $+I$ effects. When in an organic compound carbon assumes slight positive charge due to the high electronegativity of adjacent atoms, it is termed as $-I$ effect. The organic functional groups showing $-I$ effects are given in their decreasing $-I$ effect ahead:



When carbon atom is bonded with electropositive atoms or groups such as methyl group it assumes slightly negative charge and the effect is called $+I$ effect. The organic functional groups showing $+I$ effects are given in their decreasing $+I$ effect ahead:



The strength of inductive effect decreases along the C-C chain such that the greater the distance from the group, weaker the effect. Inductive effect affects several properties of the organic molecules such as their acidity and basicity. It also affects the stability of carbocations and carbanions.

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Effect on acidity and basicity

Acidity of organic compounds such as carboxylic acids is the measure of how easily they release a proton. It can also be expressed in terms of stability of conjugate bases. More stable the conjugate base more will be the acidity of carboxylic acid. Hence, substituent with -I effect increase the acidity of carboxylic acid. For example, trifluoroacetic acid is stronger acid than the acetic acid (**Figure 17**). Similarly, basicity of amine is their affinity to accept protons. Thus, substituents with -I effect decrease the basicity of amines. For example, pyridine is stronger base than the nitropyridine (**Figure 17**).

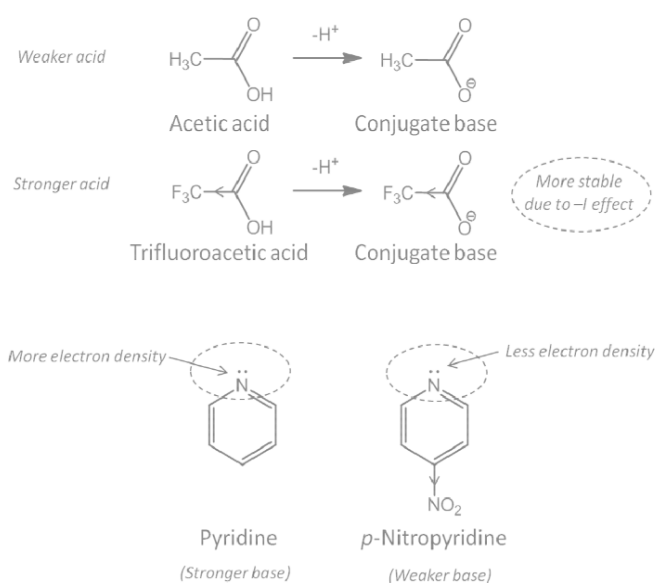


Figure 17. Effect of inductive effect on acidity and basicity.

Stability of carbocations and carbanions

Substituents with -I effect increase the positive charge density of carbocations, hence they decrease the stability of carbocations. On the other hand, substituents with +I effect stabilize the carbocations (**Figure 18**). Similarly, Substituents with -I effect decrease the negative charge density of carbanions, hence they increase the stability of carbanions. On the other hand, substituents with +I effect destabilize the carbanions.

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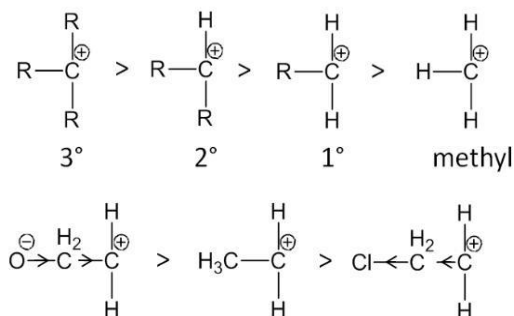


Figure 18: Effect of inductive effect on stability of carbocations.

Electromeric effect is the molecular polarization produced due to the presence of a reagent. This effect is shown by compound having double or triple bonds. For example, carbonyl bond polarizes in presence of a nucleophilic reagent such as cyanide anion. However, the polarity vanishes when the reagent is removed. Thus, electromeric effect is a temporary effect. Electromeric effect can be classified into +E and -E effects based on the direction of transfer of the electron pair. When the electron pair moves towards the attacking reagent, it is termed as the +E effect. The addition of acids to alkenes is an example of the +E effect. When the electron pair moves away from the attacking reagent, it is termed as the -E effect. The addition of cyanide ion to carbonyl compounds is an example of -E effect.

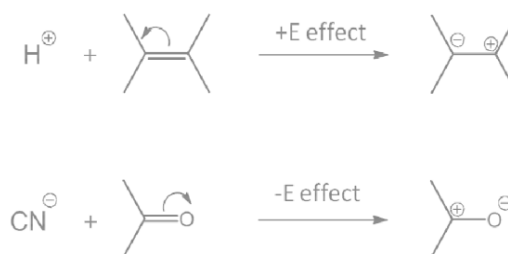
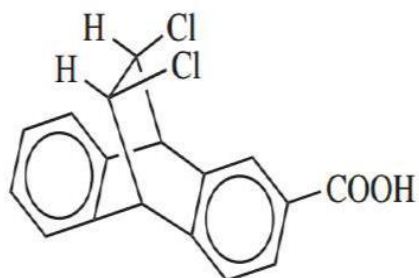


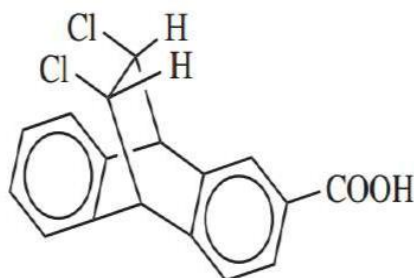
Figure 19: Schematic depiction of +E and -E effects.

The other effect operates not through bonds, but directly through space or solvent molecules, and is called the field effect. It is very difficult to separate inductive effect and field effect, but it has been done in a number of cases, generally the field effect depends on the geometry of the molecule but the inductive effect depends only on the nature of bonds. For example, in isomer 1 and 2 the inductive effect of the chlorine atoms on the position of the electrons in the COOH group should be the same since the same bonds intervene; but the field effect is different because the chlorines are closer in space to the COOH in 1 than they are in 2. This effect can be confirmed by the comparison of the acidity of 1 and 2.

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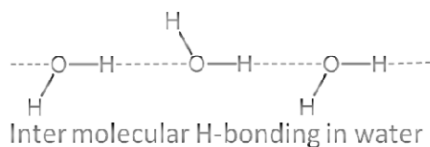
1
 $pK_a = 6.07$



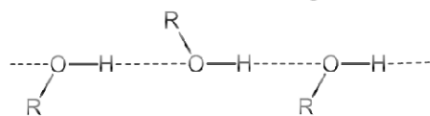
2
 $pK_a = 5.67$

1.12 HYDROGEN BONDING

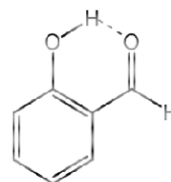
A hydrogen bond is the electrostatic attraction between two polar groups that occurs when a hydrogen (H) atom covalently bound to a highly electronegative atom such as nitrogen (N) or oxygen (O) experiences the electrostatic field of another highly electronegative atom nearby. In other words when hydrogen atom covalently connected to electronegative atom comes in vicinity to another electronegative atom, it acts as a bridge to join both entities. Hydrogen bonds can occur in same molecule (intramolecular) and between two different molecules (inter molecular). These bonds are weaker than covalent bonds but stronger than van der Waal's interactions and usually are of an order of 1-5 kcal/mol. Intermolecular hydrogen bonding is responsible for the high boiling point of water (100 °C) compared to the other compounds such as H₂S, which is gas at room temperature. Hydrogen bonding plays important role in medicinal chemistry, solid state chemistry and natural products. Stronger the hydrogen bond, higher will be the melting and boiling points of the organic molecules.



Inter molecular H-bonding in water



Inter molecular H-bonding in alcohol



Intramolecular H-bonding in
an carbonyl substituted phenol

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Figure 20. Depiction of some molecules exhibiting inter- and intra-molecular hydrogen bonding

1.13 SUMMARY

This 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, hyperconjugation, aromaticity, steric effect and electronic effects make base to comprehend organic chemistry. Other significantly important topics such as bond length, bond angles, bond energy, hydrogen bonding and van der Waal interactions are given with lucid diagrams. Introduction to the topics such as inclusion compounds, clathrates and charge transfer complexes stimulate the interest of reader to the advanced studies in organic chemistry.

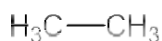
1.14 TERMINAL QUESTION

Short Answer type questions

- Q.1** What is the phenomenon of resonance in organic compounds? Explain with two examples.
- Q.2** Describe the phenomenon of hyperconjugation in 2° carbocation.
- Q.3** What is electromeric effect? Why it is called a temporary effect?
- Q.4** What is the importance of steric hinderance for SN² reactions?
- Q.5** Describe localized and delocalized bonding with one example of each.
- Q.6** Discuss the stability order of alkyl carbocations with the help of inductive effect.
- Q.7** Write a short note on inclusion compounds or clathrate compounds.
- Q.8** What is the Huckel's rule of aromaticity of organic compounds?
- Q.9** Why water is liquid at room temperature while hydrogen sulfide is a gas?
- Q.10** What is the bond angle? How will you correlate it with the hybridization?

MCQ type questions

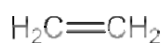
- Q.1** Find the correct decreasing order of carbon carbon bond lengths in following compounds:



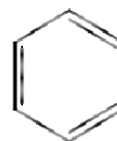
(i)



(ii)



(iii)



(iv)

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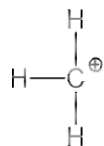
i > ii > iii > iv

i > iv > iii > ii

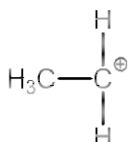
i > iii > ii > iv

ii > iii > iv > i

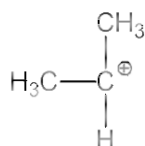
Q.2 Arrange the following carbocations in increasing order of stability:



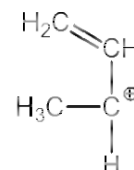
(i)



(ii)



(iii)



(iv)

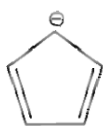
i > ii > iii > iv

i > iv > iii > ii

iv > iii > ii > i

ii > iii > iv > i

Q.3 Which one of the following is not aromatic:



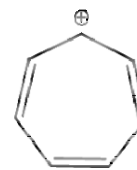
(i)



(ii)



(iii)



(iv)

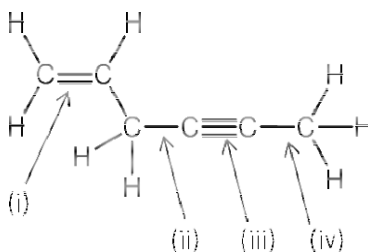
iii

i

iv

ii

Q.4 Identify the shortest carbon carbon bond length in the following compound:



i

ii

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iii

iv

Q.5 Exceptional high stability of benzene is explained by:

aromaticity

hyperconjugation

van der Waal's force

hydrogen bond

Q.6 Which of the following phenomenon explains the stability order of carbocations?

resonance effect

hyperconjugation effect

inductive effect

all of the above

Q.7 Correct order of stability of carbanions is:

$1^\circ > 2^\circ > 3^\circ > \text{methyl}$

$3^\circ > 2^\circ > 1^\circ > \text{methyl}$

$^\circ < 2^\circ < 1^\circ < \text{methyl}$

$1^\circ < 2^\circ < 3^\circ < \text{methyl}$

Q.8 Hybridization of each carbon atom in benzene is:

sp^3

sp^2

sp

none of the above

Q.9 Largest bond angle in organic compounds is observed when carbon atom is:

sp^3 hybridized

sp^2 hybridized

sp hybridized

can't say

Q.10 Hydroquinone- H_2S is a compound of following class:

charge transfer complex

clathrate compound

Coordination compound

Inorganic complex

ANSWERS

Answers to the MCQ type questions

Q.1 (b)

Q.2 (a)

Q.3 (a)

Q.4 (c)

Q.5 (a)

Q.6 (d)

Q.7 (c)

Q.8 (b)

Q.9 (c)

Q.10 (b)

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UNIT 2: MECHANISM OF ORGANIC REACTIONS

CONTENT:

2.1 Objectives

2.2 Introduction

2.3 Curved arrow notation

2.3.1 Drawing electron movements with arrows

2.3.2 Half-headed and double headed arrows

2.4 Homolytic and heterolytic bond cleavage

2.5 Type of reagents

2.5.1 Nucleophilic Reagents or Nucleophiles

2.5.2 Electrophilic Reagents or Electrophiles

2.6 Recapitulation of types of reagents

2.7 Summary

2.8 Terminal Questions

2.1 OBJECTIVES

Objective of this chapter is to provide readers with basics of organic reaction mechanisms. Like all chemical transformations, organic reactions also involve breaking and formation of chemical bonds. Thus, understanding of electron sharing between atoms and transfer of electrons is very important to understand the organic reaction mechanisms. This chapter sheds light on bond cleavage and curved arrow notations to denote the changes involving electron sharing. Concise detail on type of reagents affecting various organic reactions is also given. The chapter is developed such that the reader inculcates fundamental terminologies and notations pertaining to organic reaction mechanism. To offer students an easy and interesting learning experience, each of the topics covered is depicted with lucid

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diagrams and figures. Point to point discussion progresses as per the ORGANIC CHEMISTRY COURSE-II, BCH102 syllabus.

2.2 INTRODUCTION

Organic reactions involve breaking and formation of chemical bonds that is the changes in sharing of electrons between atoms in given molecules. Movement of electrons during organic reactions is denoted by curved arrow notations. For example, movement of odd electron is represented by half headed arrow whereas movement of electron pair is represented by full curved arrows. Understanding the correct arrow notation not only helps to describe how an organic reaction is taking place but also helps to quickly understand the peculiar mechanistic steps involved. Thus, content of this chapter is essential for beginning study of organic reaction mechanisms. Later, the chapter discusses important categories of organic reagents those are useful to carry out particular organic transformations. For example, nucleophilic reagents attack on electron deficient sites in a molecule while the electrophilic reagents react with electron rich species. Thus, this chapter is a suitable package to begin learning and understanding the organic chemistry transformations.

2.3 CURVED ARROW NOTATION

Chemical reactions involve breaking and formation of chemical bonds. It means sharing of electrons between atoms in given molecules changes during reactions. This change in sharing of electron or movement of electrons is denoted by different types of curved arrows depending on the reactions. For example, movement of odd electron (or single electron) is represented by half headed arrow whereas movement of an electron pair is represented by double headed curved arrows. How a double-headed or full-headed arrow and half-headed or fish-hook arrow is drawn in organic chemistry is depicted in Figure 2.1.

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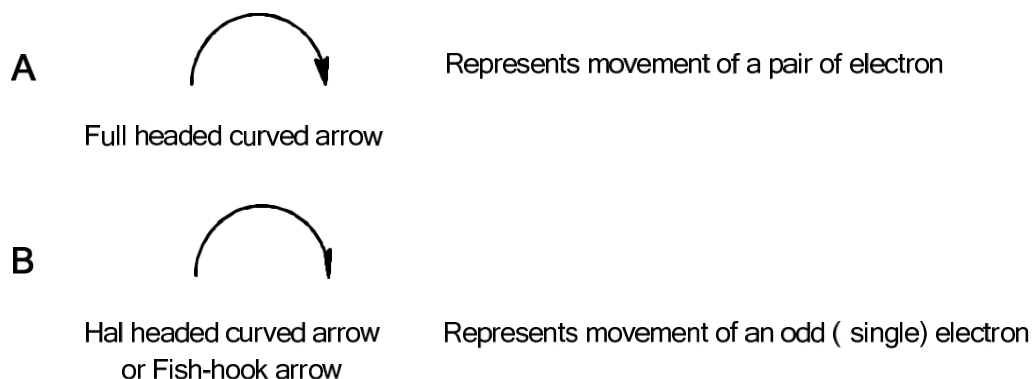


Figure 2.1 Depiction of full (A) and half (B) headed arrows

2.3.1 Drawing electron movements with arrows

Occurrence of electron movement in organic reactions or during the inter-conversion of resonating structures is obvious in organic chemistry. As the organic reactions proceed through several steps, it is important to keep track of electron movements taking place in each step to swiftly understand the mechanistic aspects. The electron movements are denoted by curved arrows as depicted in previous section. The distinct curved arrows should not be confused with other common straight arrow notations in organic chemistry. Arrow head indicates the location where electrons are moving to and the arrow tail indicates where originally electrons were located. Double headed and half headed curved arrows are discussed with some examples in the next section.

2.3.2 Half-headed and double headed arrows

Half headed arrows also referred as fish hook arrows are used to denote the movement of odd electron from one reaction site to another. Since they represent movement of single electron (odd electron) therefore, they are frequently used to depict reactions involving free radicals. Thus, mechanism of homolytic fission, reactions involving free radicals and photochemical reactions are demonstrated by half headed or fish hook arrows. Some examples are depicted in the Figure 2.2.

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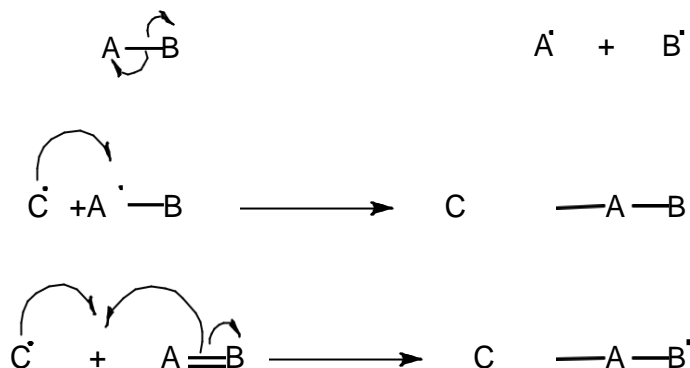


Figure 2.2 Movement of odd electrons in some processes is depicted by half headed arrows. Note the movement of electron and resulting molecular or radical species.

The first reaction indicates homolytic fission of covalent bond between atoms A and B that results in formation of free radicals $A\cdot$ and $B\cdot$. Tail of half headed arrows is on bond which is the original position of electrons and the arrow heads are pointing to the atoms A and B where the electrons locate on completion of the process. In the second example, equal sharing of odd electrons between free radicals, $C\cdot$ and $\cdot A-B$ results in a molecule $C-A-B$. The third example illustrates homolytic breaking of a π bond as a result of attack by radical $C\cdot$. C and A equally share one electron each to form new σ bond between them, whereas one odd electron resides on atom B.

Double headed arrows are used to denote the movement of electron pair from one reaction site to another. This type of arrows frequently used to depict ionic reaction mechanisms. Arrow tail and arrow head indicate initial and final locations of electron pairs respectively. Some examples are depicted in the Figure 2.3.

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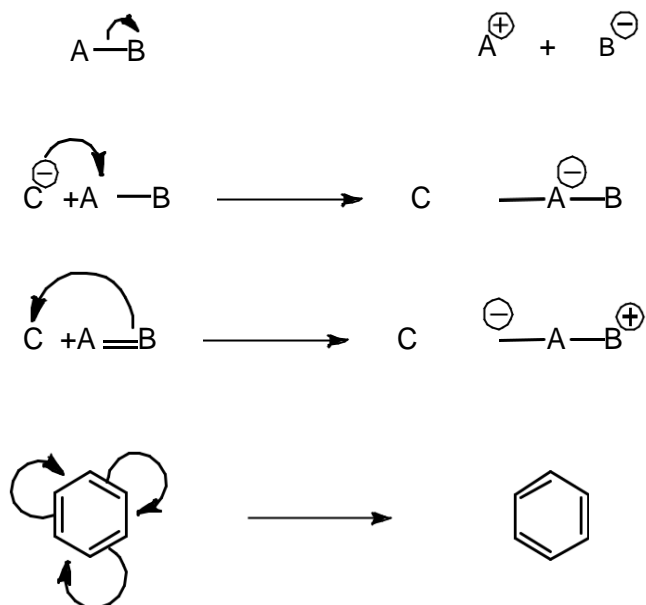


Figure 2.3 Movement of electron pairs in some processes as depicted by full headed arrows. Note the movement of electron pairs and resulting molecular or ionic species.

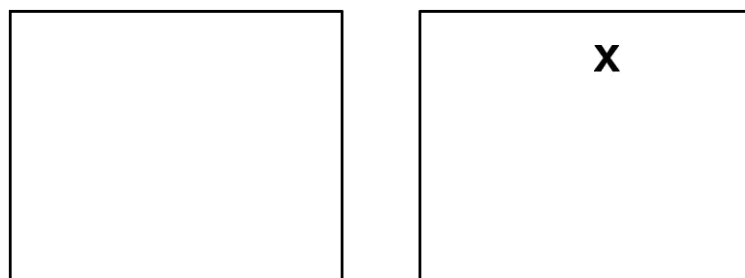
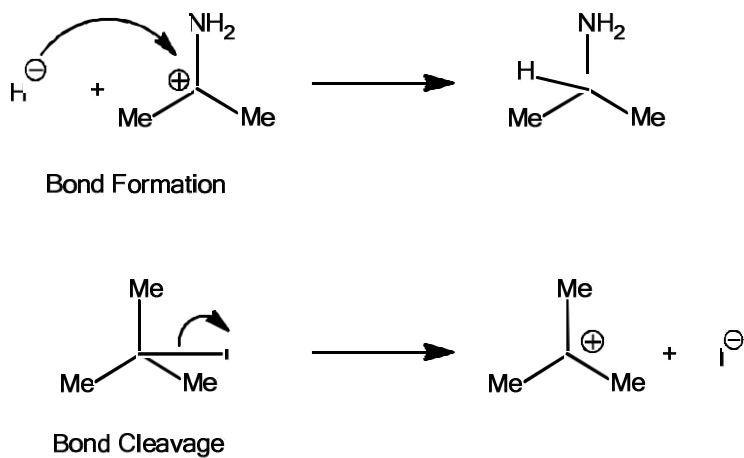


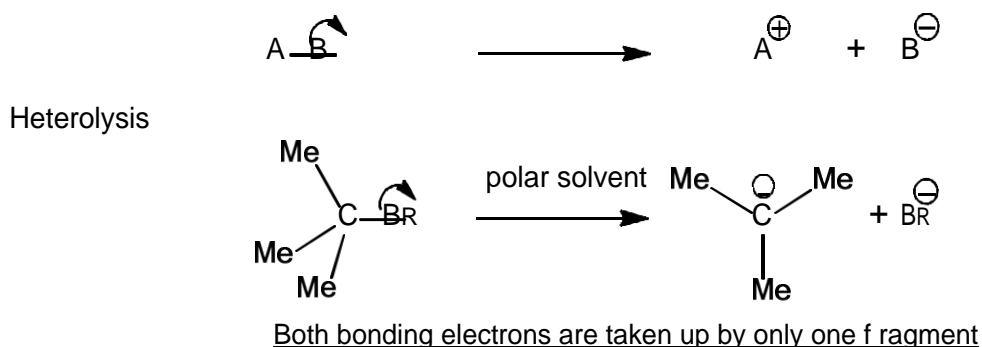
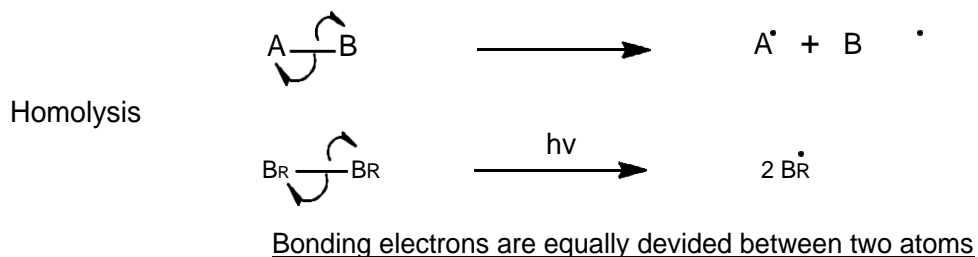
Figure 2.4 Correct depiction of curved arrow for formation and breaking of covalent bond. Inset images show correct and incorrect way to depict electron movement with curved arrows.

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The first reaction indicates heterolytic fission of covalent bond that results in formation of ions A^+ and B^- . In the second example, anion C^- attacks one electron deficient site A in a molecule A-B, i.e., C^- donates electron pair to atom A in molecule A-B resulting in the anion on product side. Third example involves attack of electron deficient atom C on the electron rich site, i.e., π bond between A and B. In the resultant species atom C assumes formal negative charge because it accepts additional electron in its orbital whereas atom B loses its electron, hence the formal positive charge on B. Fourth example depicts the concerted movement of three π electron pairs in benzene ring that inter-converts two Kekulé structures into each other.

2.4 HOMOLYTIC AND HETEROLYTIC BOND CLEAVAGE

Chemical reactions involve breaking and formation of chemical bonds. How a chemical bond will break depends on factors such as temperature, reaction medium and solvent. Organic reactions usually involve breaking of covalent bonds followed by formation of new covalent bonds. The bond breaking, also termed as bond cleavage takes place in two possible ways, namely, homolytic and heterolytic bond fission.



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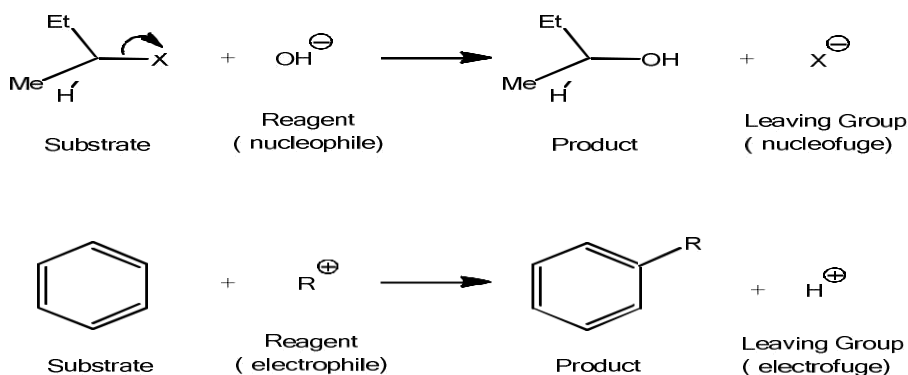
Figure 2.5 General and specific examples depicting homolysis and heterolysis of covalent bonds.

Homolytic bond cleavage is also called homolytic bond fission or homolysis. In homolysis, the two electrons in a cleaved covalent bond are divided equally between the products. On the other hand, heterolytic bond cleavage is also called heterolytic bond fission or heterolysis. In heterolysis, the two electrons in a cleaved covalent bond remain with one of the two fragments.

2.5 TYPE OF REAGENTS

Organic reactions are generally brought about by heterolysis of organic compounds. The breaking of bonds and formation of new bonds occur in presence of reagents. Thus reagents are substances or compounds that are added to bring about a reaction. In organic reactions it is convenient to call one reactant as substrate which will provide carbon to a new bond and the other is called as reagent. The attacking reagent can be (i) which provides an electron pair to the substrate, known as Nucleophile and the reaction is called a Nucleophilic reaction (ii) takes an electron pair from substrate is known as Electrophile and the reaction is called a Electrophilic reaction.

In reactions where the substrate bond is cleaved, the part that does not contain the carbon is called Leaving group. The leaving group that carries electron pair is known as Nucleofuge. If the leaving group moves out without the electron pair, it is called Electrofuge.

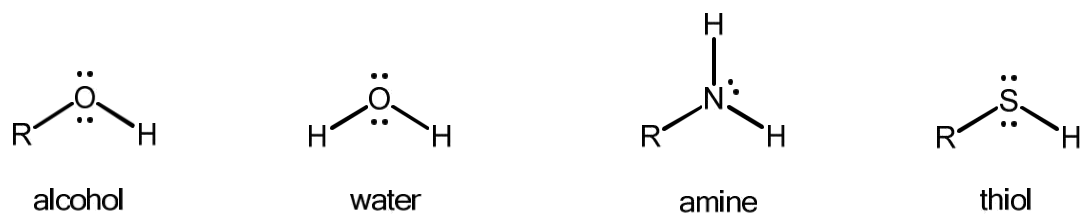


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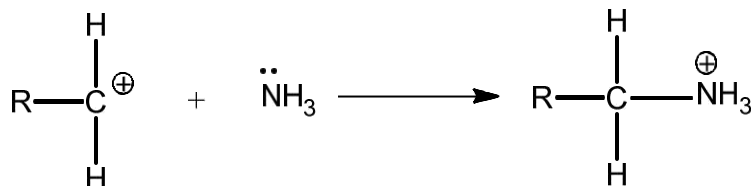
2.5.1 Nucleophilic Reagents or Nucleophiles

Nucleophile means nucleus loving. Reagents having unshared pair of electrons are known as Nucleophilic reagents or nucleophiles and they show tendency to share this lone pair of electrons with electron deficient species. They can be classified into three groups:

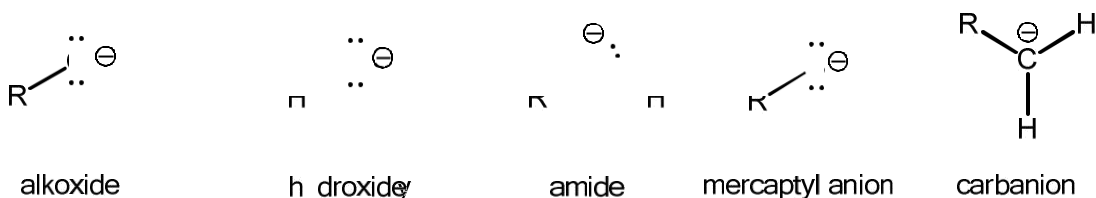
Neutral Nucleophiles: These are electron rich species due to presence of non bonding pair of electrons. Central atom of such species should have a complete octet. Neutral nucleophiles are not charged and are electrically neutral.



Organic compounds having C-C multiple bond/bonds also act as Neutral nucleophiles because these species have π electron cloud above and below the plane of the molecule. The addition reaction of a neutral nucleophile to a positively charged substrate gives a positively charged product.

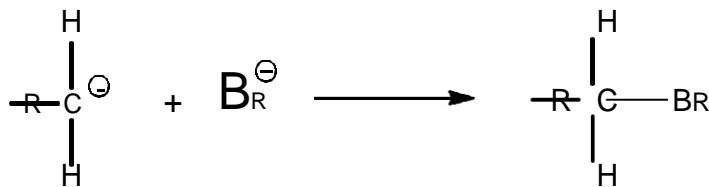


Negative Nucleophiles: These carry an electron pair and are negatively charged because of the presence of unpaired electrons.

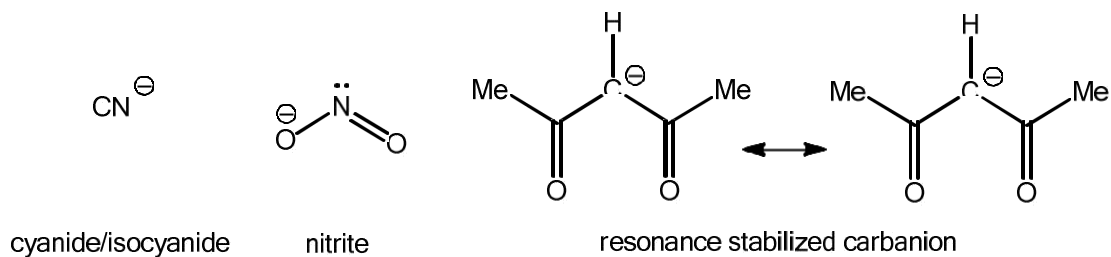


Addition reaction of a negatively charged nucleophile to a positively charged substrate results in neutral molecule.

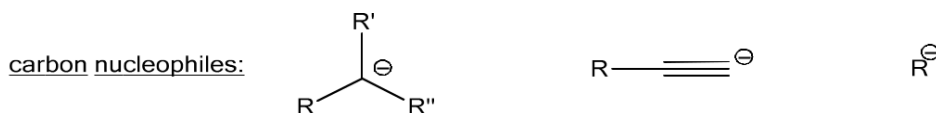
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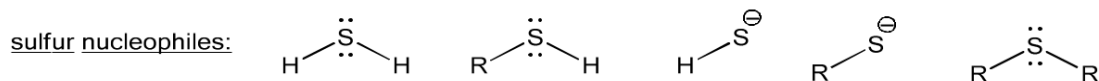
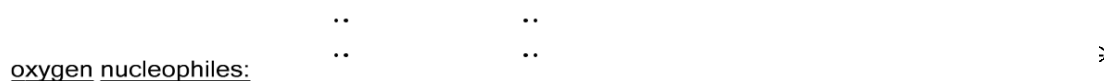
Ambident Nucleophiles: The nucleophiles which can attack through two or more atoms are called ambident nucleophiles. For Eg: CN^- can attack through N or C to give cyanide (RCN) or isocyanide (RNC) respectively.



Nucleophiles can also be classified on the basis of the kind of atom that forms a new covalent bond. The most common nucleophiles on this basis are oxygen, nitrogen, sulfur, halogen and carbon nucleophiles.



nitrogen nucleophiles: .

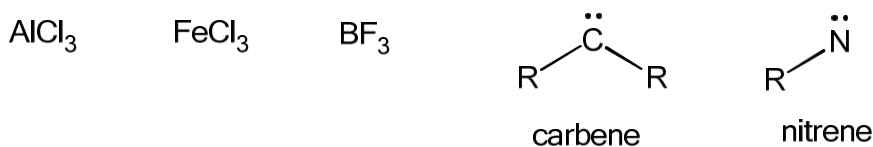


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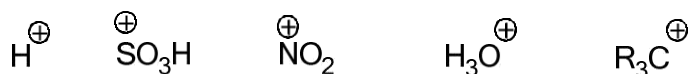
2.5.2 Electrophilic Reagents or Electrophiles

An electrophile (meaning electron loving) is a reagent that is electron deficient and due to this they show affinity for electrons. Electrophiles can also be of two types:

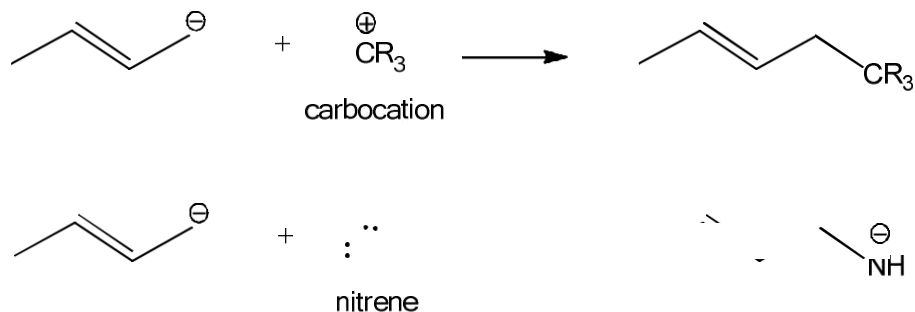
Neutral Electrophiles: These electrophiles even though electron deficient does not carry positive charge. They have incomplete valence shells. Examples: AlCl_3 , BF_3 , carbene etc.



Positive Electrophiles: These electrophiles carry positive charge on central atom and have incomplete octet.



The positive electrophile will attack the substrate (which is a negative nucleophile) and accepts an electron pair for sharing resulting in a neutral molecule. While, a neutral electrophile will attack a electron rich substrate (negative nucleophile) to form a negatively charged molecule.



2.6 RECAPITULATION OF TYPES OF REAGENTS

A nucleophile is a chemical species that donates an electron pair to an electron deficient reaction site to form a chemical bond. As the nucleophile donate electrons, they are Lewis bases. All molecules or ions with a free pair of electrons or at least one pi bond can

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act as nucleophiles. A nucleophile with higher affinity to the electron deficient site is said to have higher nucleophilicity. All carbanions, OH^- , Br^- , I^- and SH^- are few of the good nucleophiles in organic chemistry. Nucleophilic character of similar species comprising different elements increases top to down and decreases on moving left to right in the periodic table. Therefore, SH^- is better nucleophile than OH^- and CH_3^- is better nucleophile than

3

NH_2^- . Neutral nucleophilic reactions with solvents such as alcohols and water are named solvolysis. Nucleophiles may take part in nucleophilic substitution, whereby a nucleophile becomes attracted to a full or partial positive charge.

On the other hand, an electrophile is a reagent that attracts towards electrons. Electrophiles are positively charged or neutral species having vacant orbitals that are attracted to an electron rich centre. Thus, they are Lewis acids. In chemical reactions, electrophiles accept an electron pair make bond to the electron rich reaction site. Cations such as H^+ and NO^+ , polar molecules such as HCl , alkyl halide (R-X), acyl halides (R-COX), carbonyl compounds (R-CO-R or R-CHO) and polarizable molecules such as Br_2 and Cl_2 etc are commonly used electrophiles

2.7 SUMMARY

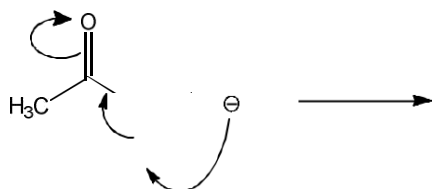
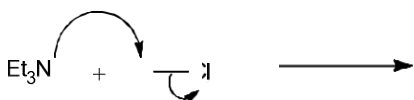
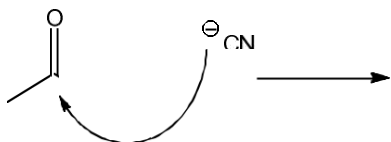
This chapter covers description of basic concepts such as curved arrow notation (arrow pushing) and bond fission, which are vital to understand and write organic reaction mechanisms. The description on topics such as full headed & half headed curved arrow, nucleophiles and electrophiles, homolytic and heterolytic bond fission is given in the chapter with sufficient details. Other significantly important terms such as nucleofuge, electrofuge, leaving group, substrate and attacking reagents are given with guiding figures. Understanding of these topics will help us to understand and gain interest in mechanisms of organic reactions.

2.8 TERMINAL QUESTIONS

Short Answer type questions

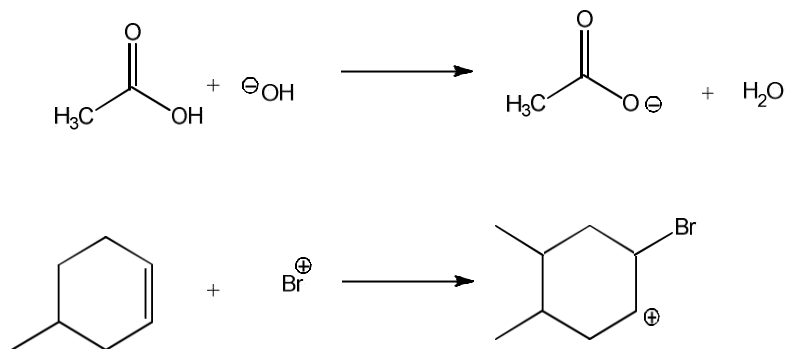
- Q.1** Briefly describe the curved arrow notation for movement of odd electrons.
- Q.2** Describe the full headed curved arrow notation used in reaction mechanisms.
- Q.3** What is an electrofuge? Give two examples of electrofuge.
- Q.4** Write short note on heterolysis of covalent bonds.
- Q.5** Describe the terms substrate, reagent and leaving group.
- Q.6** Discuss neutral nitrogen containing nucleophiles.
- Q.7** What is the difference between nucleophile and electrophile?
- Q.8** Give one example of a nucleophilic and an electrophilic substrate.

Q.9 Complete the following reactions:



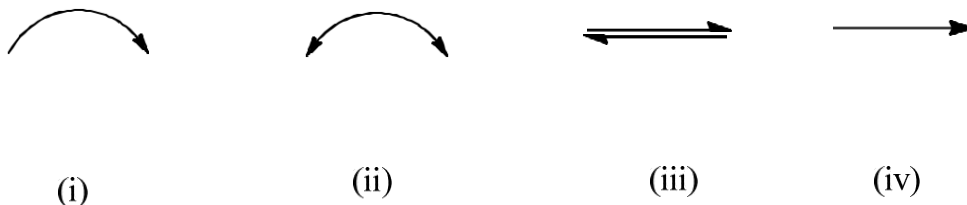
Q.10 Place the appropriate curved arrows to depict the electronic movement in following reactions.

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MCQ type questions

Q.1 Identify the correct arrow depicting movement of electron pair in organic reaction mechanisms:



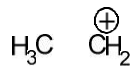
iii

i

iv

ii

SO_3

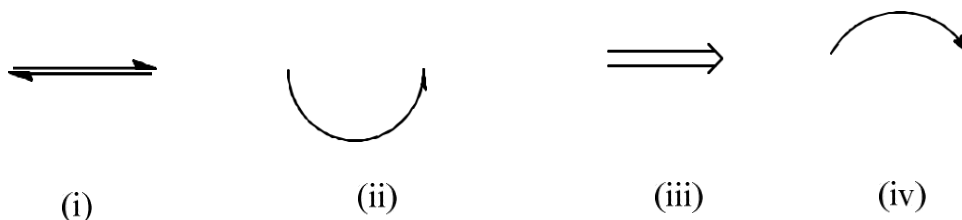


BF_3

both b and c

Q.3 Which one of the following represents movement of odd electron in organic reaction mechanisms:

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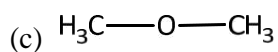
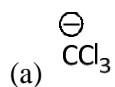
iii

i

iv

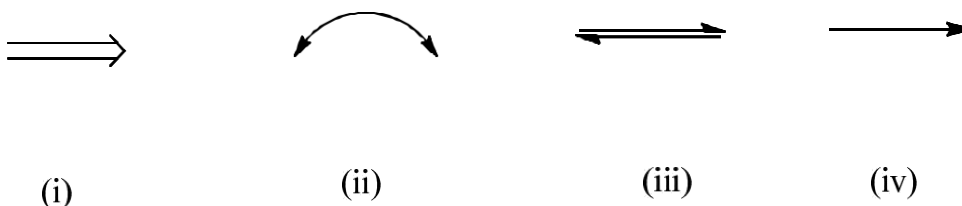
ii

Q.4 Select from the options given below the nucleophilic species:



(d) all of the above

Q.5 Find the correct depiction for fish-hook arrow:



ii & iii

iii

none

i

Q.6 Identify the electrophile from the following options:



Both a and b

Q.7 A leaving group is called so because:

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it detaches from the carbon in organic reaction

it detaches from the attacking reagent

it is part of incoming nucleophile

it is part of incoming electrophile

Q.8 Which of the species given below behaves as ambident nucleophile:



Both a and b

Q.9 Which of the species given below is an ambident nucleophile:



All of the above

substrate

leaving group

incoming group

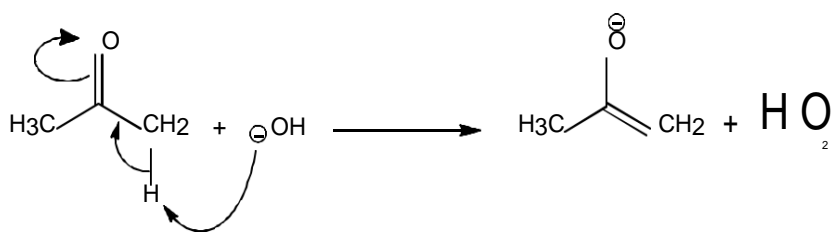
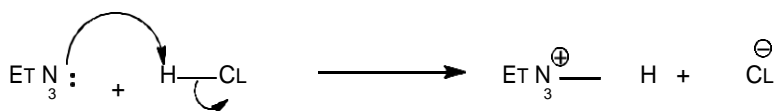
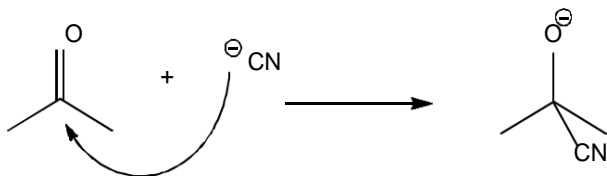
attacking reagent

ANSWERS

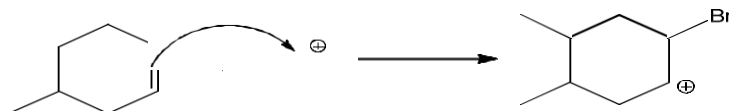
Answers to the short answer type questions

Q.9

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Q.10



Answers to the MCQ type questions

Q.1 (a)

Q.2 (d)

Q.3 (b)

Q.4 (d)

Q.5 (c)

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Q.6 (c)

Q.7 (a)

Q.8 (d)

Q.9 (b)

Q.10 (b)

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UNIT 3: REACTION INTERMEDIATE

CONTENTS:

- 3.1 Objectives
- 3.2 Introduction
- 3.3 Reaction intermediates (with examples Assigning)
 - 3.3.1 Carbocations
 - 3.3.2 Carbanions
 - 3.3.3 Free radicals
 - 3.3.4 Carbenes
 - 3.3.5 Nitrenes
 - 3.3.6 Benzyne
- 3.4 Formal charge on intermediates and other ionic species.
- 3.5 Summary
- 3.6 Terminal Question

3.1. OBJECTIVES

Explain what a reactive intermediate is, why they are important in organic reactions, and what reaction intermediates are commonly encountered.

Describe the properties of carbocations, carbanions, carbon radicals, carbenes, nitrenes and benzyne including their structure, hybridization, geometry, and reason for reactivity.

Explain how resonance stabilizes carbocations, carbanions, free radicals and other intermediates.

Explain what hyperconjugation is, and how it stabilizes carbocations and carbon radicals.

Explain how nearby electronegative atoms stabilize carbanions.

Explain how carbocations, carbanions, carbon radicals, and carbenes are formed, and recognize which of these will be formed by a given reaction.

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Explain how carbocations, carbanions, carbon radicals, and carbenes react, and what they could be expected to react with.

Explain what carbocation rearrangements are, why they occur, and the two types that can happen.

Predict whether or not a carbocation will rearrange, and if it will, draw the new carbocation and an arrow showing how it was formed.

3.2. INTRODUCTION

In the Organic Chemistry the reactions takes place in many steps. In these steps the reaction intermediates are also formed which are consumed during the reaction to give the product. So the reaction intermediates are defined as; "A neutral or charge species which is form during the reaction and by consumed gives the final product is known as reaction intermediates.

Reaction intermediates are highly reactive because they have strong tendency to convert in stable form and their life period is 10^{-12} sec.

A reactive intermediate is a short-lived, high-energy and highly reactive species. It generated in a chemical reaction and it will quickly convert into a more stable product. Only in exceptional cases can these compounds be isolated and stored, e.g. low temperatures, matrix isolation. When their existence is indicated, reactive intermediates can help explain how a chemical reaction takes place.

Most chemical reactions takes place more than one step to complete, and a reactive intermediate is a high-energy, yet stable, product that exists only in one of the intermediate steps. A reactive intermediate differs from a reactant or product or a simple reaction intermediate only in that it cannot usually be isolated but is sometimes observable only through fast spectroscopic methods. It is stable in the sense that an elementary reaction forms the reactive intermediate and the elementary reaction in the next step is needed to destroy it. Reactive intermediates based on carbon are Carbocations, Carbanions, Free radicals, Carbenes, Nirenes and Benzyne.

3.3. REACTION INTERMEDIATES

3.3.1 Carbocations

An Organic species which has a carbon atom containing only six electrons in its outermost shell and has a positive charge is called a carbocation reaction intermediate. The carbon atom of the carbocation is sp^2 hybridized, it use the three hybrid orbitals for single bonding to three substituents and remaining p- orbital is empty. The carbocations thus has a planner structure having all the three covalent bonds are in plane with the bond angle of 120^0 between them.

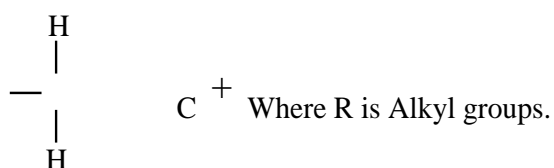
It is generated by hetrolytic bond fission and it carries + charges in its structure with six valence electrons are known as carbocation or carbonium ion.

Examples: CH_3^+ , $C_2H_5^+$, $C_3H_7^+$ etc.

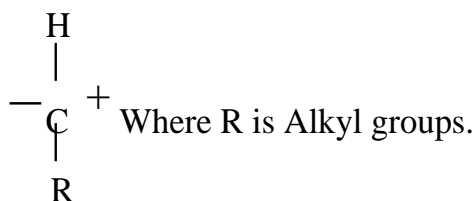
Classification of carbonium ion:

A. Alkyl Carbonium ion: Like free radical carbinium ion also classified in to three classes-

Primary carbonium ion: In this type of carbonium ion one carbon atom is attached with the + ve carbon atom.



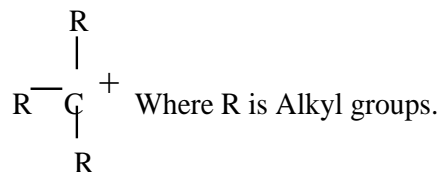
Secondary carbonium ion: In this type of carbonium ion two H atoms are replaced by two alkyl groups from the + ve charge bearing carbon.



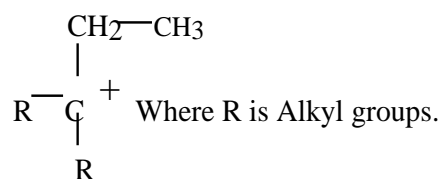
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3. Tertiary carbonium ion

In this type of carbonium ion 3 hydrogen atoms are replaced by 3 alkyl groups from the +ve charge bearing carbon.



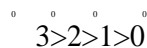
tert. Butyl carbonium ion



tert. Butyl carbonium ion

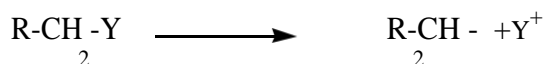
Stability of carbonium ion:

The relative stability of carbonium ion is explained with the help of Inductive effect. In the case of 1^0 carbonium ion the CH_3 group contains +I effect, so it releases the e^- towards the carbon that bears +ve charge. So some charge neutralizes and also somewhat +ve charge is created on the methyl group carbon, so the +ve charge becomes dispersed and gives stability. Hence we can say that greater the dispersion is the +ve charge, greater will be the stability. Hence 3^0 carbocation is most stable in comparison to 2^0 , 1^0 and methyl carbocation.



3.3.2 Carbanions:

These are chemical species which possess a negatively charged carbon centre. Like the Carbocations, the Carbanions are also formed by *heterolytic fission* of covalent C-Y molecules.

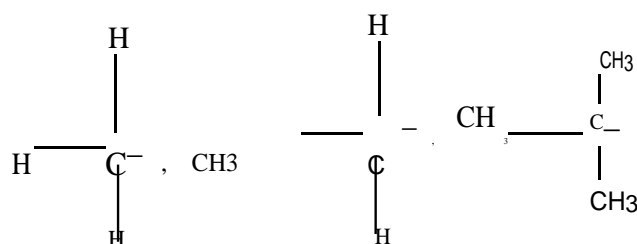


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Here Y is an atom which is more electropositive than carbon. This is why during the heterolytic fission the shared pair of electrons is drawn towards the carbon atom to develop a negative charge over it.

It is generated by heterolytic fission and bearing -ve charge and the number of valence electrons are 8 in it called carbanion reaction intermediate.

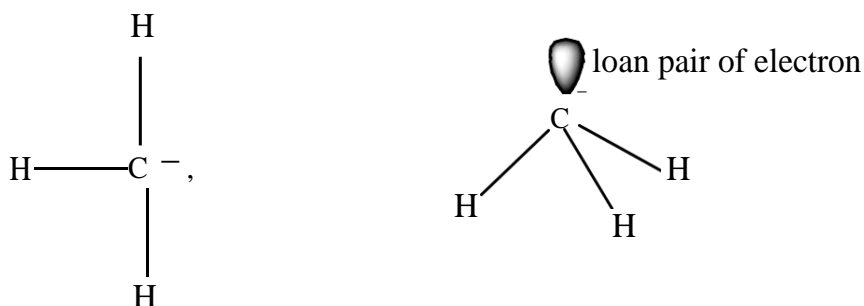
Example:



Hybridization in carbanion ion:

The carbanion ion shows sp^3 hybridization with one lone pair of electron. Hence its geometry will be tetrahedral.

E.g.

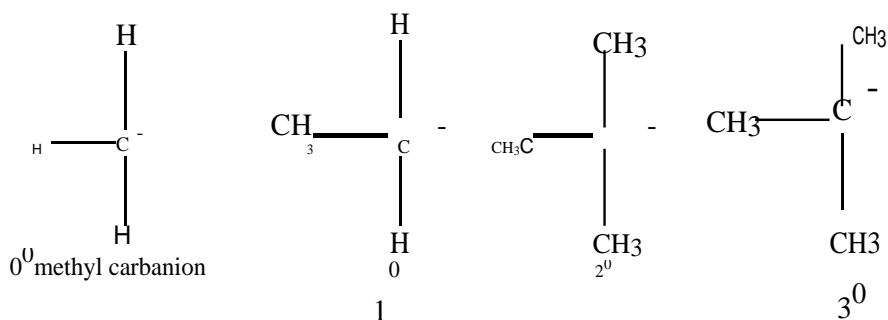


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Classification of Carbonium ion:

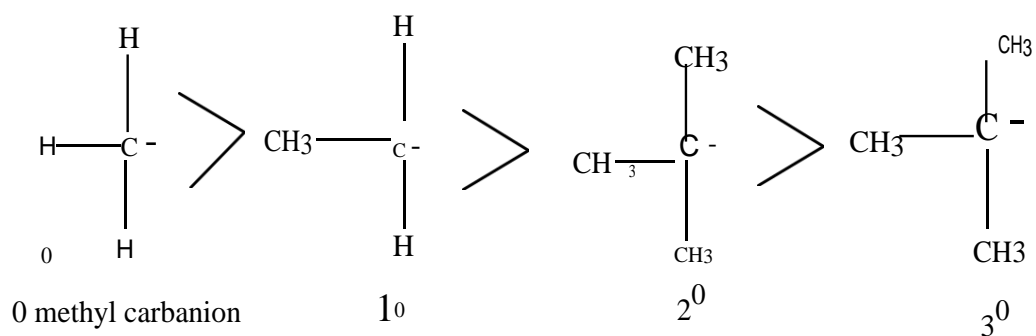
Like carbocation, carbonion ion are also classified in to three classes and it is depends upon the replacing of H from the bearing C. If only 1 H is replaced then it is primary, if two H are replaced then it is secondary, if 3 H is replaced then it is tertiary.

e.g.



Stability of carbanion ion:

The stability of carbanion ion is reverse to the stability of carbocation and free radical. Hence the order of the stability is:



Decreasing order of stability of carbanion ion.

Cause: Since $-\text{CH}_3$ group consist +I affect, so it increases the density of e^- on the carbanion ion. Hence its result is destabilization. So we can say that on increasing the +I effect stability decreases. Thus the result 0° carbanion is most stable in compare to 1° , 2° and 3° carbanion.

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3.3.3 Free radicals

These are species which are atoms or groups of atoms containing unpaired electrons. They are formed by the *homolytic fission* of covalent bond.

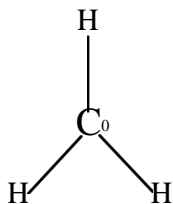


Example: CH_3^{\bullet} , $\text{CH}_3\text{CH}_2^{\bullet}$, H^{\bullet} etc.

The free radicals are strongly reactive because they have stronger tendency to become paired and their nature is paramagnetic.

Hybridization in free radical:

Free radical shows sp^2 hybridization and their geometry is triangular.



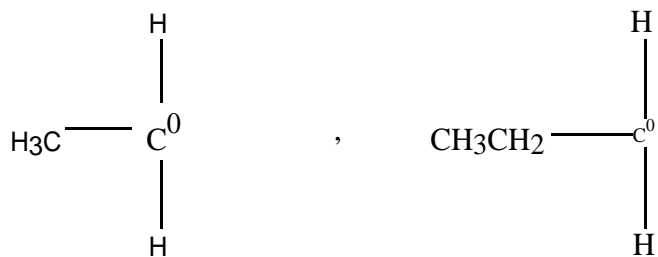
Classification of free radical:

Free radicals are classified in two following three types-

Primary free radicals: When 1 H atom of $-\text{CH}_3$ group is replaced by another alkyl group then it is called as 1° free radical.

E.g.

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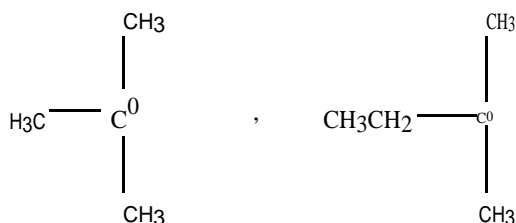


Secondary free radical: When 2 H atom of $-\text{CH}_3$ group is replaced by another alkyl group then it is called as secondary free radical.

Eg :



Tertiary free radical: When 3H atom of $-\text{CH}_3$ group is replaced by another alkyl group then it is called as tertiary free radical (3^0).

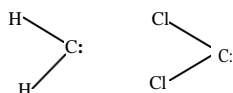


Stability of free radical: The relative stability of free radical is explained with the help of hyperconjugation concept. If the alkyl chain is longer, attached to that carbon which bears (carrying) odd electron then there is the maximum delocalization in the odd electron, hence it becomes most stable. Similarly secondary radical has more delocalization than primary free radical. So finally it is clear that tertiary free radical is most stable in compare to 2^0 , 1^0 and 0^0 free radicals.

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3.3.4 Carbenes

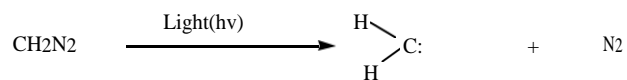
Carbenes are neutral, divalent, highly reactive intermediate carbon species. It is defined as a neutral reactive divalent species which consist six electron in its outermost shell is known as Carbene.



Carbenes are highly reactive because they have stronger tendency to complete their octate.

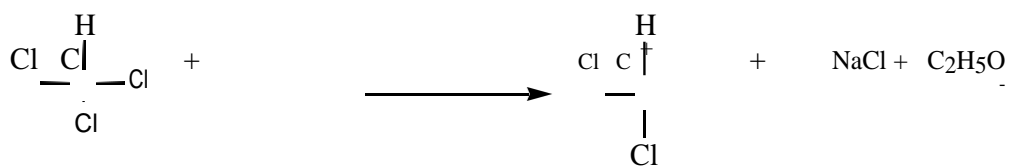
Methods of preparation:

From diazomethane-Diazomethane on decomposition under the action of light gives carbene.

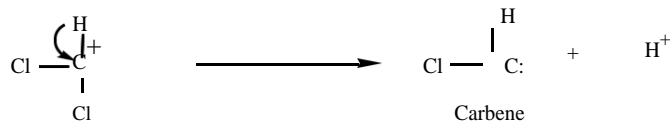


From chloroform: Chloroform on react with sodium ethoxide gives dichloro carbene by releasing $\text{C}_2\text{H}_5\text{OH}$.

Step 1



Step 2



Step 3

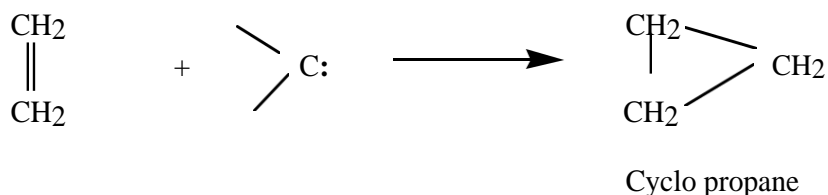


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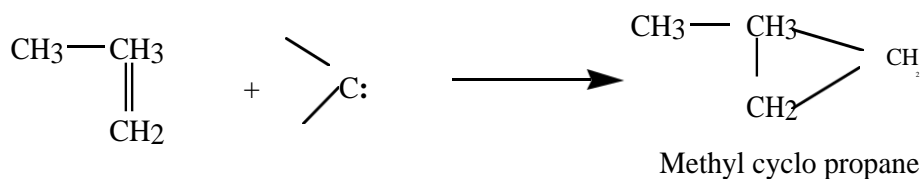
Properties of carbene:

Carbene is a highly reactive reaction intermediate and it gives easily reaction.

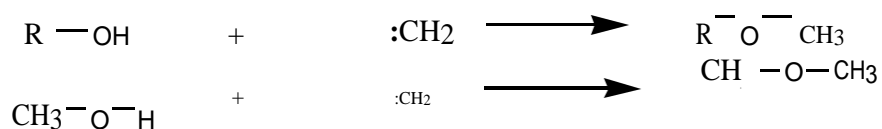
Reaction with Alkene: carbene on react alkene gives cycloalkanes.



e.g.

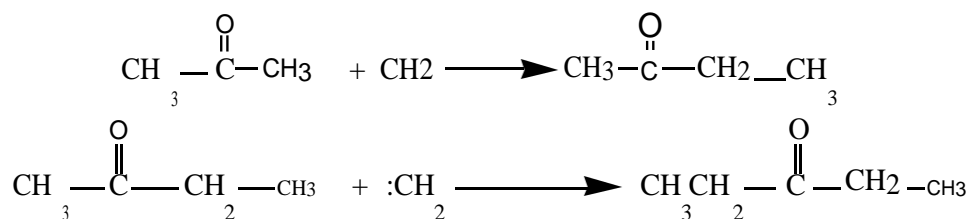


Reaction with alcohol: Carbene on react with alcohol gives addition compound ether.



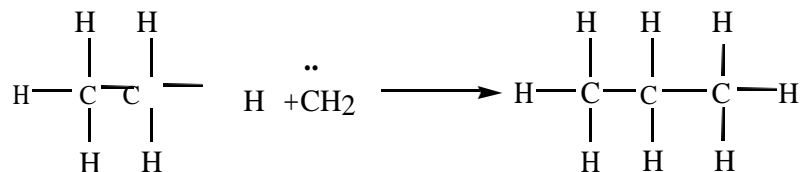
Insertion Reaction: In this reaction carbene react with those functional groups which are bi-valent and from both sides they are link with another groups undergoes insertion reaction with carbene.

Note: ketone on react with carbene gives higher member of ketone.



Reaction with alkanes: Alkanes on react with carbene gives higher number of alkane series.

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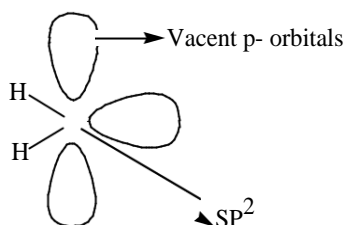


Classification of carbene: Carbenes are classified into two classes by name these are-

Singlet carbene

Triplet carbene

Singlet carbene: In this type of carbene sp^2 hybridization is observed and the unshared pair of electron is present in one p-orbital.



$$\text{Multiplicity} = S = 1/2n$$

(Where n is the number of unpaired electron)

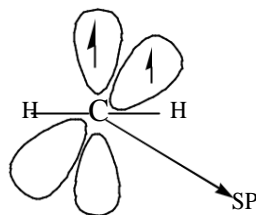
In this case $n = 0$

$$\text{Since multiplicity} = 2s + 1$$

$$2 \times 0 + 1$$

1 (singlet)

Triplet carbene: In this type of carbene the unshared pair of electron is exist in to two unhybridised p-orbital. So they show sp - hybridization with linear geometry.



$$S = \frac{1}{2} n$$

$$S = \frac{1}{2} \times 2$$

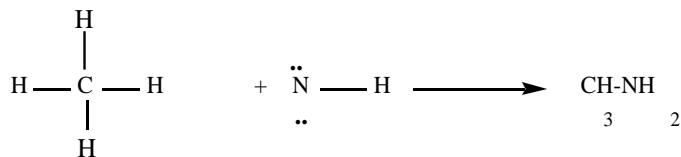
$$S = 1$$

$$\text{Since multiplicity} = 2s + 1$$

$$= 2 \times 1 + 1 = 3 \text{ (Triplet)}$$

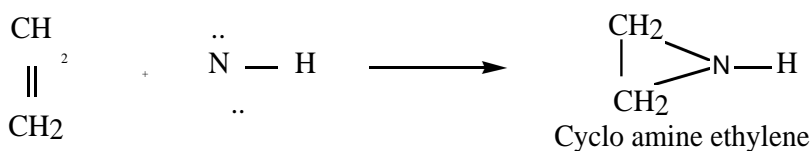
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Insertion reaction: In this type of reaction nitrene react with alkane to give amino derivative compound.

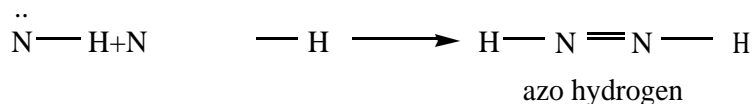


Aminomethane

Reaction with alkene: Nitrene on react with alkenes gives cyclic amino compounds.

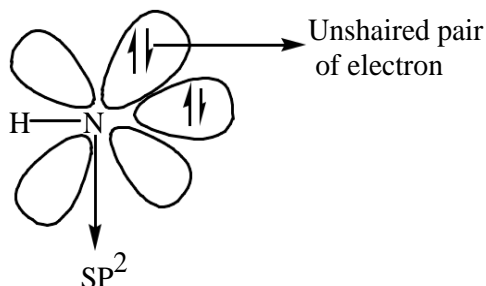


Dimerization reaction: In this type of reaction two nitrenes are combined together to form the product.



Classification of nitrenes: Nitrenes are classified into two classes one is singlet and other is triplet nitene.

Singlet nitrene: In this type of nitrene the unshared pair of electron is present in one p-orbital and it consist sp^2 hybridization, its geometry is as follow.



For multiplicity:

Unshaired pair of e^- $n = 0$

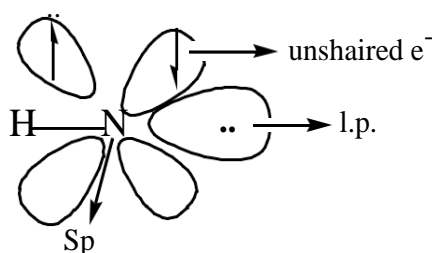
$$S = \frac{1}{2} n = \frac{1}{2} \times 0 = 0$$

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Since multiplicity = $2s + 1$

$$2 \times 0 + 1 = 1 \text{ (singlet)}$$

Triplet nitrene: In this type of nitrene N atom shows sp hybridization and the unshared electron are present in two different p - orbitals.



For multiplicity: No. of unpaired e ($n= 2$)

So multiplicity = $2s + 1$

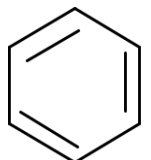
$$2 \times 1 + 1$$

3 (Triplet)

3.3.6 Benzyne:

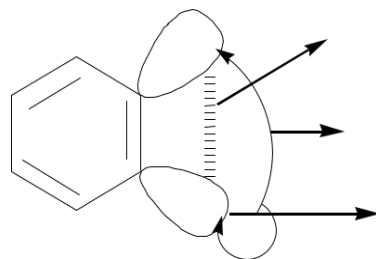
Benzyne or arynes are highly reactive species derived from an aromatic ring by removal of two ortho substituents. Arynes are usually best described as having a strained triple bond; however, they possess some biradical character as well.

The aryne nomenclature derives from the fact that the C_6H_4 can be represented as an alkyne, although systematically the species should be named as didehydro aromatic compounds, i.e. 1,2-didehydrobenzene.



Benzyne can be represented as a singlet molecule with a carbon-carbon triple bond. Although it has triple bond but it is not normal alkyne bond. In benzyne out of two π -bond of triple bond, one π -bond is normal and the other π -bond is abnormal and is formed by overlap of two sp^2 orbitals outside the ring. This is called external π -bond. It can be represented as follow.

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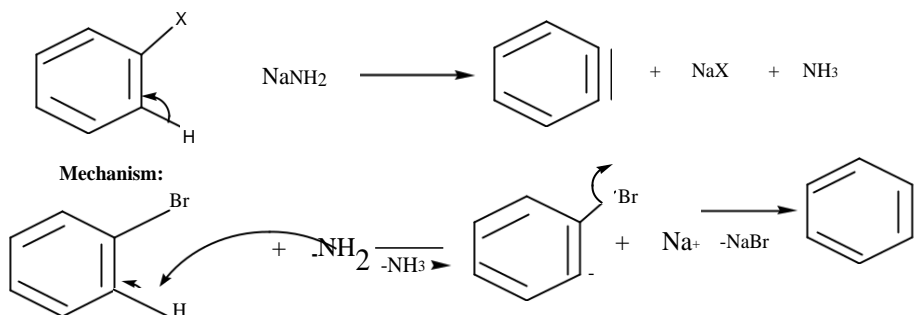


Abnormal p i-bo n d

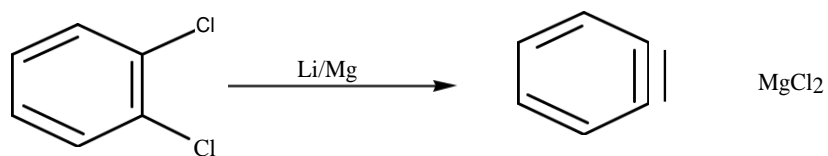
Two s p² orbitals outside the ring

Preparation of benzyne:

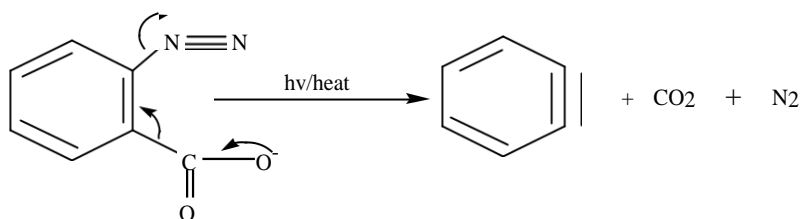
From halobenzene: When halobenzene are react with sodamide in liquid ammonia then it gives benzyne.



2. **From *o*- dihalobenzene:** When *o*-dihalobenzene is treated with lithium amalgam or Mg, then it gives benzyne.



From benzenediazonium-2- carboxylic acid: benzenediazonium-2-carboxylic acid when heated in the presence of heat and sun light then it gives benzynes.



3.4. FORMAL CHARGE ON INTERMEDIATES AND OTHER IONIC SPECIES:

The formal charge of an atom in a polyatomic molecule or ion may be defined as the difference between the number of valence electrons of that atom in an isolated or free State and the number of electrons assigned to that atom in the Lewis structure. It is expressed as:

$$\text{Formal Charge} = \text{Number of valence electron} - \text{Number of unshared electron} - \frac{1}{2} \text{Number of electrons shared in covalent bond}$$

$$\left[\begin{array}{l} \text{Formal charge (F.C.)} \\ \text{on an atom in a Lewis} \\ \text{structure} \end{array} \right] = \left[\begin{array}{l} \text{total number of valence} \\ \text{electrons in the free atom} \end{array} \right] - \left[\begin{array}{l} \text{total number of non} \\ \text{bonding (lone pair)} \\ \text{electrons} \end{array} \right] - \left[\begin{array}{l} (1/2) \text{ total number} \\ \text{of bonding (shared)} \\ \text{electrons} \end{array} \right]$$

Procedure: The procedure to determine formal charges on the atoms of an ion or molecule has three steps. The process is illustrated using hydronium ion (H_3O^+); an ion very frequently encountered in organic and biochemical reaction mechanisms.

Step 1: Draw the best Lewis structure for the molecule, including all unpaired electrons.

Be sure to show all non bonded electrons, as these influence formal charges. The best Lewis structure for the hydronium ion is shown below. The brackets indicate the positive charge belongs to the entire molecule.

Step 2. Assign the formal charge to each atom.

Formal charge is calculated using this formula:

$$\text{Formal Charge} = \text{Number of valence electron} - \text{Number of unshared electron} - \frac{1}{2} \text{Number of electrons shared in covalent bond}$$

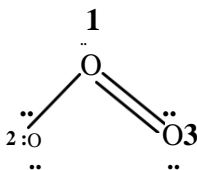
Step 3. Check your work.

The sum of the formal charges of all atoms must equal the overall charge on the structure.

For example hydronium ion, the sum of the formal charges on the hydrogen atoms (3 x zero) plus one for the oxygen gives a total charge of +1, which agrees with the overall charge. Let

us consider the ozone molecule (O_3). The Lewis structure of O_3 may be drawn as :

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The atoms have been numbered as 1, 2 and 3. The formal charge on:

The central O atom marked 1

$$6 - 2 - 1/2(6) = +1$$

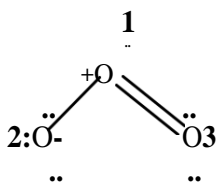
The end O atom marked 3

$$= 6 - 4 - 1/2(4) = 0$$

The end O atom marked 2

$$= 6 - 6 - 1/2(2) = -1$$

Hence, we represent O₃ along with the formal charges as follows:



3.6. TERMINAL QUESTIONS

What are carbanions? How they are generated? Discuss their stability order.

What are Carbenes? How they are generated? Give the structure of Singlet and Triplet carbenes.

Discuss some reactions of benzynes.

What are benzynes? Give their structure.

What are Singlet and Triplet nitrenes?

Give the Relative stability of free radicals with the help of hyperconjugation effect.

Give the relative stability of the alkyl carbo cations.

What are the important factors affecting the stability of carbanions? Discuss the structure of carbanions.

How will you distinguish between singlet and triplet carbenes based on their stability and stereochemical behaviour in addition reactions?

10. Explain the structure and stability of carbon free radicals

UNIT 4: STEREOCHEMISTRY-I

CONTENTS:

- 4.1 Objectives
- 4.2 Introduction
- 4.3 Concept of isomerism
- 4.4 Types of isomerism
- 4.5 Optical isomerism
 - 4.5.1 Elements of symmetry
- 4.6 Molecular chirality, enantiomers
 - 4.6.1 Stereogenic centre
- 4.7 Optical activity
 - 4.7.1 Properties of enantiomers
- 4.8 Chiral and achiral molecules with two stereogenic centres,
- 4.9 Diastereomers
 - 4.9.1 Properties of Diastereomers
 - 4.9.2 Threo and erythro diastereomers
 - 4.9.3 Meso compound,
 - 4.9.4 Resolution of enantiomers
 - 4.9.5 Inversion, retention and racemization
- 4.10 Relative configuration and absolute
 - 4.10.1 D& L system of nomenclature
 - 4.10.2 R& S system of nomenclature
 - 4.10.3 Sequence Rule
- 4.10 Summary
- 4.11 Terminal Question

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4.1 OBJECTIVES

By the end of this unit you 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

Learn chirality, enantiomers, diastereomers and their relative/absolute configurations

Learn the nomenclature (cis-trans, E/Z, D/L, d/l, erythro/threo and R/S) of different stereoisomers

4.2 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. An example of this is the drug thalidomide which was used during the 1950s to suppress the morning sickness. The drug unfortunately, was prescribed as a mixture of stereoisomers, and while one stereoisomer actively worked on controlling morning sickness, the other stereoisomer caused serious birth defects.

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.

4.3 CONCEPT OF ISOMERISATION

The word isomerism originated from Greek word *isomer* (*iso*= equal; *mers* = part). When two or more compounds having the same molecular formula but exhibit difference in their

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chemical and/or physical properties are called isomers and the phenomenon is known as isomerism.

4.4 TYPES OF ISOMERISM

Generally isomerism can be divided in to two categories;

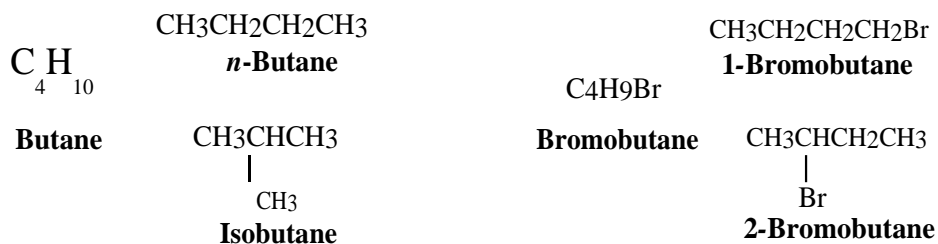
Structural (constitutional) Isomerism

Stereo (configurational) Isomerism

a. Structural (constitutional) Isomerism

Structural isomerism is also known as ‘constitutional isomerism’. Structural isomerism arises when a molecule can be represented in to two or more than two different structures. The difference in structure is due to the difference in the arrangement of atoms within the molecules, irrespective of their position in space. In other words, structural isomers are compounds those have identical molecular formulae but different structural formulae; and the phenomenon is called structural isomerism.

Examples 1: Structural isomer of Butane (C₄H₁₀) and Bromobutane (C₄H₉Br)



Structural isomerism can also be subdivided in to five types

Chain Isomerism

Functional Isomerism

Position Isomerism

Metamerism

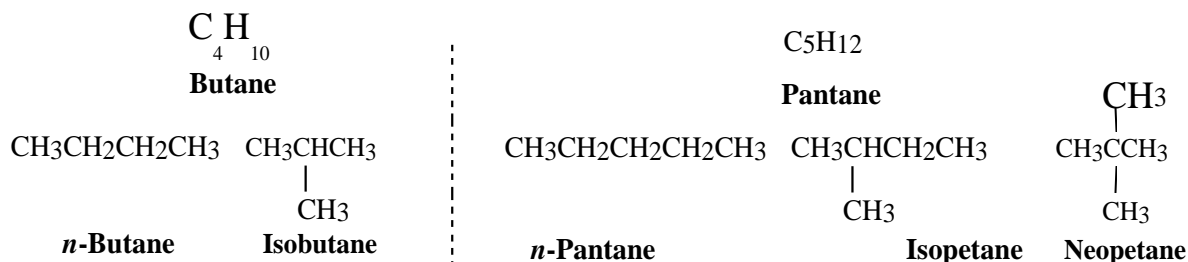
Tautomerism

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Chain Isomerism: Chain isomers are those isomers having difference in the order in which the carbon atoms are bonded to each other. In other words chain isomers have variable amounts of branching along the hydrocarbon chain.

☞ *If you observe two or more than two molecules having same molecular formulae, but difference in their hydrocarbon chain length, you should understand that these are chain isomers of each other.*

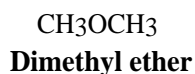
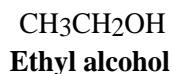
Example 2: Chain isomers of Butane (A) and Pentane (B)



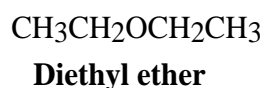
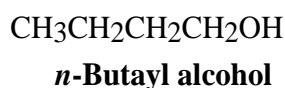
Functional Isomerism: Two or more than two molecules those having the same molecular formulae but have different functional groups are called functional isomers and the phenomenon is termed as functional isomerism.

☞ *If you observe two or more than two molecules having same molecular formulae, but difference in their functional groups, you should understand that these are functional isomers of each other.*

Example 3: Ethyl alcohol and Dimethyl ether



Example 4: *n*-Butyl alcohol and Diethyl ether



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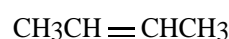
Position Isomerism: Two or more than two molecules those having same molecular formulae but having difference in the position of functional group on the carbon chain are called position isomers and the phenomenon is called as position isomerism.

☞ *If you observe two or more than two molecules having same molecular formulae, but difference in their functional groups, you should understand that these are functional isomers of each other.*

Example 5: 1-Butene and 2-Butene



1-Butene



2-Butene

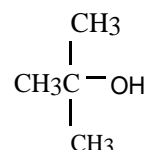
Example 6: 1-Butyl alcohol, 2-Butyl alcohol and *t*-Butyl alcohol



1-Butyl alcohol



2-Butyl alcohol



***t*-Butyl alcohol**

Metamerism: Two or more than two molecules those having same molecular formulae and functional group but having difference in the distribution of carbon atoms on either side of functional group are called metamers and the phenomenon is called the metamerism.

☞ *When you see two or more than two molecule with identical molecular formulae but while structural representation you observe there is a difference in the alkyl group attached to same functional group you should understand these molecules are metamers of each other.*

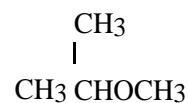
Example 7: Diethyl ether, Methyl propyl ether and isopropyl methyl ether



Diethyl ether



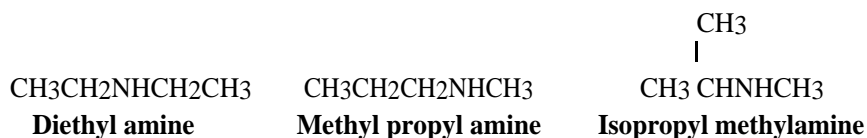
Methyl propyl ether



Isopropyl methylether

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Example 8: Diethyl amine, Methyl propyl amine and isopropyl methyl amine

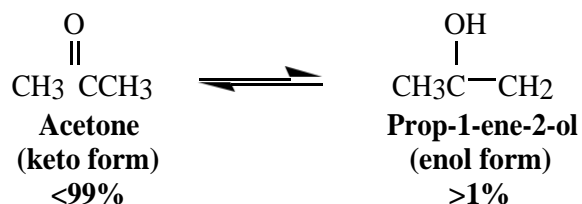


Tautomerism: This is a special kind of isomerism where both the isomers are interconvertible and always exist in a dynamic equilibrium to each other. Due to their interconversion change in functional group takes place that gives two different isomers of an organic compound. This phenomenon is called Tautomerism.

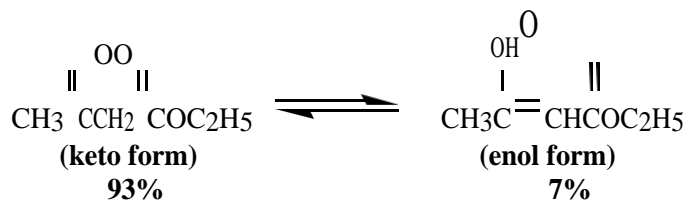
☞ When you observe two different isomeric forms of an organic compound are rapidly interconvertible to each other you should recognize them as tautomer of each other.

Remember: Tautomers are not the resonance structure of same compound

Example 9: Acetone exists in rapid equilibrium with Prop-1-en-2-ol



Example 10: Tautomeric forms of Ethyl acetoacetate under rapid equilibrium



b. Stereo (configurational) Isomerism

Stereoisomerism arises due to the difference in arrangement (configuration) of atoms or groups in space. When two or more than two isomers have the same structural formulae but

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having difference in the arrangement (configuration) of atoms in space are called stereo isomer and the phenomenon is called stereo isomerism.

Stereo isomerism can be further classified as

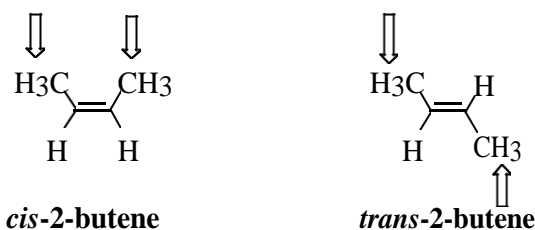
Geometrical or cis-trans isomerism

Optical isomerism

Geometrical isomerism is generally observed in alkenes and cyclic compounds due to their restricted rotation around carbon-carbon bond. For example *cis*- and *trans* 2-butene have same connection of bond and molecular formulae.

☞ *If you observe two similar groups are on the same side of C=C bond this is called cis- isomer; whereas, if two similar groups are on opposite side of C=C bond this is known as trans- isomer.*

Example 11: *cis*- and *trans*- isomerism in 2-butene

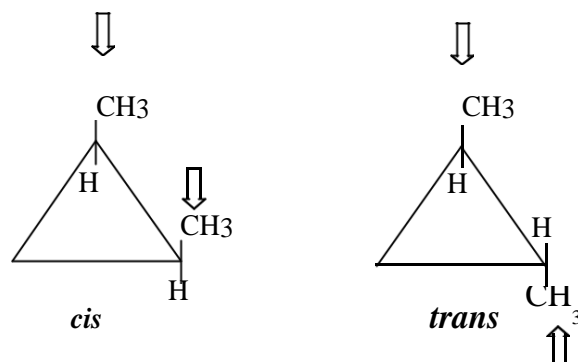


☞ *You can understand that due to the presence of one σ (sigma) and one π (pi) bond in carbon-carbon double bond, rotation around C=C bond is not possible. The restricted rotation around C=C bond is responsible for geometrical isomerism in alkenes.*

You can easily observe that rotation around C-C bond is also not possible in cyclic compounds as the rotation would break the bonds and break the ring. Thus geometrical isomerism is also possible in cyclic compounds.

Example 12: *cis*- and *trans*- isomers of 1,2-dimethylcyclopropane

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4.5 OPTICAL ISOMERISM

Optical isomerism is another class of *stereoisomerism*. The organic compounds that exhibit optical isomerism must have a unique ability to rotate the plane polarized light either towards left or towards right hand directions. This unique ability is generally known as optical activity. Optical activity of any compound is measured by analyzing the sample in an instrument called **Polarimeter**. A solution of known concentration of optically active compound is when exposed to the beam of plane polarized light, the beam of plane polarized light is rotated through a certain number of degrees, either to the clockwise (right) direction or anti-clockwise (left) direction. The compound which rotates the plane polarized light towards clockwise direction is called to be **dextrorotatory** (represented by +); whereas, the compound which rotates the plane polarized light towards anti-clockwise direction is called to be **levorotatory** (represented by -). Figure 1 shows the schematic representation of polarimeter.

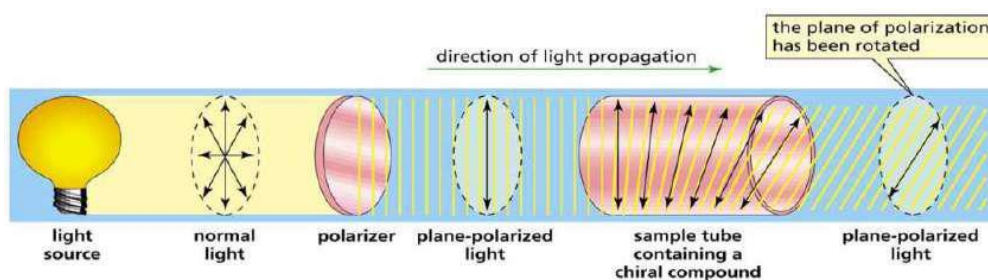


Figure 1. Schematic representation of simple polarimeter

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- ☞ The degree of rotation depends upon the number of the molecules of the compounds falls in the path of beam. To compare the rotating power of different optically active compounds, the specific rotation of each compound is calculated and then comparison should be made.
- ☞ Specific rotation is defined as the degree of rotation offered for the given wavelength of plane polarized light at given temperature by a solution of 1g/mL concentration is filled in a 10 cm length sample cell. Specific rotation is represented by $[\alpha]_t^\lambda$ and can be calculated as

$$[\alpha]_t^\lambda = \frac{100\alpha}{lc}$$

Where α is observed angle of rotation; t is the temperature of during experiment; λ is the wavelength of light used; l is the length of the tube in decimeter; and c is the concentration of the compounds per 100 mL of solution.

ii.

Remember:

Optically active compounds always exist in two isomeric forms which rotates the plane polarized light by equal degrees in opposite directions. The optical isomer which rotates the plane polarized light towards right (clockwise direction) is known as Dextrorotatory Isomer or (+)-isomer, whereas, the optical isomer which rotates the plane polarized light towards left (anticlockwise direction) is known as Levorotatory Isomer or (-)-isomer.

4.5.1 Elements of symmetry:

All optically active molecules/object are chiral and they exhibit enantiomerism (Figure 2). A chiral molecule is that which cannot be superimposed on its mirror image; however, both the non-superimposable isomers are called enantiomers. We will learn more about chirality and enantiomerism in separate section of this unit.

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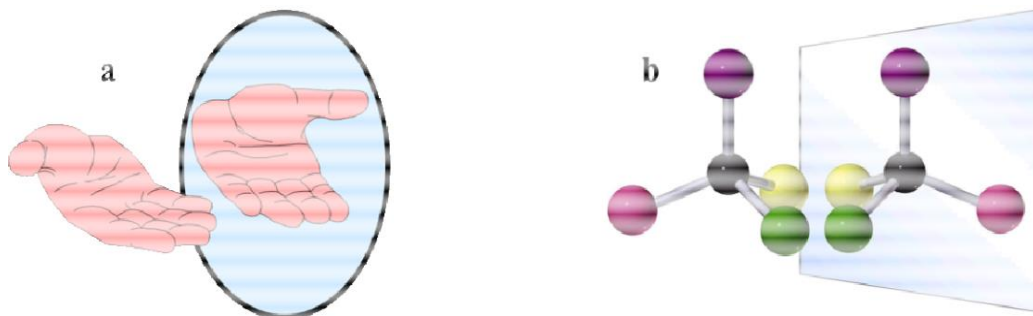


Figure 2. (a) Non superimposable mirror image relationship of right and left hands. (b) Ball and stick model of tetraivalent chiral carbon atom.

Elements of symmetry are a simple tool to identify whether a molecule is chiral or not. The necessary condition for optically active molecule to be chiral is that, the molecule should not possess any kind of symmetry elements. The elements of symmetry are generally categorized as follows:

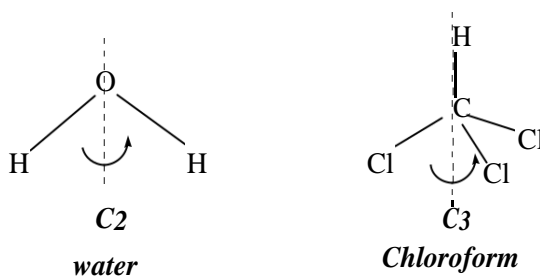
- | | |
|-------|--|
| (i) | Simple axis of symmetry (C_n) |
| (ii) | Plane of symmetry (σ) |
| (iii) | Centre of symmetry (C_i) |
| (iv) | Alternating axis of symmetry (S_n) |

Simple axis of symmetry (C_n):

When a rotation of $360^\circ/n$ (where n is any integer like 1,2,3...etc.) around the axis of a molecule or object is applied, and the rotated form thus obtained is non-differentiable from the original, then the molecule/object is known to have a *simple axis of symmetry*. It is represented by C_n .

Example 13: Water molecule has C_2 (two fold axis of symmetry) whereas chloroform has C_3 axis of symmetry.

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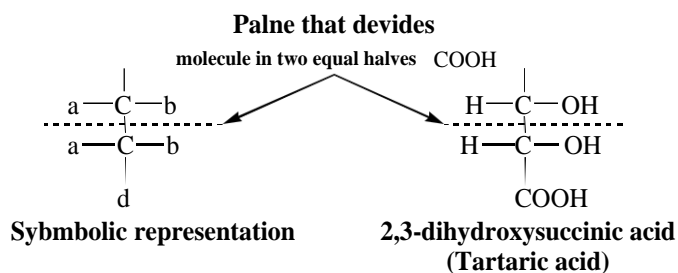


From above example you can easily understand that if you rotate the water molecule by 180° (i.e. $360^\circ/2=180^\circ$) along its molecular axis you will get the identical (non-differentiable) form of water molecule, hence water molecule has two fold of symmetry. Similarly, if you rotate the chloroform molecule by 120° (i.e. $360^\circ/3=120^\circ$) along its molecular axis you will get the identical (non-differentiable) form of chloroform molecule, hence chloroform molecule has three fold of symmetry.

(ii) Plane of symmetry (σ):

It is defined as 'when a plane that divides a molecule or object into two equal halves which are related to object and mirror image is known as *plane of symmetry*. It is represented by σ .

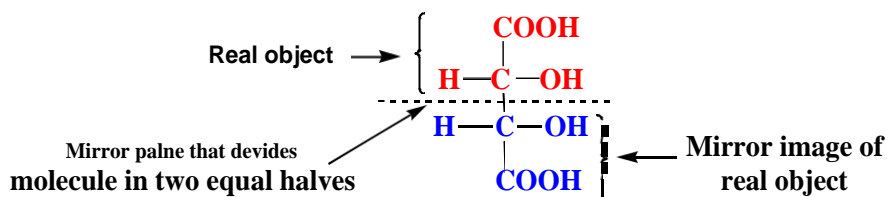
Example 14: Plane of symmetry in Tartaric acid



From above example you can easily understand that if we put a mirror plane/reflection plane exactly at the centre axis of the molecule/object; you will find that the mirror image thus

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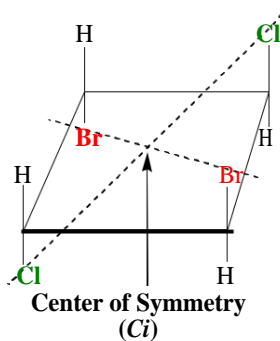
obtained is the complementary of the original and both will give us the appearance of complete molecule/object.



2,3-dihydroxysuccinic acid
(Tartaric acid)

Centre of symmetry (C_i): A molecule has a centre of symmetry when, for any atom in the molecule, an identical atom exists diametrically (diagonally) opposite to this centre and at equal distance from it.

Example 15: An isomer of 1,3-dichloro-2,4-dibromocyclobutane has a centre of symmetry

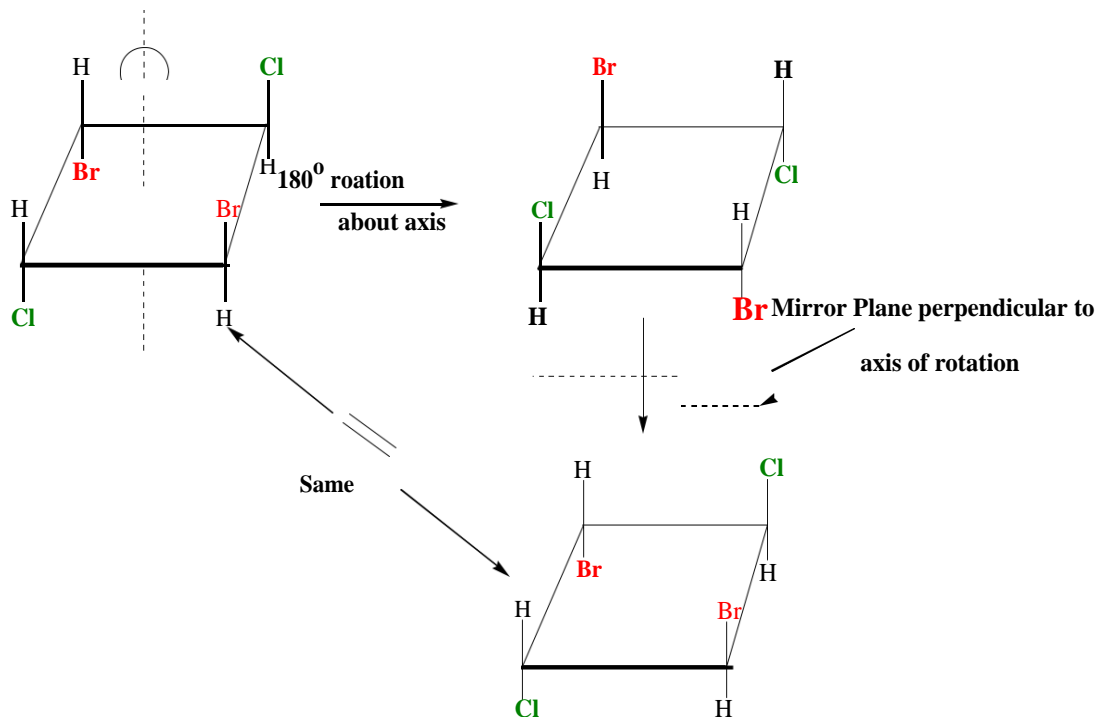


From above example you may understand that all the identical atoms are situated diagonally and at equal distance from the centre. This is called centre of symmetry.

Alternating axis of symmetry (S_n): An alternate axis of symmetry is defined as, when a molecule is rotated by $360^\circ/n$ degrees about its axis and then a reflection plane is placed exactly at perpendicular to the axis, and the reflection of the molecule thus obtained is identical to the original. It is represented by S_n .

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Example 16. An isomer of 1,3-dichloro-2,4-dibromocyclobutane has a 2 fold alternate axis of symmetry



4.6 MOLECULAR CHIRALITY, ENANTIOMERS

The necessary condition for a molecule to have optical isomerism is that molecule should not have any kind of symmetry elements present in it, in other words the molecule should be dissymmetric. Such molecules are called 'Chiral' and the property is called 'molecular chirality'. Optically active chiral molecules which are non-superimposable on their mirror images are called 'enantiomers' and the phenomenon is known as 'enantiomerism'. To exhibit optical isomerism an organic compound must have at least one asymmetric carbon atom. An asymmetric carbon atom is that which is bonded to four different atoms or groups.

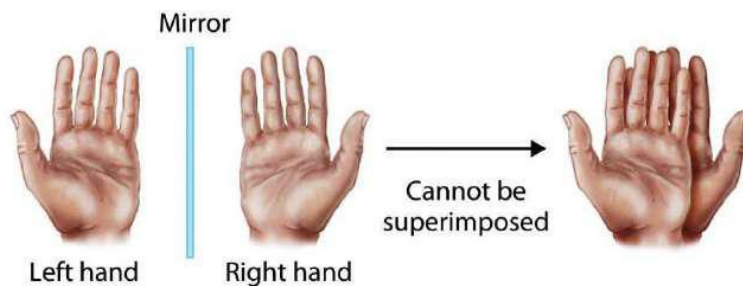


We can easily understand the chirality by comparing our hands (left hand and right hand). Our left hand and right hand are the best example of non-superimposable mirror image of each other. Each hand is therefore considered as chiral.

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iii.

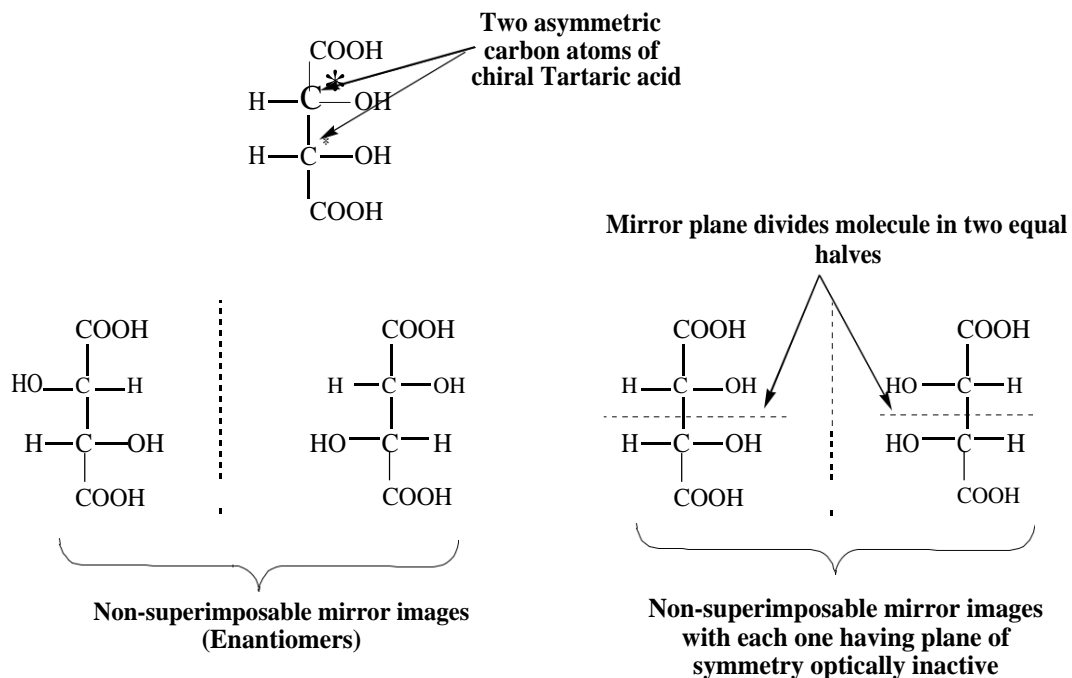
Remember: Our left hand and right hand are non-superimposable mirror image of each other each one of them is chiral.



iv.

Remember: Chirality is the necessary and sufficient condition for the existence of enantiomers.

Example 17. Tartaric acid has two asymmetric carbon and it exists in four forms, out of them two form are optically active and two are optically inactive.



4.6.1 Stereogenic Centre:

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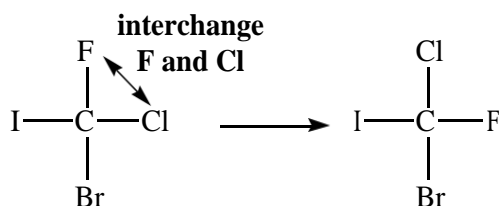
As we discussed in previous section that if a molecule contains one carbon atom which is directly bonded with four different groups or atoms, and the molecule do not have any kind of symmetry element present in it, such molecule is called asymmetric or chiral.

When the interchange of the position of two directly bonded groups or atoms of a centre carbon atom results a new stereoisomer, such chiral centre is called stereo centre or stereogenic centre.

If the new stereoisomer is a non-superimposable mirror image of the original molecule such carbon centre is called chiral carbon centre.

Remember: *All the chiral centres are stereogenic centres but all stereogenic centres are not chiral centre.*

Example 18: Bromochlorofluoriodomethane exhibits chiral carbon centre



Interchange of F and Cl results non-superimposable stereoisomers

4.7 OPTICAL ACTIVITY

It is already known to you (from section 4.5) that the optical activity is an ability of a chiral molecule to rotate the plane of plane-polarized light either towards left or right direction. The rotation is measured by an instrument called Polarimeter. When a beam of plane polarized light passes through a sample that can rotate the plane polarized light, the light appears to dim because it no longer passes straight through the polarizing filters. The amount of rotation is quantified as the number of degrees that the analyzing lens must be rotated to observe the no dimming of light appears. Optical rotation can be measured by using the following formulae

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$$[\alpha]_{\lambda}^t = \frac{100\alpha}{lc}$$

Where α is observed angle of rotation; t is the temperature of during experiment; λ is the wavelength of light used; l is the length of the tube in decimeter; and c is the concentration of the compounds per 100 mL of solution.

Optically active chiral compounds that are non-superimposable mirror image of each other are called enantiomers.

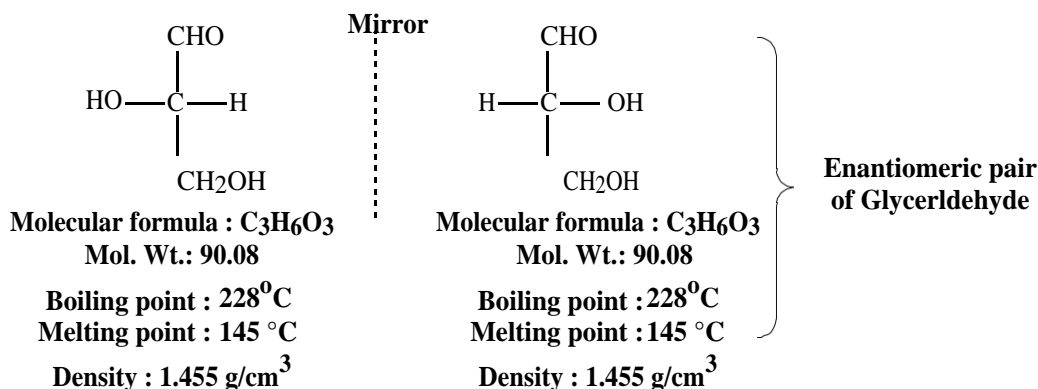
4.7.1 Properties of enantiomers:

The main properties of enantiomers are given as follow

- ✚ Enantiomers always exist in pair
- ✚ Enantiomers are non-superimposable mirror image to each other
- ✚ Enantiomers have same physical properties (like boiling point, melting point, solubility, density, viscosity, refractive index etc.) and chemical properties in achiral environment
- ✚ Each enantiomer have opposite behavior with respect to plane polarized light, if one of them will rotate the plane polarized light towards right hand direction then definitely the other will rotate the plane polarized light towards left hand direction.
- ✚ Each enantiomer shows the same chemical reactivity with achiral reagent; however they have different reactivity with chiral reagent.

Example 19: Glyceraldehyde molecule is a chiral molecule. It has a pair of enantiomer with same physical properties except their behavior towards plane polarized light

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☞ You can see that the glyceraldehyde molecule can exist in two enantiomeric forms which differ only in the arrangement of bonded atoms around the centre chiral carbon. The physical properties (like molecular formula, molecular weight, melting point, boiling point and density etc.) of both the isomers are same. But if one isomer will rotate the plane polarized light towards right hand direction (dextrorotatory) then the other one will rotate the plane polarized light towards left hand direction (levorotatory).

4.7 CHIRAL AND ACHIRAL MOLECULES WITH TWO STEREOGENIC CENTRES

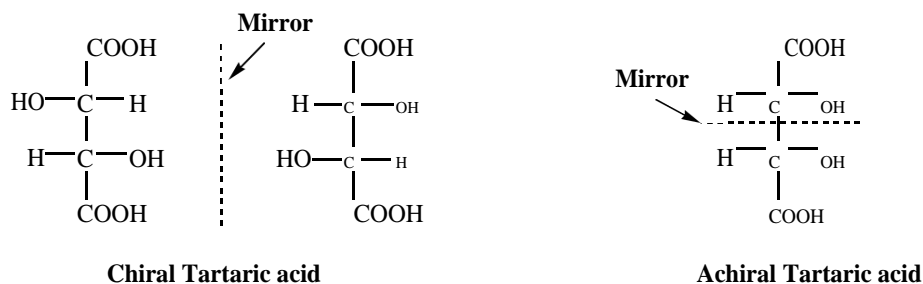
As we have discussed earlier in this unit (*sec. 4.6*) that chiral molecules are those in which the centre carbon atom is bonded directly through four different atoms/groups and do not have any kind of symmetry element present in it and the molecule has non-superimposable mirror image. However, those molecule in which centre carbon atom is directly bonded through four different atoms of groups and it satisfied any kind of symmetry elements are called achiral molecule. Achiral molecules have superimposable mirror images.

Let us consider the stereoisomers of Tartaric acid which has two stereo centres with identical atoms/groups attached to both the stereo centres. The tartaric acid have two stereo centres and can have four stereoisomers out of which two stereoisomers are non-superimposable mirror image of each other called enantiomers and chiral; and rest two are identical to each

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other and also have plane of symmetry hence it can be divided in to two equal halves, therefore are achiral.

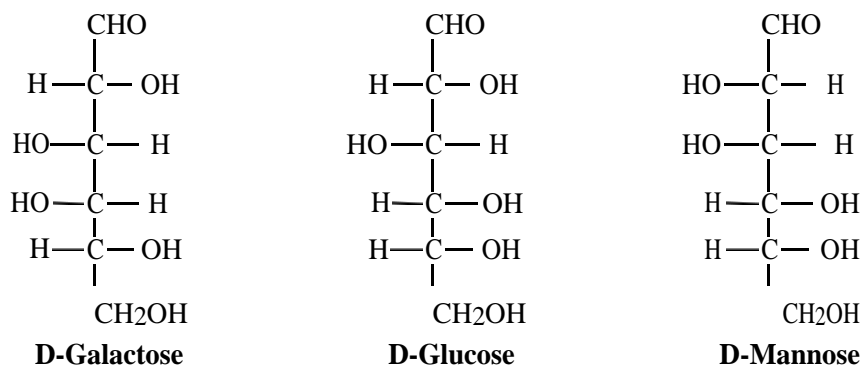
Example 20: Tartaric acid has two stereo centres with three stereoisomers (two are chiral and one achiral stereoisomer)



4.8 DIASTEREOMERS:

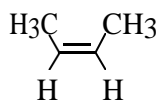
Diastereomers are those stereoisomers that are not mirror image of each other, in other words you can understand the diastereomers are stereoisomers that are not enantiomers. Diastereomers are non-enantiomeric stereoisomers with two or more stereo centres. The pair of stereoisomer that differs in the arrangement of atoms/groups bonded with at least one stereocentres is called diastereomers.

Example 21: D-Galactose, D-Glucose and D-Mannose are the non-mirror image stereoisomer of each other. Therefore are called diastereomers.

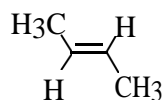


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Example 22: *cis*- and *trans*-2-butenes are non-mirror image stereoisomers of each other hence are called diastereomers.



cis-2-butene



trans-2-butene

4.9.1 Properties of Diastereomers

The main properties of diastereomers are given as follows:

- All the stereoisomers except enantiomers are diastereomers.
- Diastereomers have different physical properties like boiling point, melting point, density, solubility, density, viscosity, refractive index etc.
- Diastereomers have different chemical properties like rates of reactions, reactivity even in achiral reaction medium.
- This difference in physical and chemical properties of diastereomers is very useful in the separation of enantiomers from their mixture.

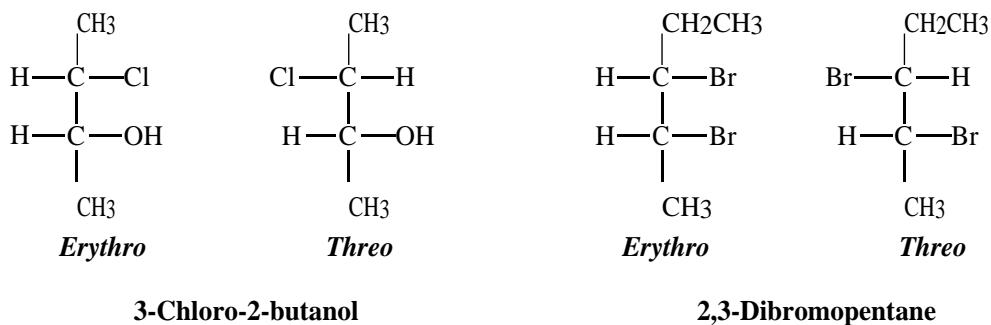
4.9.2 Threo and erythro diastereomer

Threo and *erythro* nomenclature method is designated by organic chemists to assign appropriate name to diastereomers. The *threo* and *erythro* naming is given only to those diastereomers having two adjacent stereocentres. The nomenclature is applicable to these diastereomers if there are two common atoms/groups bonded to each adjacent stereocentre. In other words the terms *erythro* and *threo* are generally applied only to those molecules which do not have symmetric ends. However, when the ends are symmetric then instead of *erythro* and *threo* the *meso* and *dl* nomenclature is preferred. We will discuss separately about *meso* and *dl* in this unit.

If the similar groups/atoms on adjacent stereocentres of diastereomer are on same (*syn*) side it is designated as *erythro*, whereas if the similar groups/atoms on adjacent stereocentres of diastereomer are on opposite (*anti*) side the diastereomer is designated as *threo*.

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Example 23: You can easily understand the erythro and threo nomenclature by taking examples of 3-bromo-2-butanol and 2,3-dibromo pentane.



☞ You can see if both the hydrogen atom on two adjacent stereocentres of 3-chloro-2butanol lies on same (syn) side the isomer is called erythro, whereas, when both the hydrogen atoms on two adjacent stereocentres of 3-chloro-2butanol lies on opposite (anti) side the isomer is called threo. Similarly you can find the same observation with 2,3-dibromopentane and designate the isomers as erythro and threo.

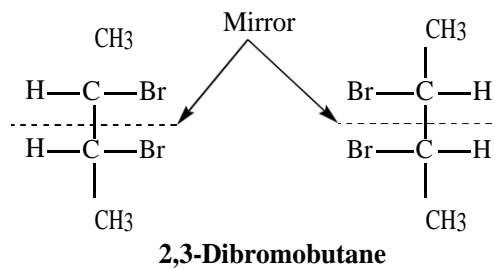
☞ You must also remember that the each erythro and threo stereo isomer can have their non-superimposable mirror image (enantiomer). Thus there will be always one enantiomeric pair of erythro and one enantiomeric pair of threo stereoisomer exists for a stereoisomer with two similar atoms on adjacent stereocentres.

4.9.3 meso- compounds

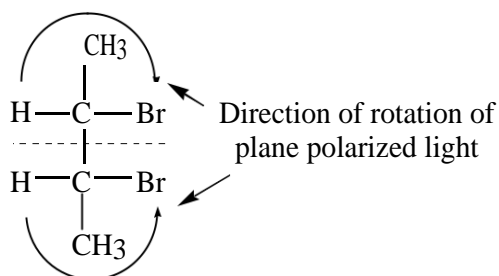
A compound with two or more carbon stereocentre but also having a plane of symmetry is called *meso* compounds. All the carbon centres have four different atoms/groups but the compound can be divided in to two equal halves which are superimposable mirror image.

Example 24: 2,3-dibromobutane have two stereocentres, but the molecule have two symmetric ends therefore it can be divided in to two equal halves. In other words the molecule have plane of symmetry.

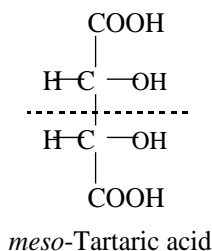
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☞ We can see that even the 2,3-dibromobutane have non superimposable mirror image but this molecule have an internal plane of symmetry hence this molecule is optically inactive or achiral. This molecule will not be able to rotate the plane polarized light in any direction. If one half of the molecule will rotate the plane polarized light towards right hand direction with some degrees; the other half will rotate the plane polarized light towards left hand direction with same degrees of rotation. Thus the net rotation of the plane polarized light is zero. Such molecules are called meso compounds.



Example 25: Another example of meso compound is one of the stereo isomeric forms of Tartaric acid (2,3-dihydroxysuccinic acid). The molecule is optically inactive because it has internal plane of symmetry.



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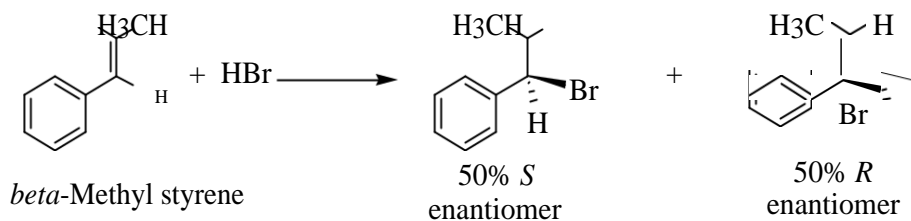
4.9.4 Resolution of enantiomers

Before we discuss about resolution of enantiomers, you must have an understanding of *racemic mixture* or *racemates*. A racemates is an equimolar mixture of a pair of enantiomers. The racemic mixture or racemates are optically inactive due to mutual or external compensation of two enantiomeric constituents. Racemic mixture in liquid and vapor phase shows physical properties (like boiling points, density, refractive index etc.) identical to those of pure enantiomers. However, the solid phase enantiomeric mixtures have some properties different from the pure enantiomers.

Remember: *Racemic mixture is not a meso compound; since both are optically inactive. The racemic mixture is an equimolar mixture of two enantiomers whereas meso is a single compound. Meso compounds are optically inactive because of the internal compensation; however, the racemic mixtures (racemates) are optically inactive because of the external compensation.*

You might have aware with that the enantiomerically pure compounds are of great importance in chemical and pharmaceutical areas. But during the synthesis of optically active compounds using achiral reaction condition and achiral reagents, it always gives racemic mixture (racemate).

Example 26: The addition of HBr on *beta*-Methyl styrene gives an equimolar mixture of enantiomers.



Therefore to obtain the pure enantiomers we must have to separate the racemic mixture in to corresponding pure enantiomers. Thus, the separation process of a racemic mixture in to its pure individual enantiomeric constituents is called resolution of racemic mixtures (resolution

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of enantiomers). Since enantiomers have identical physical properties (like solubility, boiling point, melting point, density, refractive index etc.), therefore, they cannot be separated by common physical techniques such as direct crystallization, distillation or basic chromatography. There are four general methods that are extensively being used for the resolution of racemic mixtures.

Mechanical separation (crystallization method) method

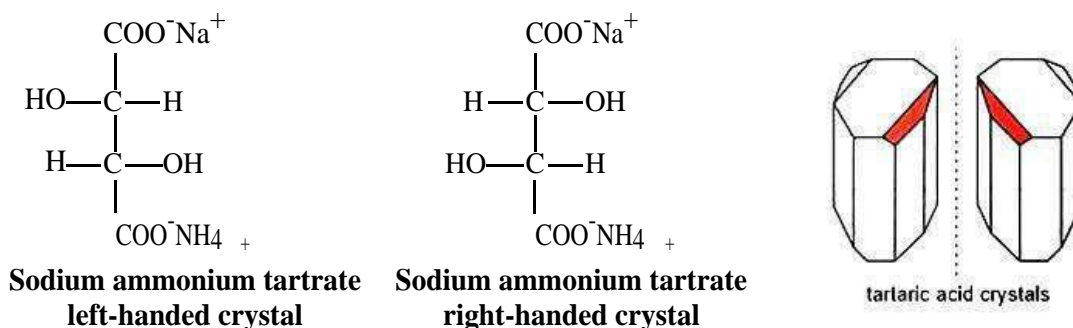
Diastereomer formation method

Chromatographic method

Biochemical/enzymatic methods

Mechanical separation (crystallization method) method: Separation of enantiomers from a racemic mixture can be achieved by direct crystallization of optically active components. The crystallization method was invented by Louis Pasteur (1848); during his pioneering work he was able to isolate the stereoisomers of tartaric acid from its racemic mixture. The stereoisomers of Tartaric acid were crystallized separately from solution and separated; since the crystals were having different symmetry and shape. This type of separation is very rare.

Example 27: Resolution of Tartaric acid was achieved by Louis Pasteur by crystallizing them as R/S form of sodium ammonium tartrate.



Diastereomer formation method: This is one of the best methods for separation of enantiomers and was also invented by Louis Pasteur (1858). In this method a racemic

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mixture is converted into a mixture of diastereomers of the enantiomeric constituents of that mixture by using a pure enantiomer of another compound.

We have already discussed in the previous section of this unit that the diastereomers have different physical (like solubility, boiling point, melting point, density, refractive index etc.) and chemical properties (like chemical rate and reactivity etc.). Therefore these diastereomers can be easily separated by either fractional crystallization or fractional distillation. After separation of diastereomers each of them is converted back into the individual enantiomers of racemate by suitable reactions.

Example 28a: R and S form of 2-hydroxypropanoic acid in an equimolar mixture can be converted into a mixture of diastereomers by reacting it with S-Brucine.

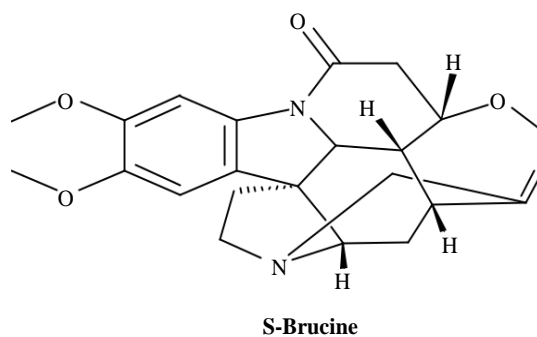
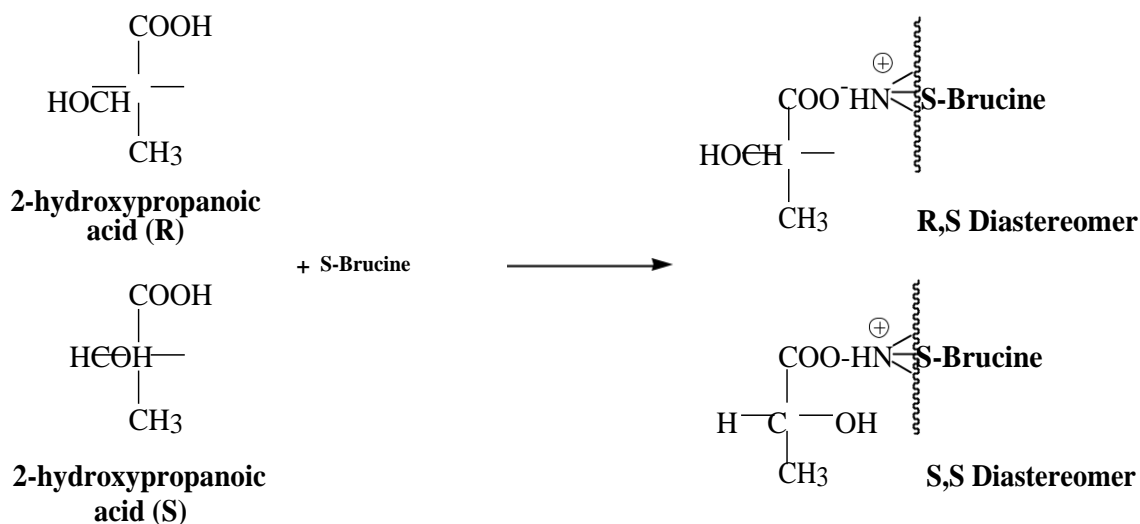
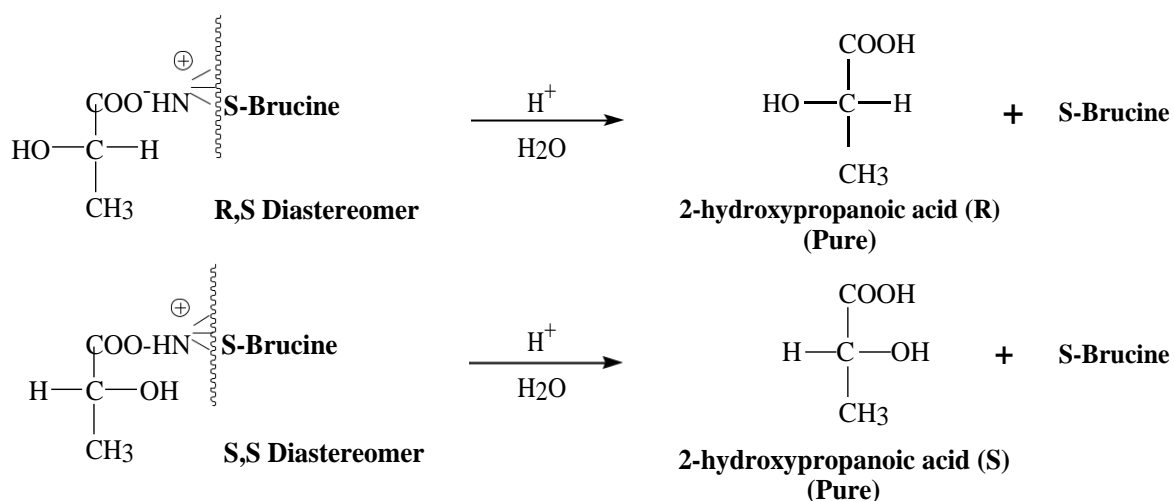


Figure 3: S-Brucine (an optically active isomer)

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We can see from above example that the enantiomeric mixture of 2-hydroxypropanoic acid can be easily converted in to corresponding diastereomeric salts by reacting with a optically pure base called S-Brucine. Both the diastereomeric salts can be separated by fractional crystallization. The separated diastereomers can be converted in to respective pure enantiomers of 2-hydroxypropanoic acid by simple acidic hydrolysis.

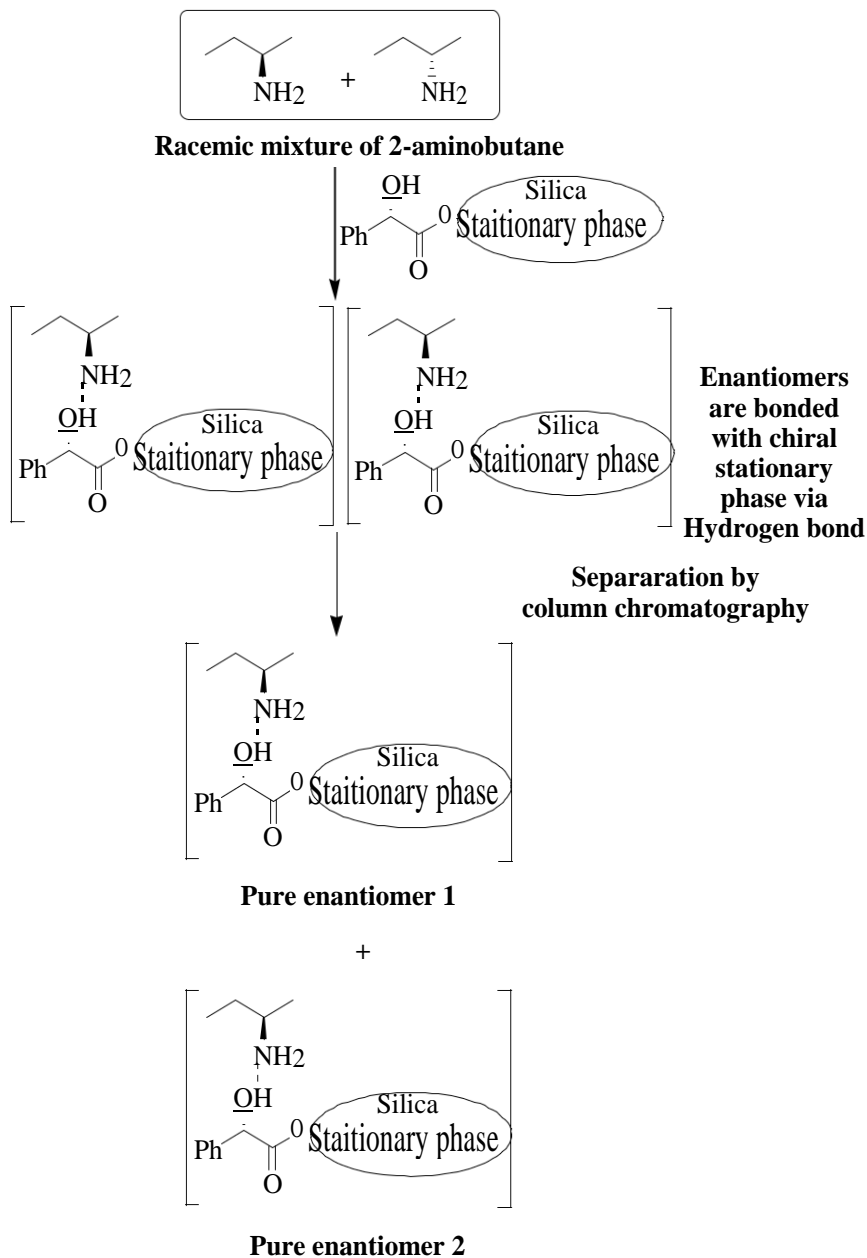
Example 28b: The acidic hydrolysis of diastereomeric salt of 2-hydroxypropanoic acid gives pure form (R/S) of 2-hydroxypropanoic acid.



Chromatographic method: Racemic mixture can also be separated by column chromatography by adsorbing the racemates on an optically active solid adsorbent or solid support. The separation of enantiomers is based on the difference in their affinity towards the adsorbent or support. Enantiomer while adsorbing on optically active solid support forms diastereomers those having different stabilities in the eluent (solvent). The enantiomer which has more affinity towards the solid adsorbent will be held more tightly than the other one which has less affinity towards solid adsorbent. Thus the diastereomeric adsorbates when filled in a column and eluted with suitable solvent system the less tightly bonded enantiomer will be eluted more rapidly and will pass through the column. However, the enantiomer which is tightly bonded with the solid support will be eluted more slowly and will come out later from the column. Hence both the enantiomers will get separated. The schematic representation of chromatographic separation of enantiomers is shown in figure 4.

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Example 29: Separation of 2-aminobutane by chromatographic separation method using chiral adsorbent (enantiomer of mandelic acid is attached to a silica stationary phase)



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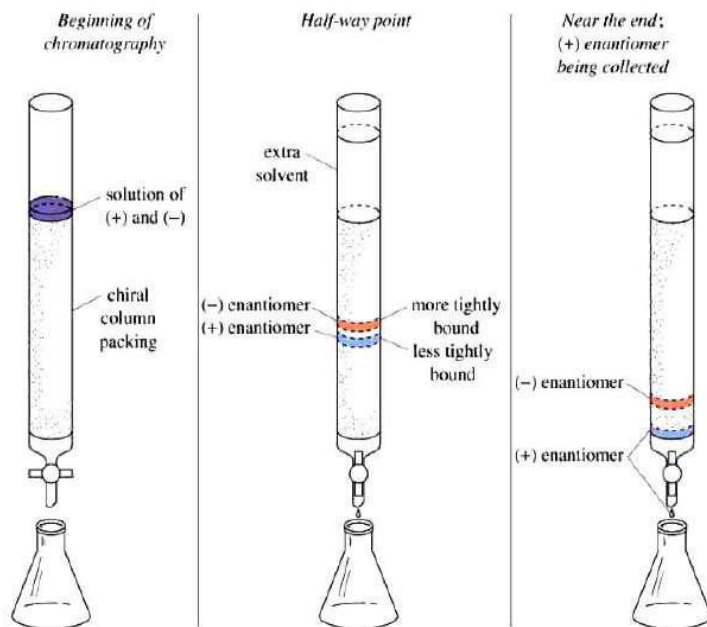
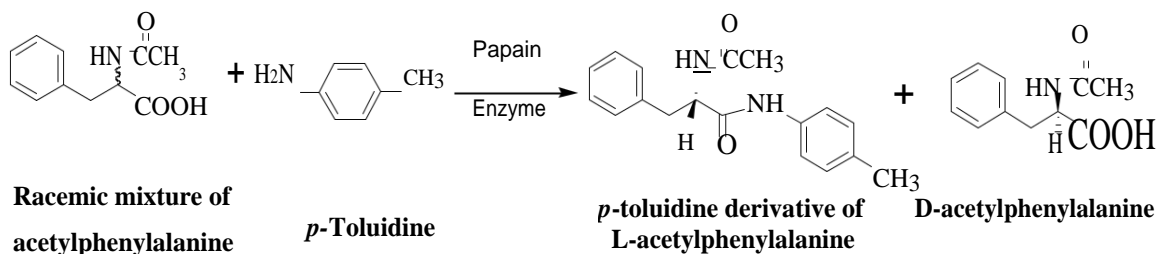


Figure 4: Schematic diagram of chromatographic separation of racemic mixture

Biochemical/enzymatic method: Enzymes are also being used for the separation of enantiomers from racemic mixture. When certain bacteria and moulds are allowed to grow in the solution of racemic mixture, they react with one enantiomer exclusively and form a derivative; as a result only one enantiomer remains in excess in the solution which can be easily separated.

Example 30: Separation of a racemic mixture of acetyl phenylalanine by reacting it with *p*-toluidine catalyzed by an enzyme called papain gives the *p*-toluidine derivative of acetyl-L-phenylalanine and leaves unchanged acetyl-D-phenylalanine.

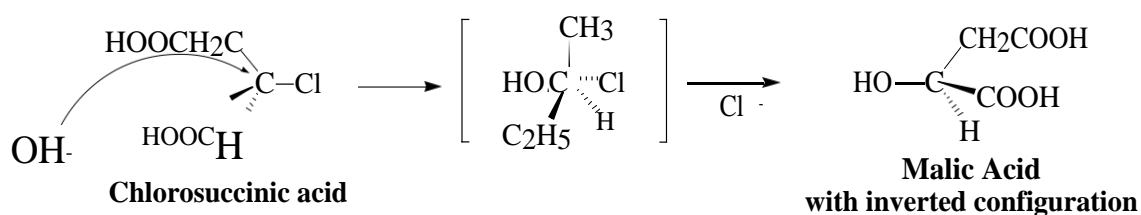


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4.9.5 Inversion, retention and racemization:

In a substitution reaction when a group/atom attached to a chiral carbon atom is replaced by any other atom as a result the configuration (*i.e.* spatial arrangement of atoms around the central atom) of central atom changes, the process is called *inversion of configuration* or simply *inversion*. The product after inversion thus obtained is the non-super imposable mirror image (enantiomer) of the original molecule. This phenomenon was first observed by the scientist P. Walden therefore it is also known as *Walden Inversion*.

Example 31: Replacement of chlorine atom of Chlorosuccinic acid by hydroxyl ion gives Malic acid with inverted configuration

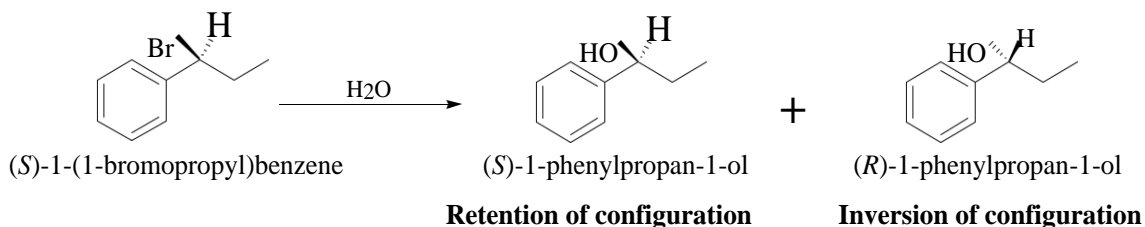


The inversion of configuration depends upon the nature of reagent, the nature of solvent, reaction temperature, the nature of substituents which is replacing the group/atom in the given molecule.

Sometimes you will observe that the replacement of any group/atom in a chiral molecule gives a new optically active isomer without the inversion of configuration. This is known as *retention* of configuration. In other words we can explain the retention of configuration is “*the preservation of the spatial arrangements (configuration) of atoms attached with a chiral centre of an optically active molecule during the chemical transformation or reaction*”. The retention of configuration is occurs when in a substitution reaction the incoming group/atom approaches to the central chiral atom from the same plane/direction of the leaving group/atom the resultant product thus obtained will have the same configuration as the reactant molecule.

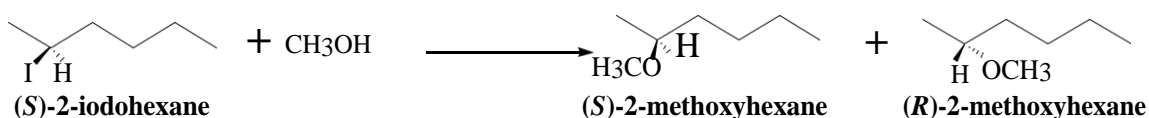
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Example 32: (*S*)-1-(1-bromopropyl)benzene on reaction with H₂O gives the mixture of (*S*)-1-phenylpropan-1-ol and (*R*)-1-phenylpropan-1-ol.



We have already discussed that the equimolar mixture of enantiomer is known as racemic mixture. The process of conversion of an optically active compound into the racemic mixture/racemate is called *racemization*. The racemization process may take place under the influence of temperature, light or chemical reagents.

Example 33: Racemization of (*S*)-2-iodohexane during reaction with CH₃OH (methanol)



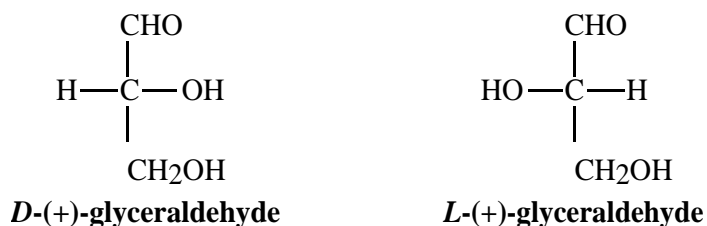
4.10 RELATIVE AND ABSOLUTE CONFIGURATION:

Relative and absolute configuration of a compound discusses about the spatial arrangement of atoms/groups around the centre chiral atom. Relative configuration is a comparison of the spatial arrangement of attached atoms/groups of two different chiral centres. Relative configuration is a geometrical property which does not change on reflection; whereas, the absolute configuration is the precise arrangement of atoms in three dimensional space. The *D/L* system is usually known as relative configuration whereas, the *R/S* stereo descriptor or nomenclature system for chiral molecules is known as absolute configuration. The absolute configuration is a topographic property which changes on reflection.

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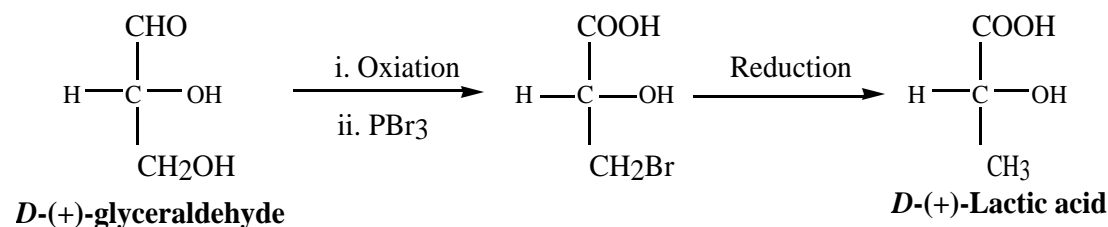
4.10.1 D/L nomenclature:

The *D/L* nomenclature is the oldest nomenclature system for enantiomers. In this nomenclature system the configuration of all the compounds were given with respect to glyceraldehyde molecule, where the configuration of glyceraldehyde molecule is taken as an arbitrary standard. According to this nomenclature if in glyceraldehyde molecule the –OH group on right and –H on left, the –CHO and –CH₂OH groups being on top and bottom, respectively the molecule is designated as (+) Glyceraldehyde and it was arbitrary given the configuration symbol *D*. The mirror image of this compound (–) glyceraldehyde was given the configuration *L*.



Any compound that can be prepared, or converted in to *D-(+)-glyceraldehyde* will belong to *D* series (relative configuration), whereas, any compound that can be prepared, or converted in to *L-(+)-glyceraldehyde* will belong to *L* series.

Example 34: Lactic acid obtained from *D-(+)-glyceraldehyde* and hence assigned *D* configuration



Remember:

There is no correlation between the D and L designation and the sign of rotation. D form of isomer may be levorotatory, and L form of isomer may be dextrorotatory and vice versa.

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The D/L nomenclature is limited to the compound that can be prepared or converted from the glyceraldehyde.

It is limited to only one chiral atom.

4.10.2 R/S nomenclature:

Since you have been noted from the above discussion on D/L configuration, there are several drawbacks associated with the D/L nomenclature system. Hence a definite and universally applicable nomenclature system was needed to specifying the absolute configuration of each chiral centre in a molecule. Cahn and coworkers (1956, 1966) have proposed a new and universally applicable nomenclature pattern for the determination of absolute configuration of any chiral molecule. This is known as the R/S system or Cahn-Ingold-Prelog (CIP) nomenclature. It involves following two steps.

In first step we need to assign the priority to the four different atoms/groups attached to a chiral centre.

Priorities to the groups/atoms can be assigned as per the **sequence rule**.

After assigning the priority to the atoms/groups attached to the chiral centre, the molecule is oriented in such a way that the lowest priority group is directed away to the observer.

Now the arrangement of the remaining atoms/groups is viewed by following decreasing order of priorities from highest priority to lowest priority.

While viewing the atoms/groups in their decreasing order if your eyes follow the clockwise direction then the chiral centre will have *R* configuration; whereas if your eyes follow anticlockwise direction the chiral centre will have *S* configuration.

When a molecule has two or more than two chiral centres then the same process should be followed to assign their configuration.

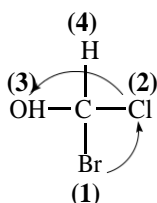
4.10.3 Sequence rule:

To assign the priorities to all four different groups/atoms attached with the chiral centre following sequence rule should be followed. The sequence rule is given by the three

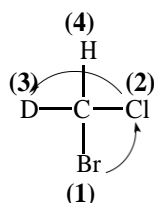
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scientists Cahn-Ingold-Prelog therefore it is also called the CIP rule. The sequence rules are arbitrary but consistent. The main observations of sequence rules are listed below.

If all the atoms directly attached to the chiral centre are different, the sequence of priorities is determined by their atomic number. The atom with higher atomic number is given higher priority. If two atoms are isotopes of same element, the isotope with higher mass number has the higher priority.



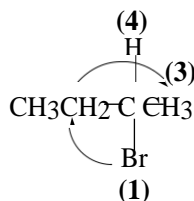
Bromochloromethanol
1-2-3 order is anticlockwise
the configuration is *S*



Deuterio bromochloromethane
1-2-3 order is anticlockwise
the configuration is *S*

Deuterium (D) is an isotope of Hydrogen with mass number 2 hence get higher priority than H

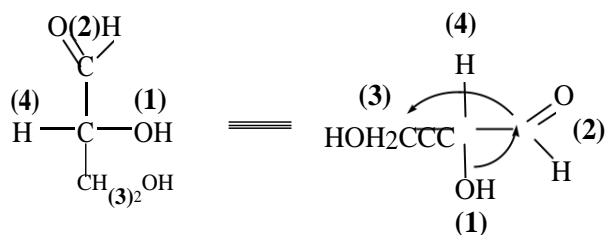
If two or more atoms attached to the chiral centre having same atomic number, the priorities are assigned by comparing the atomic numbers of the next atoms attached to each group/atom.



2-bromobutane
1-2-3 order is clockwise
configuration is *R*

If the atoms or groups attached to the centre atom are further linked with some other atoms via double and triple bonds. Then the double or triple bonded atoms are considered to be duplicated or triplicated. As per sequence rule the triple bond gets priority over double bond, similarly double bond gets priority over single bond.

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2,3-dihydroxypropanal
1-2-3 order is anticlockwise
configuration is S

4.11 SUMMARY

Stereochemistry is all about the 3 Dimensional spatial aspects of chemistry.

Molecules that differ only in the arrangement of bonds in 3Dimensional space are called "stereoisomers"

Many objects (including molecules) are non-differentiable from their mirror images, but other objects, such as your left and right hands, are differentiable. An object that has a non-superimposable mirror image 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 of 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.

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). (Think about how your feet feel if you put them in the wrong shoes).

Diastereomers are stereoisomers that are not enantiomers.

The differing interaction with plane polarized light gives rise to optical activity. Enantiomers cause the plane of polarized light to rotate in opposite directions, but

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to the same extent (clockwise = +ve, counterclockwise = -ve). This can be measured using a polarimeter. An achiral molecule is optically inactive.

A 50:50 mixture of a pair of enantiomers is called a racemic mixture. This is optically inactive since the rotations produced by each of the enantiomers must cancel each other out.

If there is more of one enantiomer than the other, then the optical purity of a sample can be determined by measuring the rotation and comparing it to that of a pure enantiomer. This can be used to establish the enantiomeric excess (ee) of the mixture.

Despite what one may observe, most molecules are not 2D objects, they are 3D as a result of the spatial arrangement of the atoms, groups and bonds. The interaction of molecules (reactions) which occur as the result of collisions between these 3D objects in 3D space can therefore also have 3D requirements and characteristics. Stereochemistry is all about the 3D properties of molecules and reactions.

4.12 TERMINAL QUESTION

What do you understand by Isomerism? Give its types.

What is chirality? Explain the necessary condition for a molecule to be chiral.

What do you understand by optical activity? How is it measured?

What are enantiomers and diastereomers?

What are symmetry elements? How they affect optical isomerism?

Explain relative and absolute configuration.

What is racemization?

ANSWERS

Ans. 1. When two or more compounds having the same molecular formula but difference in their chemical and/or physical properties are called isomers and the phenomenon is known as isomerism. Isomerism has following types:

Structural (constitutional) Isomerism

Stereo (configurational) Isomerism

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Ans. 2. An organic compound with four different atoms/groups attached to center carbon and have non-superimposable mirror image is called chiral compound and the phenomenon is called chirality. The presence of four different atoms/groups attached to center carbon and absence of any kind of element of symmetry are the necessary condition for a molecule to be chiral.

Ans. 3. The tendency of an organic compound to rotate the plane polarized light towards left or right hand direction is called optical activity. Optical activity of any compound is measured by analyzing the sample in an instrument called **Polarimeter**. A solution of known concentration of optically active compound is when exposed to the beam of plane polarized light, the beam of plane polarized light is rotated through a certain number of degrees, either to the clockwise (right) direction or anti-clockwise (left) direction. The compound which rotates the plane polarized light towards clockwise direction is called to be **dextrorotatory** (represented by +); whereas, the compound which rotates the plane polarized light towards anti-clockwise direction is called to be **levorotatory** (represented by -).

Ans. 4. Optically active chiral compounds that are non-superimposable mirror image of each other are called enantiomers. Whereas, optically active compounds which are non-mirror image of each other are called diastereomers.

Ans. 5. Elements of symmetry are a simple tool to identify whether a molecule is chiral or not. The necessary condition for optically active molecule to be chiral is that, the molecule should not possess any kind of symmetry elements. The elements of symmetry are generally categorized as follows:

Simple axis of symmetry (C_n)

Plane of symmetry (σ)

Centre of symmetry (C_i)

Alternating axis of symmetry (S_n)

Optically active compound should not have any kind of symmetry elements.

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Ans. 6. Relative and absolute configuration of a compound discusses about the spatial arrangement of atoms/groups around the centre chiral atom. Relative configuration is a comparison of the spatial arrangement of attached atoms/groups of two different chiral centres. Relative configuration is a geometrical property which do not changes on reflection. The absolute configuration is the precise arrangement of atoms in space. The *D/L* system is usually known as relative configuration whereas, the *R/S* stereo descriptor or nomenclature system for chiral molecules is known as absolute configuration. The absolute configuration is a topographic property which changes on reflection.

Ans. 7. The process of conversion of an optically active compound in to the racemic mixture/racemate is called *racemization*. The racemization process may take place under the influence of temperature, light or chemical reagents.

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UNIT 5: STEREOCHEMISTRY-II

CONTENTS:

- 5.1 Objectives
- 5.2 Introduction
- 5.3 Geometrical isomerism
 - 5.3.1 Determination of configuration of geometrical isomers
 - 5.3.2 E & Z system of nomenclature
 - 5.3.3 Geometrical isomerism in oximes and acyclic compounds
- 5.4 Conformational analysis of ethane and n-butane
 - 5.4.1 Conformational analysis of ethane
 - 5.4.2 Conformational analysis of n-butane
- 5.5 Conformation of cyclohexane
- 5.6 Axial and equatorial bond
- 5.7 Conformation of mono substituted cyclohexane
- 5.8 Newman projection and Sawhorse formula
- 5.9 Fischer and flying wedge formula.
- 5.10 Difference between configuration and conformation.
- 5.11 Summary
- 5.12 Terminal Question

5.1 OBJECTIVES:

By the end of this unit you will be able to

Learn about the stereoisomerism of those organic compounds which are not optically active

Understand the geometrical isomerism shown by olefinic compounds (double bonded compounds)

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Understand the conformational isomerism and its representation

Make a difference between configurational and conformational isomers

Learn about the conformational analysis of aliphatic and cyclic hydrocarbons

Learn how to write the Fischer projection formulae, flying wedge formula, Newman projection formulae and Sawhorse projection formulae for various conformational and configurational isomers.

5.2 INTRODUCTION

In Unit 4 we have discussed about the isomerism and its type. The difference between structural and stereoisomerism is also drawn in that Unit. However, more detail discussion on optical isomerism and its related components is presented in Unit 4. In present unit (UNIT 5) we will learn more about the isomerism exhibited by the; 1) Molecule with restricted rotation around carbon-carbon bonds (olefinic and cyclic organic compounds) is known as geometrical isomerism and; 2) Molecules which are readily interconvertible due to rotation about single bond is known as conformational isomerism. The geometrical isomerism comes under stereoisomerism whereas the conformational isomerism comes under structural isomerism. Partly, we have also discussed about stereoisomerism and structural isomerism in Unit 4.

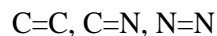
5.3 GEOMETRICAL ISOMERISM:

Geometrical isomerism is generally observed in alkenes and cyclic compounds due to their restricted rotation around carbon- carbon bond. The rotation about a double bond in alkene or about a single bond in a cyclic/ring like compound is restricted. Double bonded system consists of a σ (sigma) and a π (pi) bond perpendicular to each other. It is not possible to rotate the molecule about carbon-carbon bond. The rotation will break the π bond as a result the molecule will lose its identity. In some cases the rotation about single bond is also restricted due to steric hindrance. Geometrical isomerism is shown by various groups of

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compounds the major class of compounds that exhibit geometrical isomerism are classified as:

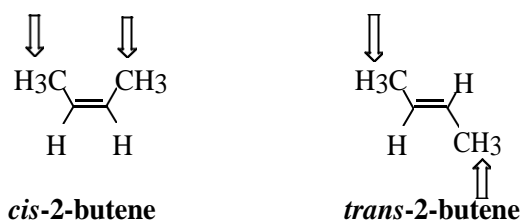
Compounds having double bond;



For example *cis*- and *trans*-2-butene have same connection of bond and molecular formulae.

☞ If you observe two similar groups are on the same side of C=C bond this is called *cis*- isomer; whereas, if two similar groups are on opposite side of C=C bond this is known as *trans*- isomer.

Example 1: *cis*- and *trans*- isomerism in 2-butene



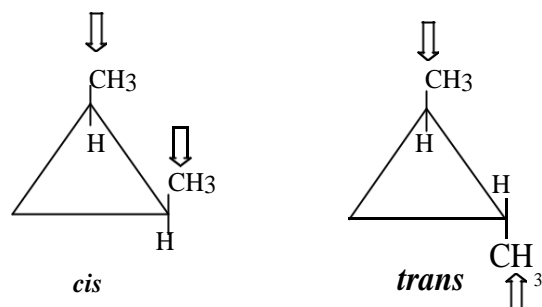
☞ You can understand that due to the presence of one σ (sigma) and one π (pi) bond in carbon-carbon double bond, rotation around C=C bond is not possible. The restricted rotation around C=C bond is responsible for geometrical isomerism in alkenes.

Cyclic compounds like homocyclic, heterocyclic and fused-ring systems

You can easily observe that rotation around C-C bond is also not possible in cyclic compounds as the rotation would break the bonds and break the ring. Thus Geometrical isomerism is also possible in cyclic compounds.

Example 2: *cis*- and *trans*- isomers of 1,2-dimethylcyclopropane

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Conditions for geometrical isomerism:

Following two conditions are necessary for any compounds to show geometrical isomerism

There should be restricted (not allowed) rotation about a bond in a molecule.

Both substituents/atoms on each carbon about which rotation is not allowed should (restricted) be different.

- ☞ **Remember:** Geometrical isomers are non-mirror image of each other hence they are called diastereomers. Therefore their physical and chemical properties are different.
- ☞ Triple bonded molecules do not exhibit any kind of stereoisomerism because such molecule shows cylindrical symmetry.

5.3.1 Determination of the configuration of geometrical isomers:

Unlike stereoisomerism of chiral compounds there is no general method for determining the configuration of geometrical isomers. You can find several methods for determination of configuration of geometrical isomers. Depending on the nature of compounds you can apply one or more methods for determination of configuration of geometrical isomers. The most commonly used methods are as follows:

Physical method

Cyclization method

Method of conversion into compound of known configuration

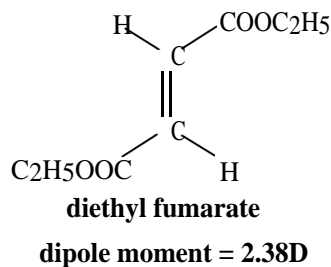
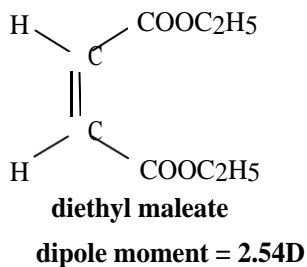
Physical method for determination of configuration:

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The geometrical isomers are non-mirror image of each other hence are called diastereomers. We have discussed in Unit 4 that diastereomers have different physical and chemical properties. Based on this fact, we can determine the configuration of geometrical isomers by comparing their physical properties. For example the melting point and absorption intensity of the *cis*-isomer are lower than the *trans*-isomer. Similarly the boiling point, solubility, heat of hydrogenation, density, refractive index, dipole moment and dissociation constant of *cis*-isomer is greater than the *trans*-isomer.

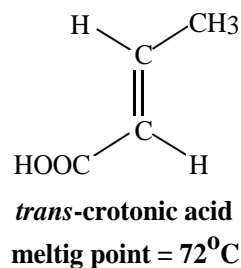
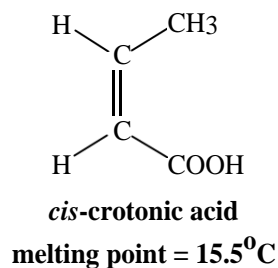
Thus if you have a set of geometrical isomers, then by comparing their above mentioned physical properties you can assign their configuration (means you can identify the *cis*- and *trans*-isomers).

Example 3: Diethyl maleate and diethyl fumarate are the *cis*- and *trans*- form to each other. The configuration of these can be determined by comparing their dipole moment. The dipole moment of diethyl maleate is 2.54D whereas the dipole moment of diethyl fumarate is 2.38D. Based on the fact that the dipole moment of *trans*- form of an isomer is lower than that of *cis*- form, you can easily predict the *cis*- and *trans*- form for diethyl maleate and diethyl fumarate.

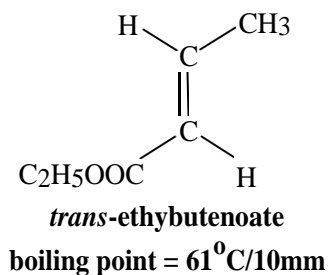
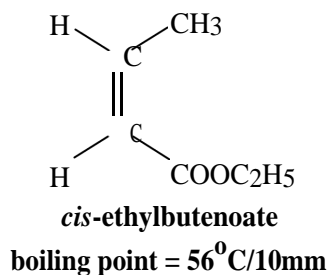


Example 4: *cis*- and *trans*- form of crotonic acid can be differentiated on the basis of their melting points. *cis*- isomer have lower melting point in comparison to *trans*- isomer.

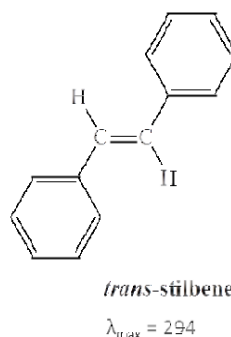
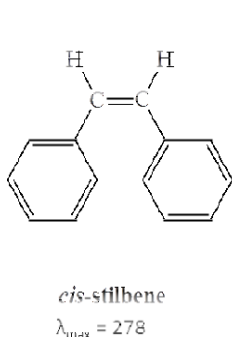
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Example 5: Ethylbutenoate exists in *cis*- and *trans*- isomeric forms. Both, the forms can also be differentiated based on their melting points.



Example 6: *cis*- and *trans*- isomer can also be identified on the basis of their absorption intensities. The UV absorption intensity (λ_{\max}) of *cis*-stilbene is lower than that of *trans*-stilbene.

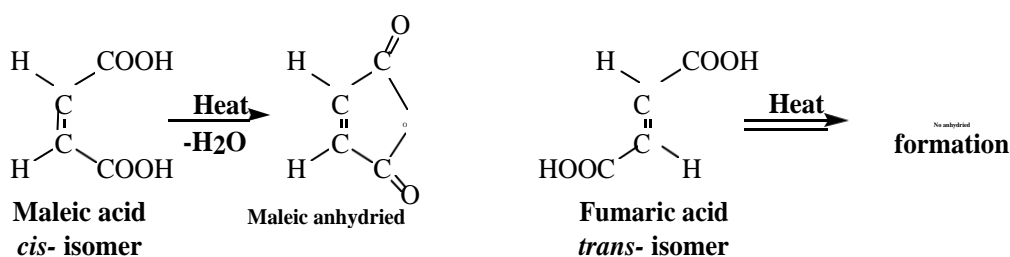


Cyclization method: Cyclization within a molecule (intramolecular) is usually depends upon the distance of two associating groups of a molecule. In other words if the reacting groups are closer to each other than the intramolecular cyclization takes place more effectively. This principal is also helps to identify the configuration of geometrical isomers.

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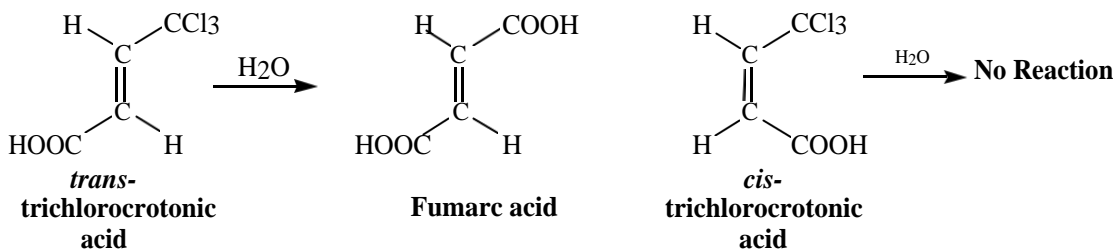
Let us take an example of two geometrical isomer of Butenedioic acid (*i.e.* Maleic acid and Fumaric acid) can be differentiated by possibility of formation of anhydride. Maleic acid which is *cis*- form of Butenedioic acid can only give the respective anhydride on heating; whereas, the *trans*- form of Butenedioic acid (*i.e.* Fumaric acid) does not give its anhydride on heating. If the Fumaric acid is strongly heated it get converted into Maleic acid.

Example 7: Cyclization of Maleic acid to Maleic anhydride. Fumaric acid does not give the anhydride on heating.



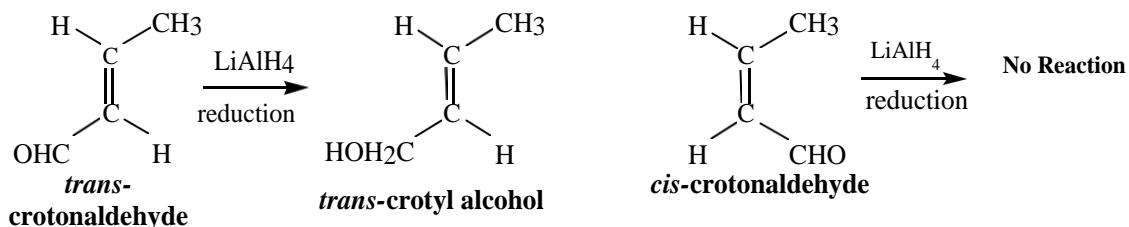
Method of conversion into compound of known configuration: The configuration of geometrical isomers can also be determined by converting them in to a compound of known configuration. For example, there are two trichlorocrotonic acid (*cis*- and *trans*-), one of which can be hydrolyzed to Fumaric acid. Therefore this isomer must be *trans*-isomer of trichlorocrotonic acid. The *cis*- isomer does not undergo hydrolysis.

Example 8: Determination of configuration of two isomers of trichlorocrotonic acid by hydrolysis method.



Example 9: Reduction of *trans*-crotonaldehyde in to *trans*-crotyl alcohol

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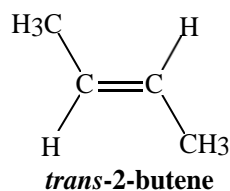
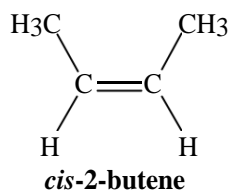
5.3.2 E & Z system of nomenclature:

We have already discussed about the *cis*- and *trans*- nomenclature of geometrical isomerism. The *cis*- and *trans*- nomenclature is the oldest and most fundamental nomenclature system for geometrical isomerism. The *cis*- and *trans*- nomenclature system is applicable only for those geometrical isomers in which at least one identical atoms/groups is bonded with each double bonded carbon. If both the identical groups/atoms are on same side of double bond the isomer is called as *cis*- isomer; whereas, if both identical groups/atoms are on opposite side of the double bond the isomer is called as *trans*- isomer (see example 1 of this unit).

The *cis*- and *trans*- nomenclature method is limited to the molecule in which identical groups/atoms are attached to double bonded carbon. If all the atoms/groups on double bonded carbon are different then the configuration of such molecule could not be assigned as *cis*- and *trans*- nomenclature. A more general nomenclature (*i.e.* E/Z nomenclature) was introduced which was based on Cahn-Ingold-Prelog system. In E/Z system the configuration is specified by the relative positions of two highest priority groups/atoms on the two carbons of the double bond.

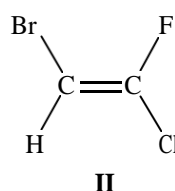
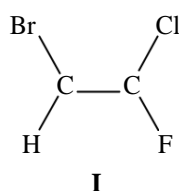
Let us understand the E/Z nomenclature system by considering an example which we have already discussed in the beginning of this Unit (example 1).

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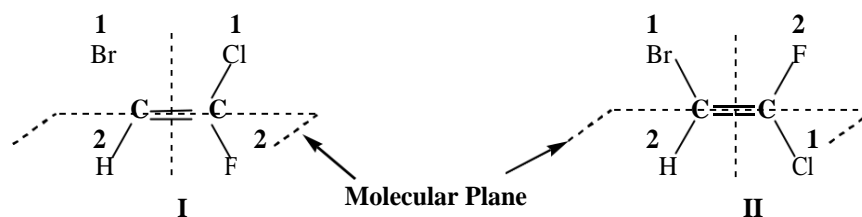


You can easily identify which one is *cis*- isomer and which one is *trans*- just by looking the position of similar atoms/groups. It is a simple and visual way of telling the two isomers apart. *So why do we need another system?*

Now consider one another example in which we will change all the atoms/groups in above example by replacing one CH₃- by Br, other CH₃- by Cl, and one H- by F. Now try to predict the nomenclature of these two isomers of 2-bromo-1-chloro-1-fluoroethene (I and II). *Could you name these isomers using cis- and trans- nomenclature?* The simplest answer is 'NO'.

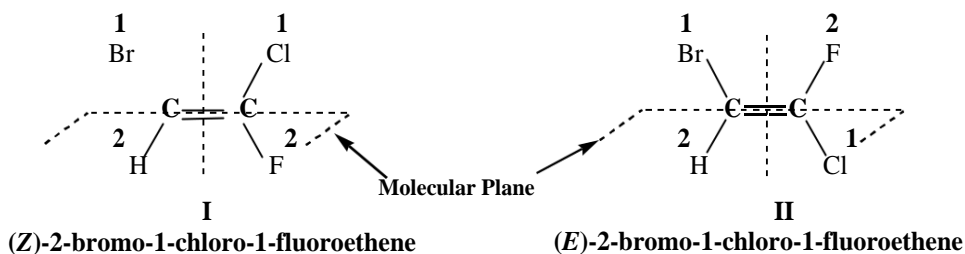


Because everything attached to the carbon-carbon double bond is different, there are not so simple so that you can predict them as *cis*- and *trans*- to each other. The E/Z system of nomenclature provides the most appropriate solution to above problem. This system is based on the priority of the attached atoms/groups on each double bonded carbon. The priority of the atoms/groups can be assigned as per the 'Sequence Rule' or 'CIP Rule' given by Cahn-Ingold-Prelog. We have already discussed the detail about 'Sequence Rule' in Unit 4. Now assign priority to atoms/groups attached to each double bonded carbon in above example.

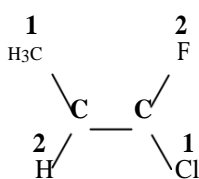


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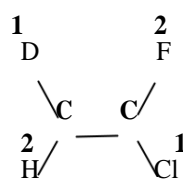
We can easily observe that the both higher priority atoms/groups on each double bonded carbon of isomer **I** are on same side; whereas, the higher priority atoms/groups on each double bonded carbon of isomer **II** are on opposite side. If the two groups with the higher priorities are on the same side of the double bond, such isomer is designated as the (*Z*)-isomer. So you would write it as (*Z*)-name of compound. The symbol *Z* comes from a German word *ZUSAMMEN*, which means together. If the two groups with the higher priorities are on opposite sides of the double bond, then such isomer is designated as (*E*)-isomer. *E* comes from the German *ENTGEGEN*, which means opposite. Thus in given example the isomer **I** is having both higher priority groups/atoms are on same side of double bond, hence it is *Z*- isomer; whereas, the isomer **II** is having both higher priority groups/atoms are on opposite side of the double bond, hence it is *E*- isomer.



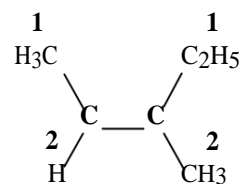
Example 10: Some other examples of geometrical isomers with *E* and *Z* configuration



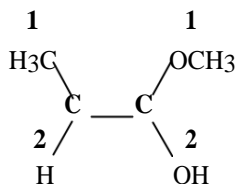
(E)-1-chloro-1-fluoroprop-1-ene



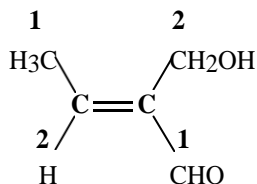
(E)-Deuterated 1-chloro-1-fluoroprop-1-ene



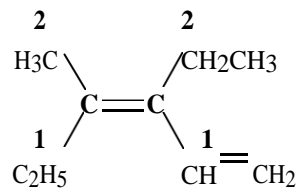
(Z)-3-methylpent-2-ene



(Z)-1-methoxyprop-1-en-1-ol



(E)-2-(hydroxymethyl)but-2-enal



(Z)-3-ethyl-4-methylhexa-1,3-diene

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5.3.3 Geometrical isomerism in oximes and acyclic compounds:

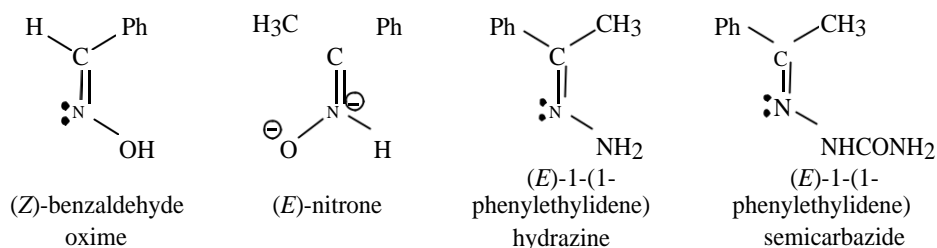
Nitrogen containing compounds like $>C=N-$ as well as $-N=N-$ bond also exhibit geometrical isomerism. The important classes of compounds that exhibit geometrical isomerism due to $>C=N-$ bond are:

Oximes

Nitrones

Semicarbazones

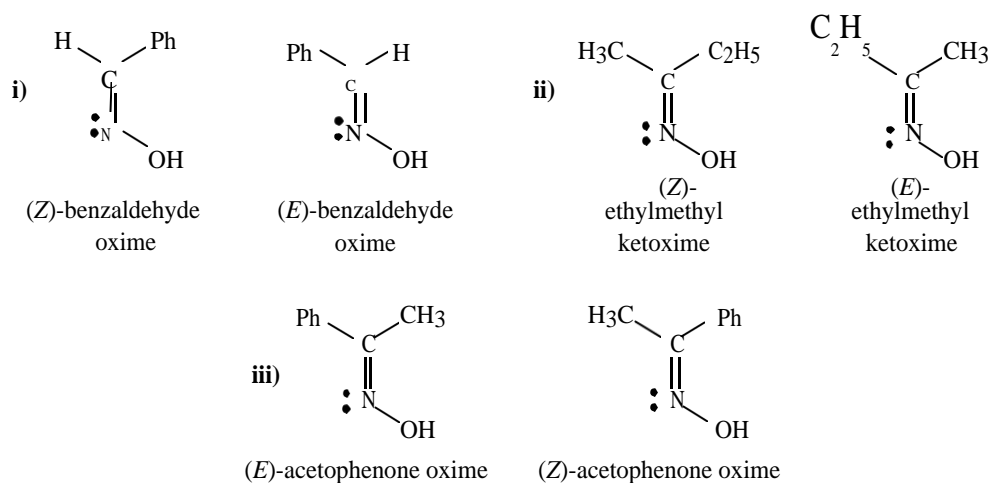
Hydrazones



Oximes are the most common compounds among all above classes. Both carbon and nitrogen atom in oxime are sp^2 hybridized the $C=N$ bond of oxime consists a sigma (σ) and a pi (π) bond. Therefore, there is no free rotation possible around $C=N$ bond; hence, oximes of aldehyde and ketones (unsymmetrical) exhibit geometrical isomerism. The configuration of such compounds is also based on priority of the groups/atoms attached to the double bonded carbon and nitrogen. Lone pair of the nitrogen always considered to be the lowest priority group. The priority of the groups/atoms is assigned as per the sequence rule which we have already discussed in Unit 4. If the higher priority groups/atom on double bonded carbon and nitrogen are on same side of the double bond the isomer is considered as *Z*- isomer, whereas if the higher priority groups/atoms are on opposite side the isomer is considered as *E*- isomer.

Example 11: *E/Z* isomerism is shown by i) benzaldoxime, ii) ethylmethylketoxime and iii) methylphenylketoxime

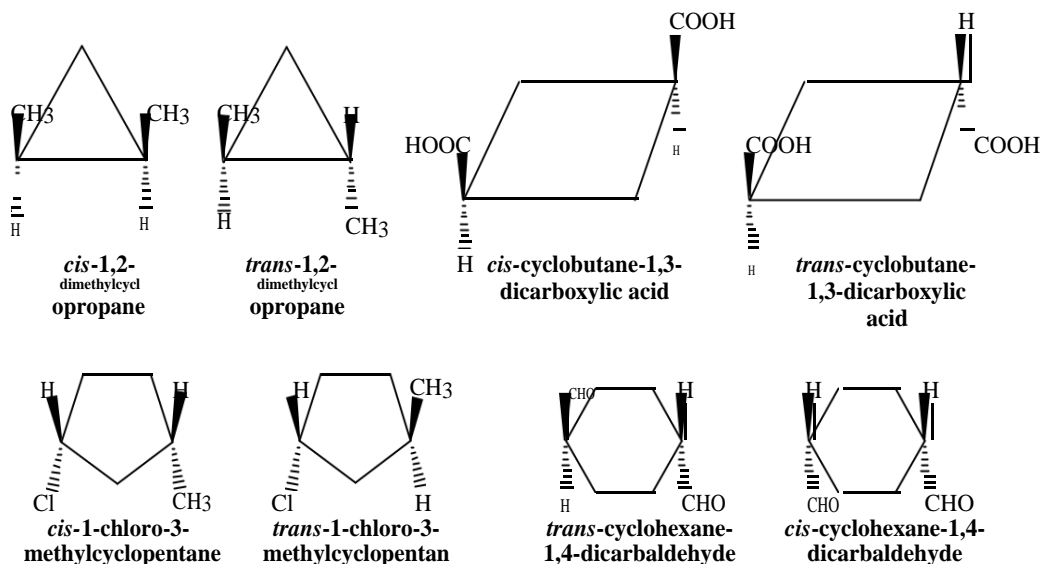
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We have already discussed that the geometrical isomerism usually arises due to restricted rotation about a bond. Since, there is no rotation possible about the carbon-carbon bond in a cyclic compound or cycloalkanes like cyclopropane, cyclobutane, cyclopentane, cyclohexane, etc. Hence, such molecule also exhibit geometrical isomerism, and can be designated as *cis*- and *trans*- isomer. In a disubstituted cycloalkanes, where the two atoms/groups are bonded on different carbons, can be represented in to two geometrical isomers. The isomer in which the two atoms/groups are located on the same side of the ring is called *cis*-isomer; whereas, the isomer in which the two atoms/groups are located on the opposite side of the ring is called *trans*-isomer.

Example 12: Geometrical isomers of disubstituted cyclopropane, cyclobutane, cyclopentane and cyclohexane.

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e

5.4 CONFORMATIONAL ANALYSIS OF ETHANE AND N-BUTANE:

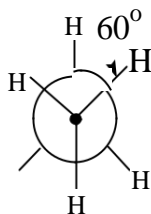
The different spatial arrangements of atoms in a molecule which is readily interconvertible by rotation about single bonds are called **conformations**. The study of various preferred conformations of a molecule and the correlation of physical and chemical properties to the most preferred conformer is called conformational analysis. Due to rapid interchange of the spatial positions of groups/atoms these conformers are non-separable under normal conditions. Since, different conformations arises because of the rotation about single bonds, hence, they are also called the rotamers. The conformational and configurational isomerisms are related to energy barrier for interconversions of different spatial arrangements of atoms in a molecule. If the energy barrier for interconversion of different spatial arrangements is between 0.6 kcal/mol-16.0 kcal/mol; it result the conformational isomers or conformers; whereas, if this energy barrier is more than or equal to 16 kcal/mol than the configurational isomers are obtained.

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5.4.1 Conformational analysis of ethane:

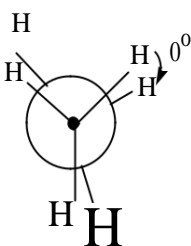
When ethane molecule rotates around carbon-carbon single bond, two extreme conformations (one is highly stable and other is highly unstable) are obtained. The highly stable conformation of ethane is called '*staggered conformation*' and the highly unstable conformation of ethane is called '*eclipsed conformation*'. In between these two extreme conformations (*i.e.* staggered and eclipsed), an infinite number of conformations are also possible.

5.4.1.1 Staggered conformation: A conformation with a 60° dihedral angle is known as a staggered conformation. The angle between the atoms attached to the front and rear carbon atom is called dihedral angle.



Staggered conformation

5.4.1.2 Eclipsed conformation: A conformation with a 0° dihedral angle is known as eclipsed conformation.



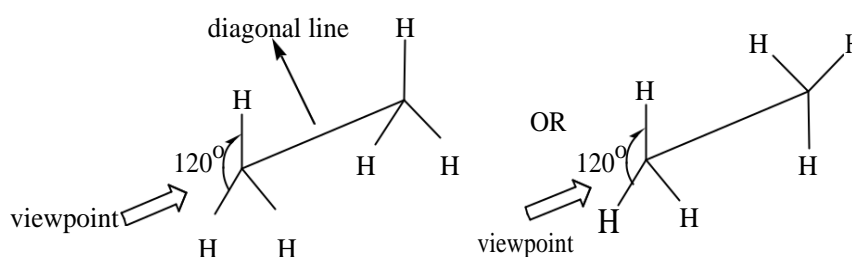
Eclipsed conformation

In staggered conformation the atoms are located at maximum possible distance from each other hence they are in their most relaxed spatial arrangement thus the staggered conformation is considered as the most stable conformation; whereas, in eclipsed conformation the atoms are located at minimum distance, hence due to repulsion between the atoms the eclipsed conformation is considered as the least stable (high energy) conformation.

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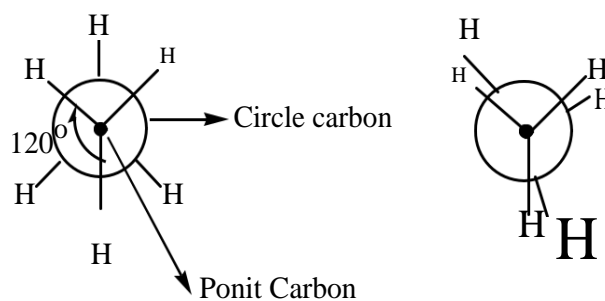
There are two methods for the representation of staggered and eclipsed conformations, a) the Sawhorse representation formula and b) the Newman representation formula.

The Sawhorse representation formula: In sawhorse representation formula the spatial arrangement of all the atoms/groups on two adjacent carbon atoms. The bond between adjacent carbon atoms is represented by a diagonal line and rest of the atoms are located on each carbon at $+120^\circ$ or -120° angles to each other. The sawhorse representation is shown as:



Sawhorse representation formula

The Newman representation formula: The Newman representation formula is a planar representation of the sawhorse formula. The molecule is viewed along the axis of a carbon-carbon bond. The carbon atom in front of the viewer is represented by a dot (\bullet), whereas the carbon atom away to the viewer is represented by circle. The rest of the atoms/groups are located on each carbon atoms at $+120^\circ$ or -120° angles to each other as shown below:



Newman representation formula

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The different conformations of ethane are not equally stable. The staggered form in which the hydrogen atoms are 'perfectly staggered' (dihedral angle is 60°) is the most stable conformation. This is because, in this conformation the all carbon hydrogen (C-H) bonds are located at maximum possible distance to each other, and hence they feel minimum repulsive energy from each other. In eclipsed conformation of ethane, the hydrogen atoms attached to each carbon are directly opposing to each other. This result the minimum separation of the atoms or groups, and hence they feel maximum repulsive energy from each other. The eclipsed conformation therefore, of highest energy and has the lowest stability. A graph plot for the energy profile for various conformations of ethane is shown on figure1. The relative stability of various conformations of ethane is

Staggered \gg Eclipsed

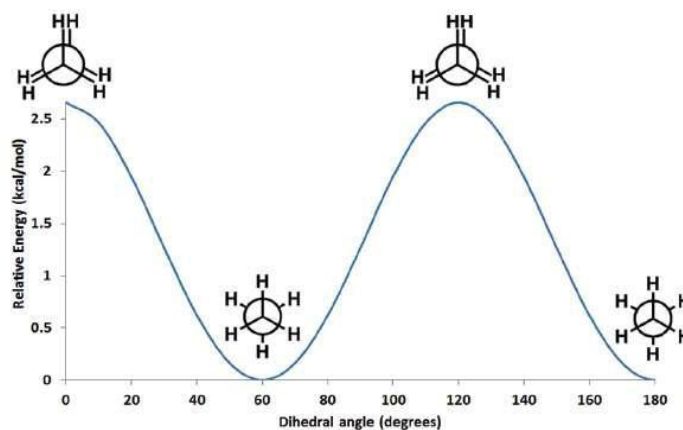


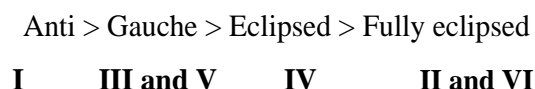
Figure 1: Energy profile diagram of conformational isomer of ethane

5.4.2 Conformational analysis of *n*-butane:

n-Butane (C_4H_{10}) has three carbon-carbon single bonds (Figure 2); therefore the molecule can rotate about each of them. The rotation about C2 and C3 bond will provide the symmetrical conformations. To study the conformational analysis of *n*-butane, we must

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also exists for *n*-butane, in which the dihedral atoms/groups are in front of each other (*i.e.* dihedral angle is 0°). The fully eclipsed conformer **IV**, in which the two methyl groups are closest to each other, has maximum steric strain; hence it is of higher energy than the other eclipsed conformers (**II** and **VI**). Thus the relative stabilities of the six conformers of *n*-butane in their decreasing order is given as follows:



5.5 CONFORMATION OF CYCLOHEXANE:

It is known to you that in cycloalkanes, all the ring carbons are sp^3 hybridized, hence must have tetrahedral geometry with all bond angles of 109.5° . But to sustain its cyclic structure the cycloalkanes could not be able to maintain the bond angle of 109.5° . As a result there is a deviation from the normal tetrahedral bond angle. This deviation leads the development of strain in the molecule. Thus the cycloalkanes exhibit angle strain, due to which cycloalkanes are not as stable as their non-cyclic homologs. To minimize the angle strain the structure of cycloalkanes is keep on changing from one cyclic form to another which are readily interconvertible by rotation about single bond. This is the reason why cyclohexane and larger rings are non-planar.

Cyclohexane exists in two readily interconvertible forms which are called the chair and boat conformations of cyclohexane (Figure 4).

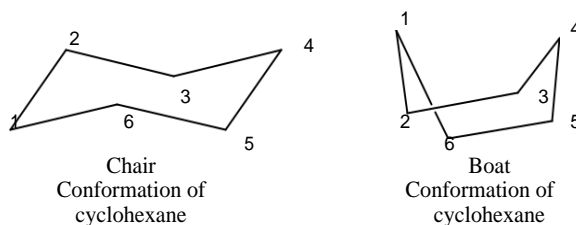
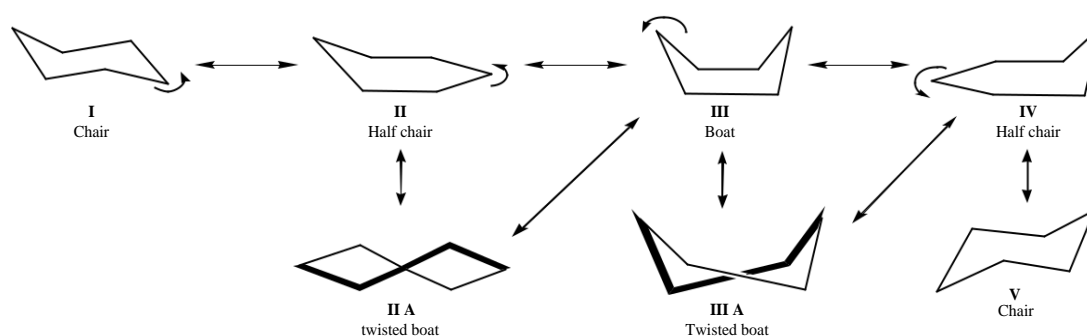


Figure 4: Two readily interconvertible conformations of cyclohexane

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Both chair and boat forms are free from angle strain. In chair form carbon C1, C3 and C5 are in one plane and carbon C2, C4 and C6 are in different plane. Similarly, in boat form carbon C1 and C4 are in one plane and carbon C2, C3, C5 and C6 are in other plane. The interconversions of chair to boat and boat to chair *via* various other intermediate conformations are shown in scheme 1. The chair conformation (**I** and **V** **scheme 1**) is considered as a rigid conformation of cyclohexane in comparison to boat conformation; because during interconversion from chair to boat conformation, some angular deformations are required. These angular deformations usually increase the energy barrier for interconversion from chair to boat conformation. Therefore the chair conformation of cyclohexane is the most stable conformation.



Scheme 1: Conformational analysis of cyclohexane

Chair form on distortion gives half chair (**II** and **IV** **scheme 1**) conformations which are of highest energy conformations. In comparison to chair conformation, the boat conformation (**III** **scheme 1**) is flexible and can readily distort in to many steps to reduce the C-H bond eclipsing. The boat conformation can be interconvertible in to twisted boat (**IIA** and **IIIA** **scheme 1**) conformations, which has comparatively less angular and steric strains. The twisted boat conformations have lower energy than the boat conformation, hence is more stable than boat conformation. At room temperature 99.9% cyclohexane molecules exist in the most stable chair conformation.

The energy profile diagram along with various possible conformations of cyclohexane is shown in figure 5.

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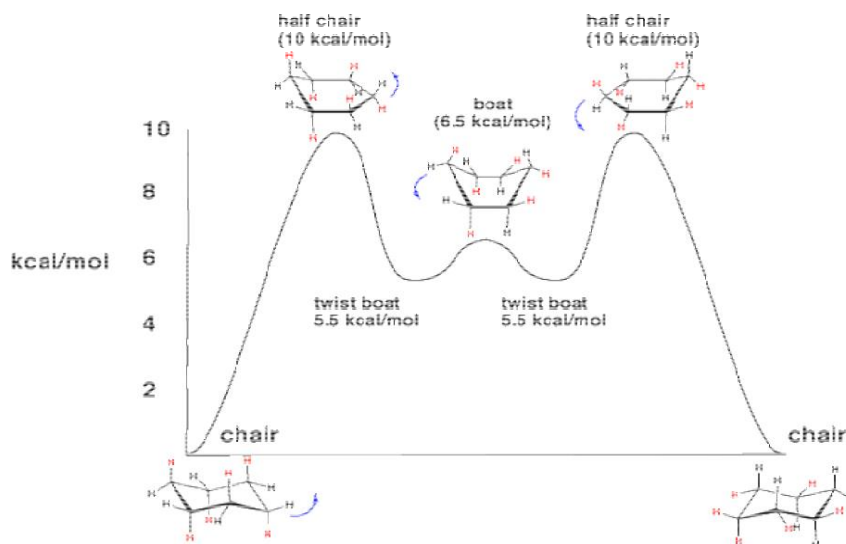
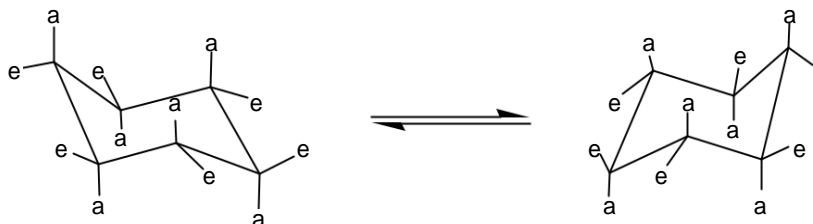


Figure 5: Energy profile diagram of conformation of cyclohexane

5.6 AXIAL AND EQUATORIAL BOND:

In chair conformation of cyclohexane, there are two different positions occupied by the 12 hydrogen atoms of cyclohexane. Out of total 12 Hydrogen atoms of cyclohexane, six hydrogen atoms are located towards perpendicular to average plane of the ring; these perpendicular hydrogen atoms are called axial hydrogens (*a*), and respective bonds are called *axial* bonds. The other six hydrogen atoms are located along with the average plane of the ring; these hydrogens are called *equatorial* hydrogens (*e*), and the respective bonds are called equatorial bond.



a = axial; e = equatorial

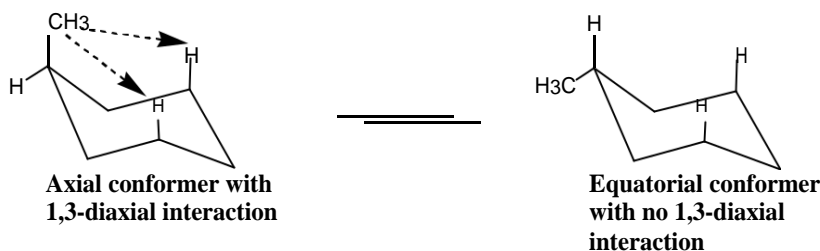
Cyclohexane is rapidly interconvertible (flips) in to its mirror image chair conformations at room temperature. During flipping all the axial hydrogens becomes equatorial and all the equatorial hydrogens becomes axial. The flipping of the cyclohexane is so rapid that it is not

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possible to differentiate between equatorial and axial hydrogens. These hydrogens can be differentiated at very low temperature (*i.e.* -80°) and analyzed by ^1H NMR spectroscopy.

5.7 CONFORMATION OF MONO SUBSTITUTED CYCLOHEXANE

If one hydrogen atom of cyclohexane is replaced by a larger atom or group, the molecule becomes highly hindered. As a result the repulsion between atoms increases. Axial atoms/groups usually face more repulsive interaction in comparison to equatorial atoms/groups. Since three axial atoms/groups are located in one side of the average plane of ring, whereas rest three atoms/groups are located in other side of the average plane of ring. The repulsive interaction experienced by three axial atoms is called *1,3-diaxial interaction*. To minimize the 1,3-diaxial interaction and resulting repulsive energy, the monosubstituted cyclohexane acquires a chair conformation in which the substituents occupies an equatorial position. There are two possible chair conformations for methyl cyclohexane. In one conformation the methyl group located at axial position (**I**), whereas in other conformation the methyl group is located at equatorial position (**II**). When methyl group is at axial position, it has 1,3-diaxial interaction with hydrogen atoms at C3 and C5 carbons due to which the energy of such conformation is very high in comparison to the conformer in which the methyl group is at equatorial position. The conformer with methyl group at equatorial position does not have any kind of 1,3-diaxial interaction hence is more stable.

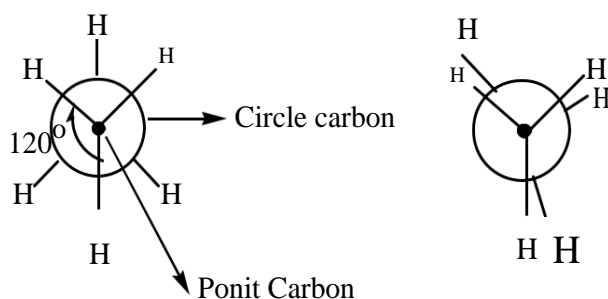


5.8 NEWMAN PROJECTION AND SAWHORSE FORMULA

The Newman representation formula: Newman Projections are used mainly for determining conformational relationships. Recall that, conformers are molecules that can be

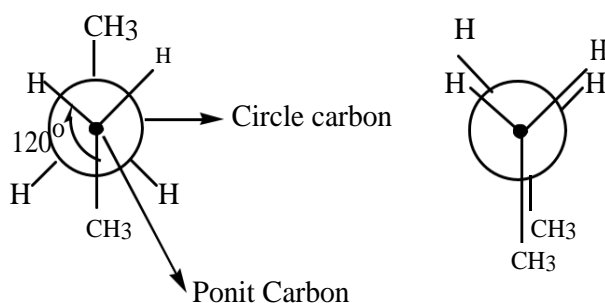
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converted into one another by a rotation around a single bond. Newman Projections are also useful when studying a reaction involving prochiral molecules that have a double bond, in which the addition of a new group creates a new stereocenter. In this notation, you are actually viewing a molecule by looking down a particular carbon-carbon bond. The Newman representation formula is a planar representation of the sawhorse formula. The molecule is viewed along the axis of a carbon-carbon bond. The carbon atom in front of the viewer is represented by a dot (\bullet), whereas the carbon atom away to the viewer is represented by circle. The rest of the atoms/groups are located on each carbon atoms at $+120^\circ$ or -120° angles to each other as shown below:



Newman representation formula of ethane

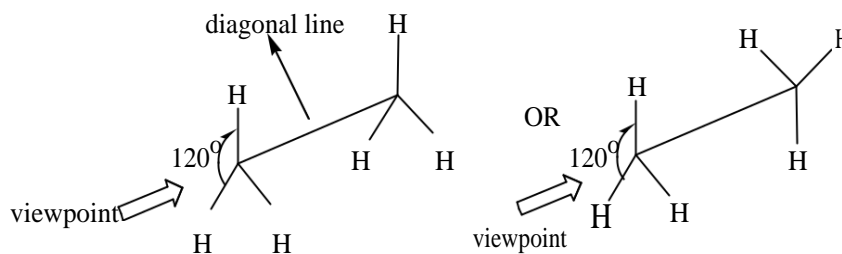
Addition of more carbons makes Newman Projections more complicated. For example, Newman Projections can be made for butane, such that it's eclipsed, gauche, and anti-conformations can be seen. (Recall that these three forms of butane are conformational isomers of one another.) In this case, the front dot represents the second carbon in the butane chain, and the back circle represents the third carbon in the butane chain. The Newman Projection condenses the bond between these two carbons.



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Newman representation formula of butane

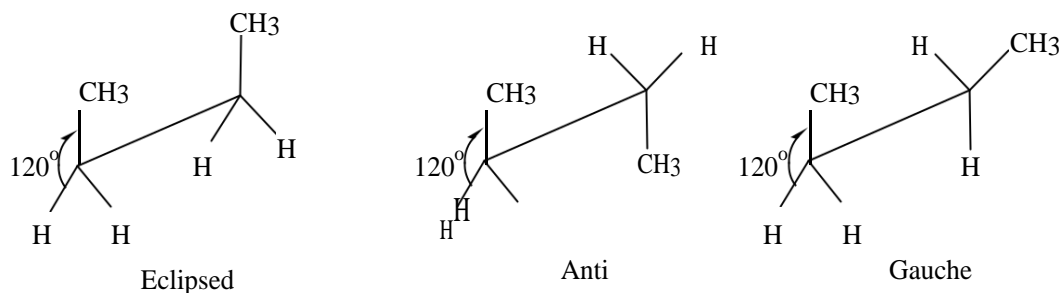
The Sawhorse representation formula: Sawhorse Projections are very similar to Newman Projections, but are used more often because the carbon-carbon bond that is compressed in a Newman Projection is fully drawn out in a Sawhorse Projection. When properly laid-out, Sawhorse Projections are useful for determining enantiomeric or diastereomeric relationships between two molecules, because the mirror image or superimposibility relationships are clearer. Like with Newman Projections, a Sawhorse Projection is a view of a molecule down a particular carbon-carbon bond, and groups connected to both the front and back carbons are drawn using sticks at 120 degree angles. Sawhorse Projections can also be drawn so that the groups on the front carbon are staggered (60 degrees apart) or eclipsed (directly overlapping) with the groups on the back carbon. Below are two Sawhorse Projections of ethane. The structure on the left is staggered, and the structure on the right is eclipsed. These are the simplest Sawhorse Projections because they have only two carbons, and all of the groups on the front and back carbons are identical. The sawhorse representation formula is the spatial arrangement of all the atoms/groups on two adjacent carbon atoms. The bond between adjacent carbon atoms is represented by a diagonal line and rest of the atoms are located on each carbon at $+120^\circ$ or -120° angles to each other. The sawhorse representation is shown as:



Sawhorse representation formula of ethane

Addition of more carbons makes Sawhorse Projections slightly more complicated. Similar to Newman Projections, Sawhorse Projections can also be made for butane, such that it's eclipsed, gauche, and anti-conformations can be seen. (Recall that these three forms of butane are conformational isomers of one another).

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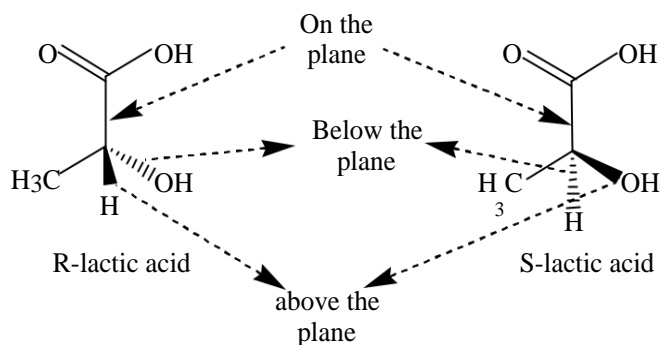
Sawhorse representation formula of butane

5.9 FISCHER AND FLYING WEDGE FORMULA:

The sp^3 hybridized tetrahedral carbon is three dimensional in nature. Generally it is very difficult to represent a three dimensional structure in a two dimensional plane paper. There are many methods have been developed for two dimensional representation of a three dimensional structure. Out of them the flying-wedge and Fischer representation methods are most commonly used for two dimensional representation of a three dimensional structure.

The flying-wedge: This is the most commonly used model for the two dimensional representation of a three dimensional molecule. In this model the bonds are presented in continuous, solid thick and dashed lines. A solid this line represents a bond projecting above the plane of the paper; it is considered that the bond with solid thick line is pointing towards observer. A dashed line represents a bond below the plane of the paper; it is considered that the bond with dashed line is pointing away to the observer. The bonds with continuous lines represent the bonds in the plane of paper. Let us consider an example of *R*-Lactic acid and *S*-Lactic acid.

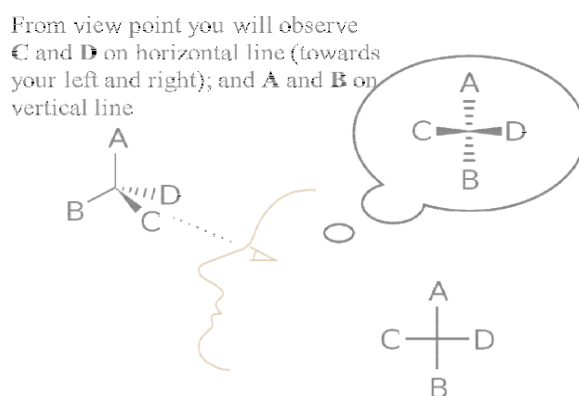
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Flying-wedge representation of *R*- and *S*-Lactic acid

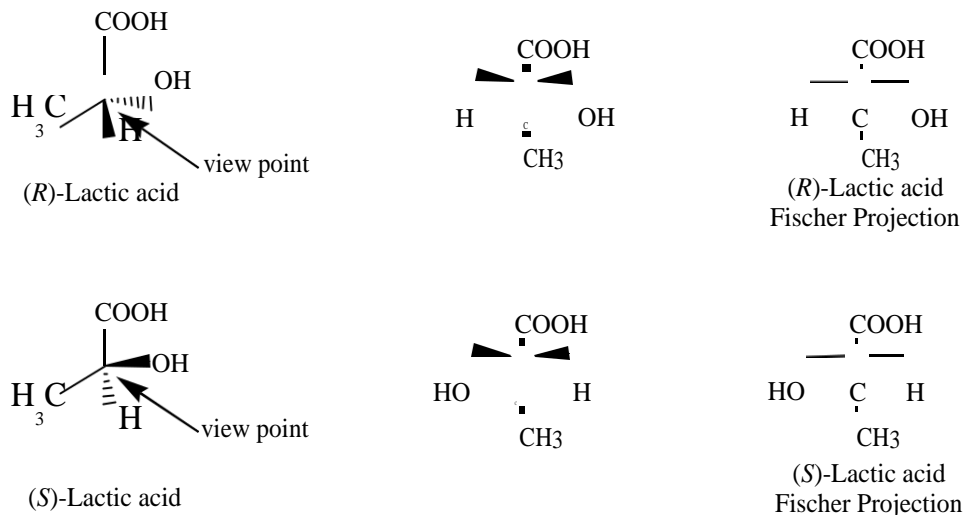
Fischer projection formula: It is a simplification of flying-wedge representation, in Fischer projection formula all bonds are drawn as solid lines in a plane paper. Fischer Projections are used often in drawing sugars and hydrocarbons, because the carbon backbone is drawn as a straight vertical line, making them very easy to draw. When properly laid-out, Fischer Projections are useful for determining enantiomeric or diastereomeric relationships between two molecules, because the mirror image relationship is very clear. In a Fischer Projection, each place where the horizontal and vertical lines cross represents a carbon. The vertical lines are actually oriented away from you (similar to dashes in the Wedge-Dash Notation) and the horizontal lines are oriented toward you (similar to wedges in the Wedge-Dash Notation).

Fischer projection is not as demonstrative as flying –wedge representation. It does not represent the actual shape of the molecule. Usually the Fischer projection formula is drawn so that the longest carbon chain in the molecule is vertical with the highly oxidized group on the top.



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Let us consider an example for conversion of flying-wedge formula to Fischer projection formula for *R*- and *S*- Lactic acid.



Conversion of flying wedge to Fischer projection formula for Lactic acid

5.10 DIFFERENCE BETWEEN CONFIGURATION AND CONFORMATION:

We have used the term conformer to explain isomers related to the rotation about C-C single bond of ethane and butane derivatives, and the term configuration to define some substituted methane and ethylene in the present unit and also in the previous unit (Unit 4). At first glance it seems straightforward to distinguish conformation and configuration. The stereoisomerism which is due to the rotation about a single bond is referred to as conformation. Conformers are easily interconvertible and it is difficult to isolate the isomer. On the other hand, when two compounds are different in their configuration, e.g., a pair of enantiomers of bromofluoromethane, or a pair of geometrical isomers, maleic acid and fumaric acid, these are distinguishable compounds, and their isolation is possible (see section 5.2.3 of this unit).

However, if maleic acid can be converted into fumaric acid by heat, there remains some ambiguity to classify conformational isomers and configurational isomers by their possibility of interconversion. It would be more practical to classify them by their facility of

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interconversion. A new nomenclature was proposed where stereoisomers with lower energy barrier of conversion are conformers (conformational isomers), while those with higher energy barrier are configurational isomers. If the barrier of interconversion is above 100 kJ mol^{-1} , these are configurational isomer while if it is lower than 100 kJ mol^{-1} , these are conformers. It was previously explained that the rotation about a C=C double bond is restricted by the overlap of p-orbitals, while the rotation about C-C single bond is relatively free. The rotation about a C=C double bond, however, can occur during the reaction; e.g., fumaric acid is converted into maleic acid by heating (see section 5.2.3 of this unit). Thus, the difference between the rotation about a C-C bond and that about a C=C bond might better be regarded as the difference of the required energy to achieve the transition state involved in the rotation.

5.11 SUMMARY:

The present unit may be summarized as:

- ✚ The stereochemistry, determines many chemical, physical and biochemical properties of the compounds.
- ✚ The types of stereo-chemical situations are divided into classes called geometrical isomers, conformational isomers and configurational isomers.
- ✚ All of the isomers are studied as a way to understand the shapes and properties of organic compounds.
- ✚ Alkenes and cyclic compounds display geometrical isomers.
- ✚ In alkenes, geometrical isomers are labeled as *cis*- or *trans*- for the longest chain in the alkene, or as *E* and *Z* for substituents of higher priority attached to the alkene.
- ✚ Cyclic alkanes are designated only as *cis*- or *trans*-.
- ✚ Rotation around bonds in alkane structures, exemplified in ethane and butane, gives rise to conformational isomers.
- ✚ There are an infinite number of conformations for any carbon-carbon single bond, but this book covers only the two extremes: the staggered and eclipsed forms.

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- ✚ In the staggered form, the torsional angle between attached groups is at 60° . In the eclipsed form, it is at 0° .
- ✚ A staggered conformation of ethane or butane has a lower rotational energy than the eclipsed conformation.
- ✚ Conformational isomers are drawn with the aid of dotted-line wedge, sawhorse, and Newman projections, and they are analyzed for internal destabilizing steric interactions.
- ✚ Wedge-and-dash representations and Newman projections are both ways of visualizing three-dimensional molecules in two dimensions.
- ✚ Anti-conformations are usually the more stable with gauche and eclipsed structures of higher energy.
- ✚ Analysis of cyclohexane derivatives pays attention to substituents in axial and equatorial positions, with equatorial substituents being more stable.
- ✚ The most stable form of cyclohexane is the chair conformation. In this form, the molecule has both axial and equatorial substituents.
- ✚ Cyclohexane undergoes a chair-boat-chair ring flip in which the axial substituents become equatorial, and vice versa.
- ✚ Interconversions between chair forms involve higher energy structures known as boat, twist and half-chair structures that are unstable.
- ✚ Cyclohexanes with axial substituents are less stable than those with the same substituents equatorial, because of unfavorable interactions among axial substituents.

5.12 *TERMINAL QUESTION*

- Q. 1 Define configurational and conformational isomers.
- Q. 2 Why the geometrical isomers are called diastereomers?
- Q. 3 What is cyclization method for determination of configuration of geometrical isomers?
- Q. 4 How do you determine the configuration of geometrical isomerism using physical method?
- Q. 5 What are staggered and eclipsed conformations of alkanes?
- Q. 6 Which conformation of cyclohexane is the most stable and why?

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Q. 7 What will be the preferred position for methyl group in the conformation of methyl cyclohexane?

ANSWERS

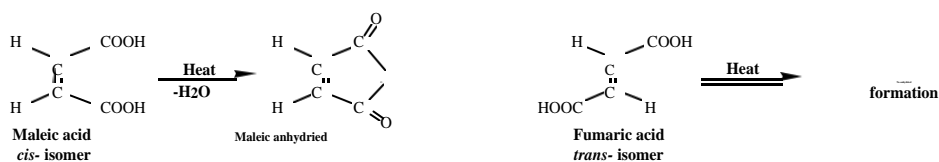
1 The stereoisomerism which is due to the rotation about a single bond is referred to as conformation. Conformers are easily interconvertible and it is difficult to isolate the isomer. On the other hand, when two compounds are different in their configuration, e.g., a pair of enantiomers of bromofluoromethane, or a pair of geometrical isomers, maleic acid and fumaric acid, these are distinguishable compounds, and their isolation is possible

2 Geometrical isomers are non-mirror image of each other hence they are called diastereomers. Therefore their physical and chemical properties are different.

3 Cyclization method: Cyclization within a molecule (intramolecular) is usually depends upon the distance of two associating groups of a molecule. In other words if the reacting groups are closer to each other than the intramolecular cyclization takes place more effectively. This principal is also helps to identify the configuration of geometrical isomers.

Let us take an example of two geometrical isomer of Butenedioic acid (*i.e.* Maleic acid and Fumaric acid) can be differentiated by possibility of formation of anhydride. Maleic acid which is *cis*- form of Butenedioic acid can only give the respective anhydride on heating; whereas, the *trans*- form of Butenedioic acid (*i.e.* Fumaric acid) does not give its anhydride on heating. If the Fumaric acid is strongly heated it get converted into Maleic acid.

Example : Cyclization of Maleic acid to Maleic anhydride. Fumaric acid does not give the anhydride on heating.



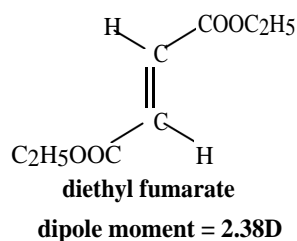
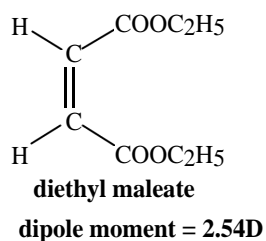
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4 The geometrical isomers are non-mirror image of each other hence are called diastereomers. We have discussed in Unit 4 that diastereomers have different physical and chemical properties. Based on this fact, we can determine the configuration of geometrical isomers by comparing their physical properties. For example the melting point and absorption intensity of the *cis*-isomer are lower than the *trans*-isomer. Similarly the boiling point, solubility, heat of hydrogenation, density, refractive index, dipole moment and dissociation constant of *cis*-isomer is greater than the *trans*-isomer.

Thus if you have a set of geometrical isomers, then by comparing their above mentioned physical properties you can assign their configuration (means you can identify the *cis*- and *trans*-isomers).

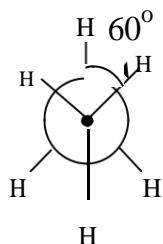
Example : Diethyl maleate and diethyl fumarate are the *cis*- and *trans*- form to each other.

The configuration of these can be determined by comparing their dipole moment. The dipole moment of diethyl maleate is 2.54D whereas the dipole moment of diethyl fumarate is 2.38D. Based on the fact that the dipole moment of *trans*- form of an isomer is lower than that of *cis*- form, you can easily predict the *cis*- and *trans*- form for diethyl maleate and diethyl fumarate.

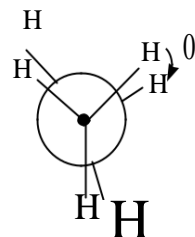


A. 5 A conformation with a 60° dihedral angle is known as staggered conformation. The angle between the atoms attached to the front and rear carbon atom is called dihedral angle. A conformation with a 0° dihedral angle is known as eclipsed conformation.

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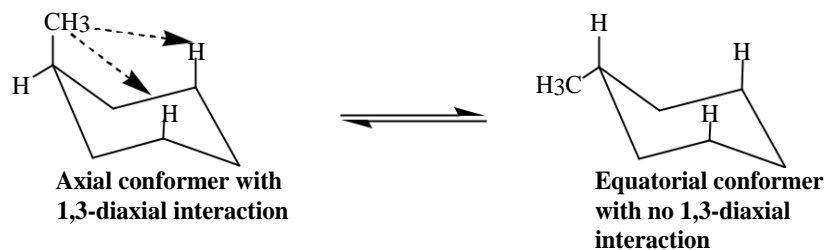
Staggered conformation



Eclipsed conformation

6 The chair conformation is considered as a rigid conformation of cyclohexane in comparison to boat conformation; because during interconversion from chair to boat conformation, some angular deformations are required. These angular deformations usually increase the energy barrier for interconversion from chair to boat conformation. Therefore the chair conformation of cyclohexane is the most stable conformation.

7 There are two possible chair conformations for methyl cyclohexane. In one conformation the methyl group located at axial position, whereas in other conformation the methyl group is located at equatorial position. When methyl group is at axial position, it has 1,3-diaxial interaction with hydrogen atoms at C3 and C5 carbons due to which the energy of such conformation is very high in comparison to the conformer in which the methyl group is at equatorial position. The conformer with methyl group at equatorial position does not have any kind of 1,3-diaxial interaction hence is more stable.



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UNIT 6: ALKANES

CONTENTS:

- 6.1 Objectives
- 6.2 Introduction
- 6.3 IUPAC nomenclature of branch and unbranched alkanes
- 6.4 Classification of carbon atoms in alkanes
- 6.5 Isomerism of alkanes,
- 6.6 Sources
- 6.7 Methods of formation (with special reactions)
 - 6.7.1 Kolbe's reaction
 - 6.7.2 Corey-House reaction of alkanes.
- 6.8 Mechanism of free radical halogenations of alkanes
 - 6.8.1 Orientation, reactivity and selectivity
- 6.9 Summary
- 6.10 Terminal Question

6.1 OBJECTIVE

By the end of the course the student should be able to:

Recognize the hydrocarbon families, functionally substituted derivatives of alkanes.

Give the IUPAC names of the branched and unbranched alkanes.

Recognize by common name and structure the alkyl.

Know the method of preparation of alkane.

Understand the constitutional isomerism in alkane.

Understand how branching affects the boiling point of an alkenes.

Mechanism of free radical substitution with reference to halogenations.

6.2 INTRODUCTION

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. The simplest alkane has only one carbon atom and is called methane. These are saturated hydrocarbons because they have the maximum number of hydrogen atoms. Alkanes are also called Paraffins because of little reactivity towards reagents.

Members of a homologous series with general formula C_nH_{2n+2} .

6.3 IUPAC NOMENCLATURE

The root or parent name for an unbranched alkane is taken directly from the number of carbons in the chain according to a scheme of nomenclature established by the **International Union of Pure and Applied Chemistry (IUPAC)**, as shown below:

Name	Condensed Structure
Methane	CH ₄
Ethane	CH ₃ CH ₃
Propane	CH ₃ CH ₂ CH ₃
Butane	CH ₃ (CH ₂) ₂ CH ₃
Pentane	CH ₃ (CH ₂) ₃ CH ₃
Hexane	CH ₃ (CH ₂) ₄ CH ₃
Heptanes	CH ₃ (CH ₂) ₅ CH ₃
Octane	CH ₃ (CH ₂) ₆ CH ₃

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Nonane	$\text{CH}_3(\text{CH}_2)_7\text{CH}_3$
Decane	$\text{CH}_3(\text{CH}_2)_8\text{CH}_3$
Undecane	$\text{CH}_3(\text{CH}_2)_9\text{CH}_3$
Dodecane	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$

The IUPAC rules for naming linear and branched alkanes are given below:

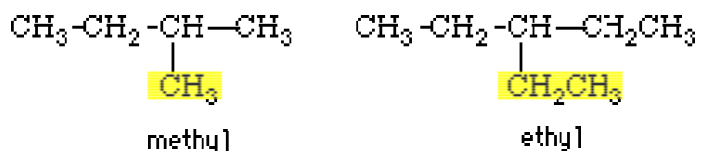
The IUPAC name for an alkane is constructed of two parts:

a prefix (meth... eth... prop..., etc.) which indicates the number of carbons in the main, or parent, chain of the molecule, and

the suffix **...ane** to indicate that the molecule is an alkane.

For branched-chain alkanes, the name of the parent hydrocarbon is taken from the **longest continuous chain** of carbon atoms.

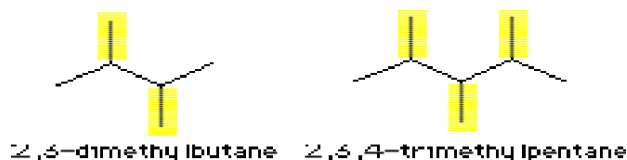
Groups attached to the parent chain are called **substituents** and are named based on the number of carbons in the longest chain of that substituent, and are numbered using the number of the carbon atom on the parent chain to which they are attached. In simple alkanes, substituents are called **alkyl groups** and are named using the prefix for the number of carbons in their main chain and the suffix **...yl**. For example, methyl, ethyl, propyl, dodecyl, etc.



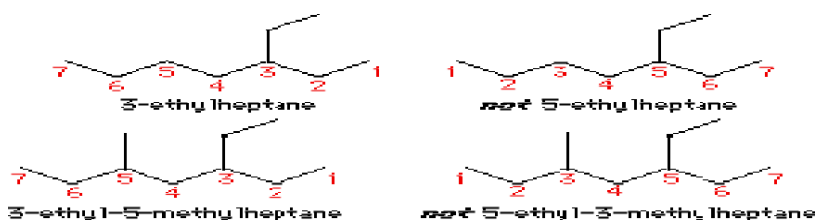
If the same substituent occurs more than once in a molecule, the number of each carbon of the parent chain where the substituent occurs is given and a multiplier is

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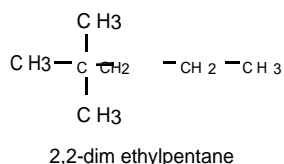
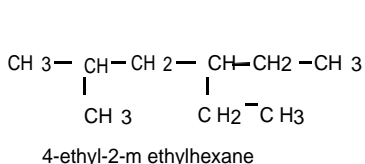
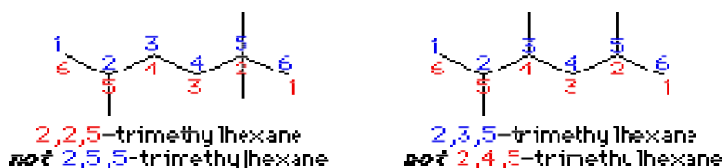
used to indicate the total number of identical substituents; i.e., **dimethyl...**
trimethyl... **tetraethyl...**, etc.



Numbering of the carbons in the parent chain is always done in the direction that gives the lowest number to the substituent which is encountered first, or, the lowest number at the first point of difference. If there are different substituents at equivalent positions on the chain, the substituent of lower alphabetical order is given the lowest number.



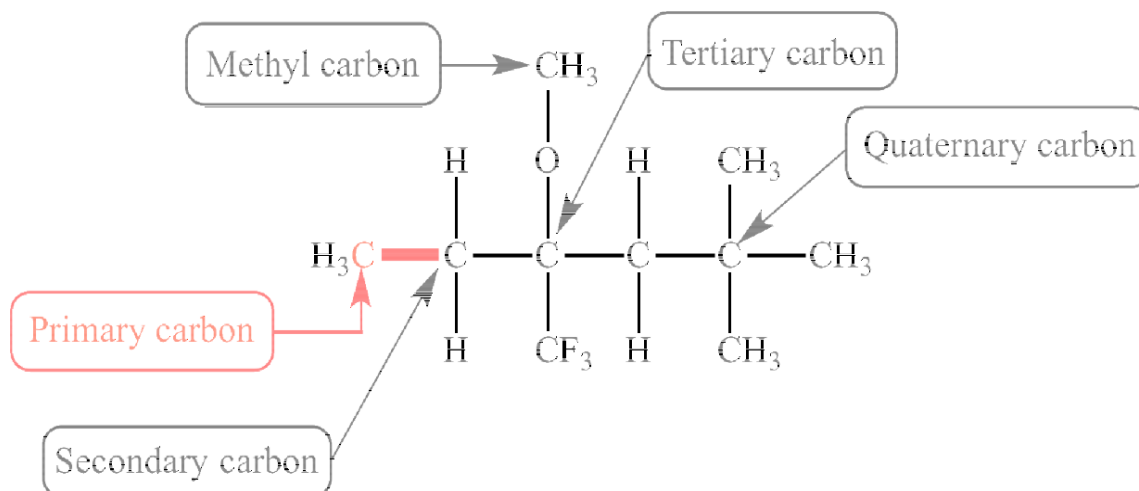
In constructing the name, substituents are arranged in alphabetical order, without regard for multipliers.



6.4 CLASSIFICATION OF CARBON ATOMS IN ALKANES

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By definition, a **primary carbon** is one which is attached to one other or no other carbon atom, a **secondary carbon** is one which is attached to two C- atoms, a **tertiary carbon** is attached to three other C-atoms, and a **quaternary carbon** is attached to four other carbon atoms; these are often abbreviated as 1°, 2°, 3° and 4° carbons.



Hydrogens always take the same class as the carbons to which they are bonded. All hydrogens on a *primary* carbon are *primary*. All hydrogens on a *secondary* carbon are *secondary*.

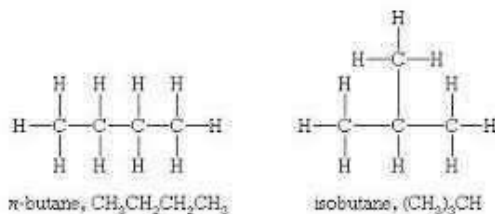
e.g., CH₃CH₂CH₃ : Propane contains **two** 1° carbons and one 2° carbon. There are six primary and two secondary hydrogens in propane.

6.5 ISOMERISM OF ALKANES

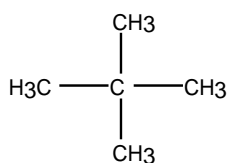
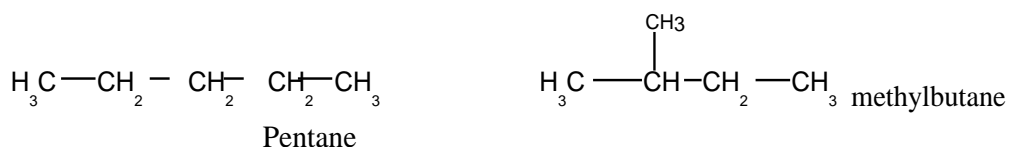
Different compounds that share the same molecular formula are known as **isomers**. Alkanes exhibit structural isomerism.

e.g., The straight-chain structure and the branched chain structure represent the two isomers of butane, C₄H₁₀.

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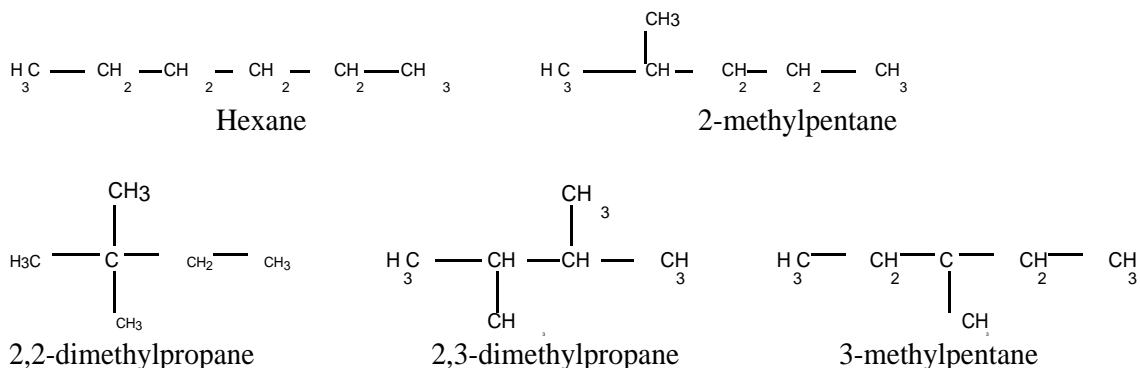


Isomers of pentane



Dimethylpropane

Isomers of hexane



6.6 NATURAL SOURCES

Petroleum and natural gas are the major sources of aliphatic hydrocarbon. The oil trapped inside the rocks is known as petroleum (PETRA – ROCK, OLEUM – OIL). The oil in the petroleum field is covered with a gaseous mixture known as natural gas. The main constituents of the natural gas are methane, ethane, propane and butane. Alkanes are

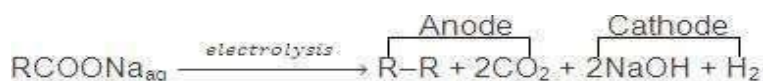
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primarily used as energy source through combustion and as raw materials for the chemical industry. The first operation in refining is fractional distillation, which yields different alkane fractions (still complex mixtures of many compounds) based on the volatility of its components. The high demand for valuable low-molecular-weight alkanes (gasoline) led to the discovery of other refining processes. Valuable industrial methods to prepare many hydrocarbons are the thermal and catalytic crackings (large hydrocarbons are broken into small fragments under the influence of heat and/or catalysts) and catalytic reforming.

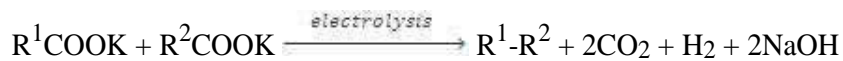
6.7 METHODS OF FORMATION

6.7.1 Kolbe's electrolysis method:

Alkanes are formed, on electrolysis of concentrated aqueous solution of sodium or potassium salt of saturated mono carboxylic acids. The electrochemical oxidative decarboxylation of carboxylic acid salts that leads to radicals, which dimerize. It is best applied to the synthesis of symmetrical dimers.



Electrolysis of an acid salt gives symmetrical alkane. However, in case of mixture of carboxylic acid salts, all probable alkanes are formed.

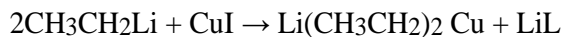


($\text{R}^1\text{-R}^1$ and $\text{R}^2\text{-R}^2$ are also formed).

6.7.2 By Corey-House synthesis:

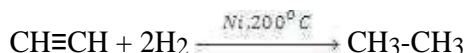
Alkyl chloride say chloroethane reacts with lithium in presence of ether to give lithium alkyl then reacts with CuI to give lithium dialkyl cuprate. This lithium dialkyl cuprate now again reacts with alkyl chloride to give alkane.

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6.7.3 By hydrogenation of alkenes: Sabatier and senderen's method:

Alkenes and alkynes on catalytic hydrogenation give alkanes. Catalyst Ni is used in finely divided form.



6.7.4 Wurtz reaction: A solution of alkyl halide in ether on heating with sodium gives alkane.

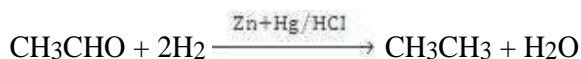


An alkyl halide on Wurtz reaction leads to the formation of symmetrical alkane having an even number of carbon atoms. Two different alkyl halides, on Wurtz reaction give all possible alkanes.

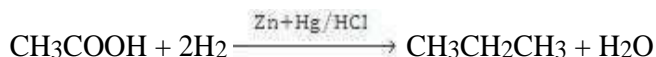


6.7.5 By Reduction of Carbonyl compounds:

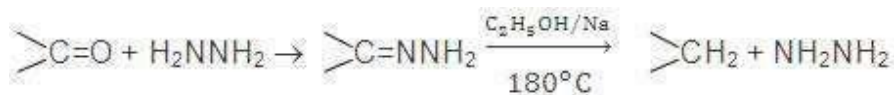
The reduction of carbonyl compounds by amalgamated zinc and conc. HCl also yields alkanes. This is Clemmensen reduction.



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Carbonyl compounds may also be reduced to alkanes by Wolf Kishner reaction



6.8 HALOGENATION OF ALKANE

Halogenation is a substitution reaction of one or more hydrogen atoms in an organic compound by a halogen (fluorine, chlorine, bromine or iodine). This reaction is a photochemical one. The products of this reaction are an alkyl halide or haloalkane and a hydrogen halide.

Alkanes are not very reactive molecules. However, alkyl halides are very useful reactants for the synthesis of other organic compounds. Thus, the halogenation reaction is of great value because it converts uncreative alkanes into versatile starting materials for the synthesis of desired compounds. This is important in the pharmaceutical industry for the synthesis of some drugs. In addition, alkyl halides having two or more halogen atoms are useful solvents, refrigerants, insecticides, and herbicides.



The reaction does not necessarily stop at one substitution, and the reaction between methane and chlorine produces dichloro-, trichloro- and tetrachloro- methane.



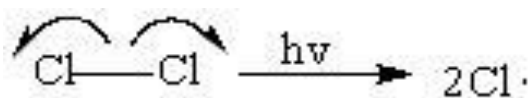
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The process of substitution is random, so all possible products result, though if there is excess methane the main one will be CH₃Cl, while a large excess of chlorine will give mainly CCl₄.

Mechanisms:

The substitution of a hydrogen atom by a chlorine atom actually takes place in a number of stages. Halogenation of an alkane takes place by a **free radical** reaction. The reaction between alkanes and these halogens requires an energy source such as ultra violet (u.v.) light. Typically, free radical reactions are described in three steps: initiation steps, propagation steps, and termination steps.

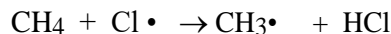
Initiation step: The photochemical energy is used to split the chlorine molecule to form two chlorine free radicals; the chlorine free radicals have an unpaired electron – such a species is called **free radical**. Single headed arrows are used during the movement of a single electron. This is called the **initiation step**.



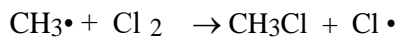
Free radicals are very reactive as they are trying to pair up their unpaired electron. If there is sufficient chlorine, every hydrogen will eventually be replaced.

Propogation Steps:

The chlorine radical then attacks the methane molecule.



The methyl radical from this reaction reacts with a chlorine molecule to form chloromethane and new chlorine radical.



The chlorine radical starts the cycle again and the process continues. In the propagation stage the Cl• at the end can go on to attack another CH₄ and so the chain can go on for

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several thousand reactions from one initiation. These two reactions are called the **propagation stage**. The propagation stage continues until two radical meet to form a molecule.

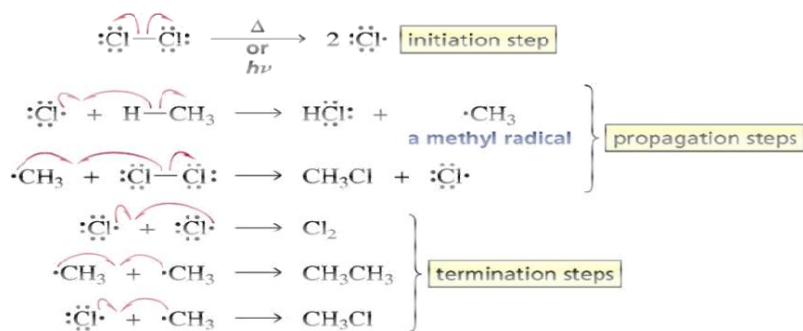
Termination Steps:

There are three possibilities for this reaction. Since the ends the sequence it is called the **termination stage**. In this step free radicals are meet to form a molecule.



The overall mechanism is called **free radical substitution**. The presence of traces of C_2H_6 in the products shows that $\text{CH}_3 \cdot$ radicals must have been formed. Of course, the $\text{Cl} \cdot$ atoms can remove a hydrogen atom from CH_3Cl , and so the reaction can go on to CH_2Cl_2 , then CHCl_3 and finally CCl_4 .

mechanism for the monochlorination of methane



The following facts must be accommodated by any reasonable mechanism for the halogenation reaction.

The reactivity of the halogens decreases in the following order: $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$.

Chlorinations and brominations are normally exothermic. Fluorination is so

explosively reactive it is difficult to control, and iodine is generally unreactive.

(iii) Energy input in the form of heat or light is necessary to initiate these halogenations.

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If light is used to initiate halogenation, thousands of molecules react for each photon of light absorbed.

Halogenation reactions may be conducted in either the gaseous or liquid phase.

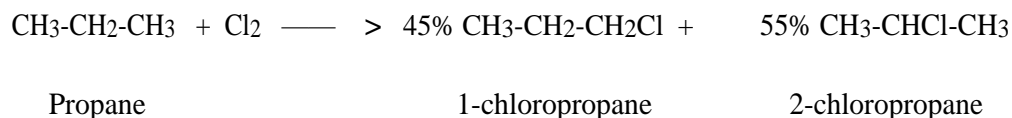
In gas phase chlorinations the presence of oxygen (a radical trap) inhibits the reaction.

In liquid phase halogenations radical initiators such as peroxides facilitate the reaction.

6.8.1 Orientation, reactivity and Selectivity:

When alkanes larger than ethane are halogenated, isomeric products are formed. All the hydrogens in a complex alkane do not exhibit equal reactivity. Hydrogens attached to more highly substituted carbons (ie. carbons with many carbons attached to them) are more reactive in free-radical halogenation reactions because the radical they form is stabilized by neighboring alkyl groups. These neighboring alkyl groups have the ability to donate some of their electron density to the electron-deficient radical carbon (a radical is short one electron of filling the atom's valence octet).

For example, propane has eight hydrogens, six of them being structurally equivalent **primary**, and the other two being **secondary**. If all these hydrogen atoms were equally reactive, halogenation should give a 3:1 ratio of 1-halopropane to 2-halopropane mono-halogenated products, reflecting the primary/secondary numbers. This is not what we observe. Light-induced gas phase chlorination at 25 °C gives 45% 1-chloropropane and 55% 2-chloropropane.



The results of bromination (light-induced at 25 °C) are even more surprising, with 2-bromopropane accounting for 97% of the mono-bromo product.



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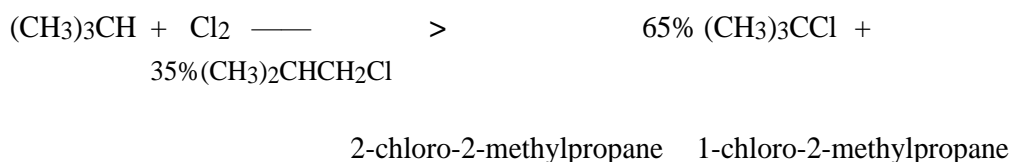
Propane

1-bromopropane

2-bromopropane

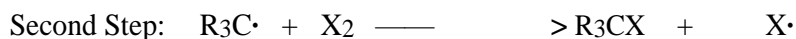
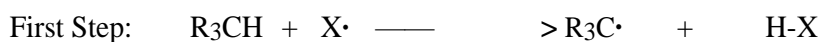
These results suggest strongly that 2°-hydrogens are inherently more reactive than 1°-hydrogens, by a factor of about 3:1.

3°-hydrogens are even more reactive toward halogen atoms. Thus, light-induced chlorination of 2-methylpropane gave predominantly (65%) 2-chloro-2-methylpropane, the substitution product of the sole 3°-hydrogen, despite the presence of nine 1°-hydrogens in the molecule.



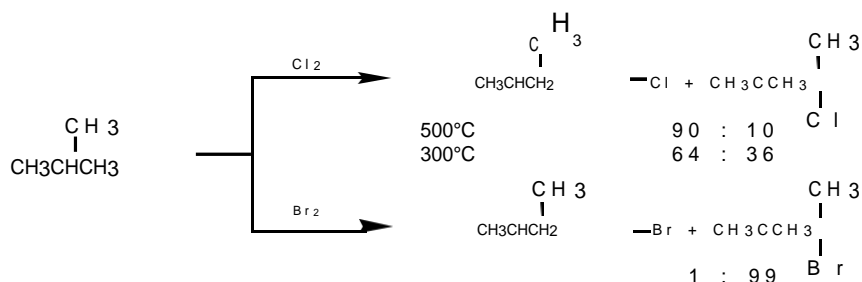
In the above reaction hydrogen on the tertiary carbon is abstracted in preference to the 9 other hydrogen atoms attached to a primary carbon (a carbon that is attached to only one other carbon atom) because it forms a more stable radical.

It should be clear from the above reactions that the hydrogen abstraction from alkane by a free radical is the product determining step. Once a carbon radical is formed, subsequent bonding to a halogen atom (in the second step) can only occur at the radical site. Consequently, an understanding of the preference for substitution at 2° and 3°-carbon atoms must come from an analysis of this first step.



Since the H-X product is common to all possible reactions, differences in reactivity can only be attributed to differences in C-H bond dissociation energies. Product distributions are governed by the number and relative reactivities of hydrogens, and the reactivities of the reactants.

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There is an activation energy difference between the formation of primary and secondary radicals; therefore, the latter is more abundant (Fig.). Furthermore, bromination is more selective than chlorination because of the much lower reactivity of the bromine radical.

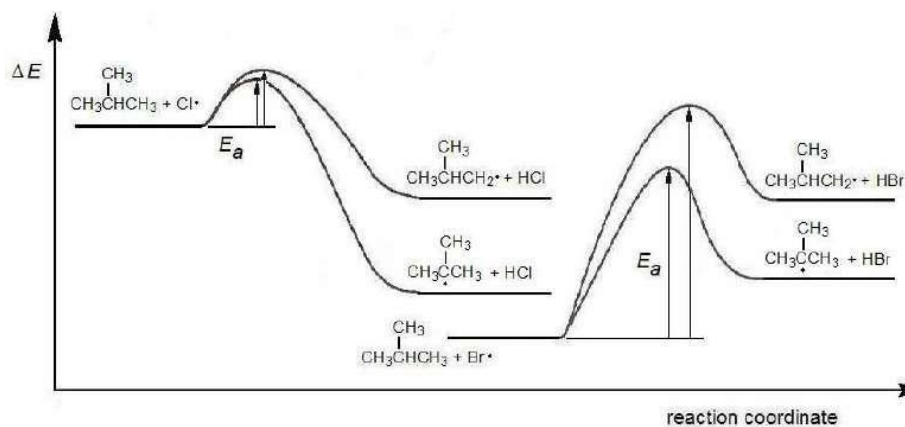
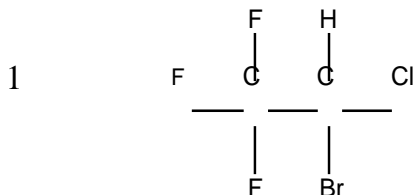


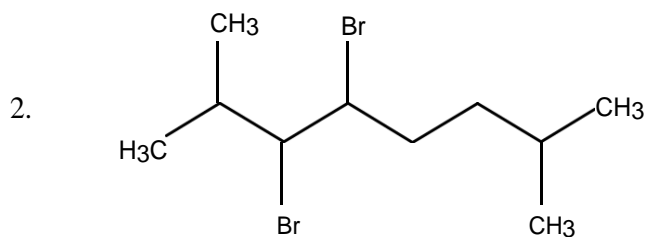
Fig. Energy changes occurring during the formation of primary and secondary radicals in free-radical chlorination and bromination of isobutane.

6.10 TERMINAL QUESTION

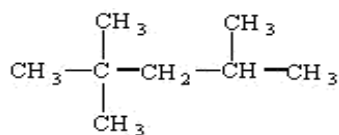
(1) Name the following alkyl halides according to IUPAC rules.



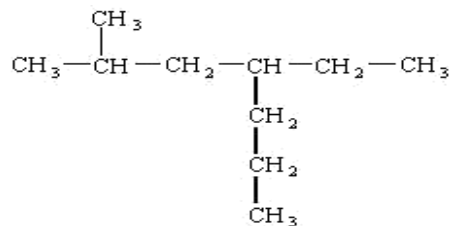
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3.



4.

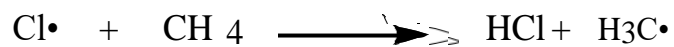


(2) Draw structures corresponding to the following IUPAC names.

(a) 2-chloro-3,3-diethylhexane (b) 4-sec-butyl-2-chlorononan

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The reaction shown below is what type?



A) addition B) termination C) propagation D) initiation

(4) Complete the following reaction.



(5) Draw out and name the structural isomers of C₅H₁₂ and C₆H₁₄.

UNIT 7: CYCLOALKANE

CONTENTS:

- 7.1 Objectives
- 7.2 Introduction
- 7.3 Cycloalkanes
 - 7.3.1 Nomenclature,
 - 7.3.2 Methods of formation,
 - 7.3.3 Chemical reactions
- 7.4 Baeyer's strain theory and its limitations
- 7.5 Terminal Question

7.1 OBJECTIVES

By the end of the course the student should be able to:

Recognize the cyclic hydrocarbon families, functionally substituted derivatives of cycloalkanes

Give the IUPAC names of the branched and unbranched cycloalkanes.

Know the methods of formation of cycloalkane.

Know the chemical reaction of cycloalkane.

Know the Baeyer's strain theory of cycloalkane and its limitations.

Know the meaning of the terms angle strain, torsional strain, and van der Waals strain.

7.2 INTRODUCTION

The cycloalkanes are the monocyclic saturated hydrocarbons. In other words, a cycloalkane consists only of hydrogen and carbon atoms arranged in a structure containing a single ring it may contain side chains, and all of the carbon-carbon bonds are single. Cycloalkanes are named like their normal alkane counterparts of the same carbon count: cyclopropane, cyclobutane, cyclopentane, cyclohexane, etc. The larger cycloalkanes,

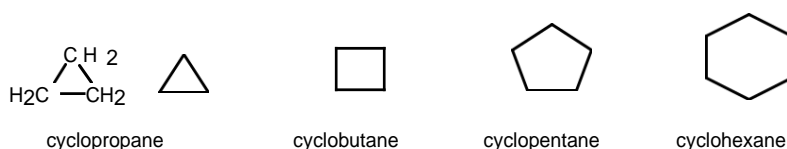
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with more than 20 carbon atoms are typically called *cycloparaffins*. In all cycloalkanes carbon of ring are saturated and sp^3 hybridized.

7.3 CYCLOALKANE

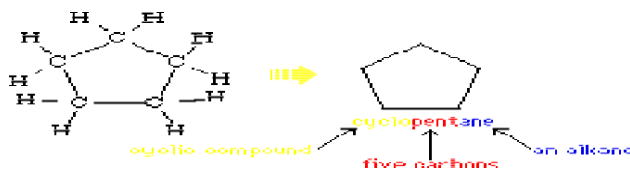
For a simple cycloalkane the general molecular formula is C_nH_{2n} , where n is the total number of carbons. This formula differs from the general formula for an alkane (C_nH_{2n+2}) by the lack of the two additional hydrogens (the "+ 2 term"). As a general rule, every ring which is constructed from an alkane reduces the number of hydrogens in the molecular formula for the parent hydrocarbon by two.

You should note that, in the smaller ring sizes (3, 4 and 5), the bond angles are significantly less than the tetrahedral angle 109.5° . This results in a significant amount of ring strain in these compounds which make many small rings susceptible to ring-opening reactions. The bond angles in a six-membered ring match well with the tetrahedral geometry of carbon and there is virtually no ring strain in these compounds. Rings which are seven-membered and larger are highly distorted, and again display significant ring strain.



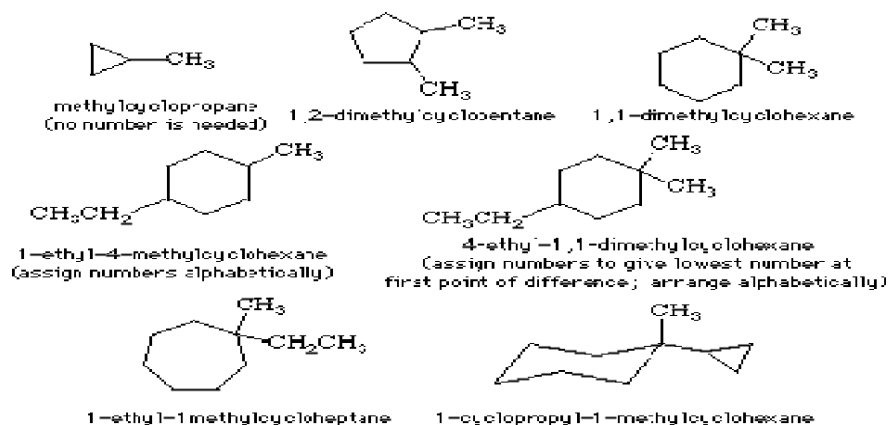
7.3.1 Nomenclature:

The nomenclature for a simple cycloalkane is based on the parent hydrocarbon, with the simple addition of the prefix **cyclo**. A three-membered ring is therefore cyclopropane, four-membered, cyclobutane, five-membered, cyclopentane, six-membered, cyclohexane, etc.



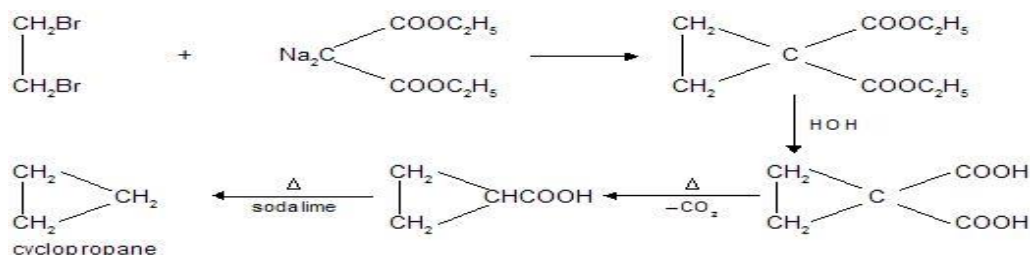
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As a convenient shortcut, cyclic structures are usually drawn using line (structural or line-angle) drawings, as shown above. Again, it is important to understand that every vertex in these drawings represents a $-\text{CH}_2-$ group, every truncated line a $-\text{CH}_3$ group and intersections of three or four lines represent 3 or 4 carbons, respectively. Substituents on cycloalkanes are named using the conventions described for alkanes, with the exception that, on rings bearing only one substituent, no number is needed. Substituted cycloalkanes are named as alkylcycloalkanes. When more than one substituents are present, number the ring beginning with one substituent in the way that gives the next substituent the lowest number possible.



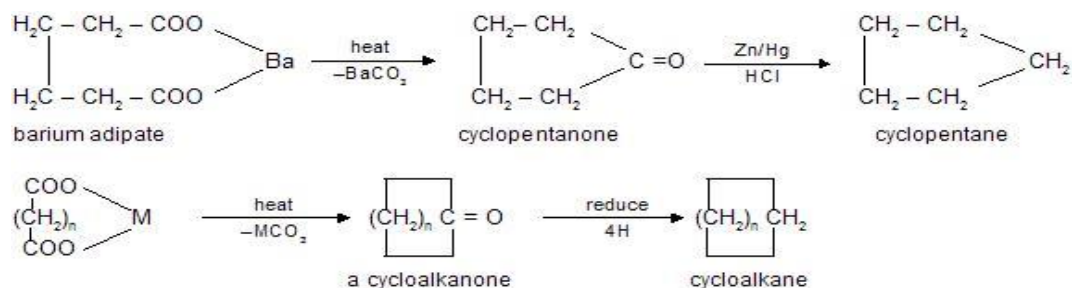
7.3.2 Preparation of cycloalkanes:

By Perkin's Method: In this method vicinal dihalide reacts with diester of dicarboxylic acid followed by hydrolysis and heated form cycloalkane.

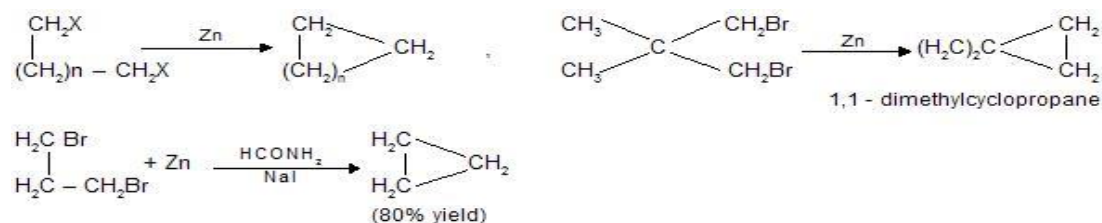


By pyrolysis of divalent metal salts of dicarboxylic acids (Wislicenus method): In this method salts of dicarboxylic acids heated followed by reduced with $\text{Zn}/\text{Hg}-\text{HCl}$ form cycloalkane.

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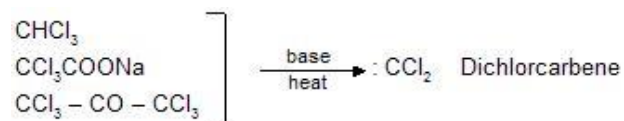


By Freund reaction: Elimination of terminal halogen atoms from dihalides with Na or Zn dust gives rise to the formation of cycloalkanes. The method can also be regarded as intramolecular Wurtz reaction. This can be used to prepare cycloalkanes from three to six carbon atoms.

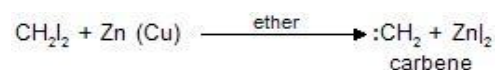


(iv) By the use of carbenes:

Carbenes are unstable intermediates in which carbon has pair of unshared electrons. These are neutral species and have no formal charge, $:\text{CH}_2$ (methylene) is the simplest member of this series. On account of greater stability di halo carbenes ($:\text{CX}_2$) are also used. Carbenes are easily prepared in solution as shown below and in the same form they are used for the reaction. This method is very useful for the preparation of small ring compounds.

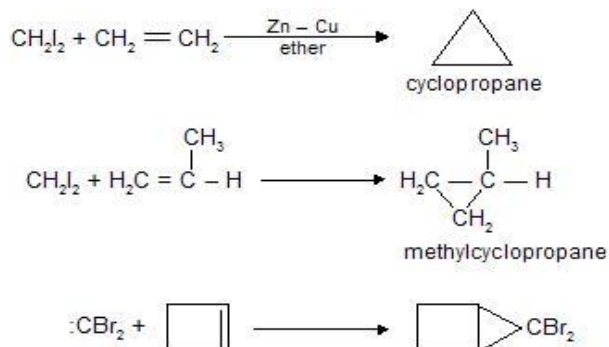


Methylene is prepared as follows



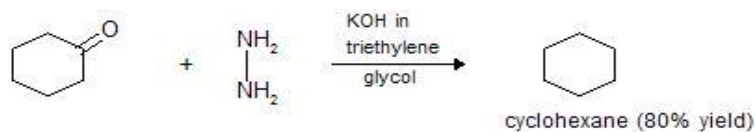
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Cyclopropane and its derivatives can easily be prepared by the use of carbenes.



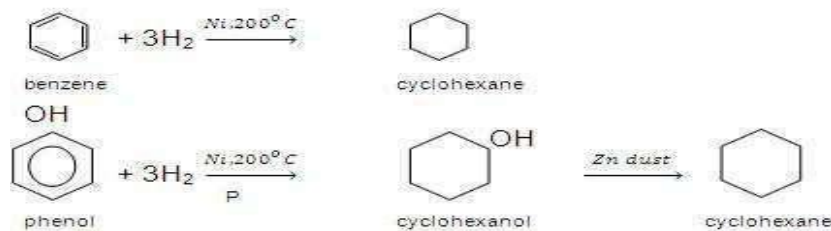
(v) Reduction of a cyclic ketone

The Wolff-Kishner carbonyl reduction is a good method for converting carbonyl group directly to methylene group. It involves heating the hydrazone of carbonyl compound in the presence of an alkali and a metal catalyst.



The Clemmensen's and Wolff-Kishner carbonyl reductions complement each other, for the former is carried out in acid solution, and the latter in alkaline solution. Thus, the Clemmensen carbonyl reduction may be used for alkali-sensitive compounds where as Wolff-Kishner carbonyl reduction is the method of choice with acid sensitive compounds.

From aromatic compounds: Six membered cyclo compounds can be easily obtained by the catalytic reduction of benzene and its derivatives.



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Physical properties:

The cycloalkanes resemble the alkanes in physical properties. They are insoluble in water but soluble in many organic solvents and are lighter than water. The melting and boiling points of cycloalkanes are ten to twenty degrees higher than the corresponding alkanes (open chain molecules). Some comparative boiling point (B.P.), melting point (m.p.) and density of alkanes and cycloalkanes are as follows:

Compounds	Bp, °C	Mp, °C	Density, d_4^{20} , g ml ⁻¹
propane	-42	-187	0.580 ^a
cyclopropane	-33	-127	0.689 ^a
butane	-0.5	-135	0.579 ^b
cyclobutane	13	-90	0.689 ^b
pentane	36	-130	0.626
cyclopentane	49	-94	0.746
hexane	69	-95	0.659
cyclohexane	81	7	0.778
heptane	98	-91	0.684
cycloheptane	119	-8	0.810
octane	126	-57	0.703
cyclooctane	151	15	0.830

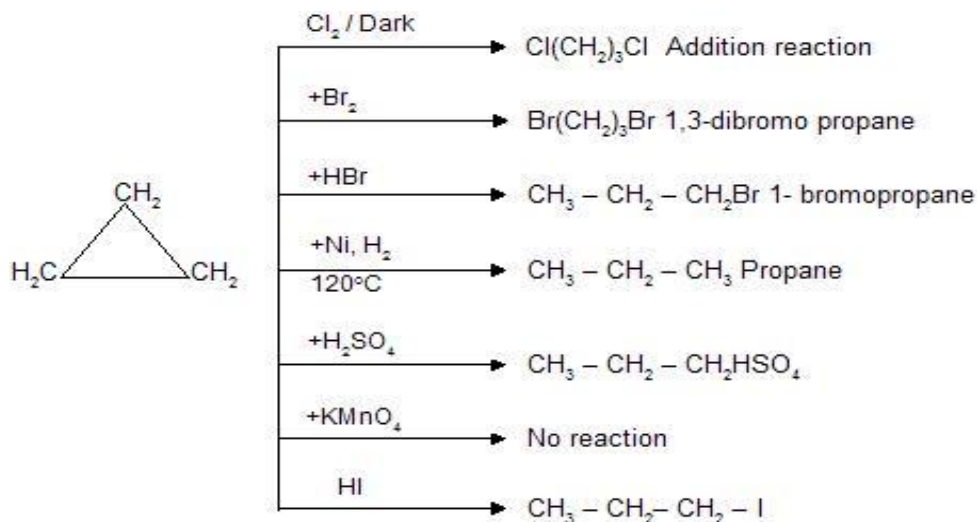
^aAt -40° ^bUnder pressure.

The melting and boiling points of cycloalkanes are somewhat higher than those of the corresponding alkanes.

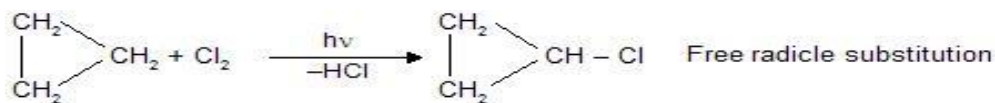
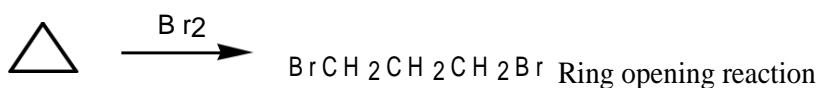
7.3.3 Chemical reactions:

Cycloalkanes are relatively inert towards the action of common reagents at room temperature. But cyclopropane and cyclobutane are exceptions and show a tendency to react with opening of the ring. Cyclopropane forms addition products with ring fission, as show:

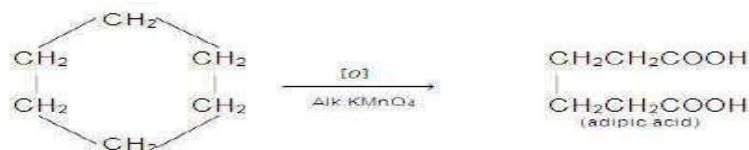
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All other cycloalkanes show the reactivity expected by alkanes, i.e. they react by substitution. In diffused light, cyclopropane reacts with chlorine to give substitution product.



Oxidation: Cycloalkanes are oxidized by alkaline potassium permanganate to dicarboxylic acids involving ring fusion.



7.4 STABILITY OF CYCLOALKANE; BAEYER STRAIN THEORY

Adolf Van Baeyer, a German chemist, in 1885, proposed a theory to explain the relative stability of cycloalkanes. The theory is based on the fundamental concept of regular

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tetrahedral structure as given by Vant Hoff and Le Bel. According to them “the tetravalency of carbon atom are directed towards the four corners of a regular tetrahedron with carbon atom at the centre making an angle of $109^{\circ}28'$ between any pair of such valencies.” He argued that because the bond angles of small rings (60° for cyclopropane and 90° for cyclobutane) are significantly lower than the tetrahedral angle (109.5°), the rings suffer from strain (angle strain) and so are highly reactive, readily undergoing strain-relieving ring opening reactions. Baeyer’s arguments for larger alicyclic were that, beyond cyclopentane and cyclohexane, the bond angles became significantly higher than the tetrahedral angle, leading to the opposite kind of ring strain and instability. This argument was erroneous, especially for the larger rings, because Baeyer assumed planar structures. In reality, only cyclopropane is truly planar, the rest having puckered structures. Despite this error, Baeyer’s ideas on angle strain are still very useful.

Strain $\beta = \frac{1}{2}(109^{\circ}28' - \text{bond angle})$ where all the carbon atoms in the ring are in the same plane. Suppose there are n carbon atoms in the ring, then the bond angle of ring would be

$$\frac{n \times 180^{\circ} - 360^{\circ}}{n} = \frac{180^{\circ} (n - 2)}{n}$$

The amount of strain (δ) in the various cycloalkanes would be as :

$$\text{cyclopropane } \beta = \frac{1}{2} (109^{\circ} 28' - 60^{\circ}) = 24^{\circ} 44'$$

$$\text{cyclobutane } \beta = \frac{1}{2} (100^{\circ} 28' - 90^{\circ}) = 9^{\circ} 44''$$

$$\text{cyclopentane } \beta = \frac{1}{2} (109^{\circ} 28' - 108^{\circ}) = 0^{\circ} 44'$$

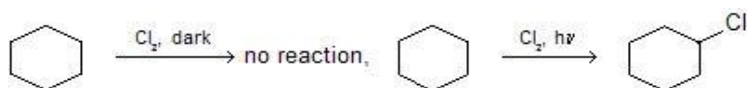
$$\text{cyclohexane } \beta = \frac{1}{2} (109^{\circ} 28' - 120^{\circ}) = -5^{\circ} 16'$$

$$\text{cycloheptane } \beta = \frac{1}{2} (109^{\circ} 28' - 128.5^{\circ}) = -9^{\circ} 33'$$

$$\text{cyclo octane } \beta = \frac{1}{2} (109^{\circ} 28' - 135^{\circ}) = -12^{\circ} 46'$$

It can be seen from the above data that the lowest value of the deviation is found in five and six-membered rings and so cyclopentane and cyclohexane are the most stable systems. The negative value of angle strain indicates that the bonds are bent outwards. The Baeyer’s strain theory could easily explain the greater reactivity of cyclopropane and cyclobutane and the stability of cyclopentane and cyclohexane rings.

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In above example cyclohexane is stable ring, so it cannot react in dark but in the presence of sunlight free radical substitution reaction occurs

Heats of Combustion and Relative Stabilities of Cycloalkanes

Stability, according to heats of combustion, reaches a maximum at cyclohexane and then decreases slightly until the ring size reaches 17, as shown in the table below.

Ring size	Heat of combustion per CH ₂ /kJ mol ⁻¹
3	696.4
4	685.5
5	663.4
6	657.9
7	661.7
8	662.9
12	658.8
17	657.1

The heat of combustion per CH₂ for alkanes is 657.9 kJ mol⁻¹.

From the above data, it is possible to calculate ring strain energy by subtracting the value 657.9 kJ mol⁻¹ from the figures in the table and multiplying by the number of CH₂ units in the rings. It can be seen that cyclopropane and cyclobutane are indeed strained, but cyclopentane is more strained than predicted by Baeyer's theory and for larger rings, there is

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no regular increase in strain. Furthermore, rings of more than 14 carbon atoms are actually strain-free.

The Nature of Ring Strain

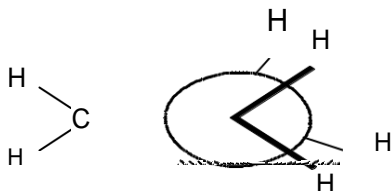
The complex picture presented above can be explained only by supposing that cycloalkane minimum-energy conformations result from the balancing of three kinds of strain:

Angle strain: It is the strain induced in a molecule when the bond angles are different from the ideal tetrahedral bond angle of 109.5° , i.e., the strain caused by distortion of bond angles.

Torsional strain – it is caused by repulsion between the bonding electrons of one substituent and the bonding electrons of a nearby substituent, i.e., the strain caused by eclipsing of bonds on adjacent atoms.

Steric strain – the strain caused by repulsive interactions when nonbonding atoms are too close to each other, i.e., it is caused by atoms or groups of atoms approaching each other too closely.

Cyclopropane and cyclobutane, with ring angles of 60° and 90° respectively, suffer from the most angle strain and even the two main conformers of cyclopentane have a small amount of angle strain. Apart from angle strain, the single planar conformer of cyclopropane has eclipsed C-H bonds, with maximum torsional strain:



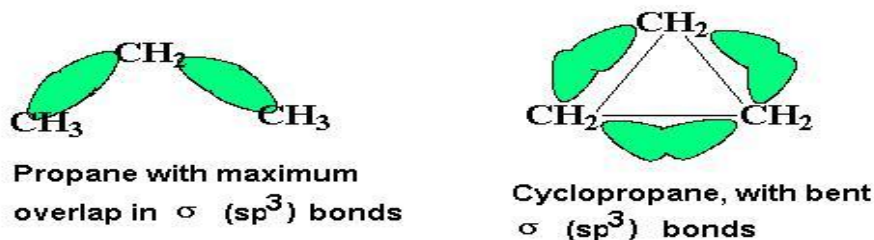
The larger rings can minimize torsional strain by adopting puckered (nonplanar) conformations.

Cyclopropane: an Orbital Picture of Ring Strain

In normal saturated compounds, the carbon atoms are sp^3 -hybridized, with C-C-C and H-C-H

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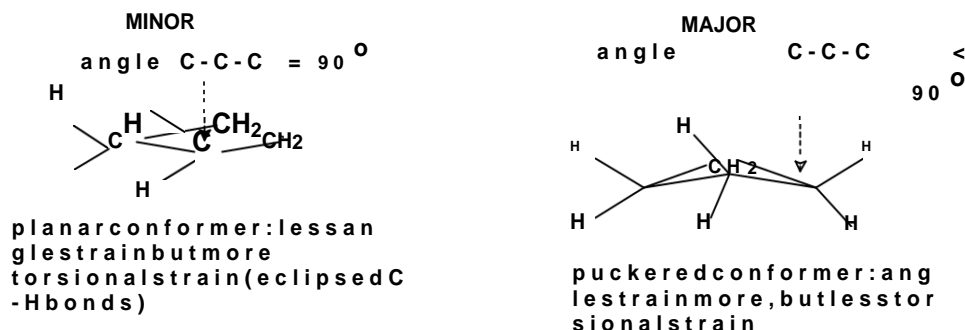
bond angles close to 109.5° . Overlap between the atomic orbitals involved in these bonds is a maximum.



In cyclopropane, the C-C-C bond angle cannot be 109.5° , so there is poor overlap making the C-C bonds weaker than in open chain equivalents.

The Conformations of Cyclobutane and Cyclopentane

Like cyclopropane, the planar conformation of cyclobutane has considerable bond strain and torsional strain and hence the more favorable conformer of cyclobutane is puckered, with one carbon atom laying some 25° out of the plane formed by the other three carbon atoms. This conformer has rather more angle strain but considerably less torsional strain, because the C-H bonds are not fully eclipsed.



A similar, but more complex situation arises in cyclopentane, the two puckered forms being (about equally) more favorable than the planar conformer. Generally cyclic alkanes found in nature have five or six-membered rings. On the other hand, compounds with three and four-membered rings are found much less frequently. This observation suggested that alkanes with five- and six-membered rings must be more stable than those with three- or four-membered rings. It was proposed that such instability could be explained on the bases of

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angle strain. Ideally, a sp^3 hybridized carbon has bond angles of 109.5° . As a result, stability of a cycloalkane may be predicted by determining how close the bond angle of a planar cycloalkane is to 109.5° . The angles of an equilateral triangle are 60° . Therefore, the bond angles in a planar cyclopropane are compressed from the ideal bond angle of 109.5° to 60° , a 49.5° deviation causing angle strain. As described earlier, normal sigma bond between two carbon atoms are formed by the overlap of two sp^3 orbitals that point directly at each other. In cyclopropane, overlapping orbitals cannot point directly at each other. Therefore, the orbital overlap is less effective than in a normal C-C bond. Hence, the less effective orbital overlap causes the C-C bond to be weaker and could be easily broken i.e. reactive.

For example, cyclopropane could be readily hydrogenated to propane. Because the C-C bonding orbitals in cyclopropane cannot point directly at each other, they have shapes that resemble bananas and, consequently, are often called **banana bonds**. In addition to angle strain, three-membered rings have torsional strain as a result of the fact that all hydrogen atoms are eclipsed.

Similarly, the bond angles in planar cyclobutane would have to be compressed from 109.5° to 90° , the bond angle associated with a planar square. Planar cyclobutane would then be expected to have fewer angles strain than cyclopropane because the bond angles in cyclobutane are only 19.5° away from the ideal angle.

Considering angle strain as the only factor, it was predicted that cyclopentane be the most stable of cycloalkanes because its bond angles (108°) are closest to the ideal tetrahedral one. In addition, it may be predicted that cyclohexane, with bond angles of 120° , would be less stable.

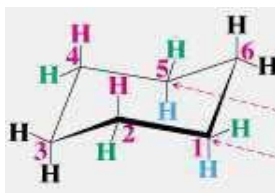
Cycloalkane	Strain Energy (kJ/mol)
Cyclobutane	110.9
Cyclopropane	114.2

In contrast to smaller rings, distortion from planarity in cyclohexane relieves both the angle and torsional strain of the planar structure. Once more, the internal angle in a planar hexagon

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is 120° , larger, not smaller, than the ideal sp^3 angle. Deviation from planarity will decrease both this angle and torsional strain from the six pairs of eclipsed hydrogens in planar model. This energy minimum cyclohexane is called the chair form. In the chair conformer of cyclohexane, all bond angles are 111° and all the adjacent bonds are staggered. Equatorial carbon-hydrogen bonds are parallel to the ring carbon-carbon bonds one bond away in chair cyclohexane. Axial carbon-hydrogen bonds are parallel and pointing either straight up or down in chair cyclohexane.

Equatorial carbon-hydrogen bonds are parallel to the ring carbon-carbon bonds one bond away in chair cyclohexane. Axial carbon-hydrogen bonds are parallel and pointing either straight up or down in chair cyclohexane. Cyclohexane rapidly interconverts between two stable chair conformations because of the ease of rotation about its C-C bonds. Such process is called ring flip. When the chair form interconverts, bonds that are equatorial in one chair conformer become axial in the other chair conformer and vice versa. Cyclohexane can also exist in a boat conformation similar to the chair conformer; the boat conformer is free of angle strain. However, the boat conformer is not as stable because some of its bonds are eclipsed, giving torsional strain to the molecule. In addition, the boat conformation is further destabilized by the close proximity of the “flagpole hydrogens” which causes steric strain.



Cyclohexane conformations:

Cyclohexane is one of the most important. If the carbons of a cyclohexane ring were placed at the corners of a regular planar hexagon, all the C-C-C bond angles would have to be 120° . Because the expected normal C-C-C bond angle should be near the tetrahedral value of 109.5° , the suggested planar configuration of cyclohexane would have angle strain at each of the carbons, and would correspond to less stable cyclohexane molecules than those with more normal bond angles. The actual normal value for the C-C-C bond angle of an open-

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chain $\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—}$ unit appears to be about 112.5° , which is 3° greater than the tetrahedral value. From this we can conclude that the angle strain at each carbon of a planar cyclohexane would be $(120^\circ - 112.5^\circ) = 1.5^\circ$. Angle strain is not the whole story with regard to the instability of the planar form, because in addition to having C-C-C bond angles different from their normal values, the planar structure also has its carbons and hydrogens in the unfavorable eclipsed arrangement, as shown in following figure.

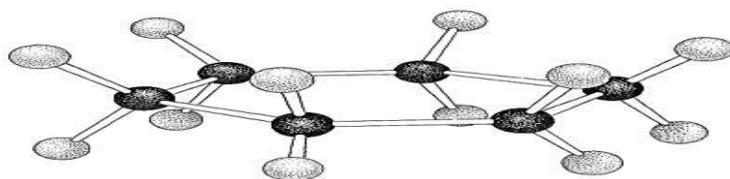
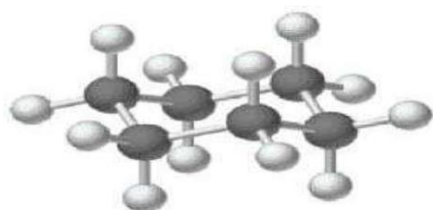
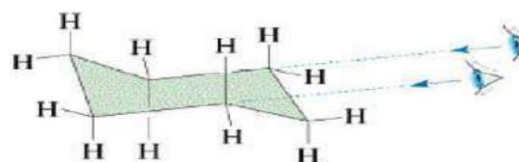


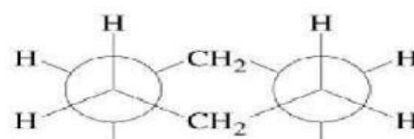
Fig: Cyclohexane in the strained planar configuration showing how the hydrogens become eclipsed



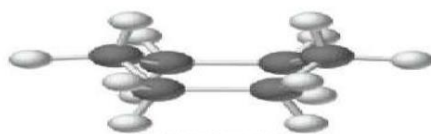
chair conformation of cyclohexane



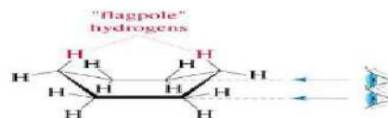
chair conformation



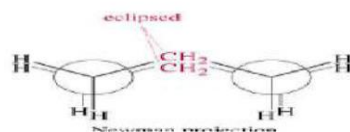
Newman projection



boat conformation of cyclohexane



symmetrical boat

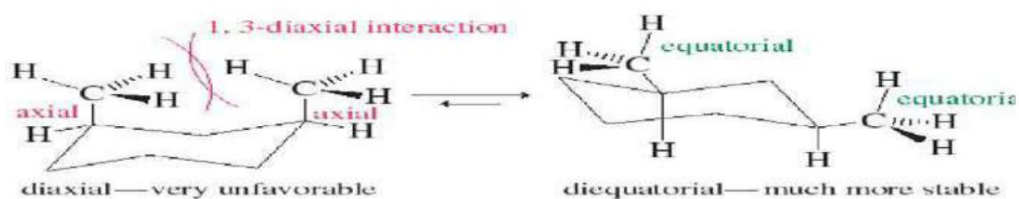
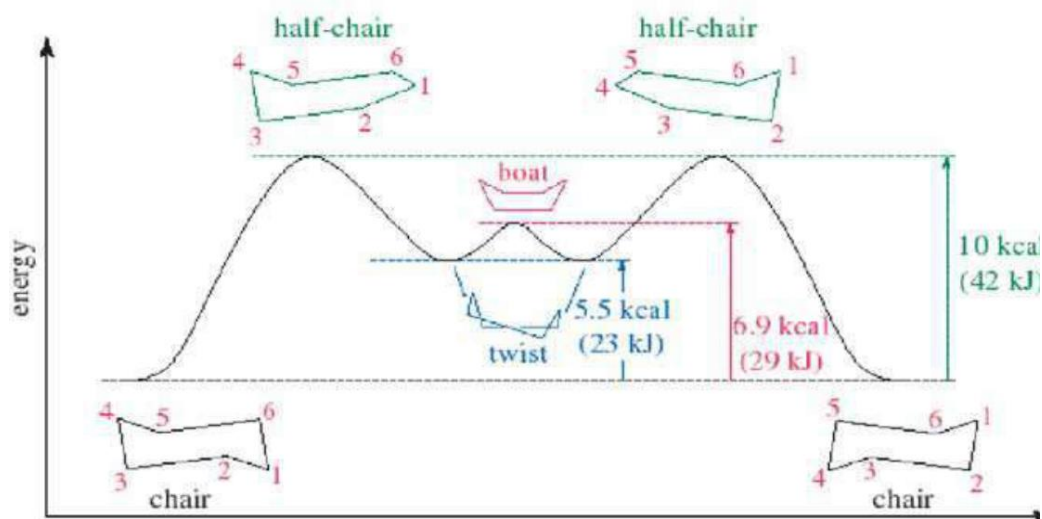


Newman projection



"twisted" boat

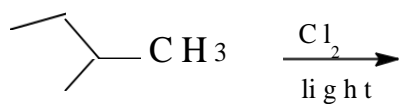
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Therefore the chair form is expected to be more stable than the boat form because it has less repulsion between the hydrogens.

7.6 TERMINAL QUESTION

1. Complete the following reaction:



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The structure of compound with molecular formula C_6H_{12} that has only 1^0 and 2^0 H atoms is :

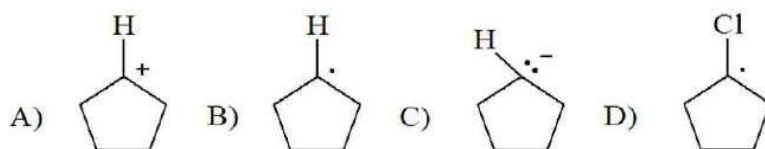
1- Methyl cyclo-pentane

1,1-Dimethyl cyclobutane

Cyclohexane

2-Methyl pent 2-ene

Which of the following is the key intermediate in the chlorination reaction below?



UNIT 8: ALKENES

CONTENTS:

- 8.1 Objectives
- 8.2 Introduction
- 8.3 Nomenclature of alkenes
- 8.4 Isomerism of alkenes
- 8.5 Methods of preparation
- 8.6 Physical properties of alkenes
- 8.7 Chemical reaction of alkenes
 - 8.7.1 Mechanism involved in hydrogenation
 - 8.7.2 Electrophilic and free radical addition
 - 8.7.3 Markownikoff's rule,
 - 8.7.4 Hydroboration oxidation,
 - 8.7.5 Oxymercuration reduction,
 - 8.7.6 Ozonolysis
 - 8.7.7 Oxidation with KMnO_4 and OsO_4
 - 8.7.8 Polymerization of alkenes
- 8.8 Industrial application of ethylene and propene
- 8.9 Summary
- 8.10 Terminal Question

8.1 OBJECTIVES

By the end of the course the student should be able to:

To name alkenes using proper IUPAC nomenclature.

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.

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Isomerism of alkenes.

Various methods of alkene preparation

Physical and chemical properties of alkene

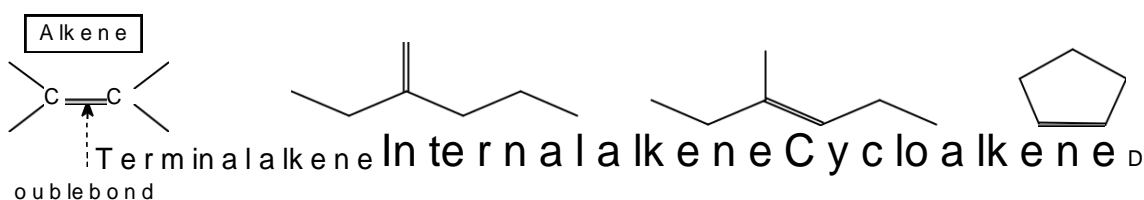
Draw the major product of the addition reaction of an alkene with diborane followed by basic hydrogen peroxide.

Use Markovnikov's rule 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

8.2 INTRODUCTION

An alkene in organic chemistry is an unsaturated acyclic hydrocarbon containing at least one carbon to carbon double bond. The simplest alkenes, with only one double bond, form a homologous series, *the alkenes* with general formula C_nH_{2n} . A double bond is a σ bond and a π bond. A π bond is weaker than a σ bond and hence more reactive than σ bonds. Due to this, π bonds are considered to be a functional group. Alkenes are also called olefins (from Greek: 'oil-formers') and vinyl compounds. Terminal alkenes have the double bond at the end of the carbon chain (on a terminal carbon), whereas internal alkenes have the double bond on non-terminal carbon atoms.

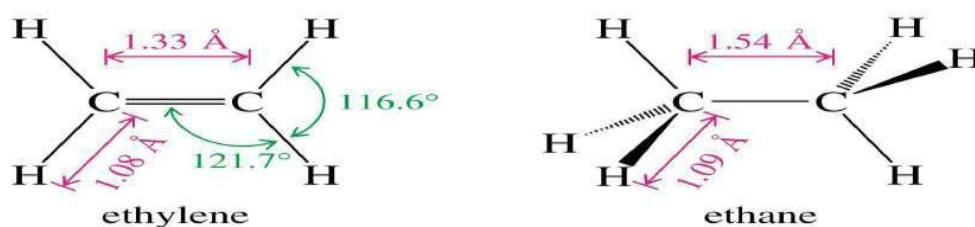


8.2.1 Structure of Alkenes:

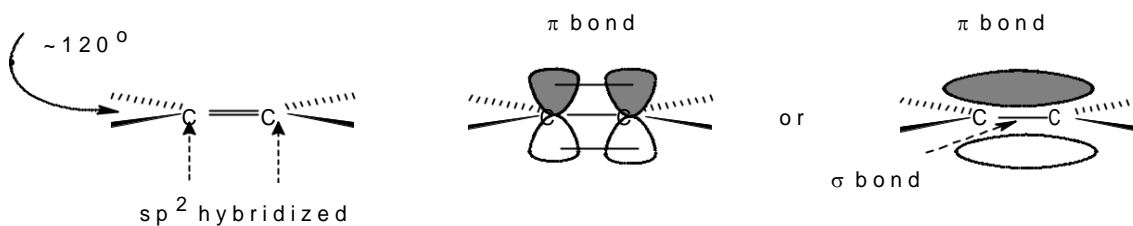
In alkenes the bond angles about each carbon in a double bond are about 120° . Both carbons

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are sp^2 hybridized and so the geometry of an alkene double bond is based on a trigonal plane. The alkene double bond is stronger than a single covalent bond and also shorter with an average bond length of 133 picometer. The C-H bonds are formed by overlap of sp^2 orbitals from the carbon overlapping with $1s$ orbital from the Hydrogen. The ethene C-H bonds contain more s character than the ethane C-H bonds and are therefore shorter and stronger. sp^2 has $1/3$ s , whereas sp^3 $1/4$ s character. s orbitals are closer to the nucleus and lower in energy. The carbon-carbon bond in ethene is shorter and stronger than in ethane partly because of the sp^2 - sp^2 overlap being stronger than sp^3 - sp^3 , but especially because of the extra bond in ethene.



The π bond exists with half its electron density above the σ bond, and half below. The unhybridized $2p$ atomic orbitals, which lie perpendicular to the plane created by the axes of the three sp^2 hybrid orbitals, combine to form the pi bond.



8.3 NOMENCLATURE OF ALKENE

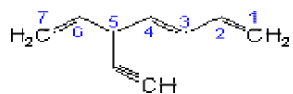
According to IUPAC nomenclature, alkenes are identified by the suffix *-ene*. Number the chain beginning at the end closest to the double bond so that the double bond will have the lowest carbon number.

Name branched or substituted alkenes in a manner similar to alkanes.

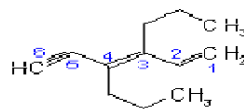
Number the carbon atoms, locate and name substituent groups, locate the double bond, and name the main chain.

Cis and *trans* isomers must be designated by the appropriate *cis-* or *trans-* prefix.

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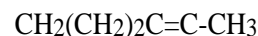
5-Ethynyl-1,3,6-heptatriene



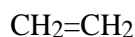
3,4-Dipropyl-1,3-hexadien-5-yne



1-octene



2-hexene



Ethene



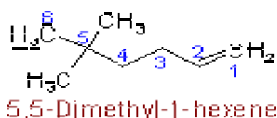
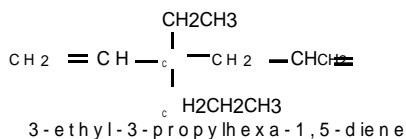
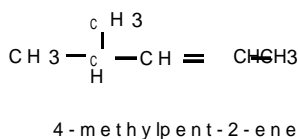
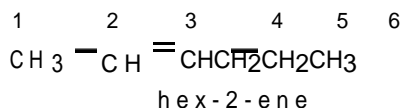
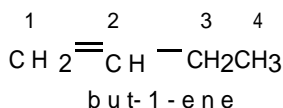
Propene



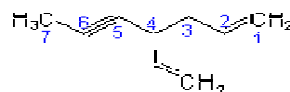
2-Methylpropene



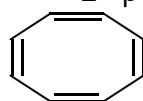
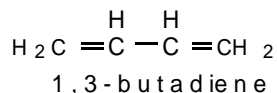
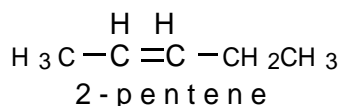
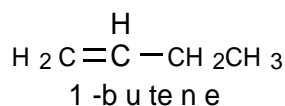
1-Hexene



5,5-Dimethyl-1-hexene



4-Vinyl-1-hepten-5-yne



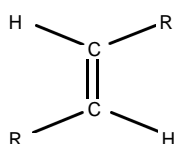
1,3,5,7-cyclooctatetraene

Compounds with two double bonds are called dienes, three double bonds are trienes, etc. For branches, each alkyl group is given a number, but the double bond is still given preference when numbering the chain.

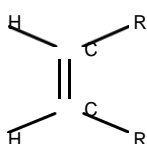
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8.4 ISOMERISM OF ALKENE

The geometry of the C=C bond is determined by the π -bond. The rotation about the carbon-carbon double bond is very difficult and therefore severely restricted. As a consequence substituted alkenes exist as one of two isomers called a cis isomer and a trans isomer. When similar 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. cis-trans isomerism to occur there must be a double bond and two different groups on each of the double bonded carbon atoms. E-Z and cis-trans are different terms for the same type of isomerism.

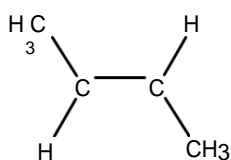


E- isomer

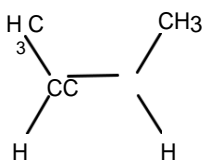


Z- isomer

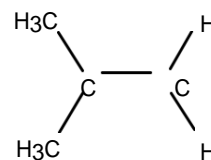
e.g., isomers of butene



trans- but-2-ene



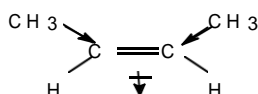
cis- but-2-ene



2-methylpropene

The cis and trans isomers will be chemically very similar, though not quite identical, and will have slightly different melting and boiling points.

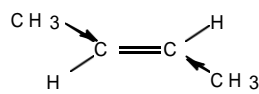
cis-2-Butene



Small net dipole

B.p. 4°C

trans-2-Butene

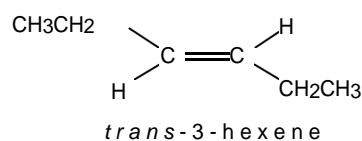
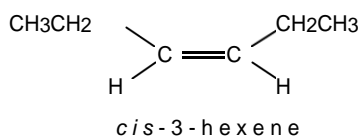


Zero net dipole

B.p. 1°C

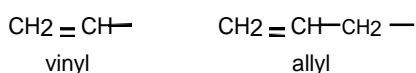
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In general, a cis alkene is more polar than a trans alkene, giving it a slightly higher b.p. and making it somewhat more soluble in polar solvents.



Common Names

Important groups derived from alkenes.



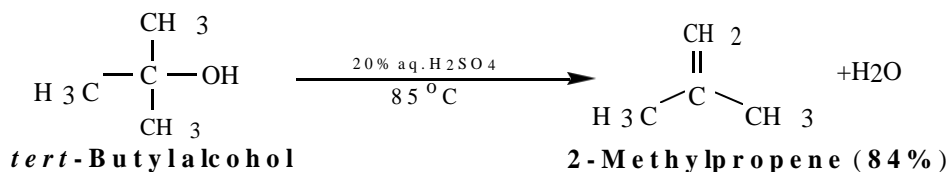
8.5 METHODS OF PREPERATION

8.5.1 Dehydration of Alcohols:

Dehydration is a process of removal of the H₂O from a substrate molecule. When heated with strong acids catalysts (most commonly H₂SO₄, H₃PO₄), alcohols typically undergo a 1, 2-elimination reactions to generate an alkene and water. The more stable alkene is the major product; this product may arise from the rearrangement of the original carbon skeleton.

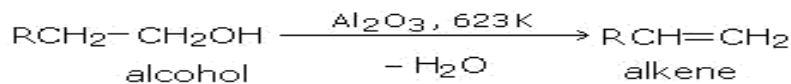


Tertiary alcohols are usually dehydrated under extremely mild conditions:

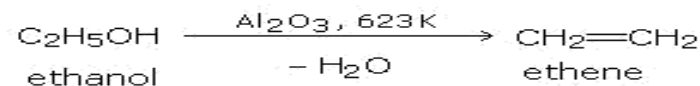


The dehydration of alcohols can also be takes place by passing the vapors of an alcohol over heated alumina(Al₂O₃) at 623K (350°C).

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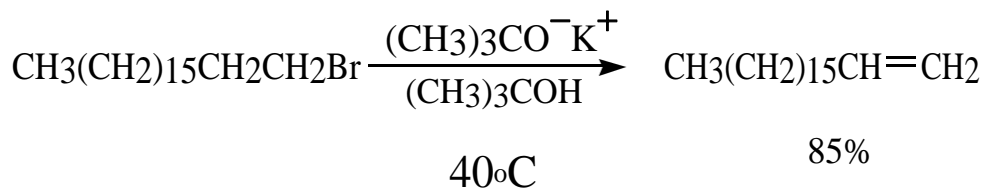
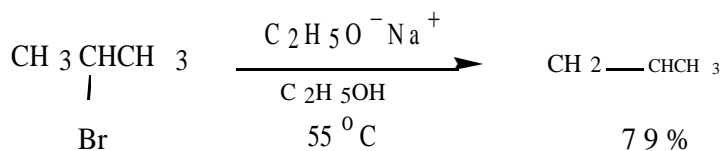
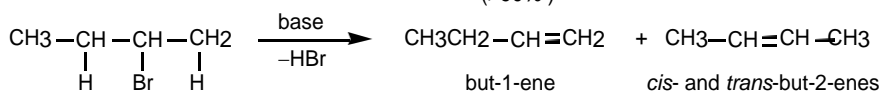
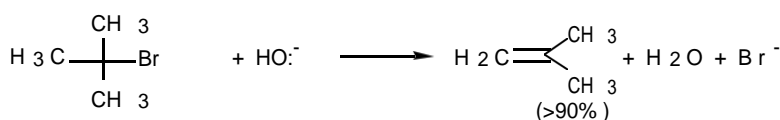
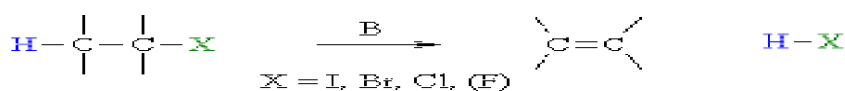
For example,



The order of the ease of dehydration of alcohols is, tertiary > secondary > primary.

8.5.2 Dehydrohalogenation of Alkyl Halides:

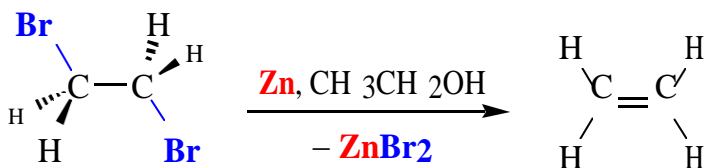
Dehydrohalogenation is the removal of a halogen atom and a hydrogen atom from adjacent carbons. When heated with strong bases (sodium or potassium hydroxides or alkoxides) in alcohol, alkyl halides typically undergo a 1,2-elimination reactions to generate alkenes. Regioselectivity is usually controlled by the relative stability of the product alkenes. The most stable alkene is usually the major product if more than one product is possible.



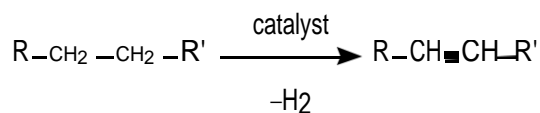
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8.5.3 Reduction of Vicinal Dibromides:

The action of zinc metal in acetic acid on vicinal dibromides to produce alkenes is elimination, a reduction and a dehalogenation reaction.



8.5.4 Dehydrogenation of alkanes:



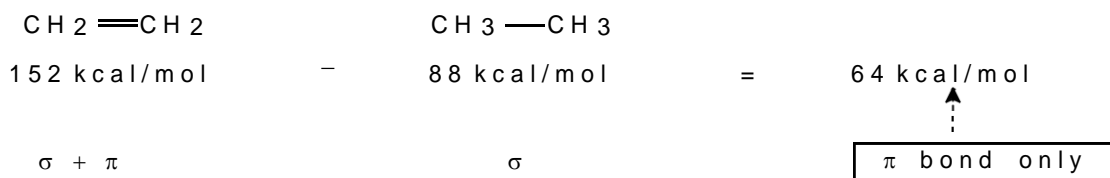
8.6 PHYSICAL PROPERTIES OF ALKENE

The physical properties of alkenes are comparable with alkanes. The physical state depends on molecular mass. The simplest alkenes, ethylene, propylene and butylene are gases. Like the alkanes, alkenes are nonpolar; insoluble in water; soluble in non polar organic solvents; less dense than water, flammable and nontoxic. Most alkenes, like alkanes exhibit only weak van der Waals interactions, so their physical properties are similar to alkanes of similar molecular weight. Alkenes have low melting points (m.p.) and boiling points (b.p.). M.p. and b.p. increase as the number of carbons increases because of increased surface area.

8.7 CHEMICAL REACTION OF ALKENE

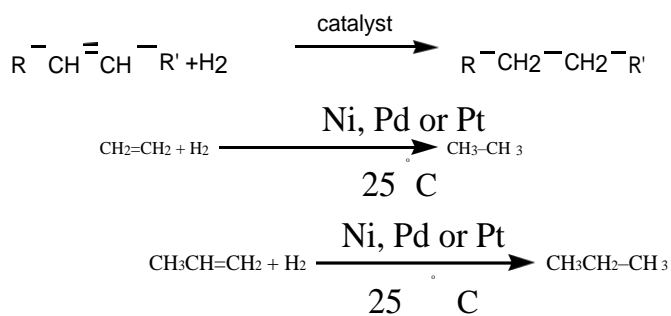
The alkenes are more reactive than the alkanes because of the C=C bond. . The carbon-carbon double bond consists of a strong sigma bond and a weak pi bond. The typical reactions of alkenes involve the breaking of this weaker pi bond and formation of two new sigma bonds. Because of the presence of the multiple bonds, characteristic reactions are the electrophilic additions. It is possible for the double bond to break, allowing each carbon to form a new bond, which is often energetically favourable.

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8.7.1 Hydrogenation:

In the presence of finely divided metals like Ni, Pt, Pd, Rh, and Ru, addition of a hydrogen molecule takes place on alkene at room temperature. When the catalyst is in a different physical state to the other reactants it is called heterogeneous catalysis (E.g. a solid catalyst with a liquid and a gas). In contrast a liquid catalyst in a reaction solution is an example of homogeneous catalysis (acid catalyzed alcohol dehydration). During catalytic hydrogenation, the hydrogen adsorbs onto the surface of the metal catalyst, and they add *syn* to the double bond. One face of the π system binds to the catalyst, then the bound hydrogen inserts into the bond, and the product is liberated from the catalyst. This is a *syn* addition reaction, i.e., both hydrogen atoms attack from the same side of the molecule.

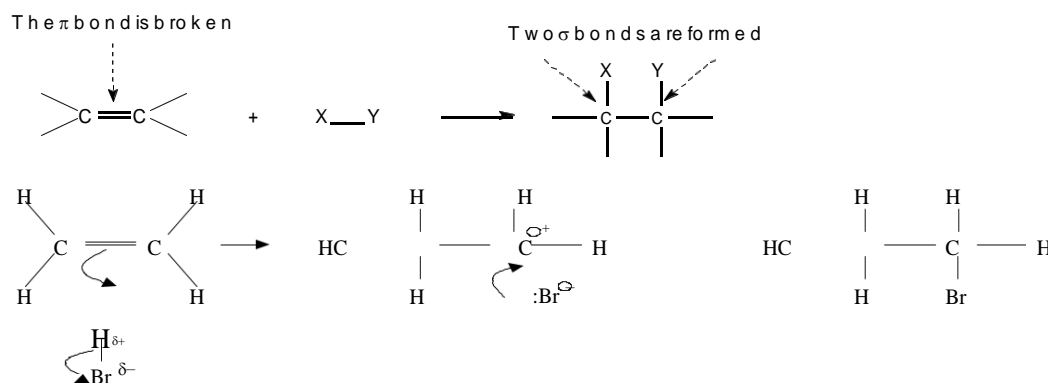


Finely divided metals activate molecular hydrogen and the hydrogen atoms add to the double bond. This is usually a *syn* addition, i.e., both hydrogen atoms attack from the same side of the molecule.

8.7.2 Electrophilic Addition. The most common chemical transformation of a carbon-carbon double bond is the addition reaction. The characteristic reaction of alkenes is electrophilic addition, because the π bond is both weak and electron rich (nucleophilic). An important feature of alkene reactivity is an ability to react with a variety of *electrophilic reagents*, those reagents attracted to the source of extra electron density. In an alkene, pi

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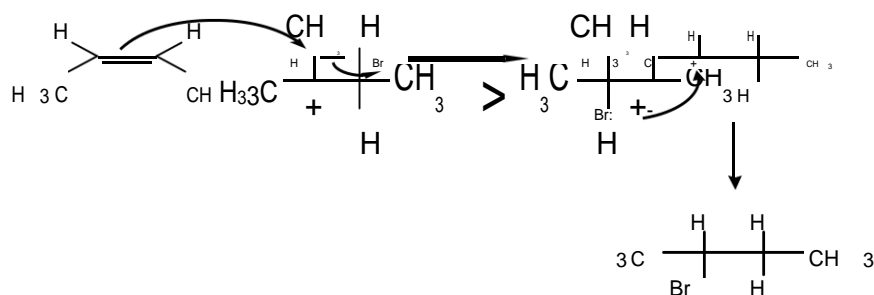
bond serves as a source of electron. An **electrophile** will attract pi electrons, and can pull them away to form a new bond. This leaves one carbon with only 3 bonds and a +ve charge (carbocation). The double bond acts as a **nucleophile** (attacks the electrophile). In most cases, the cation produced will react with another nucleophile to produce the final overall electrophilic addition product. Electrophilic addition is probably the most common reaction of alkenes.



The alkene abstracts a **proton** from the HBr, and a carbocation and bromide ions are generated.

The bromide ion quickly attacks the cationic center and yields the final product. In the final product, H-Br has been added across the double bond.

Consider the addition of H-Br to 2-methyl-2-butene:

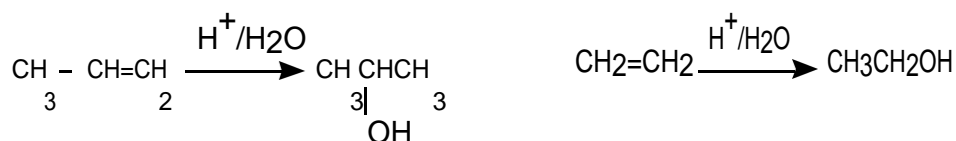


There are two possible products arising from the two different ways of adding H-Br across the double bond. But only one is observed. The observed product is the one resulting from the more stable carbocation intermediate.

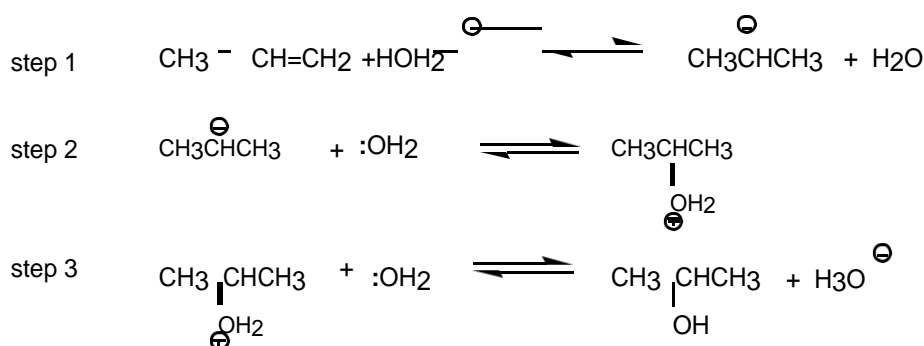
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Tertiary carbocations are more stable than secondary. The protonation occurs at the least highly substituted end so that the cation produced is at the most highly substituted end (and therefore more stable).

The acid-catalyzed process is a convenient method for the preparation of secondary and tertiary alcohols. The reaction is usually regioselective and follows *Markovnikov's rule*.



Mechanism:

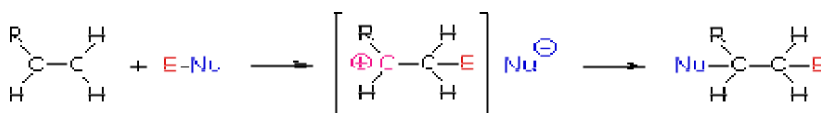


8.7.3 Markovnikov's Rule : After studying many addition reactions of unsymmetrical alkene, the Russian chemist Vladimir Markovnikov in 1869 noticed a trend in the structure of the favored addition product and formulated a rule. According to this rule “ The addition of a halogen acid to the double bond of an unsymmetrical alkene results in a product with the acid hydrogen bound to the carbon atom that already has the greater number of hydrogens attached.” Reactions that give such products are said to have Markovnikov orientation, and are Markovnikov products. The electrophilic addition of HBr is said to be **regiospecific**, since it only gives one orientation of addition.

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The regioselectivity of the above reactions may be explained by the same mechanism we used to rationalize the Markovnikov rule. Thus, bonding of an electrophilic species to the double bond of an alkene should result in preferential formation of the more stable (more highly substituted) carbocation, and this intermediate should then combine rapidly with a nucleophilic species to produce the addition product. This is illustrated by the following equation.



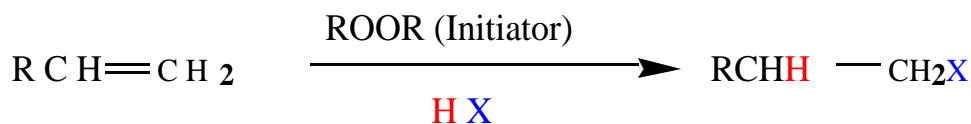
Free Radical addition to Alkenes: It is possible to obtain anti-Markovnikov products when HBr is added to alkenes in the presence of free radical initiators like peroxide. The free radical initiators change the mechanism of addition from electrophilic addition to free radical addition. This change of mechanism gives rise to the opposite regiochemistry.

Initiation: The oxygen-oxygen bond is weak, and is easily homolytically cleaved to generate two alkoxy radicals by thermal or light energy. The resulting alkoxy radical then abstracts a hydrogen atom from HX in a strongly exothermic reaction. Once a halogen atom is formed it adds to the π -bond of the alkene in the first step of a chain reaction. This addition is regioselective, giving the more stable carbon radical as an intermediate.

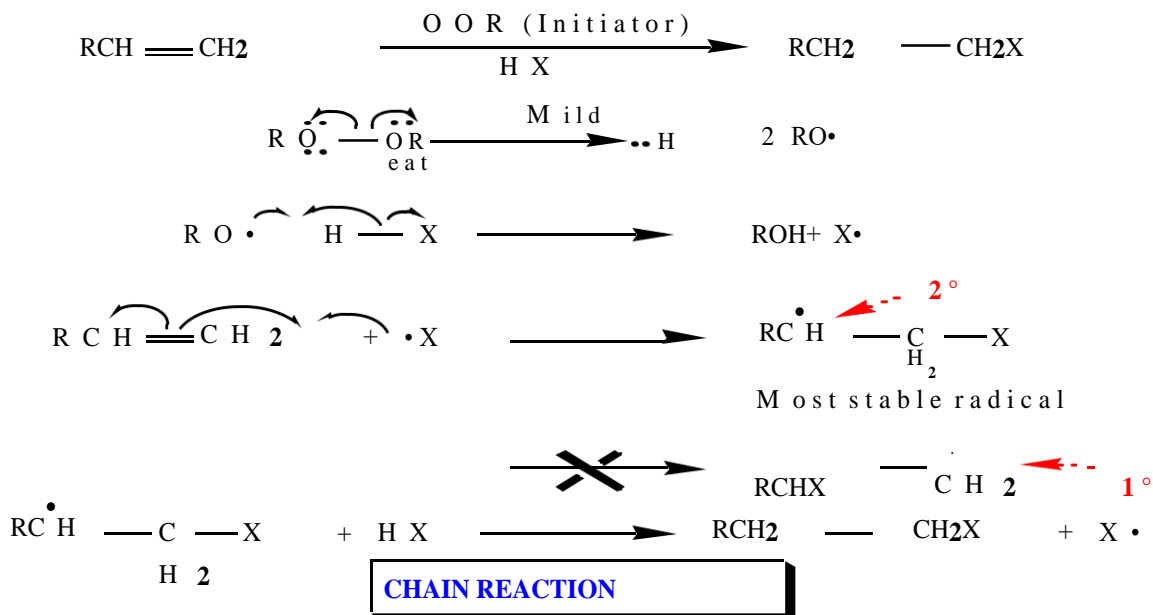
Propagation:

The halogen radical is electron deficient and electrophilic. The radical adds to the double bond, generating a carbon centered radical. This radical then abstracts hydrogen from a molecule of H-X, giving the product, and another halogen radical (Chain process). Each of the steps in this chain reaction is exothermic, so once started the process continues until radicals are lost to termination events. The orientation of this reaction is anti Markovnikov. The reversal of regiochemistry through the use of peroxides is called the **peroxide effect**.

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Tertiary radicals are more stable than secondary radicals. The reaction goes through the most stable intermediate



8.7.4 Hydroboration of Alkenes:

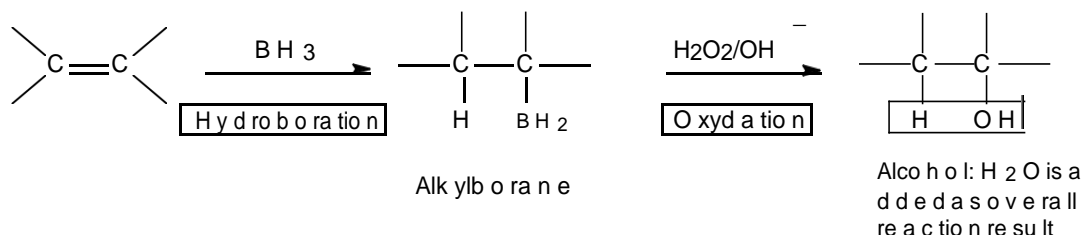
Alkenes are capable of adding diborane to yield alkylboranes. Diborane is the dimer of a hypothetical borane, BH_3 . Borane has only six valence electrons and is very electron deficient. BH_3 act as a Lewis acid and can bond to the pi-electrons of a double, i.e., borane act as an electrophilic molecule, and reacts with double bonds in a one step process to generate an alkylborane. Intermediate alkylborane is not isolated but is oxidized with alkaline H_2O_2 to yield an alcohol. This is one of the most useful methods of preparing alcohols from alkenes.

Mechanism:

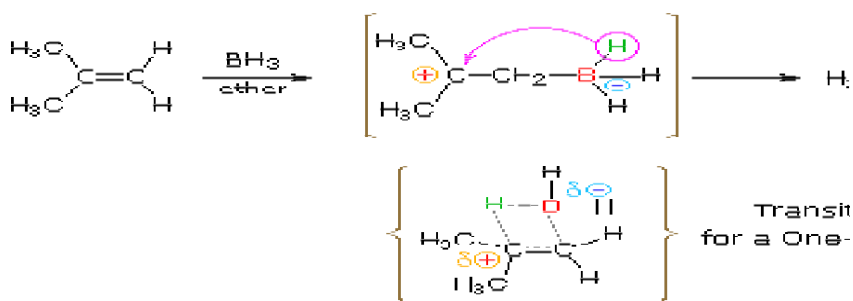
Hydroboration-oxidation is a two-step reaction sequence that converts an alkene to an alcohol. Borane adds to alkenes with anti-Markovnikov orientation. The BH_2 fragment will be directed onto the least substituted carbon and the hydride onto the most substituted carbon. In the final product the hydroxy group will replace the BH_2 group giving rise to an

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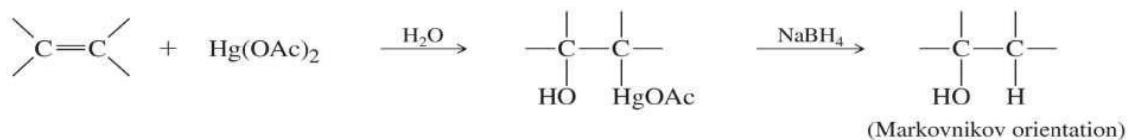
overall anti-Markovnikov addition of H₂O to an alkene. Thus, the reaction is regioselective since it represents an overall syn-addition to the double bond. The overall result of hydroboration-oxidation is the syn addition of the elements of H and OH to a double bond.



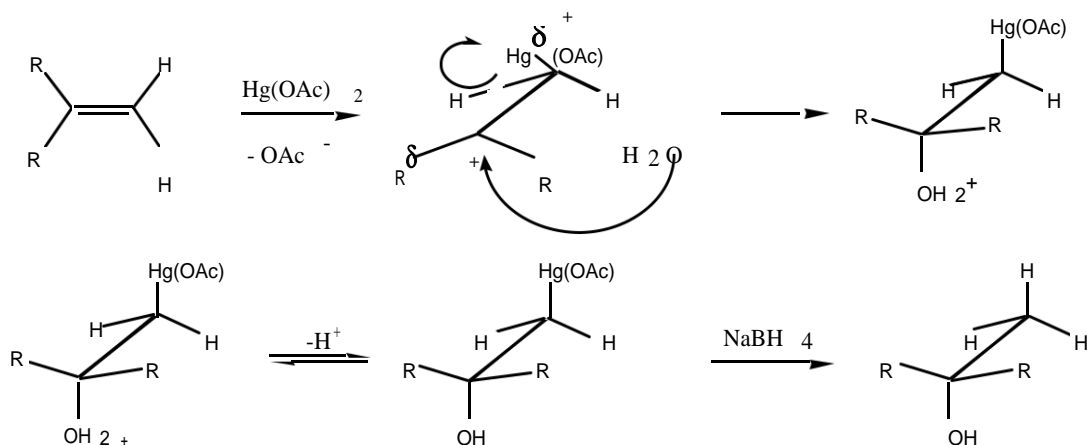
The di- and tri-alkyl boranes behave just as the alkylboranes, but for simplicity they are often written as mono alkylboranes.



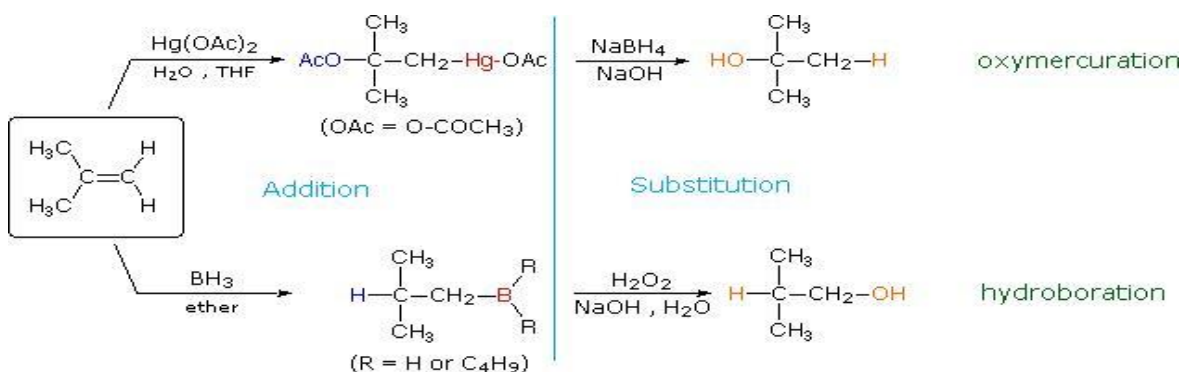
8.7.5. Oxymercuration-Demercuration: This is another alternative for converting alkenes to alcohols with Markovnikov orientation. This method has the advantage of not involving free carbocationic species, and thus removes the possibility of rearrangements. The reagent is called mercuric acetate, and is usually abbreviated to Hg(OAc)₂. In solution it ionizes into acetate ion and a positively charged mercury species which is very electrophilic and attack on a alkene double bond, giving a 3 membered ring compound called a mercurinium ion.



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When water is present, the nucleophilic oxygen will open the mercurinium ring, and generate an organomercurial alcohol. Demercuration is the removal of the mercury containing species, which is achieved by reaction with sodium borohydride, a powerful reducing agent, which replaces the mercury species with a hydrogen atom – giving the desired alcohol. The opening of the mercurinium ion proceeds in the Markovnikov fashion, with the incoming H (this time as a *hydride*) being placed on the least substituted carbon. The reaction is *regioselective* since the water nucleophile will attack the carbon with positive charge since it represents an overall anti-addition H and OH groups to the double bond. Oxymercuration-demercuration also gives Markovnikov orientation of the alcohol. The electrophile $^+\text{HgOAc}$ remains bound to the less highly substituted carbon.

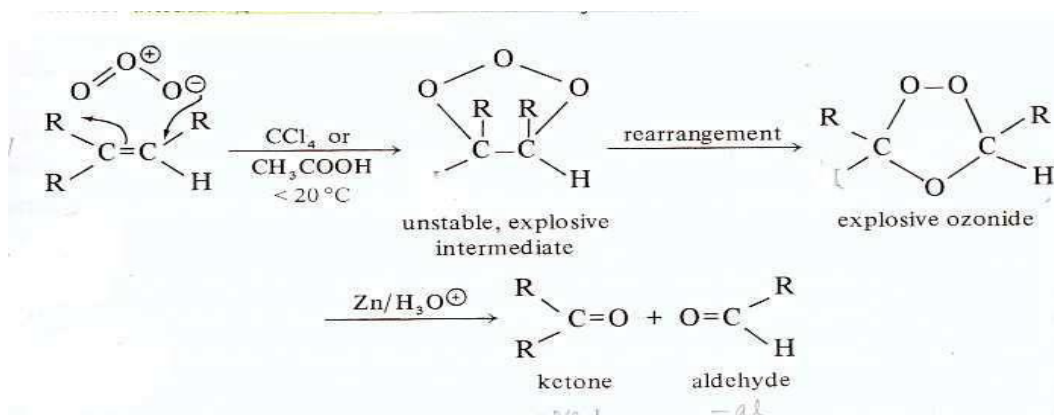


8.7.6 Ozonolysis:

Ozone, O_3 , is highly reactive electrophile. Ozone adds to carbon-carbon double bonds forming a number of intermediates the most important of which is ozonide. Reactive ozonide is reduced

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by zinc in the presence of water to give aldehydes or ketones depending on the degree of substitution of the double bond. Each double bond yields two fragments if it is substituted asymmetrically. Both acyclic and cyclic alkenes are subject to degradative ozonolysis.



After reduction step of ozonolysis:

an alkene with an unsubstituted carbon atom yields formaldehyde

an alkene with a monosubstituted carbon atom yields an aldehyde

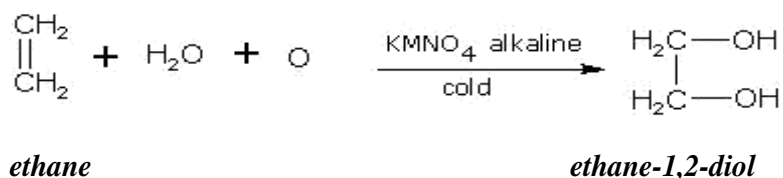
an alkene with a disubstituted carbon atom yields a ketone

Hence these reactions can be useful for the characterisation of molecules of unknown structure which contain carbon-carbon double bonds. The position of the double bond is clearly determined by ozonolysis method.

8.7.7 Oxidation with KMnO₄ and OsO₄

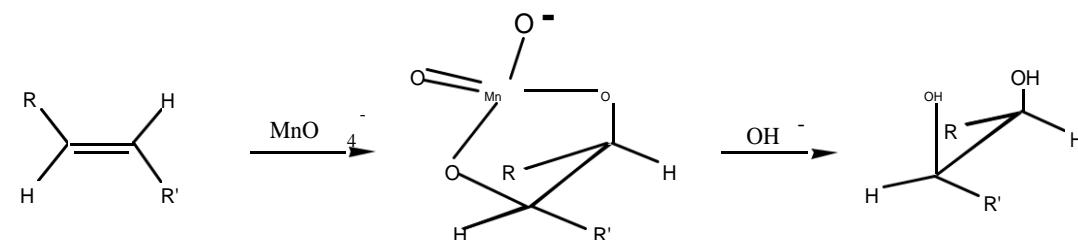
When alkenes are oxidised with cold, alkaline KMnO₄, dihydroxy compounds (diols or glycols) are obtained. The KMnO₄ gets decolourised. This reaction is therefore, used as Bayer's test for unsaturation (the presence of double or triple bonds) in any molecule.

e.g., Ethene gives ethane-1,2-diol.

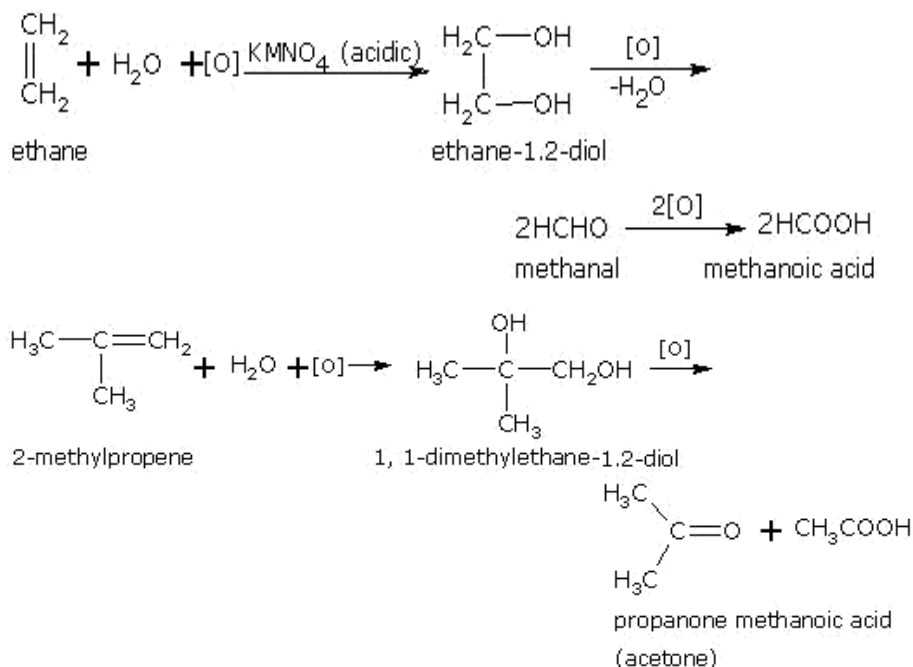


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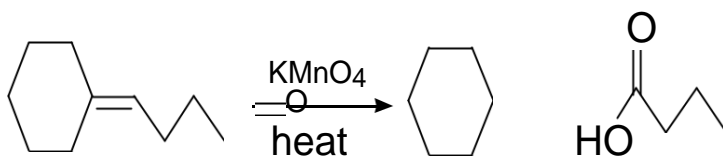
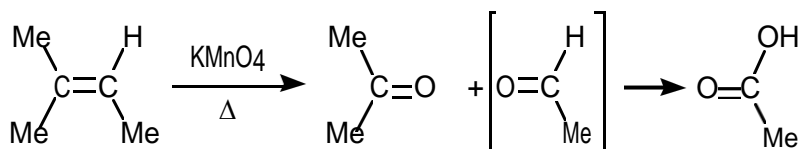
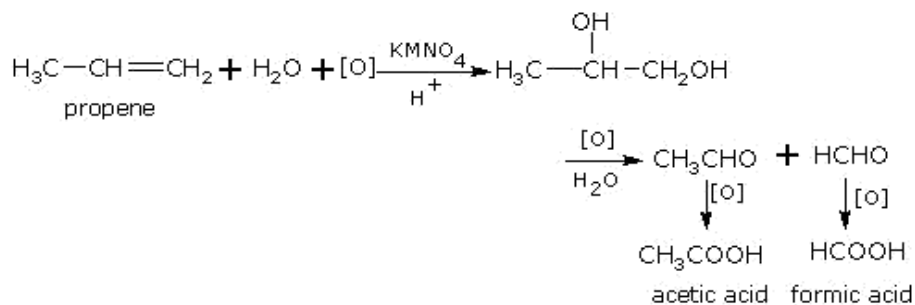
In basic solution the purple permanganate anion is reduced to the green manganate ion, providing a nice colour test for the double bond functional group. Permanganate and osmium tetroxide have similar configurations, in which the metal atom occupies the center of a tetrahedral grouping of negatively charged oxygen atoms. The reaction involves formation of the cyclic oxomanganese intermediate that is subsequently hydrolyzed in alkaline medium to give the desired product. Note that the reaction represents a syn-addition pathway and is a diastereoselective and stereospecific route to diols.



With Acidified potassium permanganate (or potassium dichromate) oxidises the dihydroxy compound so produced in reaction to ketone or carboxylic acid. For example,



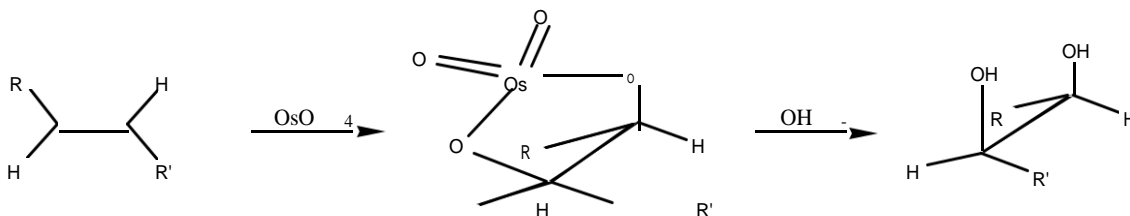
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The purpose of this reagent is to replace the double bond with two oxygen atoms.

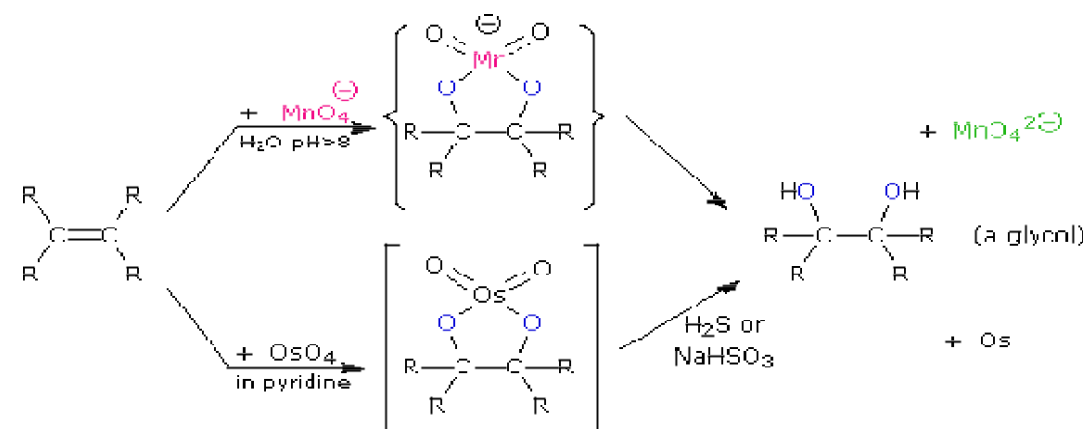
Therefore, one may expect to see two types of products: aldehydes and ketones. Hot KMnO₄ is a vigorous oxidizer. As the result, the oxidation is carried out further with aldehydes being oxidized to carboxylic acids and formaldehyde (CH₂O) to CO₂ and water. Ketones are resistant to oxidation and are therefore found as products under these conditions. Both acyclic and cyclic alkenes are subject to degradative ozonolysis.

Alkenes will also react with OsO₄ to form diols. The reaction involves formation of the cyclic osmate ester intermediate subsequently hydrolyzed in alkaline medium to give the desired product. The reaction represents a syn-addition pathway and is a diastereoselective and stereospecific route to diols.



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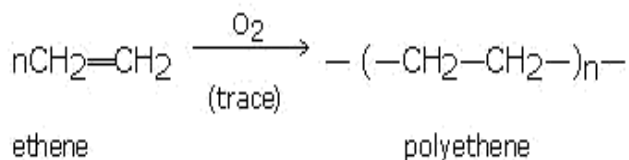
This reaction proceeds via a concerted electrophilic addition generating an osmate ester, which is hydrolyzed to a syn diol by hydrogen peroxide, which also reoxidizes the osmium catalyst. The two C-O bonds are formed at the same time with the cyclic ester, and the oxygen atoms are added at the same face of the π bond – syn orientation.



8.7.8 Polymerisation of alkenes

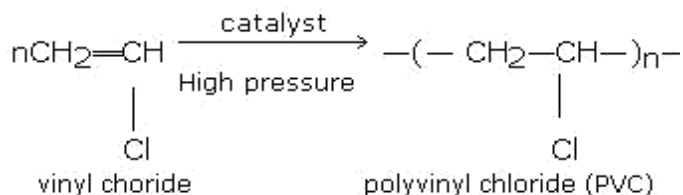
The process when monomer units are linked together to form polymeric material without the loss of material is called addition or chain-growth polymerization. The products, the addition or chain-growth polymers, are made of alkenes or substituted alkenes to produce polyethylene, polypropylene, polyisobutylene, polystyrene, polyvinyl chloride (PVC), polymethylmethacrylates, polyacrylonitriles, polytetrafluoroethylene (Teflon). Polymerization occurs in a stepwise manner through reactive intermediates. Polymerization can either proceed via a free-radical or an ionic mechanism.

When ethene is heated at high temperature under high pressure in presence of oxygen, we get polyethene

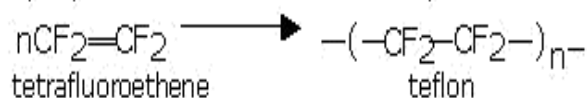


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Similarly, when vinyl chloride is polymerized in the presence of peroxide catalyst, it forms polyvinyl chloride (PVC)



Teflon is a polymer of tetrafluoroethene,



Polymerization of **alkenes** is an economically important reaction which yields polymers of high industrial value, such as the plastics polyethylene and polypropylene.

Polymerization of monomer vinyl chloride to form polymer polyvinyl chloride (PVC).

Polymerization of monomer styrene form polymer polystyrene.

8.8 INDUSTRIAL APPLICATION OF ETHYLENE AND PROPENE

Ethylene has following main industrial uses:

Ethene is used to accelerate the ripening of fruits and is most commonly used on bananas and also on citrus fruits. The ethene allows the fruit to mature in colour and ripen. This process takes place over a few days, and the more ethene that is used, the faster the fruit will ripen.

The other use of ethene is in the manufacture of plastics, such as packing films, wire coatings, and squeeze bottles.

Alkenes are useful intermediates in organic synthesis, but their main commercial use is as precursors (monomers) for polymers.

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8.9 SUMMARY

The major characteristics of the addition reactions covered in this chapter are summarized in the table below.

Reagent	Product	Mechanism	Regioselectivity	Stereochemistry
HX	Alkyl halide	2 step <i>via</i> rate-determining formation of R^+ . Rearrangements possible	Markovnikov	Syn and anti addition
H ₂ O	Alcohol	As above	As above	As above
X ₂ /H ₂ O	Halohydrin (2-haloalcohol)	3 steps, similar to halogenations	but Markovnikov: to X^+ bonds to less substituted C.	Anti addition
BH ₃ (or equivalent), then H ₂ O ₂ /OH ⁻	Alcohol	2 steps: one-step hydroboration, then oxidation. No rearrangements	Anti-Markovnikov	Syn addition in hydroboration step; retention of configuration in oxidation step

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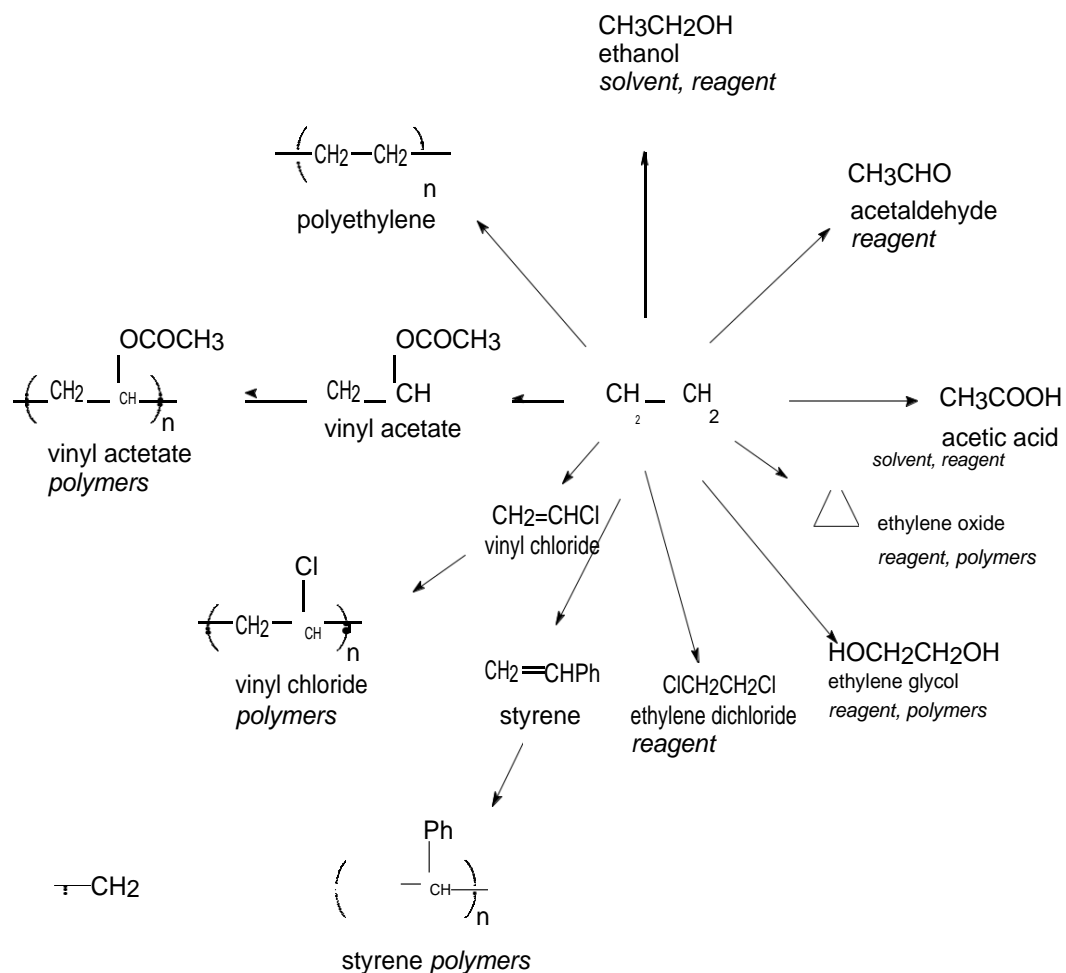
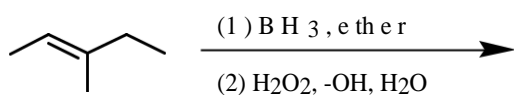
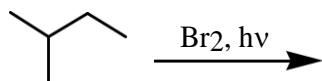


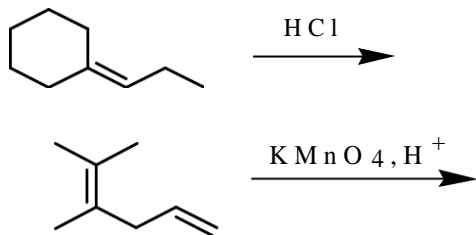
Fig: Summary of Reactions of Alkenes

8.10 TERMINAL QUESTIONS

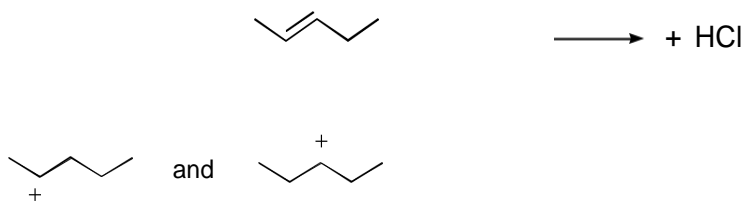
Provide the major product for each of the following reactions, showing stereochemistry where appropriate.



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(b) The intermediate of the following reaction



What are the possible products when 2-chloro-2-methylbutane

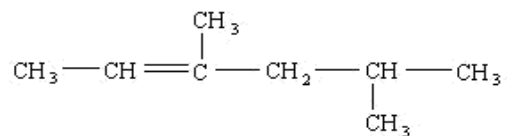
is reacted with:

aqueous potassium hydroxide

a solution of potassium hydroxide in ethanol

a solution of sodium ethoxide in ethanol?

Name the following compound.



(e) Name the straight-chain constitutional and stereoisomers of butene (C_4H_8).

UNIT 9: CYCLOALKENE

CONTENTS:

- 9.1 Objectives
- 9.2 Introduction
- 9.3 Objectives
- 9.4 Methods of formation
- 9.5 Conformation
- 9.6 Chemical reactions of cycloalkenes.
- 9.7 Summary
- 9.8 Terminal Question

9.1 OBJECTIVES

By the end of the course the student should be able to:

Recognize the cyclic hydrocarbon families, functionally substituted derivatives of cycloalkenes

Give the IUPAC names of the branched and unbranched cycloalkenes.

Know the methods of formation of cycloalkene.

Know the chemical reaction of cycloalkene.

9.2 INTRODUCTION

A hydrocarbon that contains carbon atoms joined to form a ring with double bond is called cycloalkene. The only difference in reactivity or energetics from acyclic systems occurs when there is significant ring strain in the cycloalkene.

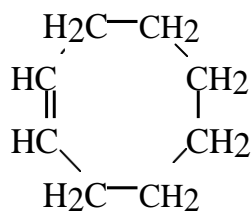
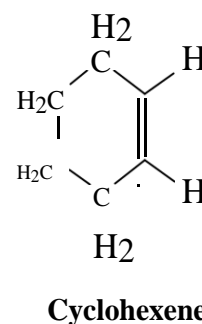
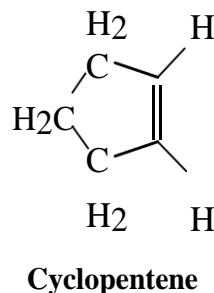
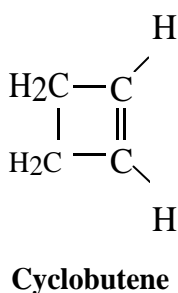
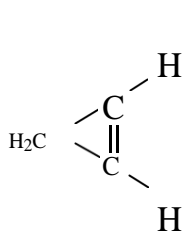
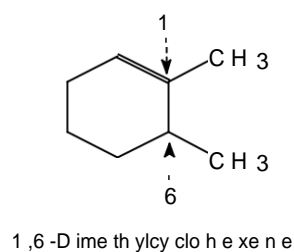
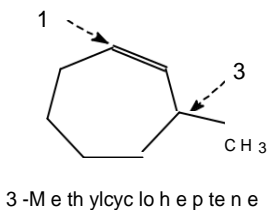
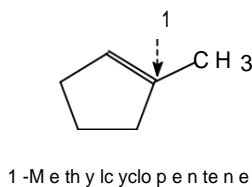
9.3 NOMENCLATURE

In naming cycloalkenes, the double bond is located between C-1 and C-2 and the "1" is usually omitted in the name. The ring is numbered clockwise or counterclockwise to give the

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first substituent the lowest number.

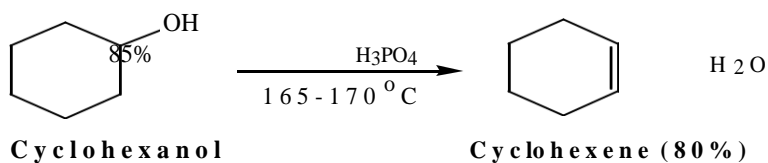
Examples:



9.4 METHOD OF FORMATION

9.4.1 From cyclic alcohol:

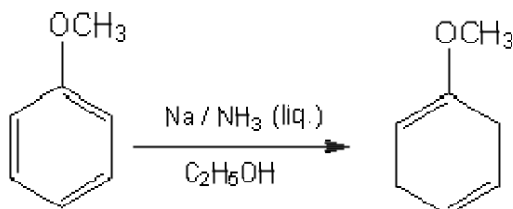
Secondary alcohols usually dehydrate under milder conditions: The loss of water from a cyclic alcohol gives a cycloalkene.



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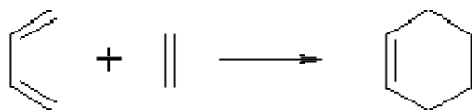
9.4.2 By Birch reduction:

The 1,4-reduction of aromatic compounds to the corresponding unconjugated cyclohexadienes by alkali metals dissolved in liquid ammonia in the presence of an alcohol is called *Birch* reduction. The reaction proceeds *via* a one-electron transition mechanism.



9.4.3 By Diels-Alder reaction:

The cycloaddition of a conjugated diene and an alkene leads to a cycloalkene. In this reaction, participating bonds are broken and new bonds are simultaneously formed.



9.4.4 By Electrocyclic reaction: Conjugated double-bond systems can be cyclized in a reversible reaction either by heating or using photolysis and form cycloalkene.



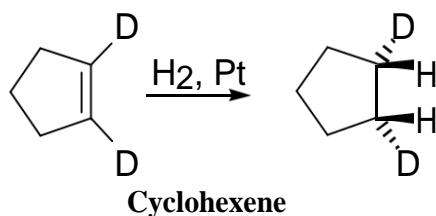
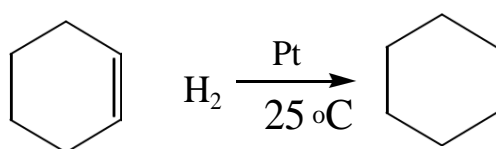
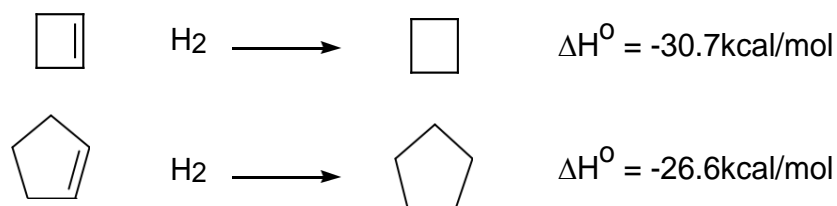
9.6 CHEMICAL REACTIONS

9.6.1 Hydrogenation:

This is the addition of a hydrogen molecule to a compound using a (usually Pt, Pd, Ni) catalyst. When the catalyst is in a different physical state to the other reactants it is called heterogeneous catalysis (E.g. a solid catalyst with a liquid and a gas). In contrast a liquid catalyst in a reaction solution is an example of homogeneous catalysis (acid catalyzed alcohol dehydration).

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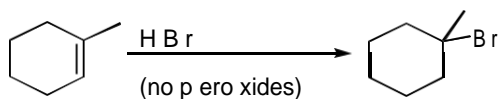
During catalytic hydrogenation, the hydrogen adsorbs onto the surface of the metal catalyst, and they add syn to the double bond.



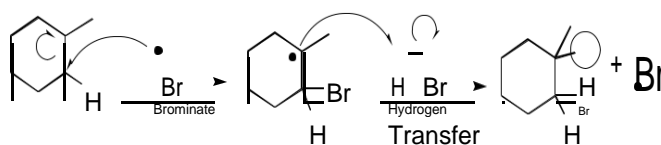
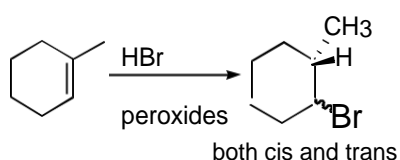
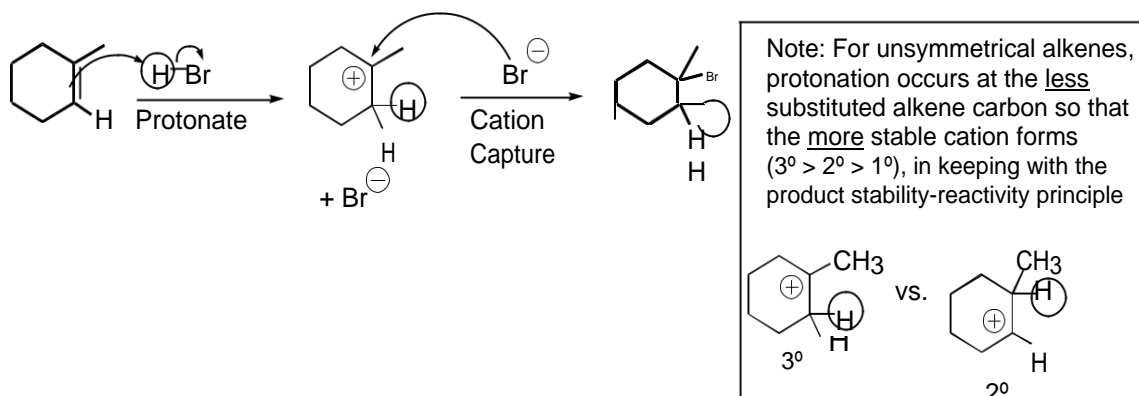
One face of the π system binds to the catalyst, then the bound hydrogen inserts into the π bond, and the product is liberated from the catalyst and stereospecific cis-addition of hydrogen takes place.

9.6.2 Reaction with halogen acid:

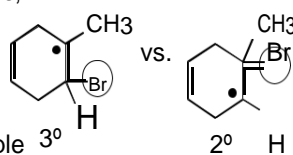
Addition of halogen acid like HCl to cycloalkene form stereoisomers according to Markovnikov rule.



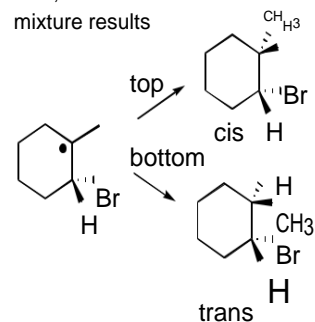
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Note 1: For unsymmetrical alkenes, bromination occurs at the less substituted alkene carbon so that the more stable radical forms ($3^\circ > 2^\circ > 1^\circ$), in keeping with the product stability-reactivity principle



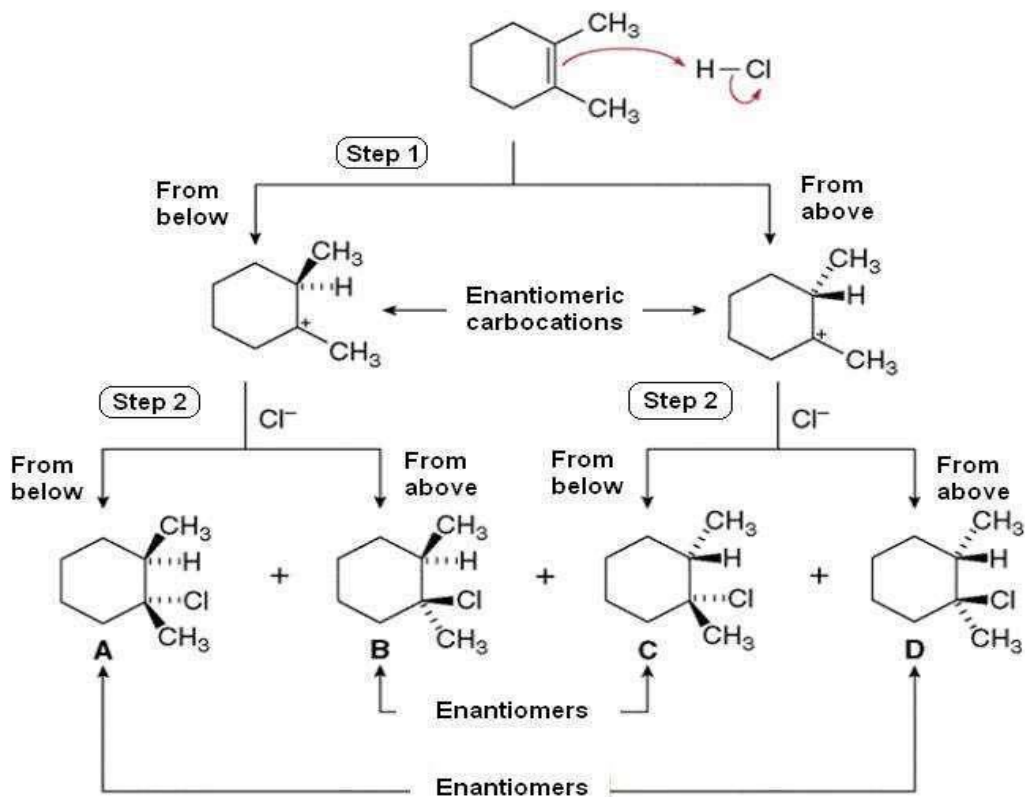
Note 2: Hydrogenation of the radical comes from either face, thus cis/trans mixture results



1, 2-dimethylcyclohexene forms two stereoisomers as follows:

Initial attack of H^+ to 1, 2-dimethylcyclohexene forms two enantiomeric carbocations. These carbocation react with Cl^- from two directions, forming a total of four stereoisomers, A-D – two pairs of enantiomers. Overall **anti-addition** to the double bond takes place.

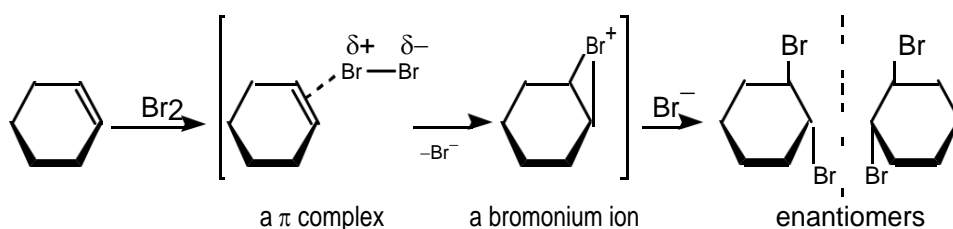
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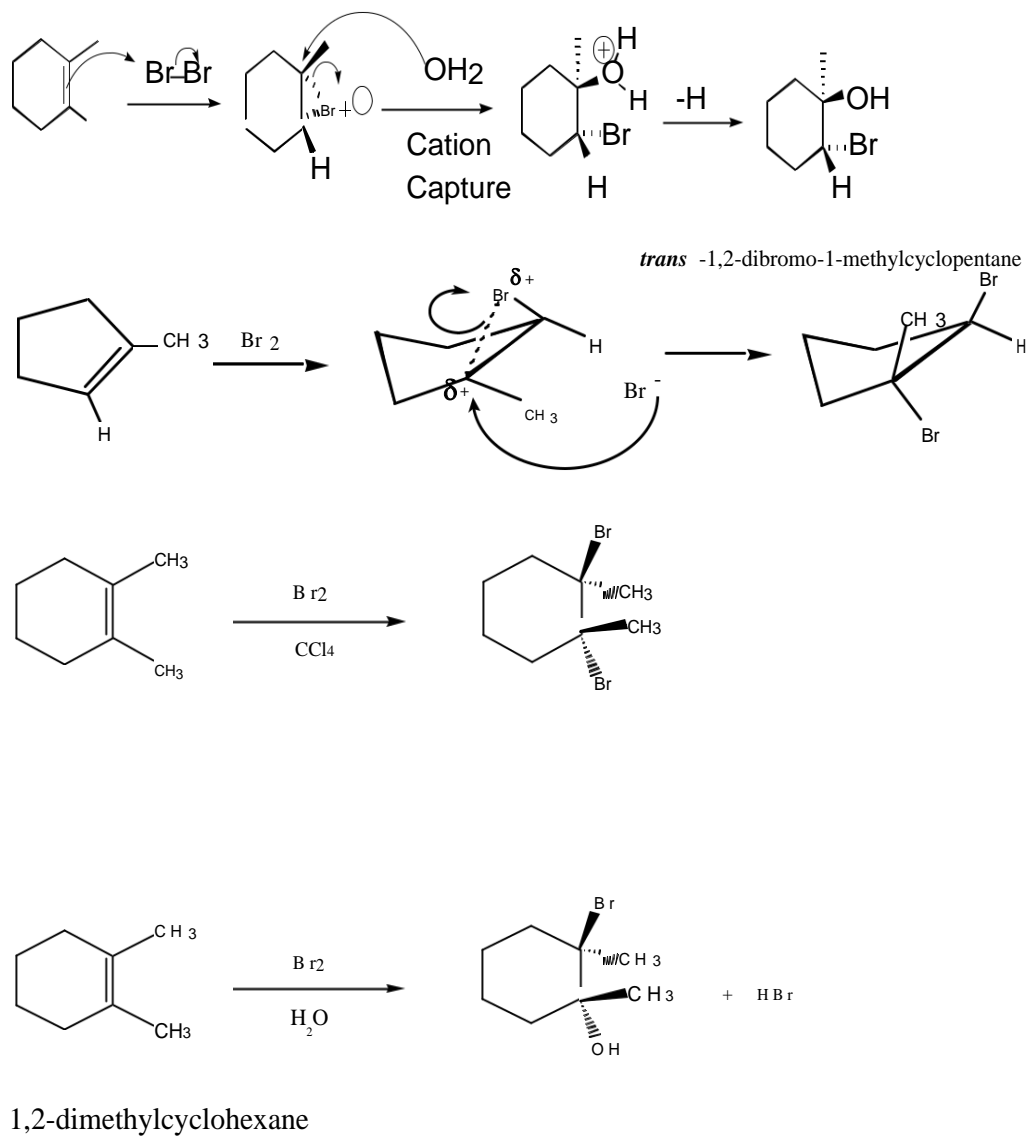
9.6.3 Addition of halogens:

Alkenes react rapidly with halogens (Cl_2 , Br_2) even in the dark (rapid decolorization of bromine in carbon tetrachloride – a test reaction for alkenes).

e.g., bromination of cyclohexene and its derivative. As a result of its interaction with the double bond bromine is polarized and forms a weak π complex. The latter breaks down to form a cyclic bromonium ion, which then reacts with bromide ion attacking from the opposite side to form *trans*-1,2-dibromocyclohexane.



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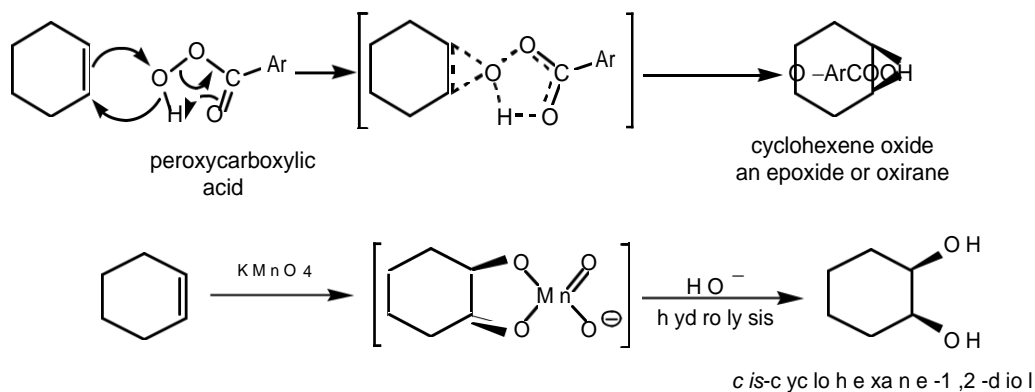
1,2-dimethylcyclohexane

9.6.4 Oxidations:

Depending on the reaction conditions, breaking of the pi bond or cleavage of both the sigma and pi-bonds can occur.

i. Epoxidation and *syn* hydroxylation yield epoxides (oxiranes) and 1,2-diols, respectively, through breaking of the σ bond.

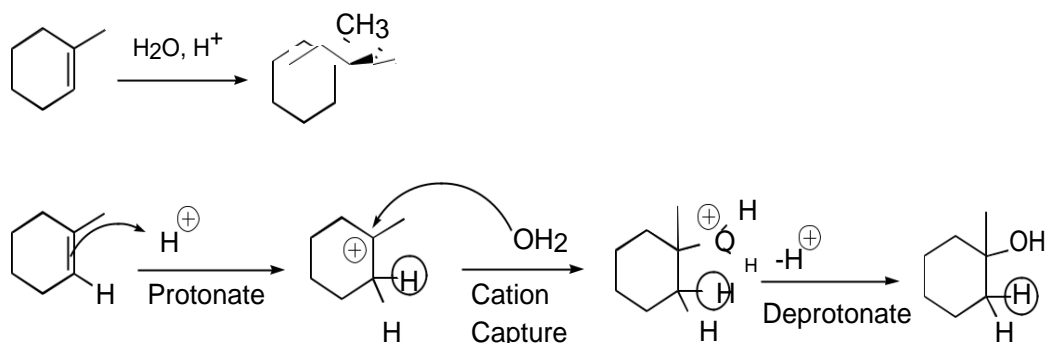
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This is one of the most useful methods of preparing alcohols from cycloalkenes.

9.6.5 Hydration:

This reaction takes place according to Markovnikov rule.



For unsymmetrical alkenes, protonation again occurs at the less substituted end of the alkene, in order to produce the more stable radical intermediate ($3^\circ > 2^\circ > 1^\circ$)

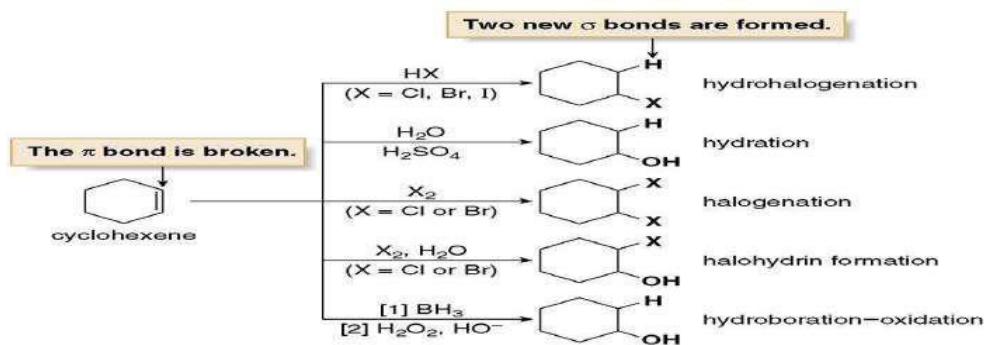
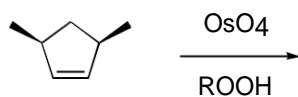


Fig: Various reactions of Cycloalkene

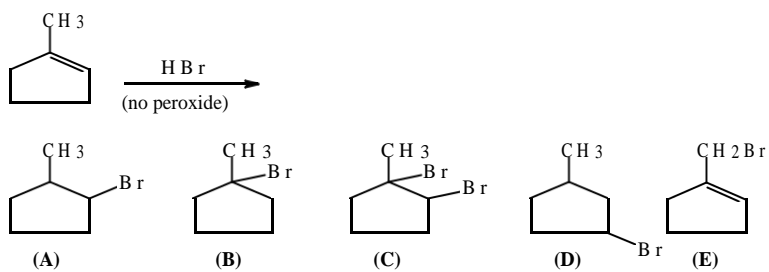
9.7 TERMINAL QUESTIONS

(a) Draw the major product of the following reaction:

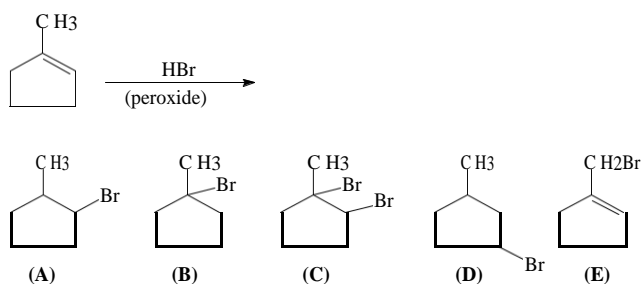


Find out the structure of the major product formed from the following reactions. Justify your selections.

(i)



(ii)



UNIT 10: DIENE

CONTENTS:

- 10.1 Objectives
- 10.2 Introduction
- 10.3 Nomenclature and classification of dienes
- 10.4 Isolated, conjugated and cumulated dienes
- 10.5 Structure of allenes and butadienes
- 10.6 Methods of formation
- 10.7 Polymerization.
- 10.8 Chemical reactions
 - 10.8.1- 1,2 and 1,4 addition
 - 10.8.2 Diels – Alder reaction
- 10.9. Summary
- 10.10. Terminal Question

10.1. OBJECTIVES

Explain the difference between cumulated, isolated, and conjugated dienes, and be able to draw or recognize examples of these compounds.

Give the relative energy of the three types of dienes. Cumulated dienes

Explain the geometry and hybridization of cumulated dienes, as well as the orientation of substituents to each other.

Explain why conjugated dienes have two preferred conformations (s-cis and s-trans), and how this is different from cis and trans stereoisomers of alkenes.

Explain how the p orbitals from the four carbons of 1,3-butadiene come together to form four pi orbitals, including which are bonding and which are antibonding, how their energy compares, which are occupied, and what they look like.

Draw the mechanism for a Diels-Alder reaction.

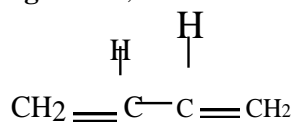
Explain what kinds of starting materials can form two constitutional isomers as products of a Diels-Alder reaction, and how to determine which will be the major product.

10.2. INTRODUCTION

Those compounds which have two C-C double bonds are known as Dienes or alkadienes.

Their suffix is -adiene.

e.g. buta-1,3-diene

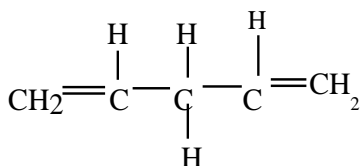


10.3. NOMENCLATURE AND CLASSIFICATION OF DIENES

Dienes can be divided into three classes, depending on the relative location of the double bonds:

Non- conjugated dienes (isolated dienes): In this type of dienes the two double bonds are separated by more than one single bond are known as Non- conjugated dienes.

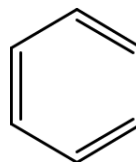
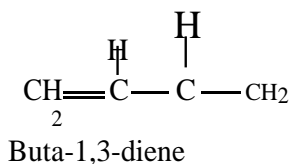
Examples:



Penta-1,4-diene

Conjugated dienes: In this type of dienes the two double bonds are separated by only one single bond are known as conjugated dienes.

Examples:

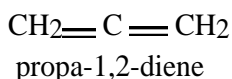


benzene

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Cumulated dienes: In this type of dienes the two double bonds are continuous, so these are named as cumulated dienes.

Examples:



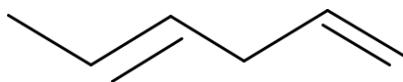
Nomenclature of dienes:

Dienes are alkenes with two double bonds. IUPAC name is same as alkene, but change -ene to -adiene and use two numbers to locate the two double bonds (number from the end of the chain which makes the smaller of these numbers smaller).

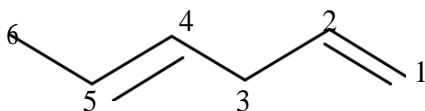
A type of organic compounds, called **polyenes**, contains two or more double bonds. For example, **dienes** have two double bonds, and **trienes** have three. To name a diene or a triene, follow the same steps for naming an alkene with these exceptions.

Step 1 Write the numbers indicating the locations of the double bonds separated by commas and followed by a hyphen.

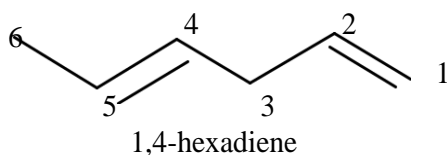
Step 2 After the hyphen; write the parent name of the compound, changing the ending from —ene to —diene, if there are two double bonds, or —triene, if there are three, etc. The following example demonstrates how to name a polyene.



Step 1 Determine the length of the parent chain and the positions of the double bonds. The parent chain is six carbons long. There are two double bonds, and their positions are C1 and C4.

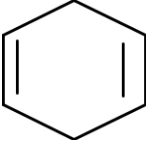
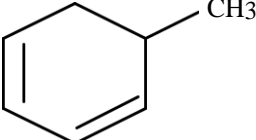


Step 2 Write the numbers of the locations of the double bonds followed by a hyphen: 1,4-. **Step 3** After the hyphen write the name of the parent chain with the —diene ending. The name of the compound is 1,4-hexadiene.



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Some common diens and their IUPAC Nomenclature:

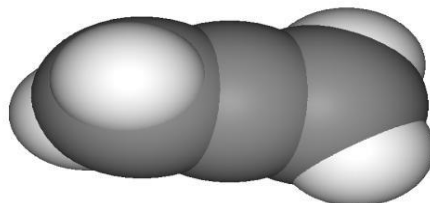
- $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ ————— 1,3-butadiene
- $\text{CH}_2=\text{CH}-\text{CH}=\underset{\text{CH}_3}{\text{C}}-\text{CH}_3$ ————— pent-4-methyl-1,3-diene
-  ————— 1,4-cyclohexadiene
-  ————— 5-methyl-1,3-cyclohexadiene

10.5. STRUCTURE OF ALLENES AND BUTADIENES

10.5.1. Structure of allenes:

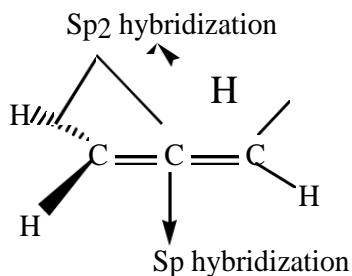
An allene is a compound in which one carbon atom has double bonds with each of its two adjacent carbon centres. Allenes are classified as polyenes with cumulated dienes. The parent compound of allene is propadiene. Compounds with an allene-type structure but with more than three carbon atoms are called cumulenes. Allenes are much more reactive than most other alkenes.

The central carbon of allene forms two sigma bonds and two pi bonds. The central carbon is sp -hybridized, and the two terminal carbons are sp^2 -hybridized. The bond angle formed by the three carbons is 180° , indicating linear geometry for the carbons of allene. It can also be viewed as an "extended tetrahedral" with a similar shape to methane.



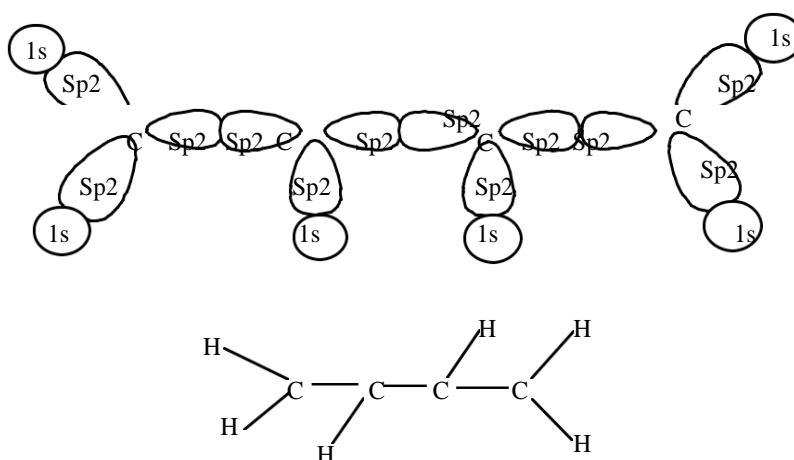
3-D- structure of Allene

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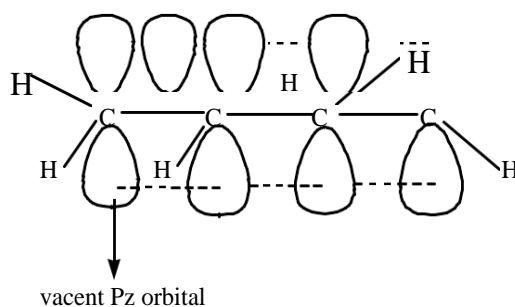


10.5.2. Structure of 1,3-butadiene:

Each carbon in buta-1,3-diene is Sp^2 hybridization and the sp^2 hybridized orbital of C_1 is overlap with $1s$ orbital of 2 H atom to form sp^2 -s σ -bond and also sp^2 orbital of C_2 to form sp^2 - sp^2 σ -bond. Similarly C_4 and C_2 overlap with $1s$ of 1H atom to form sp^2 -s σ -bond and it is also overlapped with C_1 and C_3 . Hence the σ bond structure of 1,3-butadiene is represented as

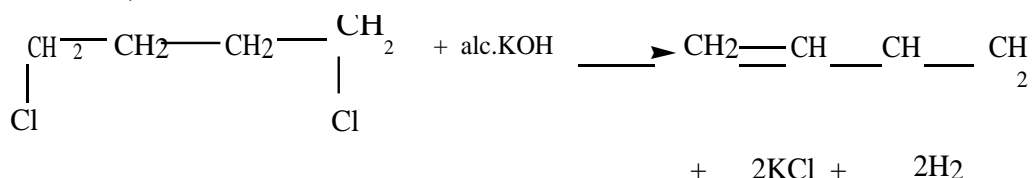


In 1,3-butadiene each carbon consist of one unhybridized p-orbital which overlap from the nearest carbon atoms to form the π -bond by π -electron cloud. This is known as delocalization of π -electrons.

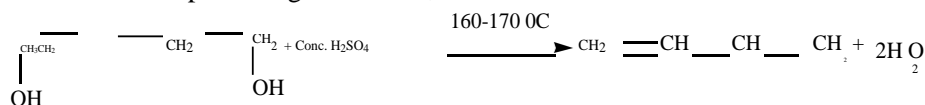


10.6. METHODS OF FORMATION

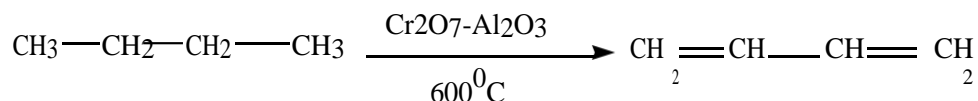
From 1,4-dichloro butane: 1,4-dichloro butane on react with alc. KOH gives buta-1,3-diene.



From 1,4-butane diol: Bute 1,4- diol on react with conc. H₂SO₄ from 160-170 °C temperature gives bute-1,3-diene.

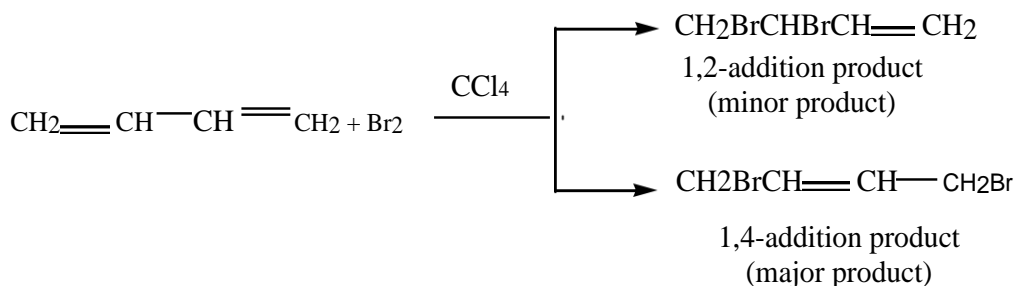


From n-butane: n-butane on heating in the presence of Cr₂O₇-Al₂O₃ at 600°C than it gives 1,3-butadiene.



10.7. CHEMICAL REACTIONS

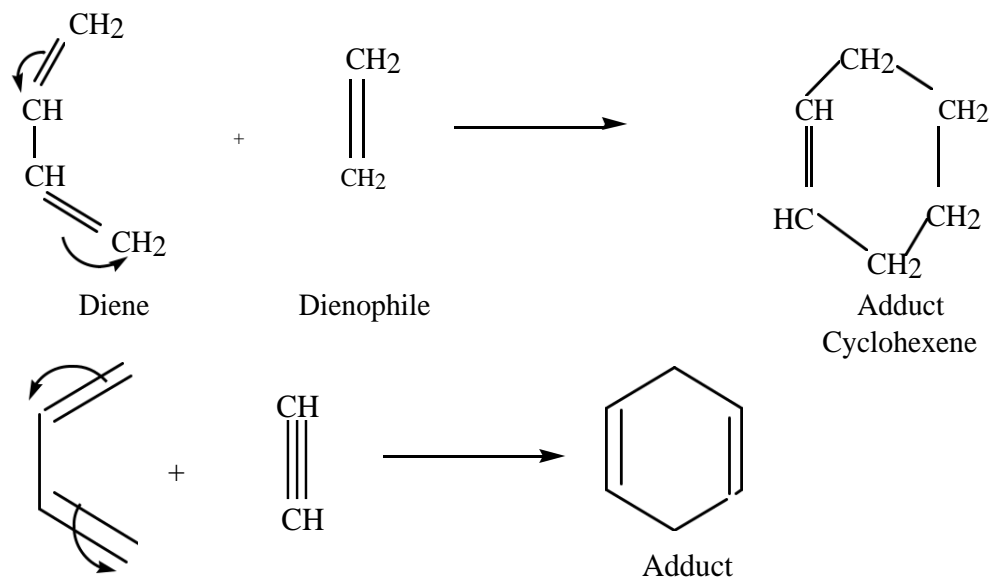
Addition of halogens: 1,3- butadiene when react with halogens in the presence of catalyst than it gives 1,2 and 1,4 addition products.



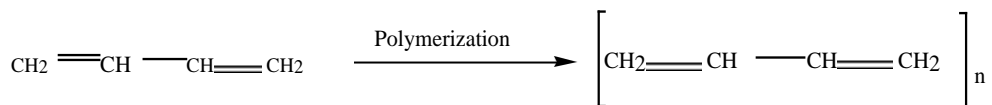
Diels-Alder reaction: In this reaction buta-1,3- diene is react with unsaturated compound such as alkene, alkyne etc. to form the product without any catalyst. This reaction is known as Diels-alder reaction and the product formed by the reaction is known as adduct.

E.g.

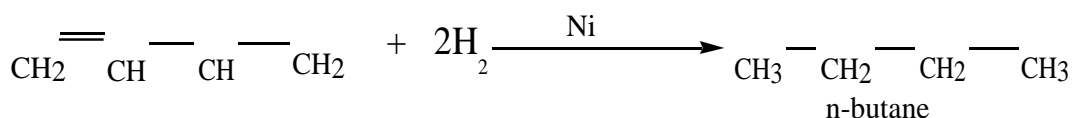
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Polymerization Reaction: n - molecules of 1,3-butadiene are polymerize to give the addition polymer.



Hydrogenation: In the presence of Ni catalyst buta-1,3-diene on react with H_2 gives n -butane.



10.8. SUMMARY

Dienes are unsaturated hydrocarbons with two double bonds. In case of Conjugated dienes, the Conjugated double bonds are separated by one single bond and isolated double bonds are separated by more than one single bond while Cumulated double bonds are adjacent to each other. A conjugated diene is more stable than an isolated diene, which is more stable than a cumulated diene.

An isolated diene, like an alkene, undergoes only 1,2- addition. If there is only enough electrophilic reagents to add to one of the double bonds, it will add preferentially to the more reactive bond. A conjugated diene reacts with a limited amount of electrophilic reagent to form a 1,2-addition product and a 1,4-addition product.

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In a Diels–Alder reaction, a conjugated diene ($4\pi e^-$) reacts with a dienophile ($2\pi e^-$) to form a cyclic compound; in this concerted cycloaddition reaction, two new bonds are formed at the expense of two bonds. The reactivity of the dienophile is increased by electron-withdrawing groups attached to the carbons.

10.9 TERMINAL QUESTION

Give the products obtained from the reaction of 1 mole HBr with 1 mole 1,3,5-hexatriene.

Which dienophile is more reactive in a Diels–Alder reaction?

Discuss the effect of temperature on 1,2 and 1,4 addition to conjugated diene.

Discuss why conjugated diene is more stable than non-conjugated diene.

Give the mechanism of 1,2 and 1,4 addition reaction of 1,3-butadiene.

Explain why conjugated dienes are more stable than the isolated diene.

Give the mechanism of electrophilic addition to conjugated dienes.

What are dienes? Write the difference between conjugated and cumulative diene.

What happens when 1,3-butadiene is treated with 2-moles of HBr.

Write a short note on Diels–Alder reaction.

Explain the structure of conjugated diene.

What are dienes? How are they classified with suitable examples.

What are the various classes of dienes? Give their structures.

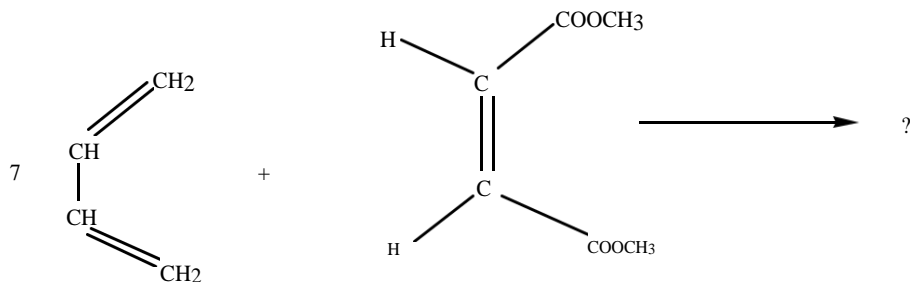
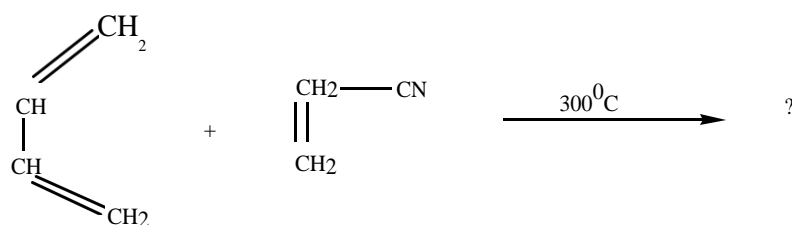
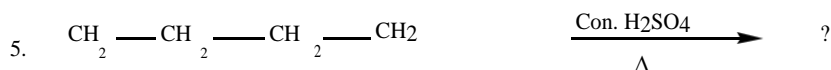
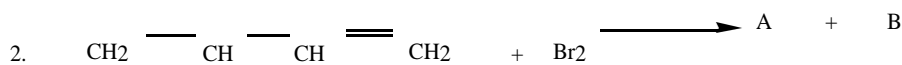
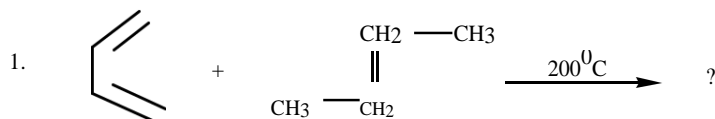
What are conjugated dienes? Why are they more stable than isolated dienes?

Give the mechanism of 1,2- and 1,4-addition reaction to 1,3-butadiene. What is the effect of temperature on the addition of HBr to 1,3-butadiene.

On the basis of molecular orbital diagram, explain why conjugated diene is more stable than non-conjugated dienes.

Complete the following reactions:

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References:

1. Advanced Organic Chemistry by, Jagdamba Singh and L.D.S. Yadav, Pragati Prakashana.

Paula Yurkanis Bruice 4th edition.

Organic Reactions and Their Mechanisms, by P. S. Kalsi, New edge Science.

R. L. Madan, S. Chand and company Pvt. Ltd.

UNIT 11: ALKYNES

CONTENTS:

11.1 Objectives

11.2 Introduction

11.3 Nomenclature and classification

11.4 Structure and bonding in alkynes

11.5 Methods of formation

11.6 Physical properties

11.7 Chemical reactions of alkynes

11.7.1 Acidity of alkynes

11.7.2 Mechanism of electrophilic and nucleophilic addition reactions

11.7.3 Oxidation and polymerization

11.8 Summary

11.9 Terminal Question

11.1. OBJECTIVES

Explain the difference between alkynes and unsaturated compounds with carbon carbon triple bonds.

Nomenclature of Alkynes

Hybridization and bond formation of Alkynes

Explain how the sigma and two pi bonds are formed in a C \equiv C.

Explain how carbon-carbon single, double, and triple bonds compare in length.

Give the physical properties of alkynes, including polarity, water solubility, flammability, and odor.

Chemical Reactions of Alkynes.

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11.2. INTRODUCTION

Alkynes are hydrocarbons which contain carbon-carbon triple bond. The triple bond is indicated by changing the ending of the name to -yne, in the same manner as the double bonds in alkenes are indicated by the ending -ene. Alkynes, like alkenes are unsaturated hydrocarbons with the general formula C_nH_{2n-2} . Their suffix is -yne and the IUPAC name of them is written as Alkane-ane+ yne = Alkyne. For example, ethyne the simplest alkyne,



Structure of Ethyne, Acetylene

Which is more commonly known by its common name **acetylene**, is a gas often used as a fuel for cutting and welding torches because it burns with a very hot flame?

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

The first few members of this series are represented by the following structures:

Name	Structure	Condensed structure
Ethyne	$H-C \equiv C-H$	$HC \equiv CH$
Propyne	$\begin{array}{c} H \\ \\ H-C \equiv C-C-H \\ \\ H \end{array}$	$HC \equiv CCH_3$
But-1-yne	$\begin{array}{c} H \quad H \\ \quad \\ H-C \equiv C-C-C-H \\ \quad \\ H \quad H \end{array}$	$HC \equiv CCH_2CH_3$
But-2-yne	$\begin{array}{c} H \quad \quad H \\ \quad \quad \\ H-C-C \equiv C-C-H \\ \quad \quad \\ H \quad \quad H \end{array}$	$CH_3C \equiv CCH_3$
Pent-1-yne	$\begin{array}{c} H \quad H \quad H \\ \quad \quad \\ H-C \equiv C-C-C-C-H \\ \quad \quad \\ H \quad H \quad H \end{array}$	$HC \equiv CCH_2CH_2CH_3$
Pent-2-yne	$\begin{array}{c} H \quad \quad H \quad H \\ \quad \quad \quad \\ H-C-C \equiv C-C-C-H \\ \quad \quad \quad \\ H \quad \quad H \quad H \end{array}$	$CH_3C \equiv CCH_2CH_3$

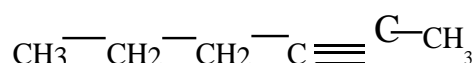
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11.3. NOMENCLATURE AND CLASSIFICATION

The naming of the alkynes follows the exact rules as those used for naming alkenes except, of course, that the suffix *-yne* is used to indicate that a triple bond is now present.

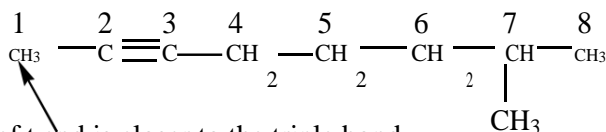
Naming Alkynes:

STEP 1: Name the main chain. Find the longest carbon chain of carbons containing the triple bond. The names of alkynes end with *-yne*. When there is more than one multiple bond, use numerical prefixes (diene, diyne, triene, triyne, etc.)



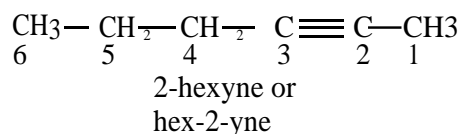
Name as *hexyne* - a six C chain containing a triple bond.

STEP 2: Number the carbon atoms in the main chain. Begin at the end nearer the multiple bond. If the multiple bond is at the same distance from both ends, begin numbering at the end nearer the first branch point.



The left end is closer to the triple bond.

STEP 3: Write the full name. Assign numbers to the branching substituents, and list the substituents alphabetically. Indicate the position of the multiple bond(s) in the chain by giving the number of the first multiple-bonded carbon. If more than one multiple bonds is present, identify the position of each multiple bond and use the appropriate ending diene, triene, tetraene, and so forth.



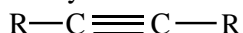
Some common alkynes and their naming:

Structure	Common Name	IUPAC
$\text{CH}\equiv\text{CH}$	Acetylene	ethyne
$\text{CH}\equiv\text{C---CH}_3$	methyl acetylene	propyne
$\text{CH}_3\text{---C}\equiv\text{C---CH}_3$	dimethyl acetylene	2-butyne
$\text{CH}\equiv\text{C---CH}_2\text{---CH}_3$	ethyl acetylene	1-butyne

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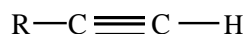
11.3.1. Classification of Alkynes: Generally alkynes can be categorized into the following two categories.

Terminal Alkyne: A Terminal Alkyne is an alkyne in whose molecule there is at least one hydrogen atom bonded to a triply bonded carbon atom. Or simply, the alkynes in which the triple bonded carbon atoms are at the extreme positions.



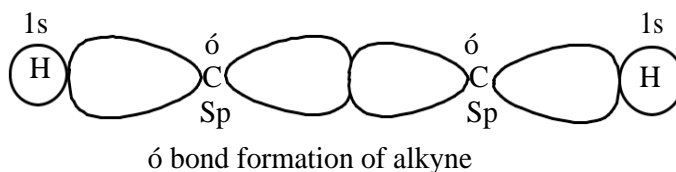
Where, both R will be H or same alkyl group

Non-terminal alkynes: Non-Terminal Alkynes, on the other hand have triple bond at any place other than the end positions.

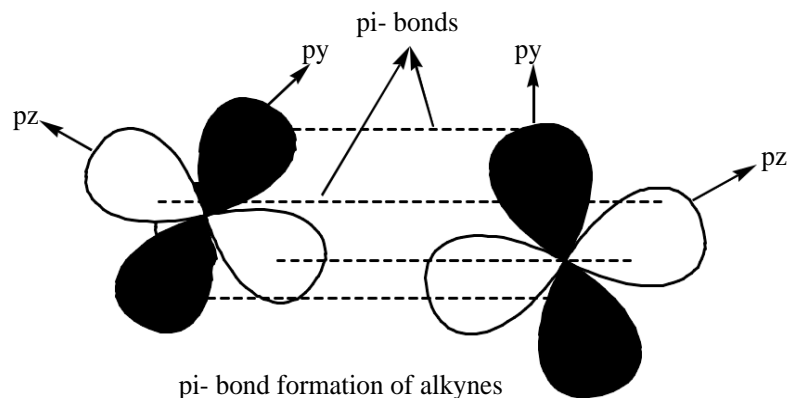


11.4. STRUCTURE AND BONDING IN ALKYNES

Each carbon atom of ethyne has two sp hybridised orbitals. Carbon-carbon sigma (σ) bond is obtained by the head to head overlapping of the two sp hybridised orbitals of the two carbon atoms. The remaining sp hybridized orbital of each carbon atom undergoes overlapping with the $1s$ orbital of each of the two hydrogen atoms in the same plane to form two C-H sigma bonds. The H-C-C bond angle is of 180° . Each carbon has two unhybridised p orbitals which are perpendicular to each other as well as to the plane of the C-C sigma bond. The $2p$ orbitals of one carbon atom are parallel to the $2p$ orbitals of the other carbon atom, which undergo sidewise overlapping to form two π bonds between two carbon atoms. Thus ethyne bonds. Thus, σ bonds and two C-C π bond, two C-H σ molecule consists of one C-C σ ethyne is a linear molecule.

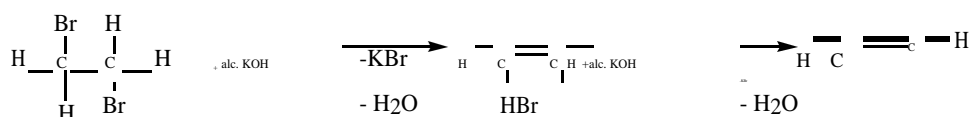


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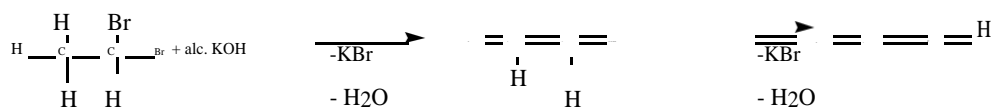


11.5. METHODS OF FORMATION

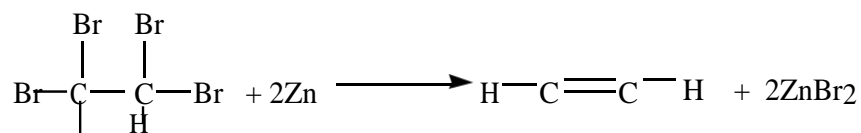
From Vicinal di-halides: Vic. di halides on react with alc. KOH gives alkynes.



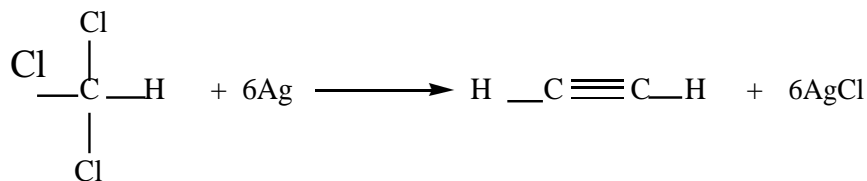
From gem. dihalides: 1,1- dihalides are known as gemdihalides, gem-dihalides on react with alc. KOH gives alkyne.



From tetra halides: Tetra halides on react with Zn form alkynes.

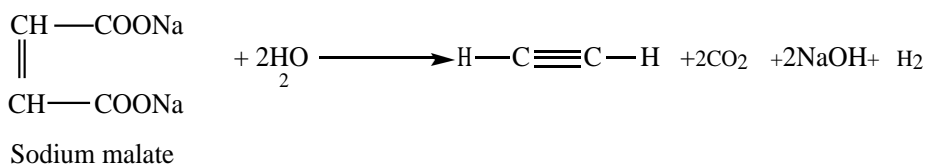


From Chloroform: The trihaligen derivatives of CH₄ are known as haloform. Such as CHX₃ (X= Cl, Br, I). Chloroform on react with Ag powder gives acetelene.



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From Kolbey's electrolysis method: The Na or K salt of malic acid on react with H₂O and after electrolysis gives acetylene and CO₂ at anode and H₂ and NaOH at cathode.



11.6. PHYSICAL PROPERTIES

Physical State:

The first three members of alkynes are gases while those containing five to thirteen carbon atoms are liquids and higher alkynes are solids.

Melting and Boiling Points:

The melting and boiling points of alkynes are quite low and increase regularly with increase in molecular mass. Alkynes are less volatile than alkanes and alkenes.

Solubility:

Alkynes are insoluble in water but are soluble in organic solvents such as benzene, hexane, ether, carbon tetrachloride, etc.

Density:

All alkynes are lighter than water. Their densities increase regularly with increase in molecular mass.

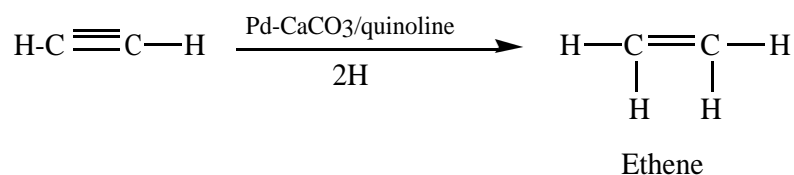
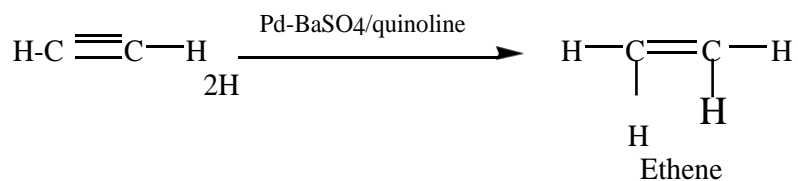
11.7. CHEMICAL REACTIONS OF ALKYNES

Electrophilic Addition Reactions

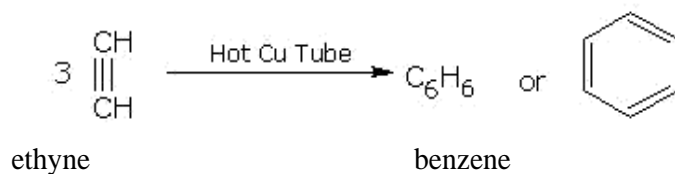
Carbon-carbon triple bond, C≡C, is a combination of one and two bonds. Alkynes give electrophilic addition reactions as they show reactivity due to the presence of bonds. This property is similar to alkenes but alkynes are less reactive than alkenes towards electrophilic addition reactions due to the compact CC electron cloud. Some typical electrophilic addition reactions given by alkynes are:

Addition of hydrogen: An alkyne reacts with hydrogen in the presence of catalyst (Pt or Ni) at 250°C, first forming alkenes and finally alkane.

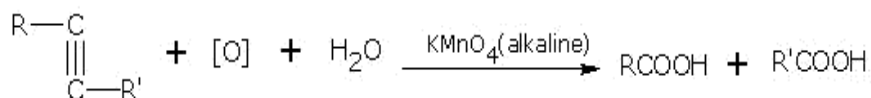
ORGANIC CHEMISTRY



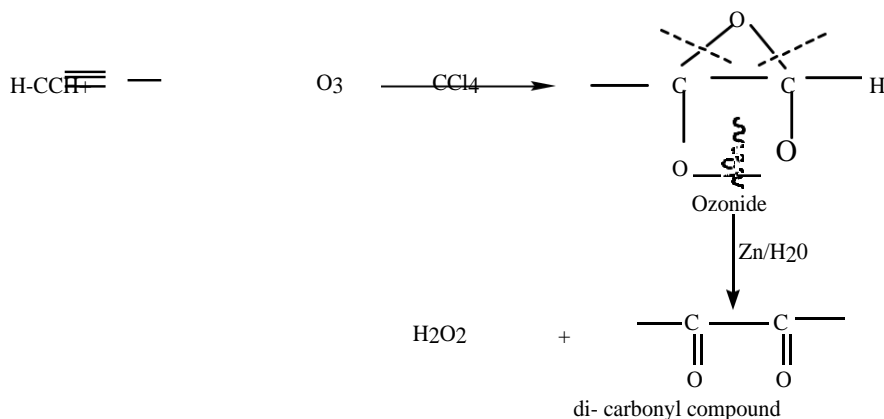
Polymerization: In the presence of red hot Cu tube, three molecules of C_2H_2 are undergoes polymerization and give a polymer C_6H_6 . This reaction is known as polymerization of C_2H_2 .



Oxidation: Oxidation of alkynes gives mono or dicarboxylic acids.



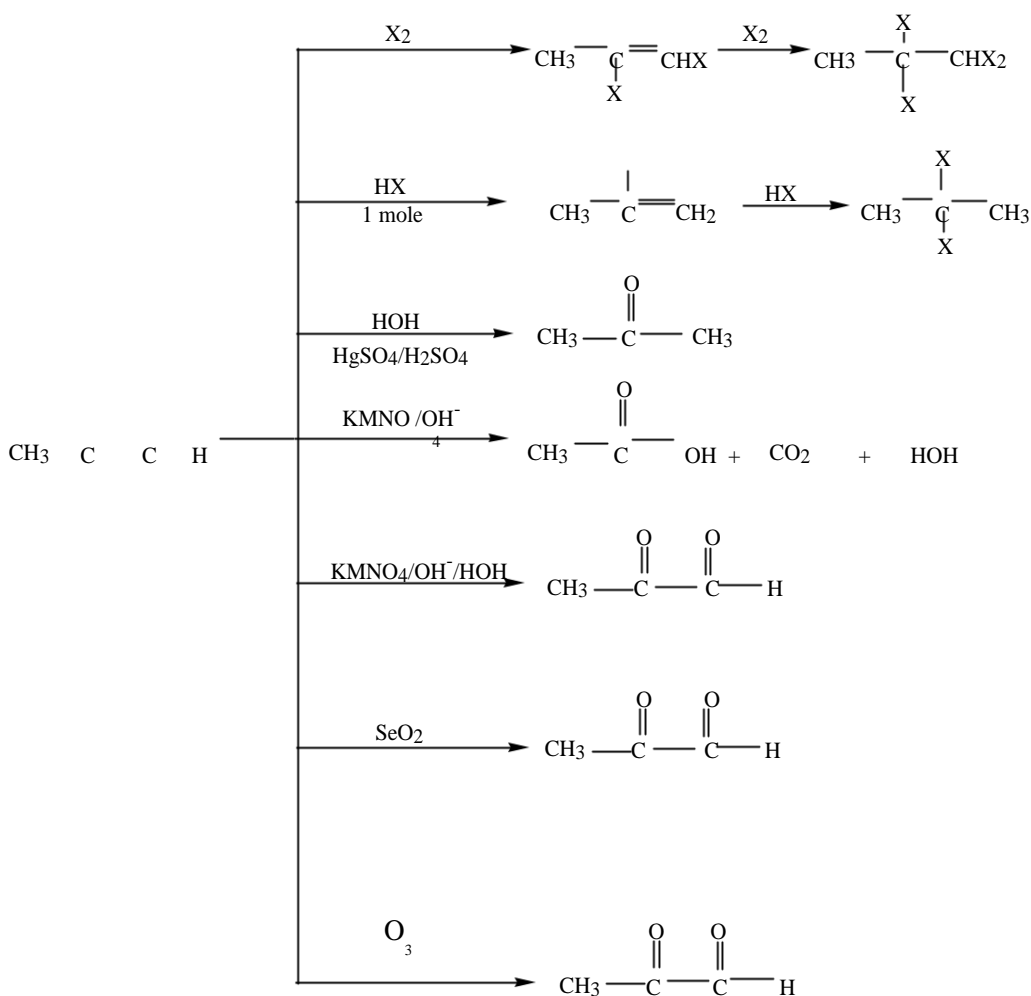
Ozonolysis: In the presence of CCl_4 alkyne on react with O_3 gives alkyne ozonimide which on react with $\text{Zn}/\text{H}_2\text{O}$ gives di-carbonyl compound.



11.8. SUMMARY

Alkynes contain the doubly unsaturated $C\equiv C$ functional group. Terminal alkynes, $R-C\equiv C-H$, are quite acidic for hydrocarbons and can be deprotonated to form a carbanion that can then be alkylated. Like alkenes ($C=C$), the alkyne $C\equiv C$ undergoes a variety of addition reactions.

Summary of the Key reaction of Alkynes:



11.10 TERMINAL QUESTION

Discuss Kolbe's electrolytic method to prepare acetylene.

Convert Chloroform into acetylene.

Alkynes do not exhibit geometrical isomerism while alkenes do so why?

Alkynes are less reactive than alkenes towards electrophilic addition reaction why?

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Convert acetylene into ethanol.

Why does acetylene behave like a weak acid?

Alkynes undergo both electrophilic and nucleophilic addition reactions. Why?

Discuss structure of alkyne.

Alkynes are acidic in nature. Explain.

Give mechanism of addition of halogens to alkynes.

Why alkynes undergo nucleophilic addition reactions while simple alkenes do not?

How will you distinguish between Ethane and Ethyne? Give reaction.

How will you distinguish between Ethene and Ethyne? Give reaction.

Objective Type Questions:

Odor of ethyne is:

Onion like

Garlic like

Vinegar like

fruity

Acetylene is another name of:

Ethane

Propyne

Butane

Pentane

The compound C_2H_2 belongs to the series of hydrocarbons with the general formula.

C_nH_n ;

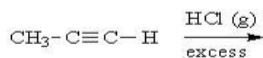
C_nH_{2n}

C_nH_{2n-2}

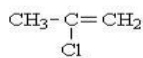
C_nH_{2n+2} .

What is the major product expected from the following reaction?

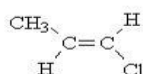
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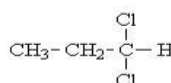
(a)



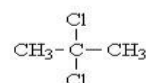
(b)



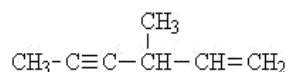
(c)



(d)



What is the IUPAC name for the following compound?



- 4-vinyl-2-pentyne
- 4-methylhex-2-yn-5-ene
- 3-methylhex-4-yn-1-ene
- 3-methylhex-1-en-4-yne

The reaction of ethyne with which of the following gives $\text{CH}_2\text{Br-CHBrCl}$?

- (a) HCl, then HBr
- (b) HCl, then Br_2
- Cl_2 , then HBr
- Cl_2 , then Br_2
- H_2 , then Br_2

Which of the following metals is used as a catalyst in the catalytic hydrogenation of both alkenes and alkynes?

- a. Palladium
- b. Iron
- c. Magnesium
- d. Copper

What product(s) will be obtained from the acid-catalysed hydration of pent-2-yne?

- Pentanal Pentan-2-one
- pentan-3-one
- Pentan-2-one
- Pentan-3-one

Answers: 1. b, 2. b, 3. 3, 4. C, 5. d, 6.

UNIT 12 ARENES AND AROMATICITY

CONTENT:

- 12.1 Objectives
- 12.2 Introduction
- 12.3 Nomenclatures of benzene derivatives
- 12.4 The aryl group
- 12.5 Aromatic nucleus and side chain
- 12.6 Structure of benzene
 - 12.6.1 Molecular formula and Kekule structure
 - 12.6.2 Resonance and MO picture
- 12.7 Aromaticity: the Huckel's rule, aromatic ions
- 12.8 Methods of preparation
- 12.9 Properties (Physical and Chemical properties of benzene)
- 12.10 Reduction of benzene (Birch reduction)
- 12.11 Orientation and ortho/para ratio.
- 12.12 Summary
- 12.13 Terminal Question

12.1 OBJECTIVE

In this chapter we have to study about Arenes.

Arenes: Nomenclature of Benzene derivatives, The aryl group, Aromatic nucleus and side chain Structure of benzene, molecular formula & Kekule's structure Resonance and MO pictures, Aromaticity: the Huckel's Rule, Aromatic ions.

Chemical reactions of benzene : Aromatic electrophilic substitution ,General pattern of nitration, halogenations & sulphonation & Friedel-Crafts reactions, Activating and deactivating substituent, Orientation and ortho / Para ratio, Reduction of benzene (Birch reduction),Summary & Terminal questions & Answers

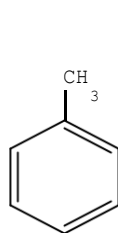
12.2 INTRODUCTION

Arene is generally used for aromatic hydrocarbons. Benzene and its alkyl derivatives are important parts of arenes. The general formula of arenes is C_nH_{2n-6y} (where y = Number of rings) so the percentage of carbon in arenes is more than that of aliphatic hydrocarbons. In 1834, Eilhardt Mitscherlich correctly determined benzene's molecular formula and decided to call it benzin because of its relationship to benzoic acid, a known substituted form of the compound. Further its name was changed to benzene. Compounds like benzene, which have relatively few hydrogens in relation to the number of carbons, are typically found in oils produced by trees and other Natural Plants. Early chemists called such compounds aromatic compounds because of their pleasing smell. In this way, they were differentiating from aliphatic compounds, with higher hydrogen-to-carbon ratios, that were obtained from the chemical degradation of fats. The chemical meaning of the word "aromatic" now signifies certain kinds of chemical structures. We will now examine the criteria that a compound must satisfy to be classified as aromatic. Aromatic compounds are now regarded as a class of compound which contains at least one benzene ring. They are also known as benzenoids. In other cases compound which do not contain benzene ring but they still behave as aromatic compounds. Such compounds are known as non-benzenoids.

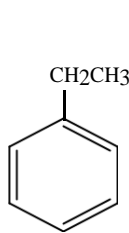
In this series benzene is first and most important member. These are called benzenoid compounds.

Example:

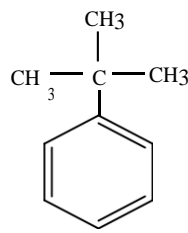
1. Alkyl benzenes:



Toluene



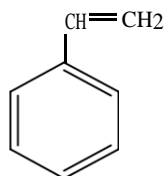
Ethyl benzene



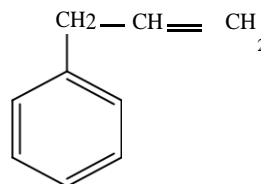
tert-Butyl benzene

2. Alkenyl benzenes:

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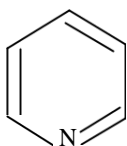
Styrene



3-Phenyl propene-1

Aromatic hydrocarbons which have different those chemical properties than benzene are called non benzenoid aromatic compound.

Example:



Pyridene



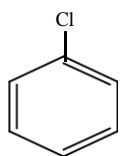
Cyclopenta dienyl anion

12.3 NOMENCLATURE OF BENZENE DERIVATIVE

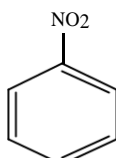
Nomenclature of benzene derivatives depends on IUPAC system and some derivatives have common names.

Monosubstituted benzene: These are named by prefixing the name of the substituent to 'benzene'

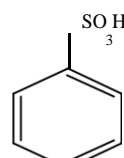
Example:



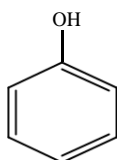
Chloro benzene



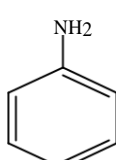
Nitrobenzene



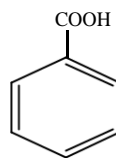
Benzene sulphonic acid



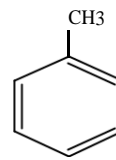
Phenol



Aniline



Benzoic Acid

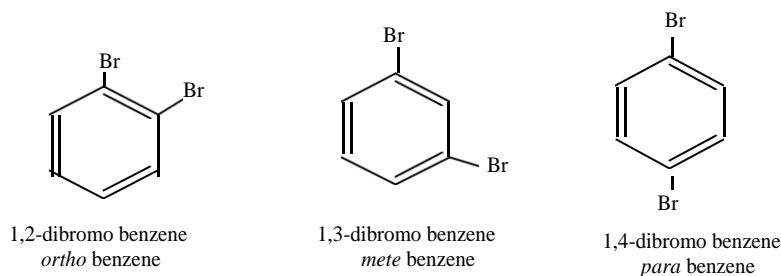


Toluene

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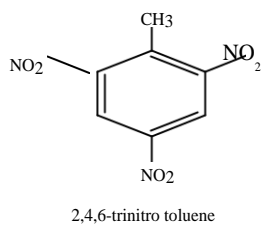
Disubstituted benzene: When there are two substituents on the ring, three positional isomers are possible and their positions are indicated by ortho, meta and para or by numbers.

Example:



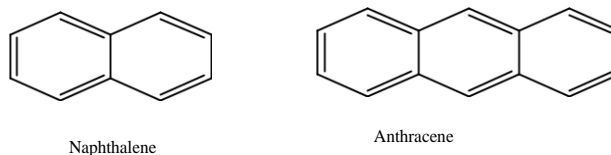
Polysubstituted benzene: When three or more substituents are placed on benzene then numbers are used to indicate the position.

Example:



Fused polycyclic arenes: There are many polycyclic arenes having one or more benzene rings fused in ortho positions.

Example:

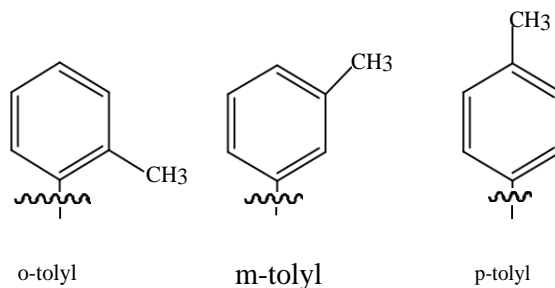


12.4 THE ARYL GROUP

The univalent group which is derived by any other aromatic hydrocarbon is known as aryl group (Ar-)

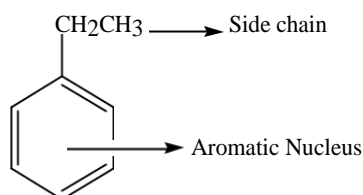
Example:

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12.5 AROMATIC NUCLEUS AND SIDE CHAIN

The basic carbon structure of benzene is called aromatic nucleus. When alkyl group attached to the aromatic ring is called side chain.



12.6 STRUCTURE OF BENZENE

12.6.1 Molecular Formula and Kekule structure: The structure of benzene is deduced by the following points.

A. Molecular Formula:

By the analytical measurement its empirical formula is observed as CH and its molecular mass is 78.

Empirical formula = CH

Empirical weight = $12 + 1 = 13$

Molecular weight = 78

Empirical weight $\times n$ = Molecular weight

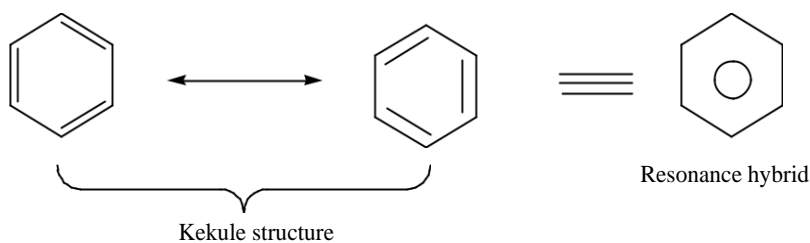
$13 \times n = 78$

Since molecular formula = CH $\times 6 = C_6H_6$

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B. Kekule structure of benzene:

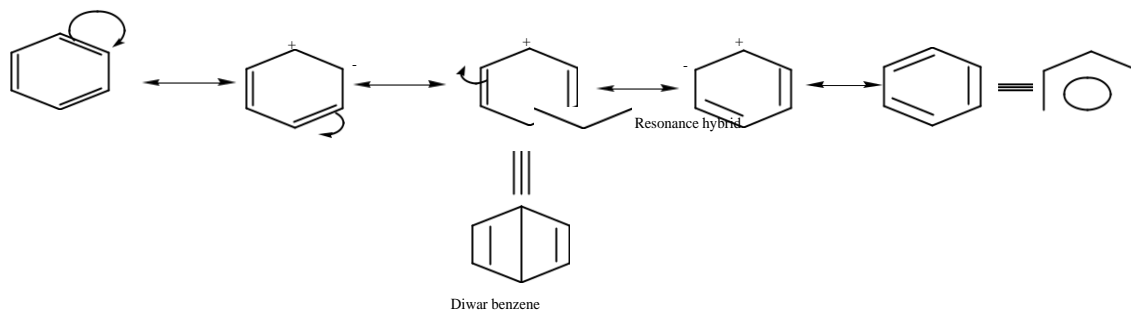
In 1865 a scientist Kekule gives the special structure of C_6H_6 and he represents that C_6H_6 shows two resonating structures which are known as Kekule structures and these structures cannot explain all properties of benzene so they have resonance hybrid and the resonating energy for it is 36 K Cal/mol.



It is cyclic planer structure of six carbons with alternate single and double bonds. Each carbon attached with one hydrogen so two structures are in a state of continuous oscillation.

12.6.2 Resonance and MO picture:

A. Resonance Structure:



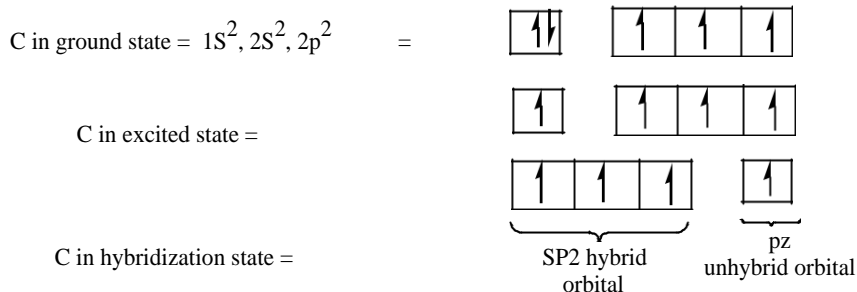
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According to valence bond theory, benzene is considered as resonance hybrid of two Kekulé and three Dewar structures, the Kekulé structure making major contributions. Because resonating structures are more stable so benzene should be more stable than other structure.

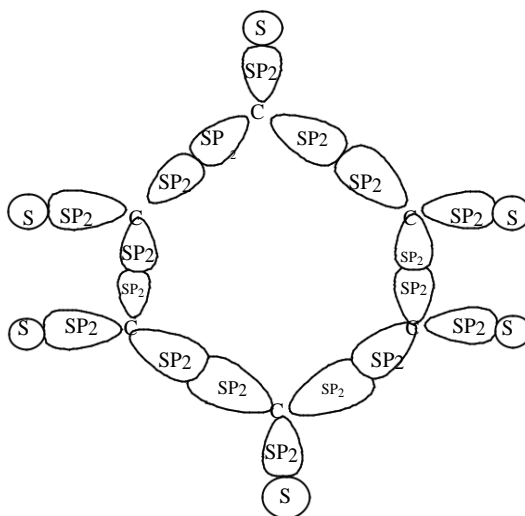
B. Molecular Orbital (MO) picture:

All six carbon atoms in benzene are sp^2 hybridized. All hybrid orbitals overlap each other and with s-orbitals C-C and C-H bonds to form σ bond.

It is the modern view of structure, in benzene each carbon is sp^2 hybridized with bond angle 120° . So it is cyclic and planar. Each carbon contains one unhybrid p orbital (p_z) which is perpendicular to the σ plane and π - e^- undergoes delocalization, each carbon overlaps with two carbon atoms to form sp^2 - sp^2 σ bond and with H-atom to form sp^2 -S σ bond.

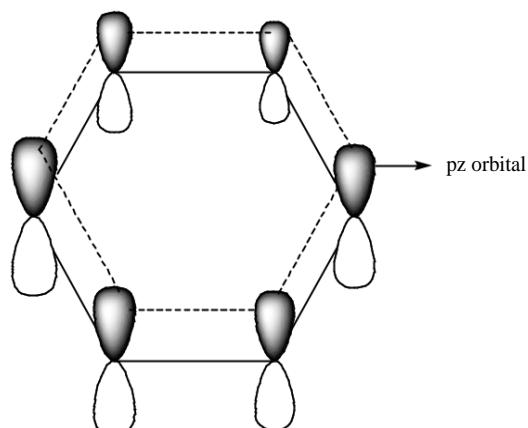


Frame work of benzene

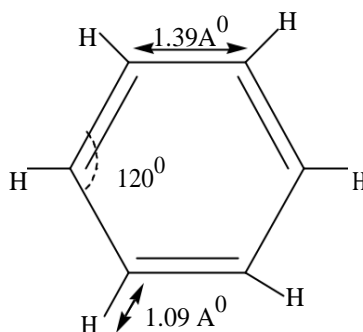


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π -Frame work of benzene:



Complete structure of benzene:



12.7 AROMATICITY: THE HUCKEL'S RULE

An aromatic compound is more stable than an analogous cyclic compound with localized electrons. In contrast, an antiaromatic compound is less stable than an analogous cyclic compound with localized electrons. Aromaticity is characterized by stability, whereas antiaromaticity is characterized by instability.

Aromatic compound > cyclic compound with localized electrons > antiaromatic compound

The aromatic compounds have alternate single and double bond due to this those compounds have special stability, which is known as Aromaticity. These are the following rules for compound to be aromatic.

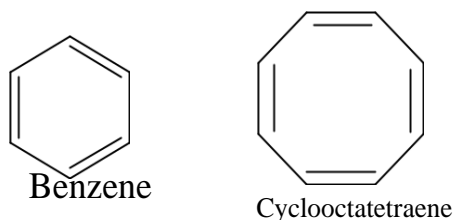
1. An aromatic compound is cyclic and planer.

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There is a p-orbital on every atom of an aromatic ring.

The cyclic arrangement of p-orbitals in an aromatic compound, must contain $(4n+2) \pi$ electrons. This is known as Huckel rule. If such systems contain $4n\pi$ electron then it will be anti aromatic.

Example:

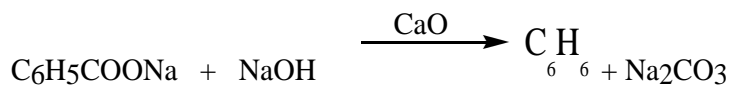


These all compounds follows Huckel rule.

12.8. METHODS OF PREPARATION

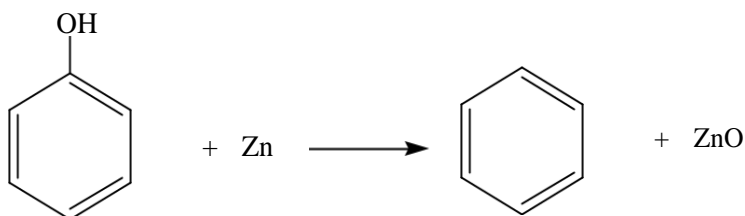
1. From sodium benzoate:

From sodium benzoate C_6H_5COONa on react with sodalime ($NaOH$ and CaO) to give benzene.

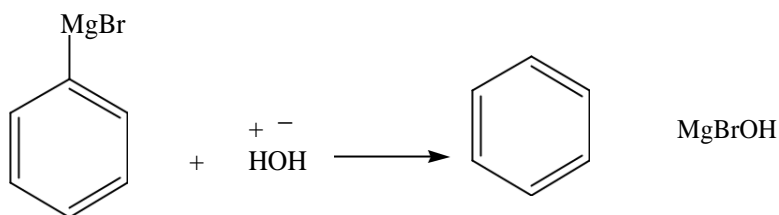


2. From Phenol:

Phenol on react with Zn power gives benzene by removing ZnO .

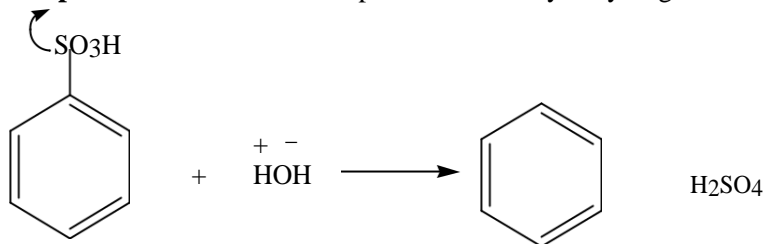


From Grignard Reagent: Grignard Reagent (C_6H_5X) on hydrolysis gives benzene.

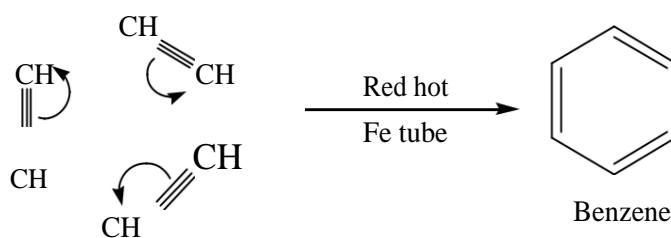


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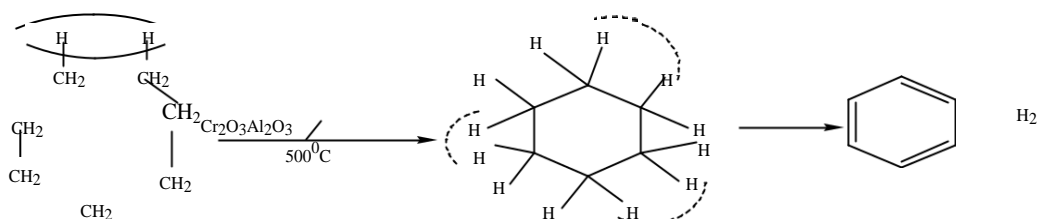
From Benzene sulphonic acid: Benzene sulphonic acid on hydrolysis gives benzene.



5. from acetylene (By polymerization reaction): Acetylene (Ethyne) on polymerization gives benzene.



Industrial Preparation of benzene: n-hexane on heating at 500°C temperature in the presence of Cr_2O_3 supplied by Al_2O_3 gives cyclohexane, which on again dehydrogenation gives C_6H_6 .



12.9. PROPERTIES (PHYSICAL AND CHEMICAL)

A. Physical properties:

Benzene is a colorless liquid

It is insoluble in liquid but soluble in Organic solvent.

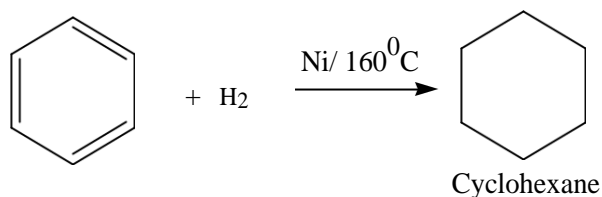
Benzene itself is a good solvent.

Its vapour is poisonous.

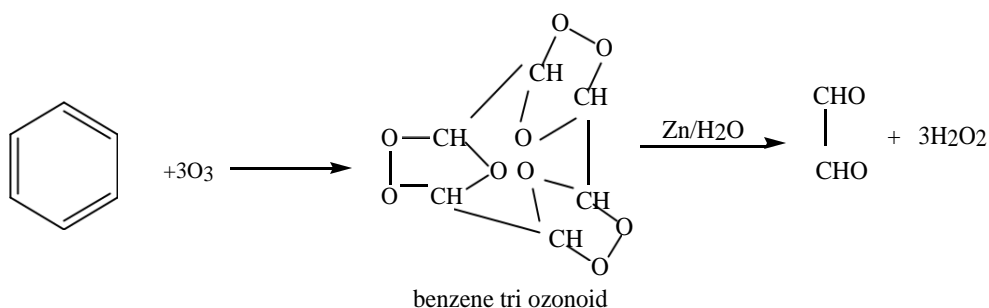
B. Chemical properties of benzene:

Hydrogenation: In the presence of Ni catalyst at 160°C temperature benzene on react with H_2 gives an additional product cyclohexane.

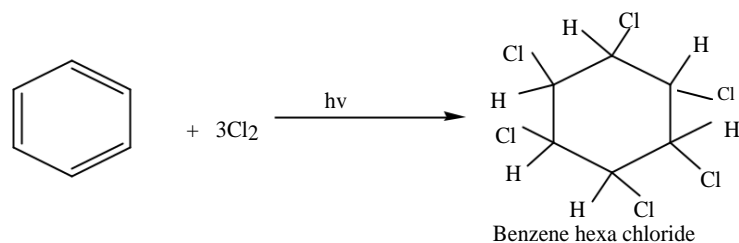
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Ozonolysis: In the presence of CCl₄ benzene on react with O₃ gives benzene tri ozonoid. This on hydrolysis in the presence of Zn gives glyoxal.

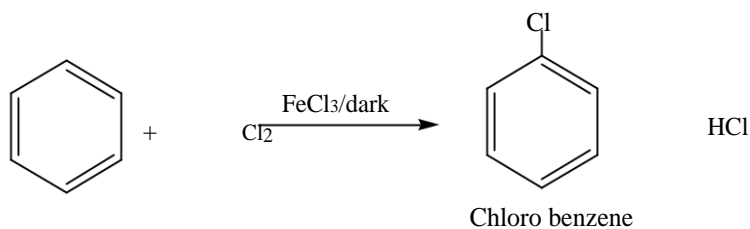


Chlorination: In the presence of sun light benzene on react with Cl₂ gives an additional product benzene hexa chloride (C₆H₆Cl₆, BHC). It is also known as Gamaxine, lindane or 666. It is used as apesticide



4. Electrophilic Substitution reaction:

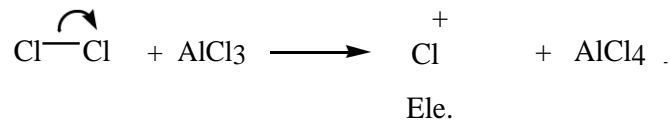
i. Chlorination: In the absence of sun light and in the presence of FeCl₃ or AlCl₃, benzene on react with Cl₂ gives C₆H₅Cl. This reaction known as electrophilic substitution reaction of benzene.



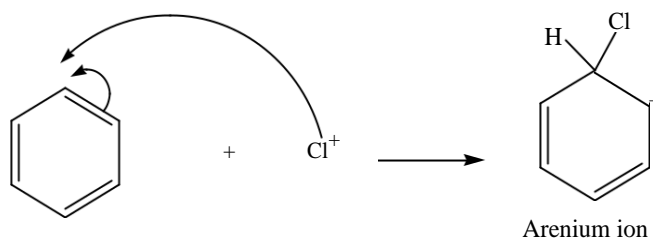
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Mechanism:

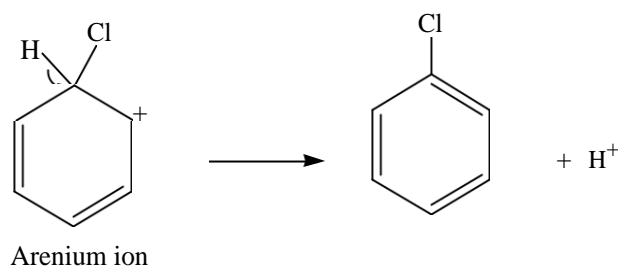
Step I: Formation of electrophile:



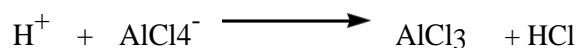
Step II: Attack of electrophile (formation of arenium ion):



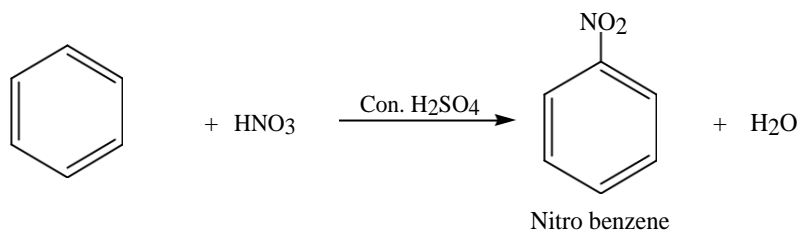
Step III: Formation of product:



Step IV: Formation of catalyst:

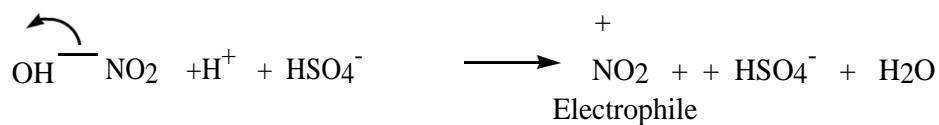


Nitration: In the presence of H_2SO_4 benzene on react with HNO_3 gives nitrobenzene. This reaction is known as nitration.



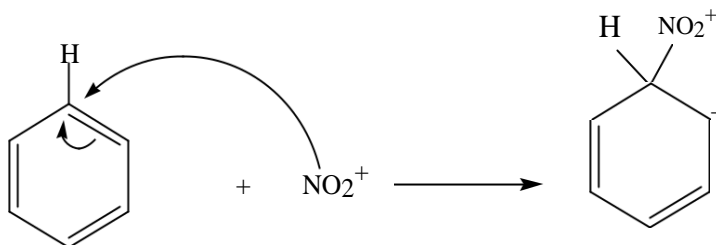
Mechanism:

Step I: Formation of electrophile:

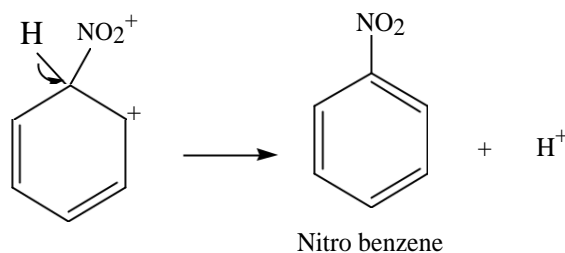


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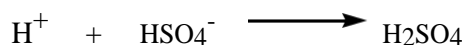
Step II: Attack of Electrophile (NO_2^+)



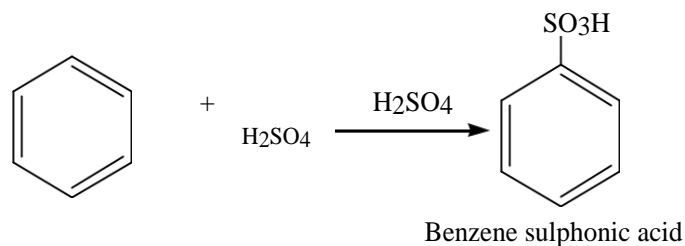
Step III: Formation of product:



Step IV: Formation of catalyst:



Nitration: In the presence of H_2SO_4 , benzene on react with H_2SO_4 gives benzene sulphonic acid. This reaction is known as sulphonation reaction.



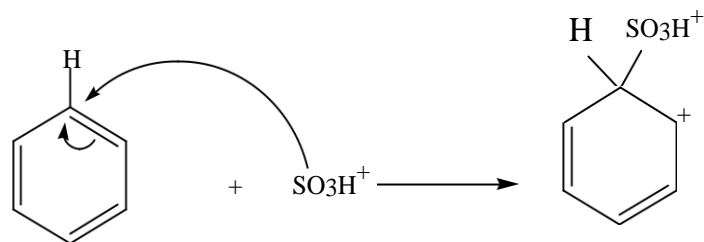
Mechanism:

Step I: Formation of electrophile:

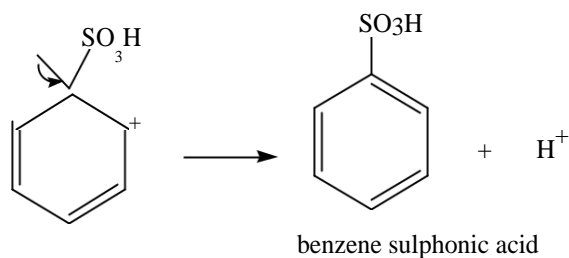


Step II: Attack of electrophile:

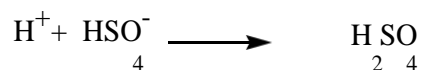
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Step III: Formation of product:

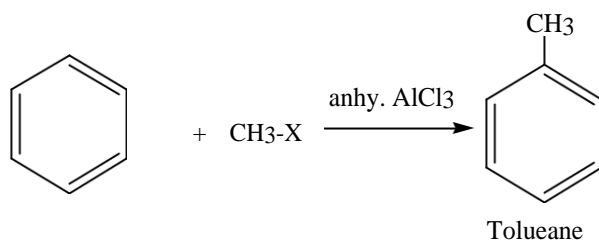


Step IV: Formation of catalyst:

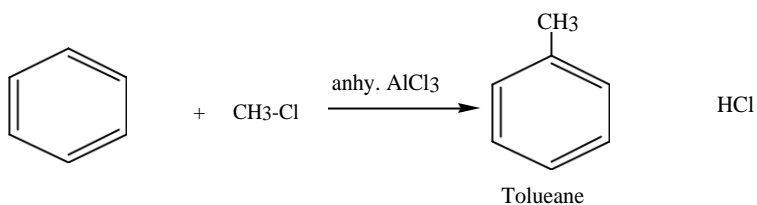


iv. Friedel Craft reaction:

a. Friedel craft alkylation: In the presence of anhydrous AlCl_3 , benzene reacts with R-X to give alkyl benzene. This reaction is known as Friedel Craft acylation.



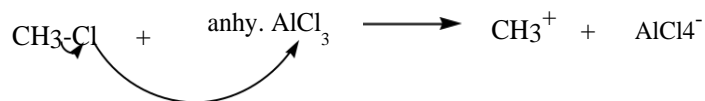
Eg.



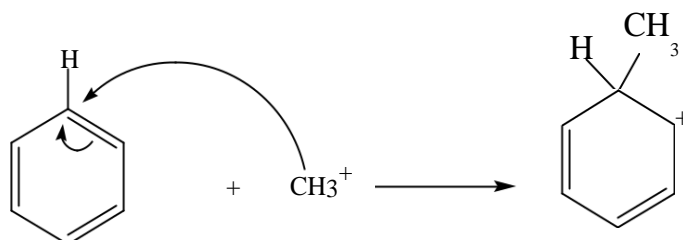
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Mechanism:

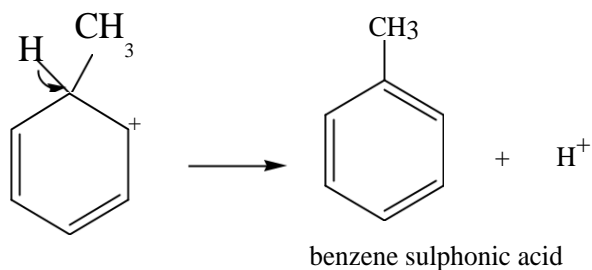
Step I: Formation of electrophile:



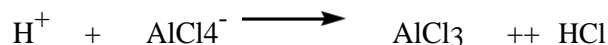
Step II: Attack of electrophile:



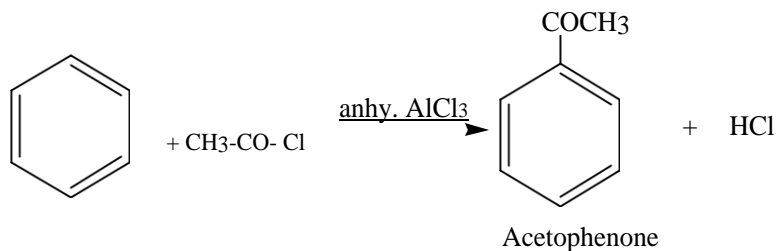
Step III: Formation of product:



Step IV: Formation of catalyst:



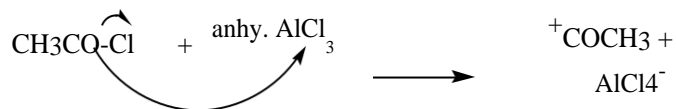
Friedel craft acylation: In the presence of anhydrous AlCl_3 , benzene reacts with R-CO-X to give aceto phenone. This reaction is known as Friedel Craft acylation.



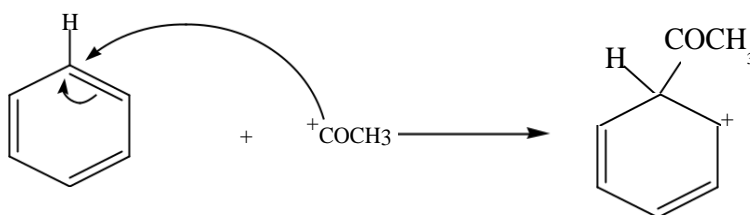
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Mechanism:

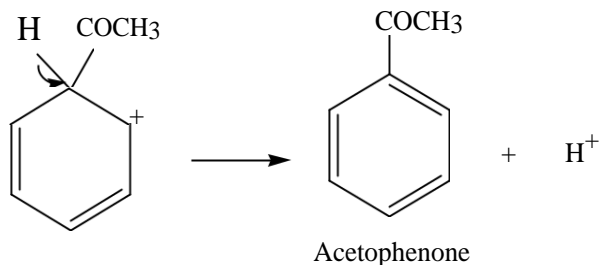
Step I: Formation of electrophile:



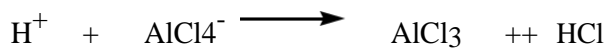
Step II: Attack of electrophile:



Step III: Formation of product:



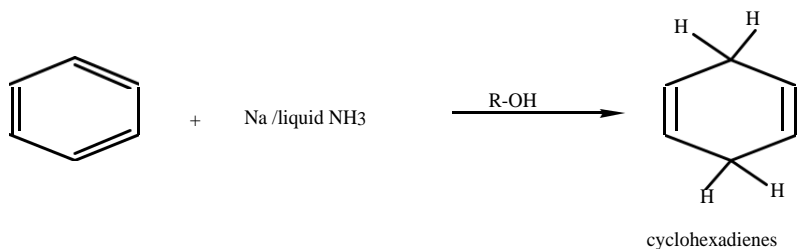
Step IV: Formation of catalyst:



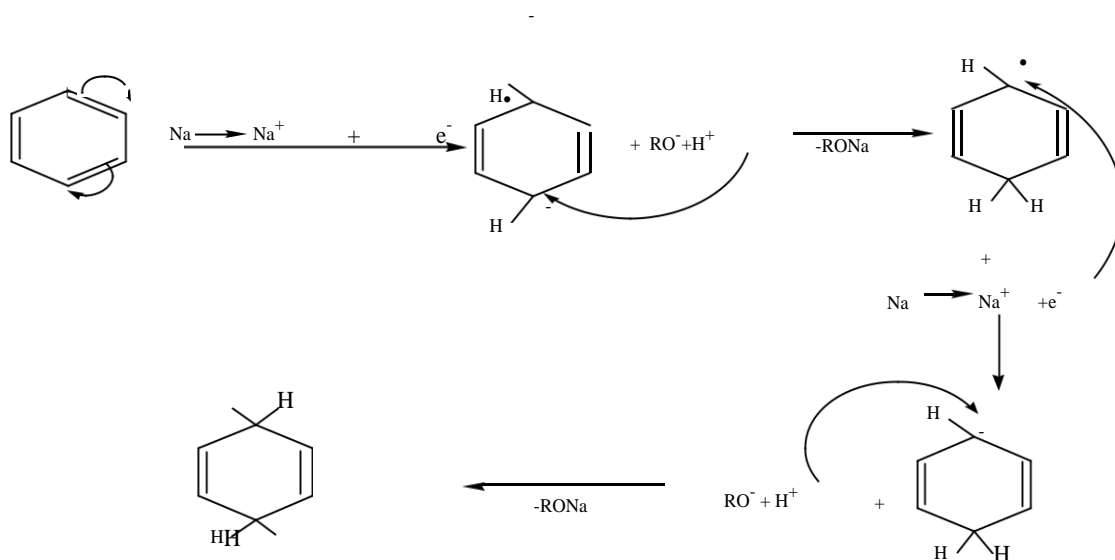
12.10. Reduction of benzene (Birch reduction)

The Birch reduction is an organic reaction where aromatic rings undergo a 1,4-reduction to provide unconjugated cyclohexadienes. The reduction is conducted by sodium or lithium metal in liquid ammonia and in the presence of an alcohol.

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Mechanism:



12.11. Orientation and ortho/para ratio.

As we know that all six hydrogen atom in are identical. So they form only monosubstitute derivative. The next incoming electrophile will forward to the other condition by the I substituent group. Hence, "The tendency of I substituent group for forwarding the II incoming substituent group on ortho, pera or meta positions is known as directive influence." Directive influence is depends upon the nature of I substituent group.

Classification of groups according to directive influence:

According to directive influence the groups are classify into two classes-

Ortho pera director.

Meta director.

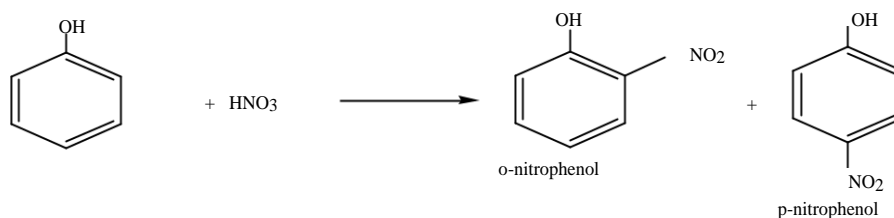
In a C₆H₆ ring the position 2, 6 are equivalent and form ortho product.

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The position 3, 5 are equivalent and gives meta product. The position 4 is unique and gives para product.

Ortho/para directing: If the first substituent group forward to the incoming second substituent group primarily to ortho and para position then it is known as *o*, *p* director.

Example: When C_6H_5OH undergoes nitration then it form 57% *o*-nitro phenol and 43% *p*-nitro phenol.



Condition for *o*-*p* director:

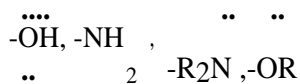
o, *p*-directors are saturated in nature.

They are electron rich, hence they consist lone pair of electrons (except $-R$ groups).

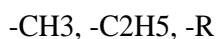
These are ring activator (except, halogen family due to $-I$ effect).

Examples of *o*,*p*-directors-

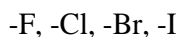
Strongly activator-



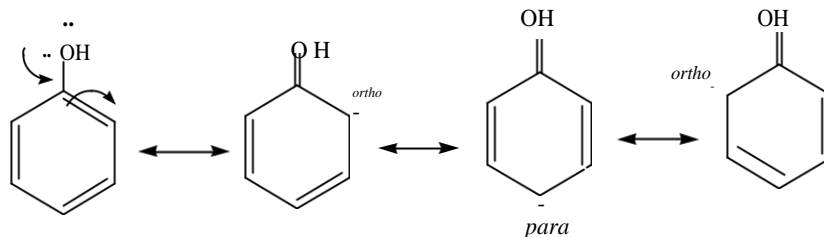
Weak activator-



Ring deactivator-



Mechanism of *o*, *p*-director: The mechanism of *o*, *p*-director group increases the density of e^- at *o*, and *p*-position due to which the incoming electrophile will easily attack at those positions. Hence these are ring activator.

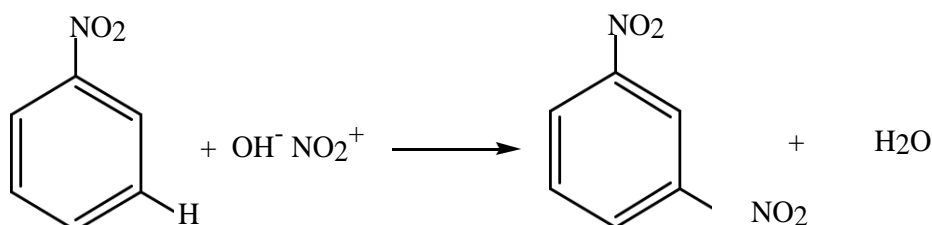


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Thus it is clear from above mechanism that the -OH group increases the density of e^- at o & p-position so the incoming electrophile will easily attack at o and p-positions so, o, p-directors are ring activator. But halogen (-F,-Cl,-Br,-I) are o,p directors but ring deactivator due to -I effect (inductive effect).

Meta-directors- If the first substituent groups forward to the incoming substituent group at meta position then it is referred as meta director.

Example: When undergoes nitration then it form 1, 3 dinitro benzene.



Condition for meta directors-

They have multi bonded (except $-NR_3^+$).

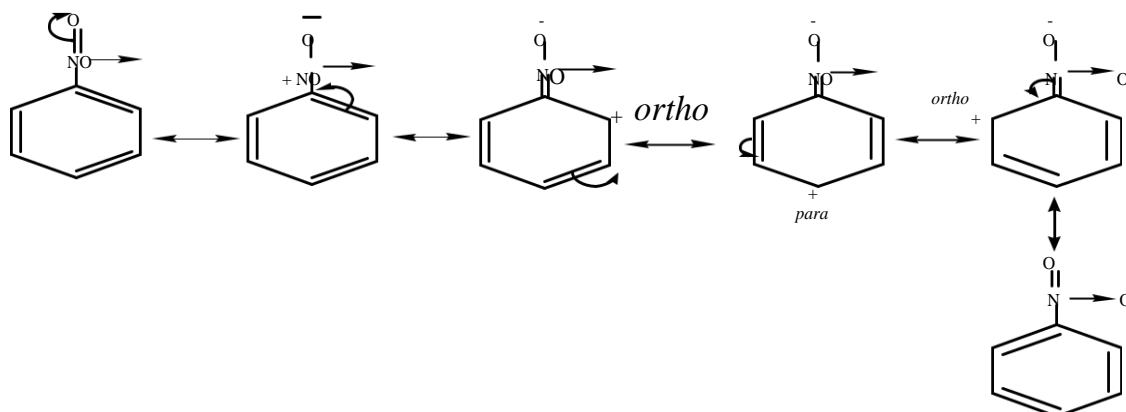
These are electron deficient.

These are ring deactivators because they withdraw the electron from the ring towards itself.

Examples of Meta directors:

$-NO_2$, $-COOH$, $-CHO$, $-SO_3H$, $CONH_2$, $-CN$, $-NR_3^+$ etc.

Mechanism of meta directors:



Thus it is clear from above mechanism that m-directors withdraw the electron from ring. As a result the *ortho* and *para* position becomes partially +ve. Hence the incoming second

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electrophille will attack at neutral meta position. So these are meta directors and also ring deactivator.

12.12. SUMMARY

Aromatic hydrocarbons are known as arenes. In arenes, Benzene is most important compound.

Nomenclature of benzene derivatives is depending on the substituent which added with benzene. By substituent, benzene derivative have several names as Toluene or Methylbenzene.

Benzene aromaticity causes it to undergo electrophilic aromatic substitution reactions. 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.

Some monosubstituted benzenes are named as substituted benzenes (e.g., bromobenzene, nitrobenzene)

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.

Stability of benzene depends on the resonating structures. By resonance we can easily define the stability of benzene.

Aromaticity of benzene and some other stable compounds can easily be given by Huckel Rule.

12.13 TERMINAL QUESTIONS

A. Short answer type question:

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Discuss the orbital structure of benzene,

State Huckel rule. Give the suitable example.

Give the mechanism of Friedel Crafts acylation reaction.

Explain meta directing nature of nitro group.

Methyl group attached to benzene ring has no lone pair of electrons but is still ortho and para directing in nature. Explain why?

What are non benzenoid compounds?

What is aromaticity?

What is the cause of aromatic character of benzene in terms of Huckels rule?

Explain why methyl group in toluene is ortho and para directing in nature.

Give the mechanism of nitration of benzene.

Explain the stability of benzene on the basis of orbital structure.

How will you prepare the following compounds from benzene?

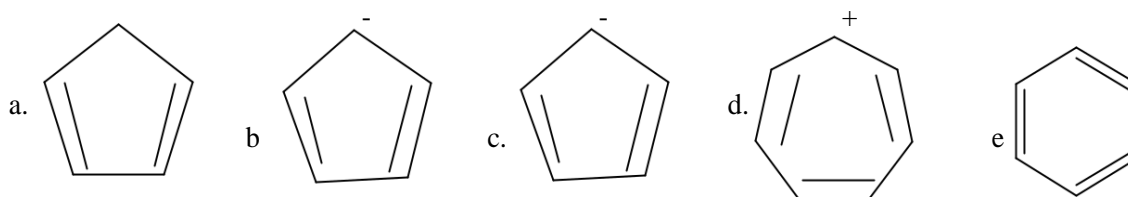
a. Acetophenone b. Toluene c. Chlorobenzene d. Benzene hexa chloride

Discuss the orientation of electrophilic substitution in nitrobenzene.

What are electrophilic substitution reactions? Discuss the mechanism of sulphonation of benzene.

Explain why $-NH_2$ group when attached to benzene ring is ortho and para directing in nature.

Which of the following have aromatic and why?



16. List the following compounds in order of decreasing reactivity toward nucleophilic aromatic substitution: chlorobenzene, 1-chloro-2,4-dinitrobenzene, p-chloronitrobenzene.

17. Show how each of the following compounds could be synthesized from benzene:

a. nitrophenol

b. p-nitroaniline

c. p-bromoanisole.

18. Draw the structure of each of the following compounds:

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- a. m-chlorotoluene b. p-bromophenol c. o-nitroaniline d. m-dichlorobenzene
- e. 2,5 dinitrobenzaldehyde f. m-chlorobenzonitrile g. o-xylene

B. Objective type question:

- In nitration of benzene, the electrophile is-
a. H^+ b. SO_2 c. SO_3 d. NO_2^+
- Benzene reacts with chlorine in the presence of $FeCl_3$ catalyst to form.
a. Hehachlorobenzene b. Chlorobenzene
c. Hexachlorocyclohexane d. benzyl chloride
- Gammexene is:
a. hexachloroethane b. DDT c. TNT d. Hexachlorocyclohexane
- Ozonolysis of benzene gives:
a. formic acid b. glyoxal c. formaldehyde d. glycine
- Which of the following compounds undergoes nitration most easily?
a. Benzene b. toluene c. Nitrobenzene d. Benzoic acid
- Toluene reacts with bromine in the presence of UV light to give.
a. m-bromotoluene b. benzyl bromide c. o-bromotoluene d. benzoyl bromide

With respect to the electrophilic aromatic substitution of benzene which of the following is:

- A non-aromatic intermediate is formed
- Benzene acts as an electrophile
- A proton is lost in the final step
- Resonance forms are important

Which of the following statements is **incorrect**: aromatic compounds?

- Are planar
- Have $4n$ π -electrons
- Are cyclic
- Are generally less reactive than similarly substituted alkenes

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When considering electrophilic aromatic substitution reactions electron withdrawing substituents (e.g. nitro) are described as:

- Ortho/para directing and activating
- Ortho/para directing and deactivating
- Meta directing and activating
- Meta directing and deactivating

The Friedel-Crafts alkylation.

- Works very well for primary chlorides
- Works very well for tertiary chlorides
- Works very well for acyl chlorides
- Works very well without a catalyst

With respect to the electrophilic aromatic substitution of benzene which of the following is not true:

- A non-aromatic intermediate is formed
- Benzene acts as an electrophile
- A proton is lost in the final step
- Resonance forms are important

Which of the following is not associated with electrophilic aromatic substitution?

- The formation of nitrobenzene
- The formation of benzyne
- The formation of bromobenzene
- The formation of benzene sulfonic acid

Answers

1. c, 2. b, 3. b, 4. b, 5. b, 6. b, 7. b, 8. b, 9. d, 10. b, 11. b, 12. b

References:

Advanced Organic Chemistry by, Jagdamba Singh and L.D.S. Yadav, Pragati Prakashana.

Paula Yurkanis Bruice 4th edition.

Organic Reactions and Their Mechanisms, by P. S. Kalsi, New edge Science.

R. L. Madan, S. Chand and company Pvt. Ltd.

UNIT 13: ALKYL HALIDE

CONTENTS:

- 13.1 Objectives
- 13.2 Introduction
- 13.3 Nomenclature and classification of alkyl halides
- 13.4 Methods of formation
- 13.5 Physical properties
- 13.6 Chemical reactions
- 13.7 Mechanism of nucleophilic substitution reactions of alkyl halides
 - 13.7.1 SN1 and SN2 and SNI reaction with energy profile diagrams
- 13.8 Elimination reactions (Types of elimination reactions)
- 13.9 Polyhalogen compounds-Chloroform, carbon tetra chloride
- 13.10 Summary
- 13.11 Terminal Question

13.1 OBJECTIVE

In this chapter we have to study about Alkyl halide: Its classification, Nomenclature. Describe the reactions involved in the preparation of alkyl halide (haloalkanes) and understand various reactions that they undergo. . Correlate the structures of alkyl halide with various types of reactions. Use stereochemistry as a tool for understanding the reaction mechanism. Nucleophilic Substitution Reaction of Alkyl Halides as S_N^1 Reaction, S_N^2 Reactions and its mechanism, Elimination Reactions as E1 and E2 reaction and its mechanism, Poly halogen compound and Terminal Questions

13.2 INTRODUCTION

The replacement of hydrogen atom(s) in a hydrocarbon, aliphatic by halogen atom(s) results in the formation of alkyl halide (haloalkane). Haloalkanes contain halogen atom(s) attached to the sp^3 hybridized carbon atom of an alkyl group. Many halogen containing

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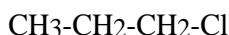
organic compounds occur in nature and some of these are clinically useful. These classes of compounds find wide applications in industry as well as in day-to-day life. They are used as solvents for relatively non-polar compounds and as starting materials for the synthesis of wide range of organic compounds. Chlorine containing antibiotic, chloramphenicol, produced by soil microorganisms is very effective for the treatment of typhoid fever. In this Unit, you will study the important methods of preparation, physical and chemical properties and uses of alkyl halide.

13.3 NOMENCLATURE AND CLASSIFICATION OF ALKYL HALIDES

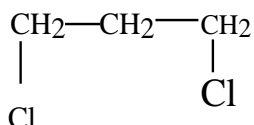
A. Classification on the basis of number of halogen atom:

Aliphatic halogen compound (alkyl halide) can be classified in to following classes:

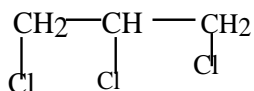
Monohalogen compounds: Compound which contains one halogen in the molecule is called Monohalogen compounds.



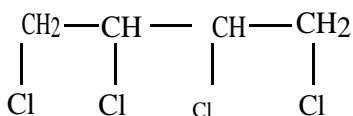
Dihalogen compounds: Compound which contains two halogens in the molecule is called Monohalogen compounds.



Trihalogen compounds: Compound which contains three halogens in the molecule is called Monohalogen compounds.

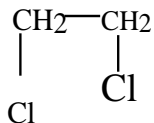


Tetrahalogen compounds: Compound which contains four halogens in the molecule is called Monohalogen compounds.

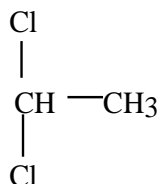


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Vicinal dihalide: Compounds containing two halogens on adjacent carbon in the compound is called vicinal dihalide.



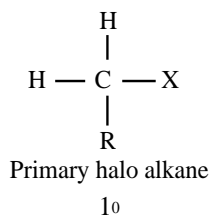
Geminal dihalide: Compound containing two halogen on the same carbon atom is called Geminal dihalide.



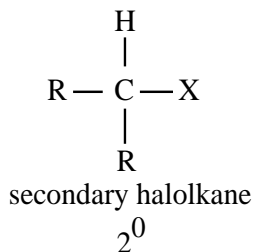
B. Classification On the basis of the nature of the carbon attached to the halogen atom:

On the basis of the nature of the carbon attached to the halogen atom, alkyl halides are classified in three types.

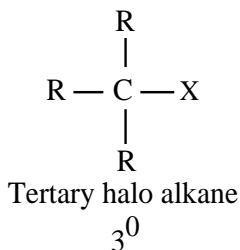
1. Primary alkyl halide:



2. Secondary alkyl halide:



3. Tertiary alkyl halide:



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Here R = Alkyl group CH₃, C₂H₅, C₃H₇ etc.

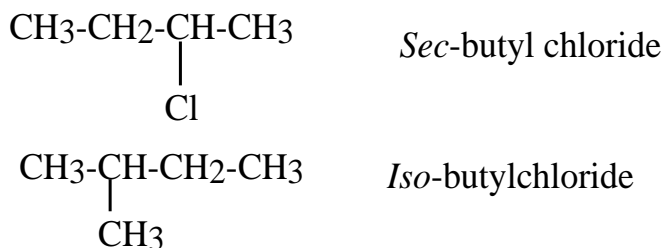
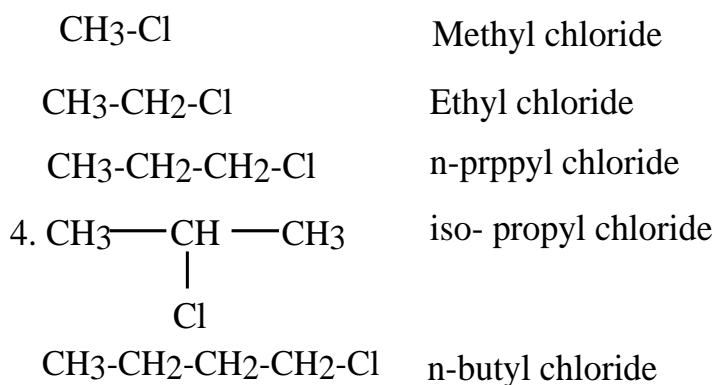
X = Halogen atom (Cl, Br, Ietc.)

Nomenclature:

Alkyl halides are named into two ways

A. Common System: In this system the alkyl group attached to the halogen atom is named first. This is then followed by an appropriate word chloride, bromide or fluoride.

Example:



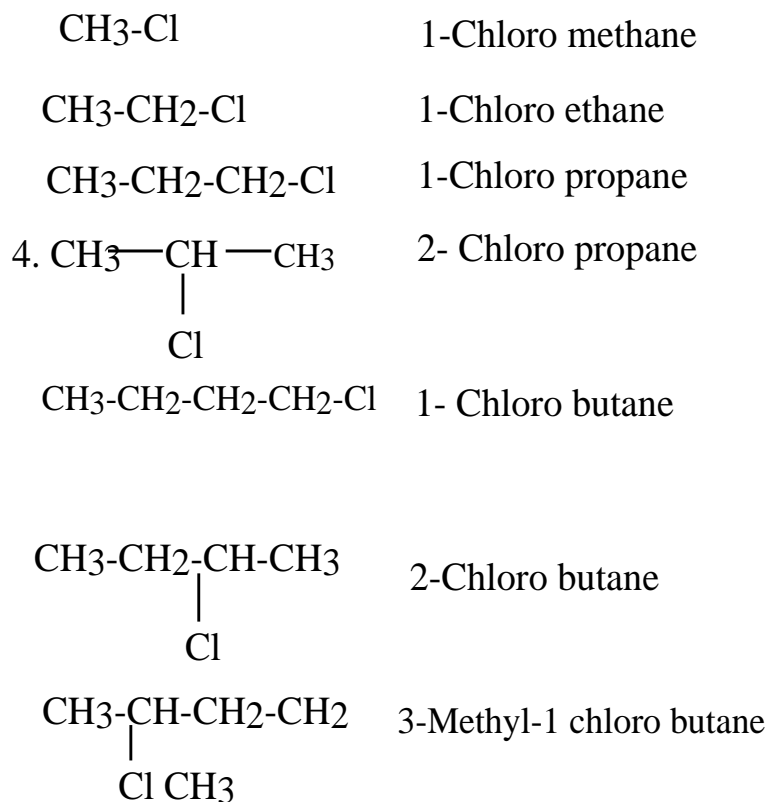
B. IUPAC System: It has following rules-

1. Select the longest carbon chain containing the halogen atom.
2. Number the chain so as to give the carbon carrying the halogen atom the lowest possible number.
3. Indicate the position of the halogen atom by a number and by the fluoro, chloro, bromo.

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4. Name other substituent and indicate their position by numbers.

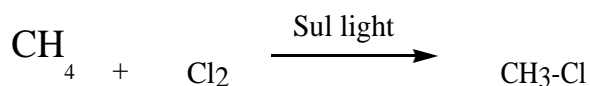
Example:



13.4. METHODS OF FORMATION

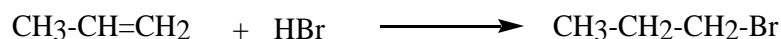
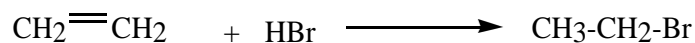
Alkyl halides can be prepared by the following methods:-

Halogenation of Alkanes: Alkanes react with Cl_2 or Br_2 in the presence of UV light or at $^\circ\text{C}$ to give alkyl halides along with polyhalogen derivatives.



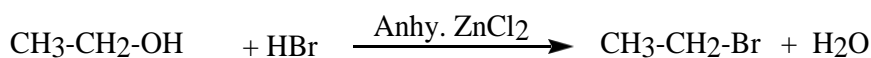
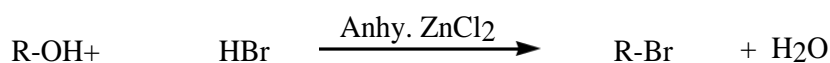
From alkene (Addition of Halogen acids to Alkenes): Halogen acids add to alkenes to yield alkyl halides. The mode of addition follows Markonikoff rule, except in presence of organic peroxides.

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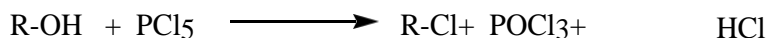
3. From Alcohol:

a. Reaction with Hydrogen halide: When any alcohol react with hydrogen halide in the presence of anhydrous ZnCl_2 , then it gives corresponding alkyl halide.



b. Reaction with phosphorus penta chloride (PCl_5):

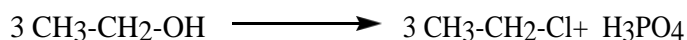
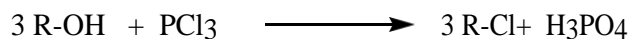
Alcohol on react with PCl_5 gives alkyl halide by removing phosphoryl chloride (POCl_3).



Ethyl chloride

c. Reaction with phosphorus tri chloride (PCl_3):

Alcohol on react with PCl_3 gives alkyl halide by removing of H_3PO_4 .

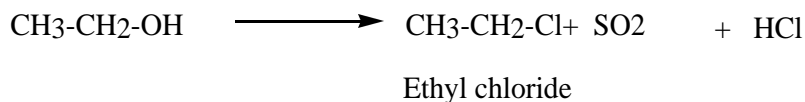
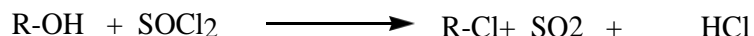


Ethyl chloride

d. Reaction with thionyl chloride (SOCl_2).

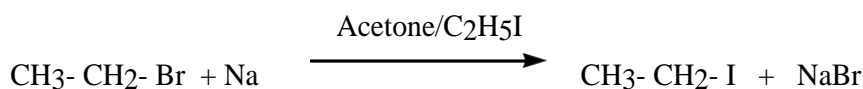
Alcohol on react with SOCl_2 gives alkyl halide by removing of CO_2 and HCl .

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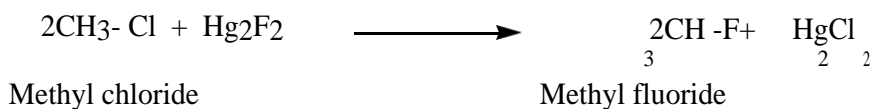


4. From halogen exchange reaction:

This reaction is particularly suitable for preparing alkyl iodides. The alkyl bromide or chloride is heated with a conc. sodium iodide in acetone.



Alkyl fluorides are also prepared by treating alkyl chloride or bromide with inorganic fluorides.

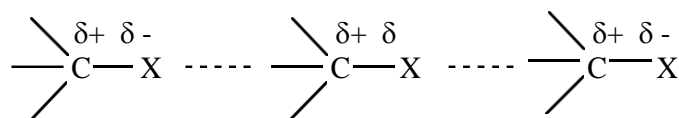


13.5 PHYSICAL PROPERTIES

The lower alkyl halides (CH_3F , CH_3Cl , CH_3Br , $\text{C}_2\text{H}_5\text{Cl}$) are gases at room temperature. The other alkyl halides containing upto C18 are liquids having high boiling points.

Haloalkanes are moderately polar molecules. Still they are immiscible in water. It is due to their inability to form hydrogen bonds with water molecules.

The melting and boiling points of haloalkanes are higher than those of their parent hydrocarbons (Table 13.1) This is due to (i) the greater molecular mass and hence greater magnitude of van-der Waals forces of attraction in halo compounds than in the parent hydrocarbons and (ii) the existence of intermolecular dipole-dipole interaction, as shown below:



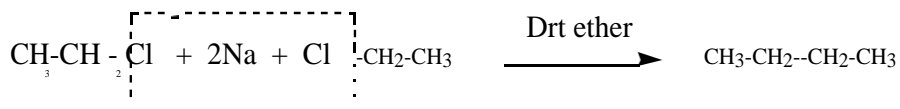
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For a given alkyl group, the boiling points increase from fluoro to iodo compounds as the size of halogen atom increases. The boiling points of halomethanes, haloethanes and halobenzene given in the Table 13.1 to show this variation.

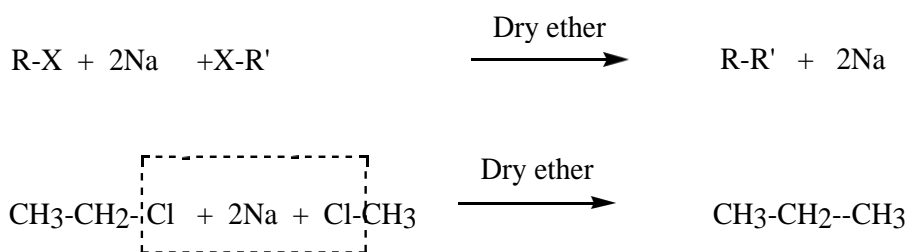
Compound	Melting point (K)				
	X=H	X=F	X=Cl	X=Br	X=I
CH ₃ -X	111.5	194.6	248.8	276.6	315.4
C ₂ H ₅ -X	184.3	241	285	311.4	345
C ₆ H ₅ -X	351	358	405	429	461

13.5. CHEMICAL REACTIONS

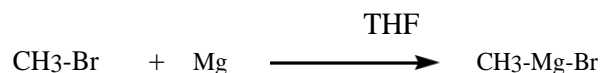
Wurtz reaction: In this reaction R-X is treated with Na in the presence of dry ether to give alkane. This reaction is also known as coupling reaction.



Wurtz Fittig reaction: When two different alkyl halides react with Na metal in the presence of dry ether then it gives odd number containing alkanes. This reaction is known as Wurtz Fittig reaction.

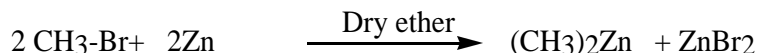


Reaction with Magnesium (Mg): When any alkyl halide reacts with Magnesium metal then it gives Organometallic compound.

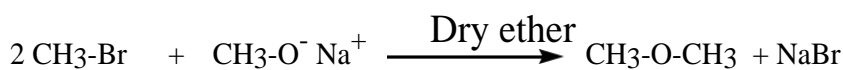


Frankland Reaction: In this reaction R-X is treated with Zn in the presence of dry ether to give di-alkyl-Zn compound.

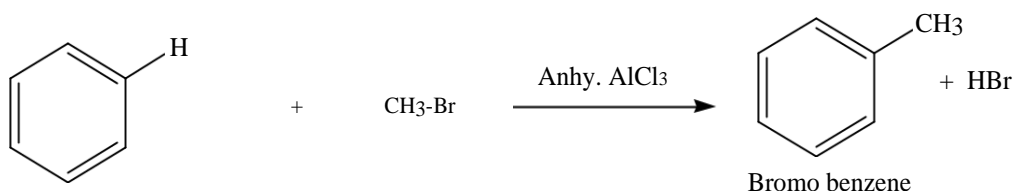
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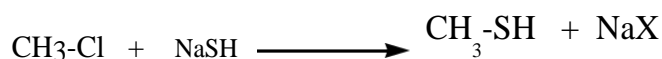
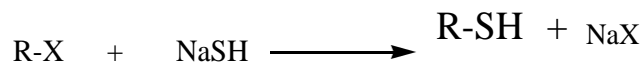
Williamson synthesis: In this reaction R-X is treated with R-O-Na (sodium alkoxide) in the presence of dry ether to form ether and this reaction has great importance to form both types of ether symmetrical and unsymmetrical.



Friedal Craft reaction: In this reaction when an alkyl halide react with aromatic hydrocarbon like benzene then it gives alkyl benzene.



Reaction with Sodium hydro sulphide (NaSH): In this reaction when an alkyl halide reacts with Sodium hydro sulphide then it give thio alcohol.



13.6 MECHANISM OF NUCLEOPHILIC SUBSTITUTION

REACTIONS OF ALKYL HALIDES

During nucleophilic substitution reaction the C-X bond undergoes to the breaking and the C-nucleophile bond to be formation. In the case of R-X this processes takes place any of the three types.

The breaking of C-X bond takes place followed by the formation of C-Nu bond.

The formation and the breaking takes place simultaneously.

The formation of C-Nu bond takes place followed by the breaking of C-X bond. Generally the initial two types takes place in aliphatic alkyl halides and the third types takes place in aryl halides (Ar-X).

Classification of Nucleophilic substitution reaction:

The Nucleophilic substitution Reaction is classified in to following two classes.

(1) SN1 (Unimolecular Nucleophilic Substitution reaction):

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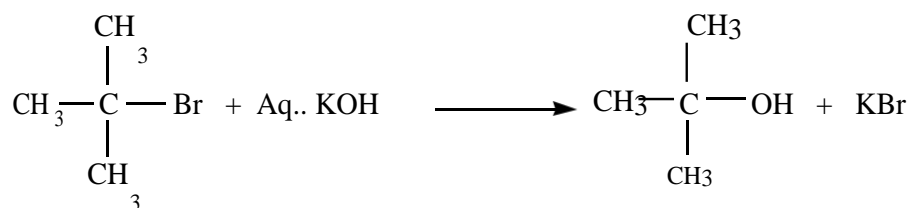
It represents that Mononucleophilic substitution reaction. Generally such type of mechanism is carried by tert. alkyl halides and it is the two step mechanism.

Step-I

In this step the C-X bond undergoes heterolytic fission to give an intermediate carbonium ion and it is the slowest step. So it is the rate determining step.

Step-II

It is the faster one and in it the nucleophile is attacked to the carbonium ion to form the required compound.

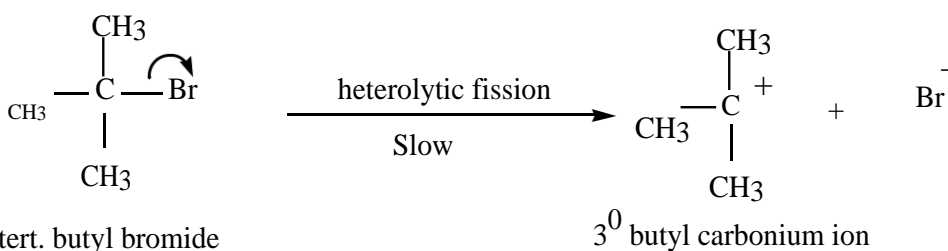


Mechanism:

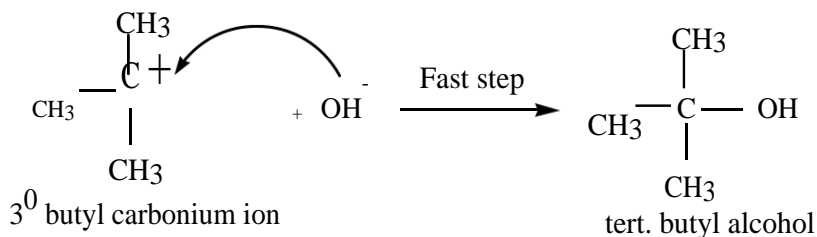
Formation of Nucleophile:



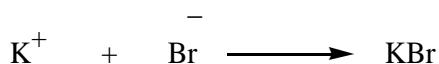
Step I- Slow step:



Step II Fast step:



Formation of KBr:



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It is clear from above mechanism that in the slowest step only one reactant (ter. butyl bromide) takes place, hence the rate of reaction depends upon the concentration of it, so it is a first order reaction. So this reaction is known as uni-molecular nucleophilic substitution (SN^1) reaction.

Mathematically:

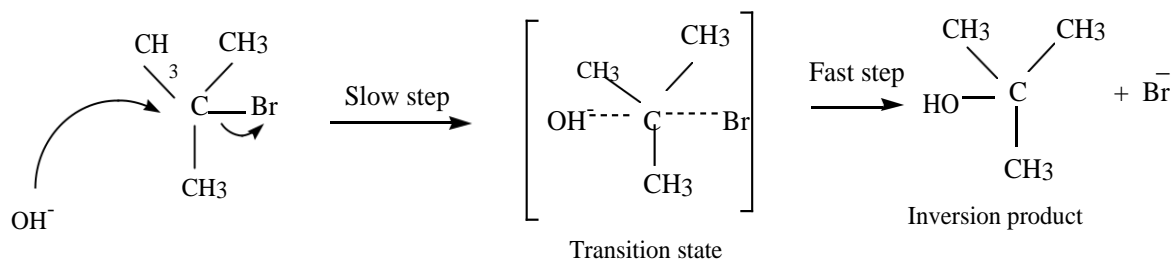
$$\frac{dx}{dt} = k [\text{Alkyl halide}]$$

(2) SN^2 (Bi-molecular nucleophilic substitution reaction) Reaction:

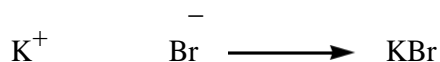
This type of mechanism is generally followed by primary alkyl halides and it is the one step mechanism. In this type of mechanism Nu^- attacks that carbon which is attached from the halogen atom, from the opposite side of the halogen carrying carbon atom because there is repulsion between nucleophilic and halogen. It is the slowest step.

Mechanism:

Formation of Nucleophile:



Formation of KBr:



In the transition state or activated complex the C-Nu bond is partially formed and the C-Br bond is partially breaking. Hence in this stage the C-Nu bond starts to form and the C-Br bond starts to break and finally is formed. In this mechanism the C-H bonds are like the spokes and are along the axis.

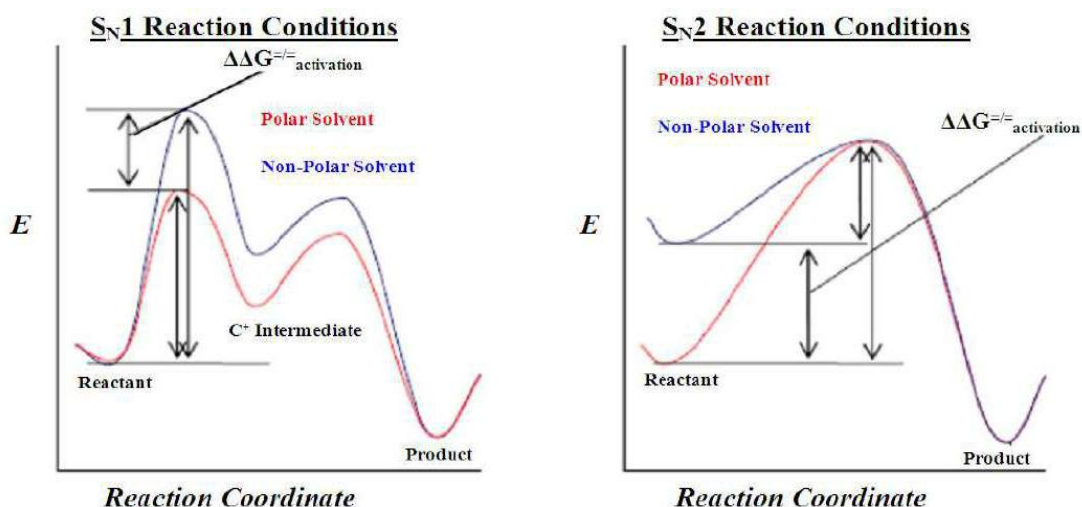
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Since in the slowest step there are two reacting species one is alkali & other is R-X. So its rates depends upon the concentration of both. So its is Bi-molecular Nucleophilic Substitution reaction reaction S_N^2 .

Mathematically:

$$\frac{dx}{dt} = K [\text{Alkyl halide}] [\text{KOH}]$$

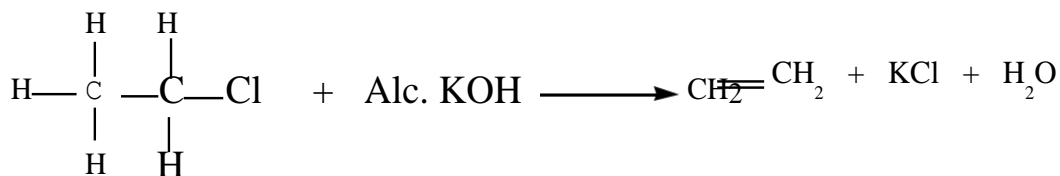
13.6.1. S_N1 and S_N2 reaction with energy profile diagrams



13.7. ELIMINATION REACTIONS (TYPES OF ELIMINATION REACTIONS)

In this type of reaction the atoms or group of atoms are eliminated from two adjacent C-atoms to give the product.

Example: R-X on react with KOH (alc.) gives alkene by undergoing dehydrohalogenation



Types of elimination reaction:

Elimination reactions are classified into two classes. One is E^1 and other is E^2 reaction.

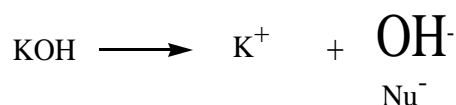
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E¹ Elimination (Uni-molecular Elimination Reaction): Generally such type of mechanism is observed in tert. alkyl halides and it is two step mechanism.

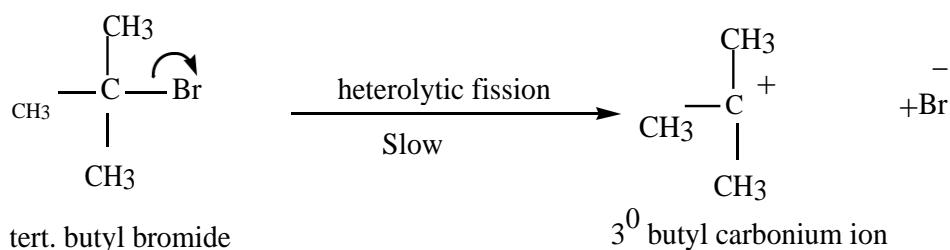
Step I: It is the slowest step. In this step the C-X bond undergoes heterolytic fission to form an intermediate carbonium ion and this step is also known as rate determining step.

Step II: It is the faster one. In this step the Nu⁻ is eliminate a β- hydrogen from the carbonium ion and form alkene.

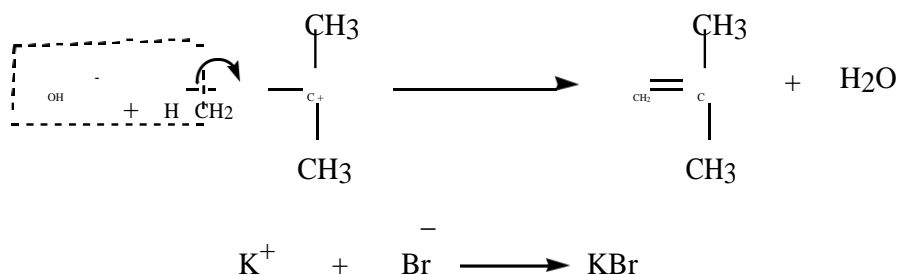
Mechanism:



Step I:



Step II:



2. E² Elimination (Bi-molecular Elimination Reaction): E2 mechanism is concerted process and a bimolecular reaction. Because the base removes a hydrogen at the same time the C—X bond is broken to form a halide ion the rate law for the rate determining step is dependent on both the alkyl halide and the base :

$$\text{Rate} = k [\text{alkyl halide}] [\text{base}]$$

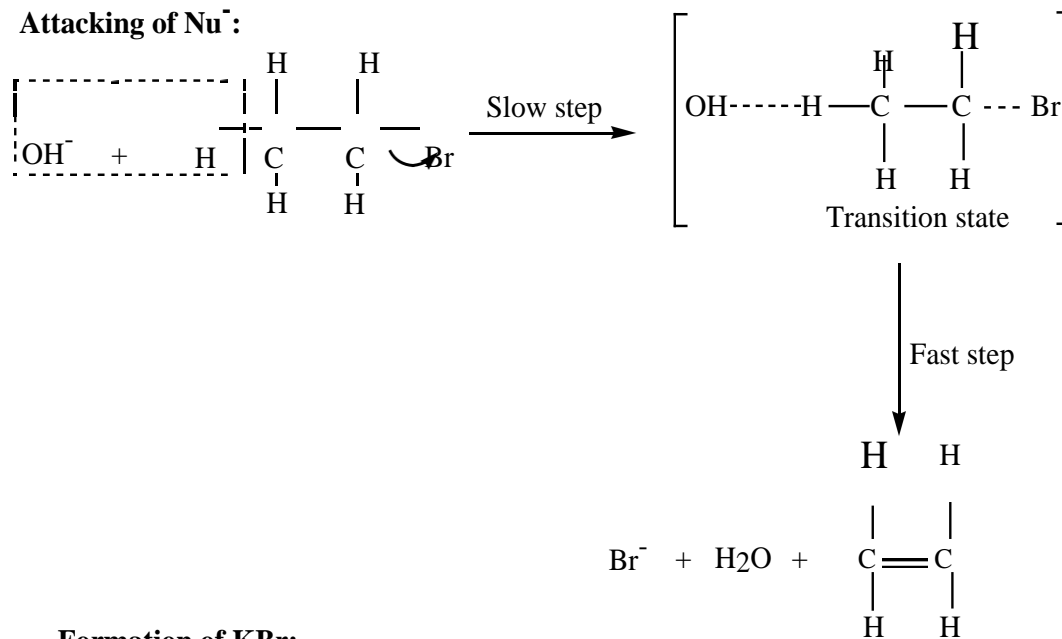
The stronger the base the more likely it is that E2 mechanism will be in operation. E2 mechanism illustrate by reaction of 1-bromopropane with sodiummethoxide.

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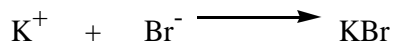
Formation of Nucleophile:



Attacking of Nu⁻:



Formation of KBr:



Thus it is clear from above mechanism in the slowest step, which is rate determining step two reacting species takes place. Hence the rate of reaction depends upon both concentrations. So it is of two order reaction.

13.8. POLYHALOGEN COMPOUNDS- CHLOROFORM, CARBON TETRA CHLORIDE

A large number of polyhalogen aliphatic and aromatic halogen compounds are known. These are extensively used as solvents, pesticides, anaesthetics etc. Some of the important compounds are chloroform (CHCl₃), iodoform (CHI₃), carbon tetrachloride (CCl₄), benzene hexachloride (BHC), DDT, etc.

A. Chloroform (CHCl₃): Chloroform is an important trihalogen derivative of methane. In the past chloroform was extensively used as general anesthetic for surgery but it is rarely

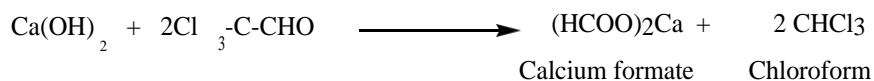
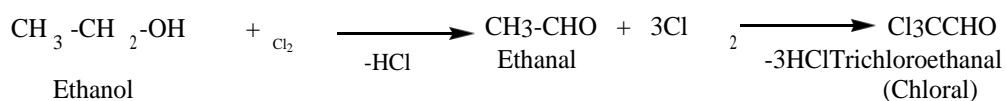
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used for this purpose now because it causes extensive liver damage. Its IUPAC name is trichloromethane

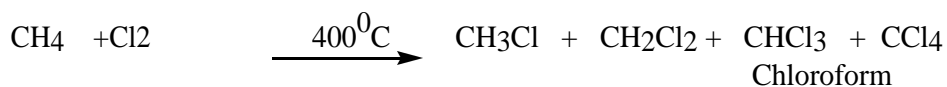
Preparation of Chloroform:

1. From Ethanol:

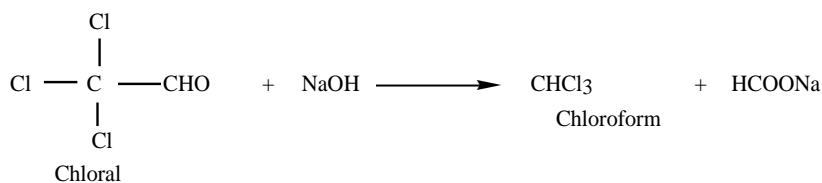
Chloroform is prepared in the laboratory by treating ethanol or propanone with chlorine gas in the presence of an alkali. Following is the reaction sequence in this process-



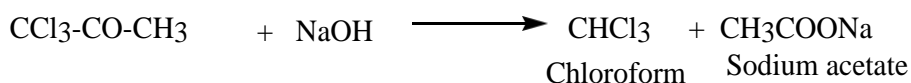
From Methane: Methane on chlorination gives CHCl_3 which is separated from the mixture.



From Chloral (Trichloro acetaldehyde): Chloral on react with NaOH or Ca(OH)_2 to give chloroform.

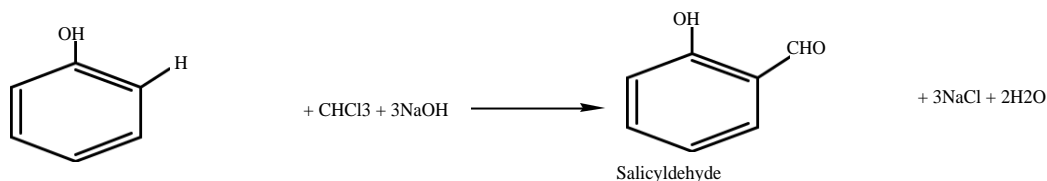


From trichloroacetone: Trichloro acetone on react with NaOH gives CHCl_3 by removing sodium acetate.



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Rimer-Tieman Reaction- Chloroform reacts with phenol in the presence of sodium hydroxide to form salicylaldehyde.



Uses:

i. Chloroform is used as a solvent for fats, waxes and rubber.

In the preparation of chloropicrin and chloretone.

As a laboratory solvent

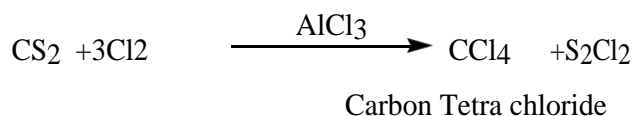
As an anaesthetic.

In medicines such as cough syrups.

B. carbon tetra chloride:

Preparation: Carbon tetrachloride is manufactured by following process:

From Carbon Disulphide: By the action of chlorine on carbon disulphide. Aluminium chloride is used as catalyst



Carbon tetrachloride is removed from the mixture by fractional distillation.

2. From Chloroform:



3. From methane:



Physical properties:

Carbon tetrachloride is colourless liquid.

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It is insoluble in water but soluble in ethanol and ether.

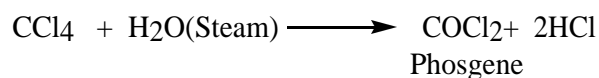
It is an excellent solvent for oils, waxes, fats and greases.

It is used as a fire- extinguisher under the name Pyrene because it is non-inflammable. When a spray of carbon tetrachloride is directed at fire, its dense vapours prevent the oxygen of air from reaching the burning articles.

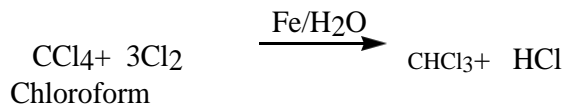
Chemical Properties:

Carbon tetrachloride is inert to most organic reagents. It gives the following reaction-

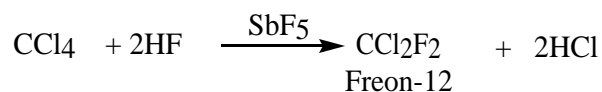
Reaction with Steam: Carbon tetrachloride vapours react with steam at 500°C to give phosgene.



Reduction- Carbon tetrachloride can be reduced moist iron filling to give chloroform.



Reaction with HF: Carbon tetrachloride reacts with hydrogen fluoride in the presence of antimony penta fluoride to form dichlorodifluoromethane.

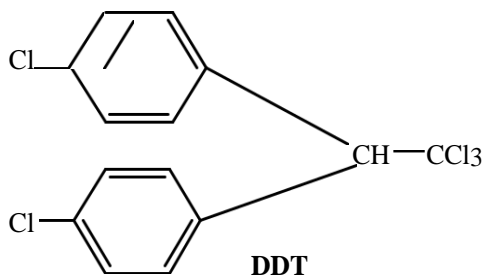


Freon-12 is widely used as a refrigerant and propellant in aerosol sprays of all kinds.

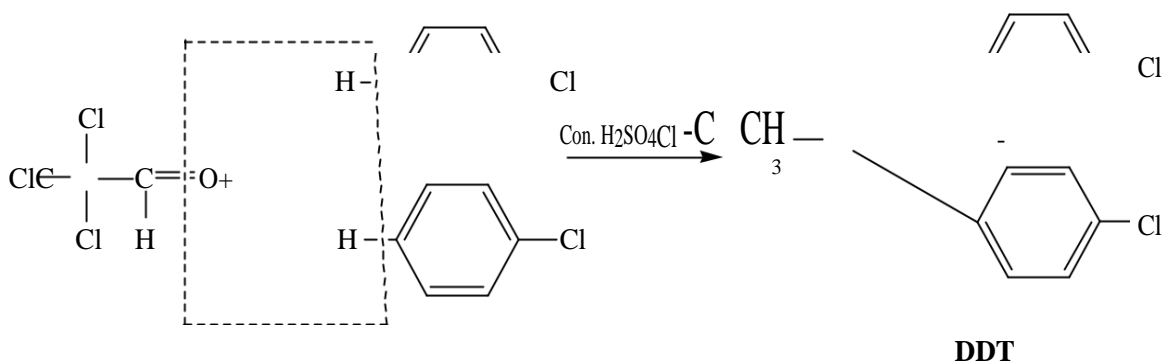
C. Dichlorodiphenyltrichloroethane (DDT):

It is available in several different forms: powder, aerosols, granules, etc.

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Methods of preparation: Chloro benzene on react with CCl_3CHO (Chloral) in the presence of Con. H_2SO_4 form DDT by removing H_2O .

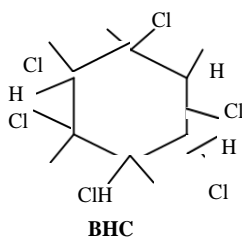


Uses:

It is used mainly to control mosquito-borne malaria. It is also used as an agricultural insecticide. The use of DDT has been banned in many countries because being non-biodegradable, it accumulates in environment. It is toxic to other living organisms such as: mammals, birds, fishes, etc.

D. Benzene Hexa Chloride (BHC):

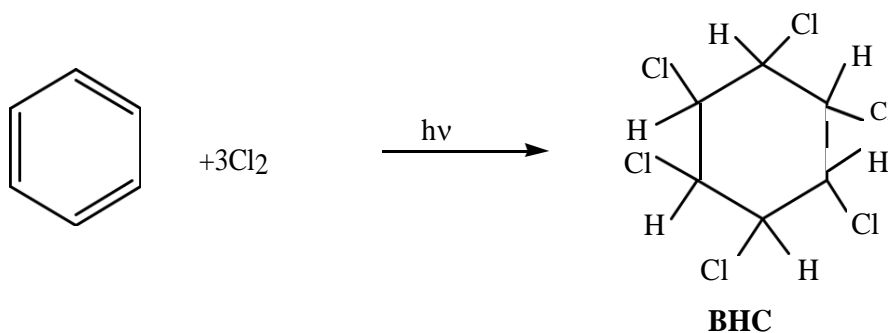
It is sold under the name gammexane, lindane or 666 and has the formula $\text{C}_6\text{H}_6\text{Cl}_6$.



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Methods of the preparation:

In the presence of sun light benzene on react with Cl_2 gives an additional compound B.H.C., it is also known as 666 or Gamexene or lindane.



Uses: It is used as a pesticide in agriculture.

13.10 SUMMARY

Alkyl halides may be classified as mono, di, or polyhalogen (tri-, tetra-, etc.) compounds depending on whether they contain one, two or more halogen atoms in their structures.

Alkyl halides are prepared by the free radical halogenation of alkanes, addition of halogen acids to alkenes, replacement of $-\text{OH}$ 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. These are slightly soluble in water but completely soluble in organic solvents.

In addition to undergoing nucleophilic substitution reactions, alkyl halides undergo β -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.

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A number of polyhalogen compounds e.g., dichloromethane, chloroform, iodoform, carbon tetrachloride, Freon and DDT have many industrial applications. However, some of these compounds cannot be easily decomposed and even cause depletion of ozone layer and are proving environmental hazards.

13.11 TERMINAL QUESTION

Draw structural formulae of the following compounds:

- (i) 2-Bromo-3-methylbutane
- (ii) 3-Chloro-4-methylhexane
- (iii) 3-Bromochlorobenzene
- (iv) 2,4-Dibromotoluene

Although haloalkanes are polar in nature, they are insoluble in water. Explain.

Why is chloroform stored in dark coloured bottles?

Name two commonly used polyhalogen compounds.

What products will be obtained when ethylbromide reacts with

- (i) aq. KOH and (ii) alc. KOH

What is the major product of elimination reactions of 2-bromobutane?

What is a Grignard reagent? How is it prepared?

What are nucleophilic substitution reactions? Explain the mechanism of S_N1 and S_N2 reactions in aliphatic compounds.

Write down the $E1$ and $E2$ mechanism of dehydrohalogenation in detail.

Write down the detail mechanism of reaction of halogen acid on alcohols.

Arrange each set of compounds in order of increasing boiling points.

Bromomethane, Bromoform, Chloromethane, Dibromomethane.

1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.

12. What happens when?

n-butyl chloride is treated with alcoholic KOH,

Bromobenzene is treated with Mg in the presence of dry ether,

Chlorobenzene is subjected to hydrolysis,

Ethyl chloride is treated with aqueous KOH,

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Objective Type Question:

(1) Freon-12, CCl_2F_2 is used as a:

- (a) Local anesthetic (b) Dry-cleaning agent
(c) Refrigerant (d) Disinfectant

(2) Which of the following reagents can be used to prepare an alkyl chloride from an alcohol?

- (a) PCl_5 (b) SOCl_2
(c) NaCl (d) $\text{HCl} + \text{ZnCl}_2$

(3) Alkyl halides undergo-

Electrophilic substitution reactions

Electrophilic addition reactions

Nucleophilic addition reactions

Nucleophilic substitution reactions

(4) 1-Bromobutane reacts with alcoholic KOH to-

- (a) 1-Butene (b) 2-Butene
(c) 1-Butanol (d) 2-Butanol

1

- (a) Methyl chloride (b) Isopropyl chloride
(c) Ethyl chloride (d) 3°- butyl chloride

UNIT 14: ARYL HALIDES

CONTENTS:

- 14.1 Objectives
- 14.2 Introduction
- 14.3 Nomenclature and classification of aryl halides
- 14.4 Methods of formation of aryl halides
- 14.5 Chemical reactions
- 14.6 Relative reactivity of alkyl halides vs allyl vinyl and aryl halides.
- 14.7 Synthesis and uses of DDT and BHC
- 14.8 Summary
- 14.9 Terminal Question
- 14.10 Answers

14.1 INTRODUCTION

Alkyl halides have vast importance as it can be used for the preparation of a variety of organic functional groups. In this unit we shall discuss the halogen derivatives of benzene-Aryl halide, which are normally less reactive than alkyl halide, have their own pattern of reactivity, and these reactions are novel, useful and productive. The aryl halides produced on the largest scale are chlorobenzene and isomers of dichlorobenzene. Several aromatic chloro compounds are used extensively as insecticides, herbicides, fungicides and bactericide.

14.2 OBJECTIVES

Name Aryl halide according to the IUPAC system of nomenclature from their given structure.

Describe the reactions involved in the preparation of Aryl halides.

Identify reactions involving aryl halides.

Synthesis of DDT and BHC.

Relative reactivities of alkyl halide VS vinyl and aryl halide.

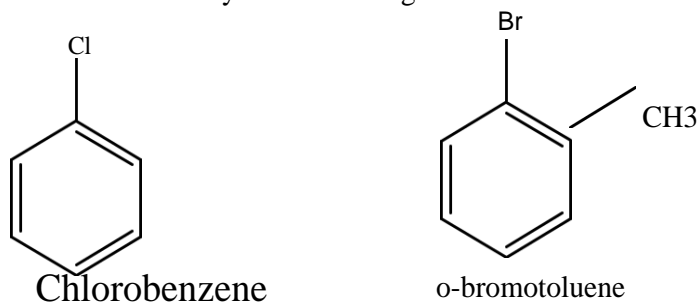
14.3 NOMENCLATURE AND CLASSIFICATION OF ARYL HALIDES

(1) Classification of Aryl halides

Aryl halides are those compounds which contain at least one benzene ring and one halogen atom in the molecule. They are as follows:

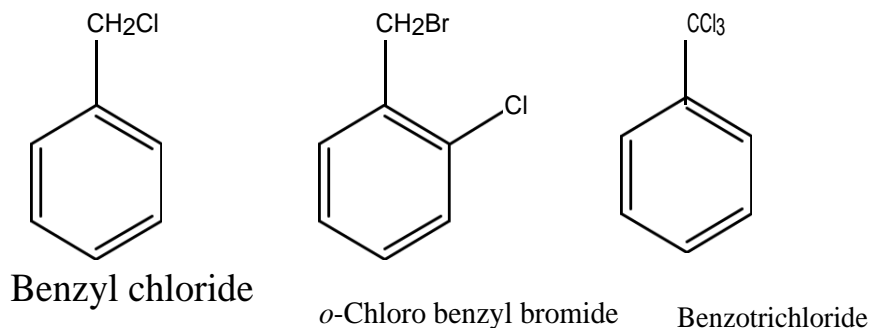
(i) Nuclear halogen compounds

These compounds have directly attached halogen atoms to the benzene ring. For example,



Side-Chain halogen Compound

These compounds have side chain attached with halogen. There may be more than one halogen in the side chain.



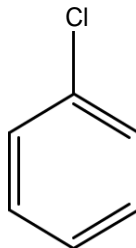
(2) Nomenclature of aryl halide

Aryl halides are also termed as haloarenes in IUPAC as well as common system. There are some rules for nomenclature of aryl halide.

If there is only one halogen group bonded directly to benzene ring, it is numbered as one position and written as prefix followed with benzene as main ring. For example Chlorobenzene or aryl chloride. All six position of benzene

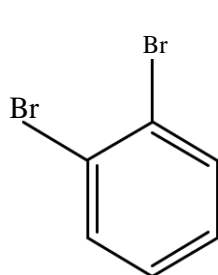
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are equivalent. Hence monohalogen compounds could be represented by attaching the halogen to any of the six position.

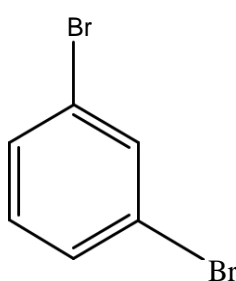


Chlorobenzene

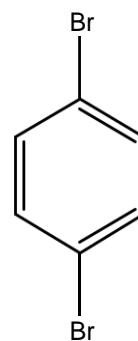
For dihalogen derivatives containing same type of halogen, the prefix *o*- (ortho) *m*- (meta) and *p*- (para) are used in common system. If the two group are located in neighboring position the two groups are ortho to each other. If there is a gap of one position, the groups are meta to each other and if the gap is of two position the groups are para to each other. However in IUPAC nomenclature of dihalogen derivatives, numerical prefixes 1,2 , 1,3 , 1,4 are used to assigned the position of halogen.



o- (ortho)
(1,2dibromo benzene)



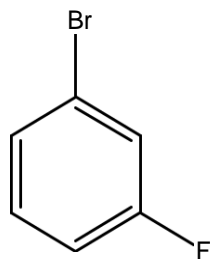
m- (meta)
(1,3dibromobenzene)



p- (para)
(1,4dibromobenzene)

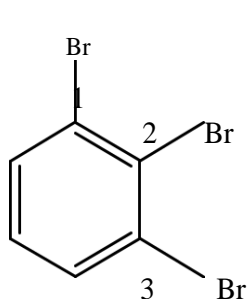
In the presence of two different halogen group attached to benzene ring, halogen numbered alphabetically and written in the same way. For eg. If there are two halogen groups like bromo and fluoro bonded to benzene ring bromo group will be written first followed by fluoro group.

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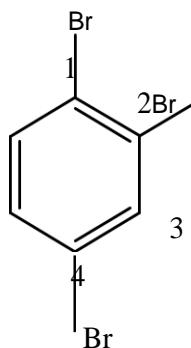


1-Bromo3- fluoro benzene

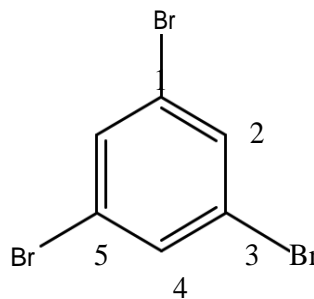
For naming trihalogen compounds, we use the number system. Number 1 is given to the position of the groups and then the other groups are numbered accordingly. Clockwise direction is followed for this purpose.



1,2,3 Tribromobenzene

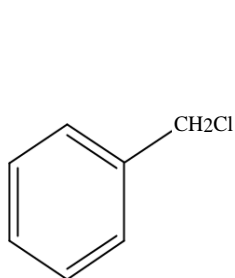


1,2,4 Tribromobenzene

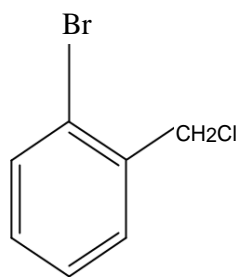


1,3,5tribromobenzene

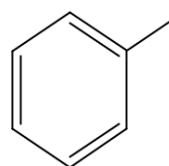
Side chain halogen compounds are named as follows :



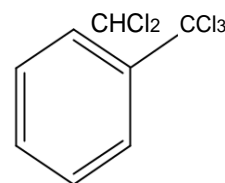
Benzyl Chloride
Chloride



o-Bromo benzyl chloride



Benzo Trichloride



Benzal

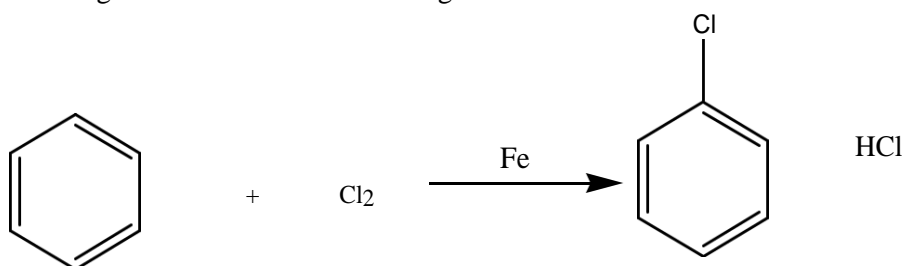
14.4 METHODS OF FORMATION OF ARYL HALIDES

Aryl halides are prepared by following methods:

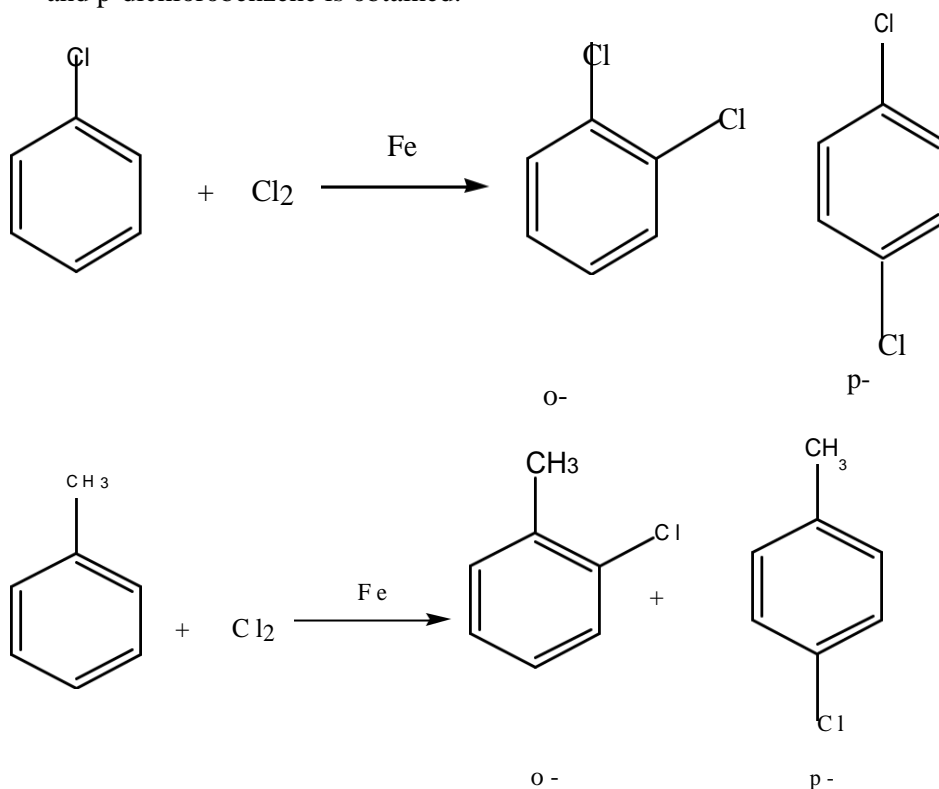
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Direct halogenations of benzene - Chlorination and bromination is very conveniently carried out at ordinary temperature in the absence of light and in the presence of metallic iron or lewis acids such as chlorides or bromides of Fe, Al, Sb. Fluorination and Iodination of benzene, are rarely performed because fluorine is too reactive to control the reaction and iodine is too unreactive for a favorable equilibrium constant.

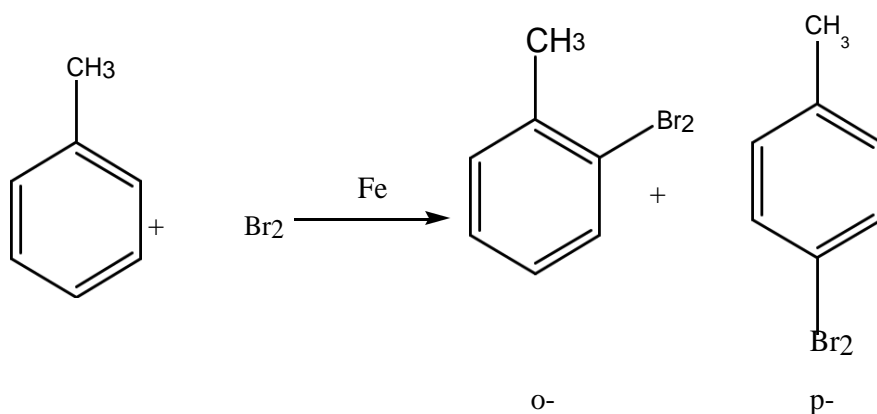
This reaction stops at the monosubstituted stage due to the deactivating influence of the halogen atom on the aromatic ring.



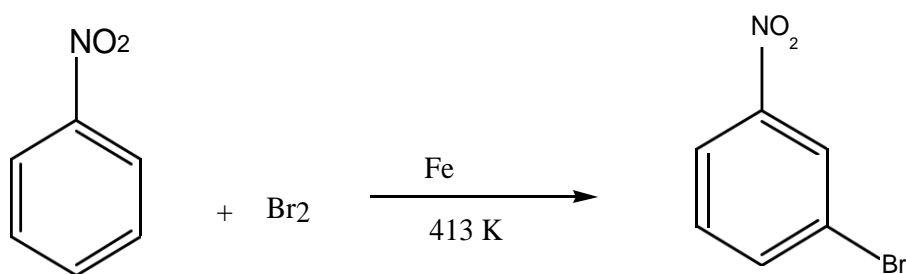
However, if chlorine is used in excess, further substitution takes place and a mixture of o- and p-dichlorobenzene is obtained.



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When aromatic compounds contain strongly deactivating group such as $-\text{NO}_2$, $-\text{COOH}$ etc., high temperature is required and the halogen enters then meta position.

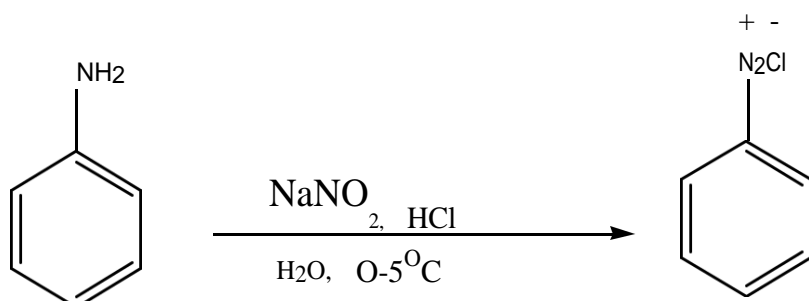


Nitrobenzene

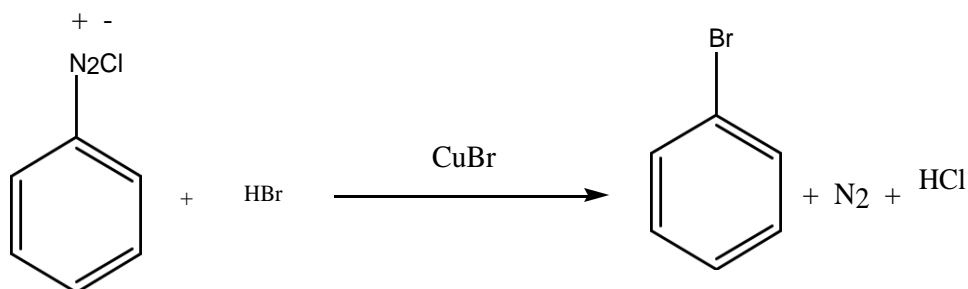
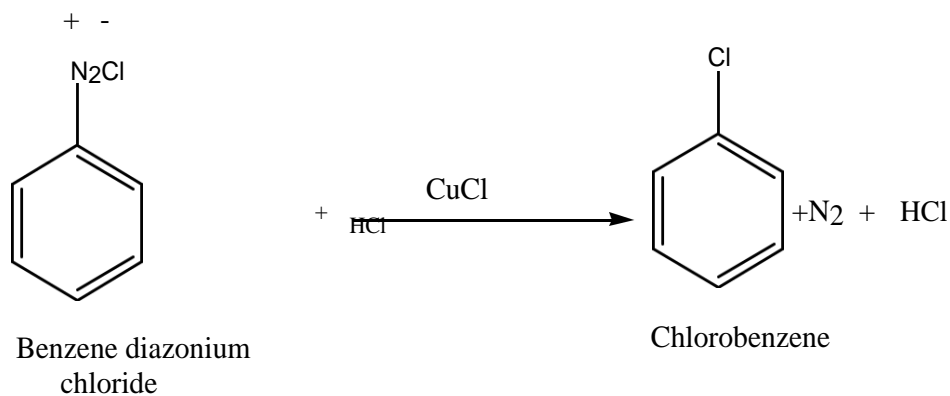
m- Bromo nitrobenzene

Decomposition of aryl Diazonium salts (Sandmeyer's reaction)- This is an important method for the preparation of aryl halides, specially those which cannot be prepared by the direct halogenations.

Aryl amines when treated with acidified sodium nitrite at low temperature ($0-5^\circ\text{C}$), result in the formation of Aryldiazonium salts.

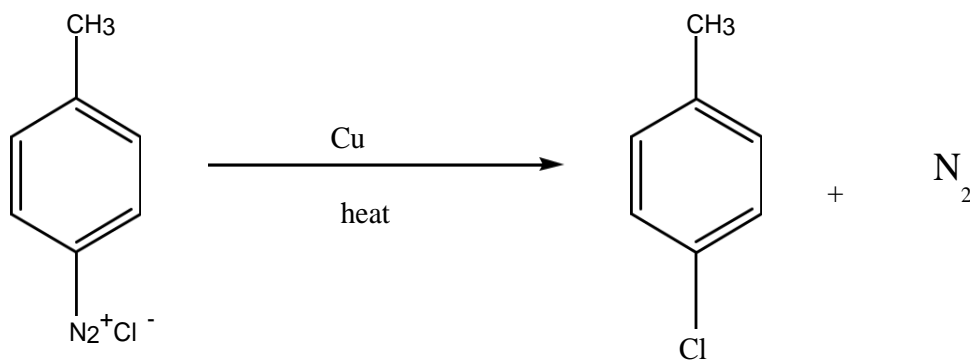


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Gattermann Reaction:

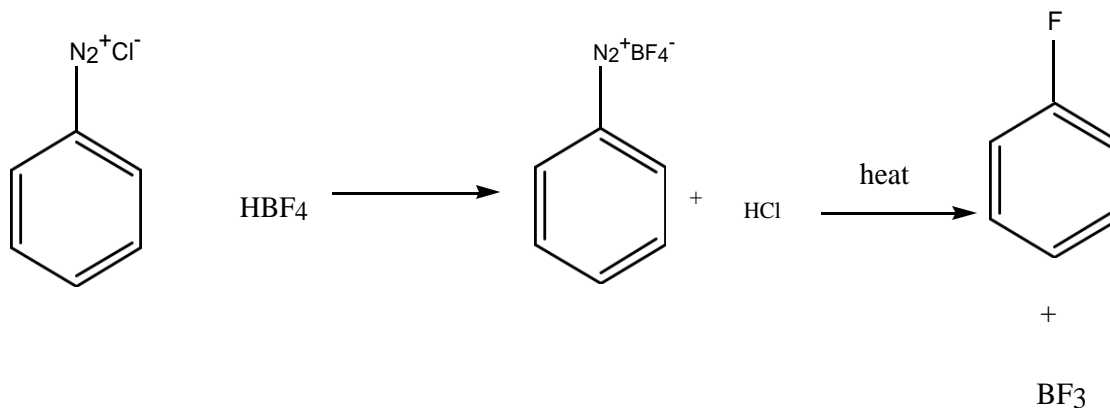
Gattermann reaction is the modified form of above mentioned reactions. This reaction requires the diazonium salt to be warmed in presence of copper powder when it decomposes to give the halobenzene.



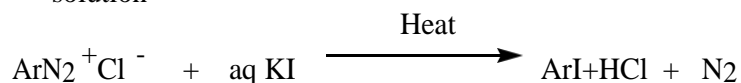
Schiemann reaction:

This is a good method for introducing fluorine atom in the ring. Addition of fluoroborate, to aryldiazonium salt solution gives the insoluble diazonium fluoroborate, which on gentle heating gives the aryl fluoride.

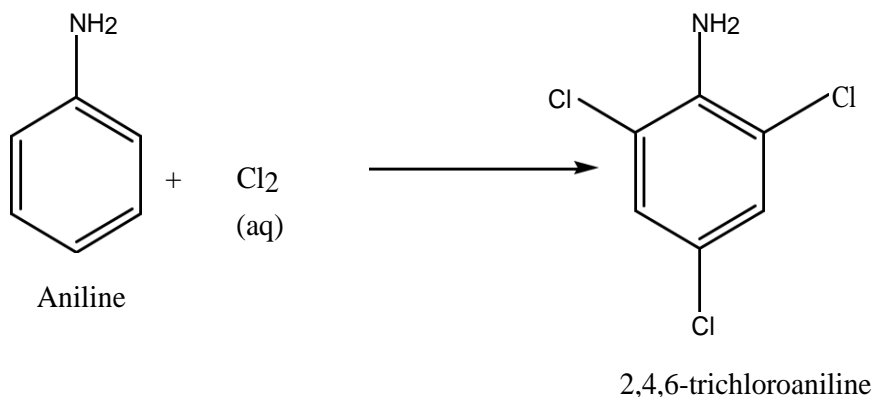
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Aryl iodides are obtained by warming the diazonium salt solution with potassium iodide solution

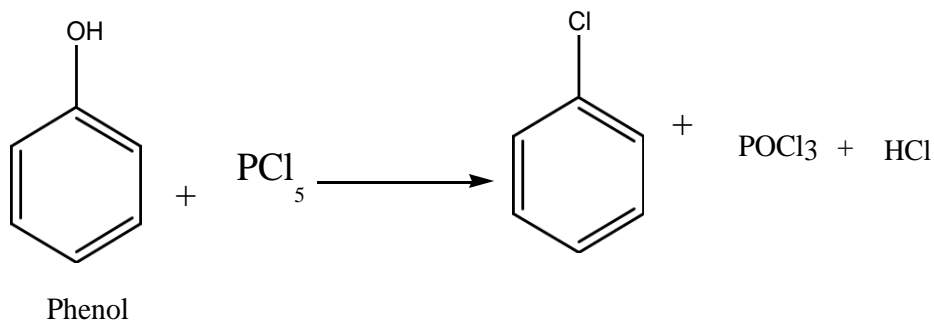


When aromatic compounds contain highly activating group such as $-\text{OH}$, $-\text{NH}_2$ etc. They undergo halogenation in the absence of halogen carrier and halogen enters the *ortho* and *para* position.

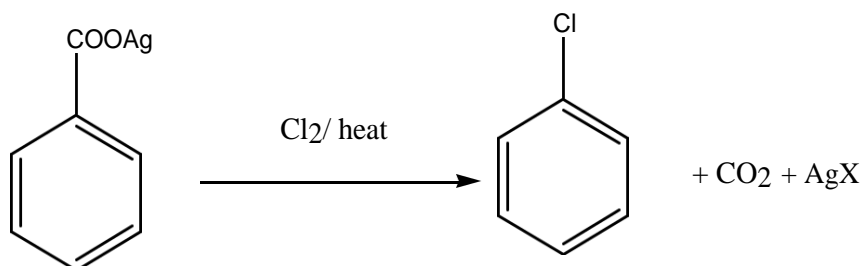


From phenols – Reaction of phenol with PCl_5 yields aryl chloride.

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From silver salt of benzoic acid (Hunsdiecker reaction) :

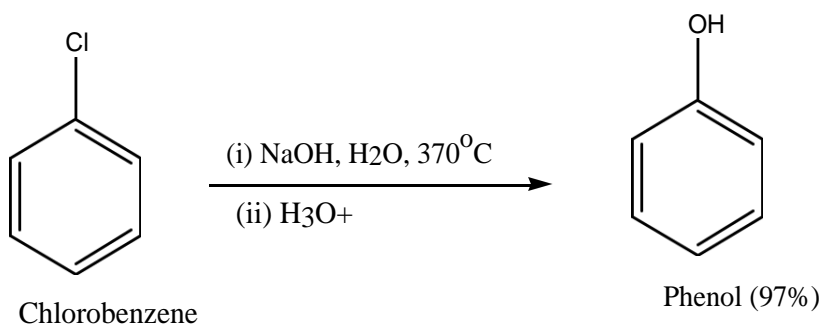


14.5 REACTIONS OF ARYL HALIDES

The reactions of aryl halide are due to the halogen atom (nucleophilic substitution reactions) and the aromatic ring (Electrophilic substitution reaction).

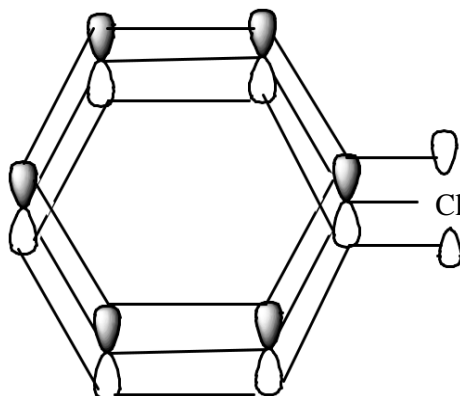
Nucleophilic substitution reactions

Aryl halides are relatively unreactive towards nucleophilic substitution reactions. For example Chlorobenzene is essentially inert to aqueous sodium hydroxide at room temperature. To proceed reaction at reasonable rate temperature over 300°C are required.

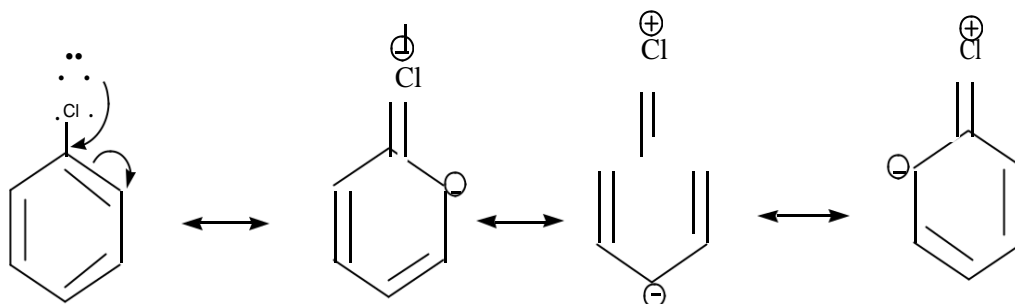


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Aryl halides are less reactive than alkyl halide in nucleophilic substitution reaction. This lack of reactivity is due to several factors. In aryl halide the carbon chlorine bond is σ bond. However, one of the p -orbital of chlorine having a pair of electrons is parallel to the delocalized p -orbitals of the benzene nucleus. This p -orbital of chlorine can also overlap with the delocalized p -orbitals of benzene nucleus. Thus the bond between carbon and chlorine becomes strong.



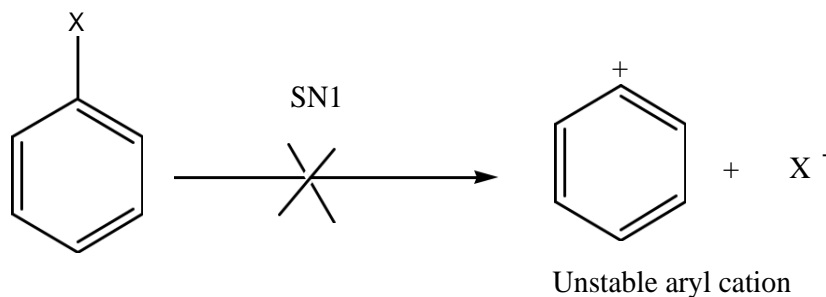
The delocalized π MO gives partial double bond character to C-Cl bond in aryl halides.



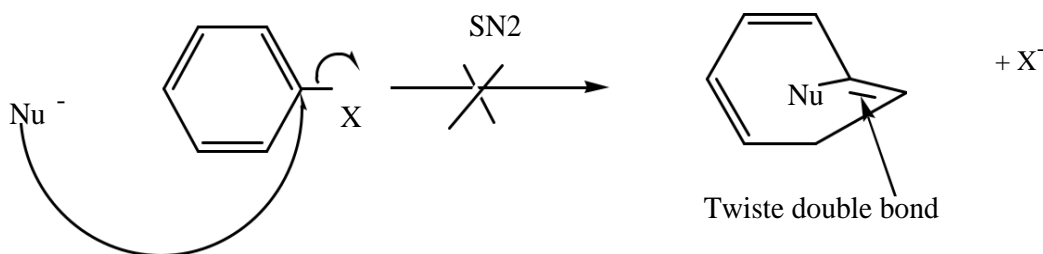
Another reason for the low reactivity of aryl halide towards nucleophilic substitution reaction is the π electron cloud in aromatic ring with which does not allow the nucleophile to attack easily on benzene ring.

Aryl halides cannot proceed through S_N1 -type processes because carbon-halogen bonds of aryl halides are too strong, and aryl cations formed during the reaction are highly unstable due to high in energy.

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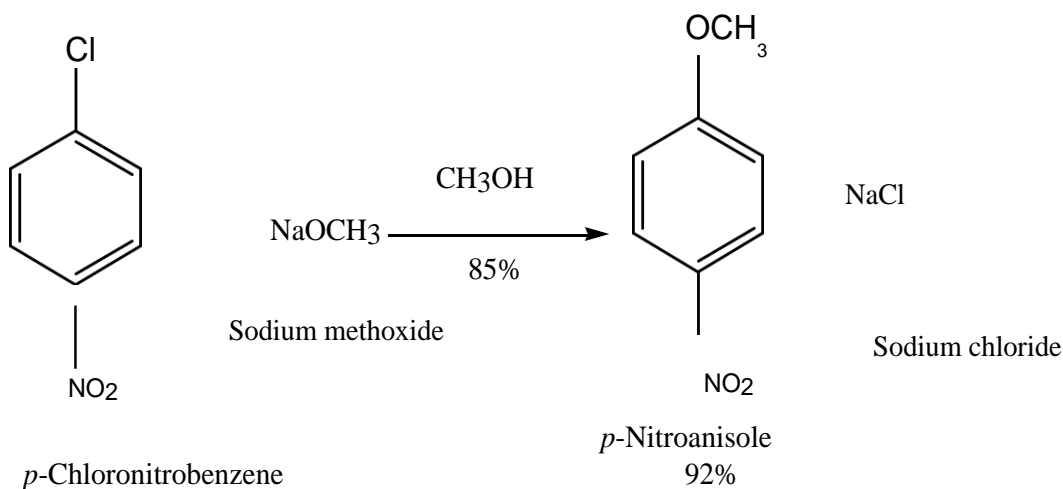


Aryl halides also cannot be proceeding through SN2-type process, because the aromatic ring blocks the approach of the nucleophile to carbon at the side opposite the bond to the leaving group. Inversion of configuration is impossible.

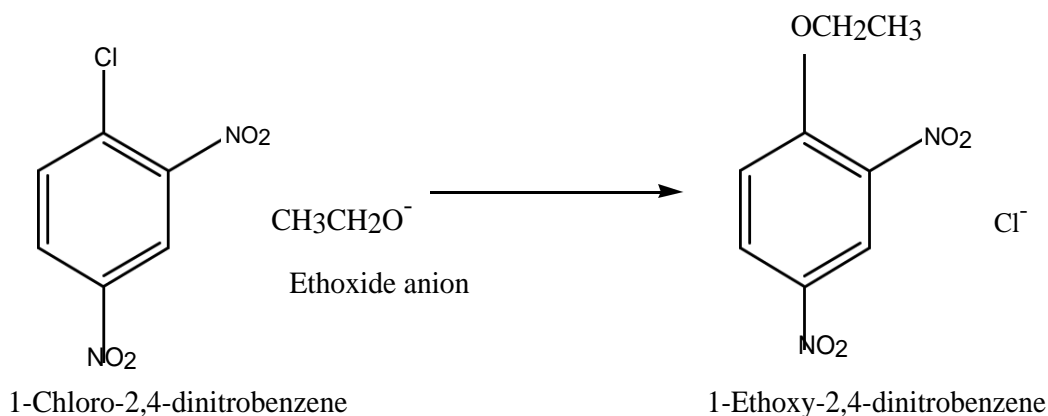
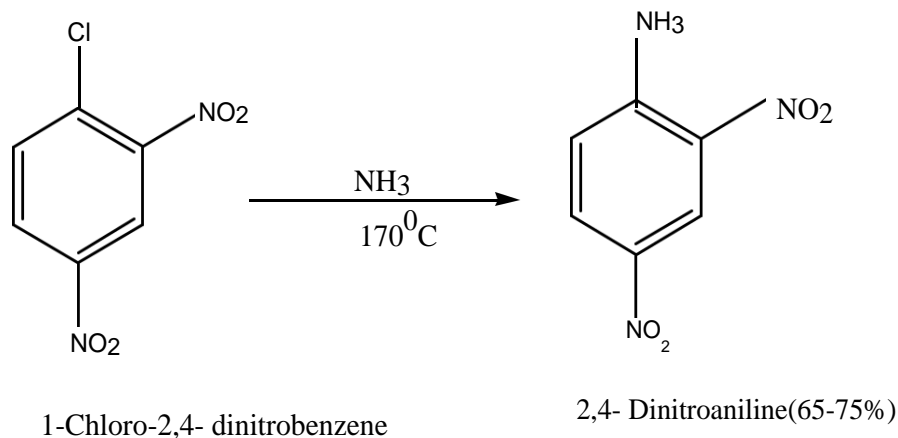


(1) Nucleophilic substitution in nitro substituted aryl halides (SNAr)

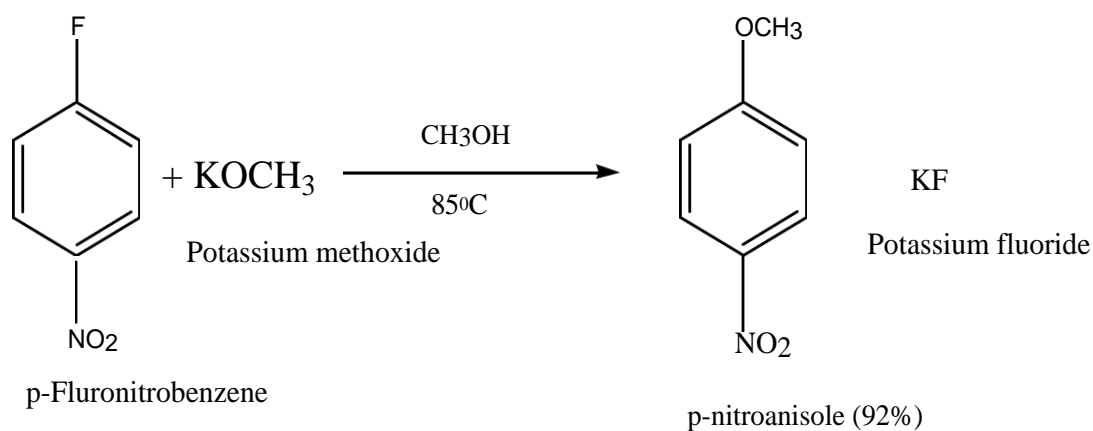
Aryl halides consists of strong electron withdrawing group such as a nitro group *ortho* or *para* to the halogen undergo nucleophilic substitution readily



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Aryl fluorides undergo nucleophilic substitution reaction when ring bears an *o*- or a *p*- nitro group.



These reactions follow a second order rate law:

$$\text{Rate} = k[\text{Aryl halide}][\text{Nucleophile}]$$

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Mechanism of second order nucleophilic aromatic substitution reaction (S_NAr) can be of following two types.

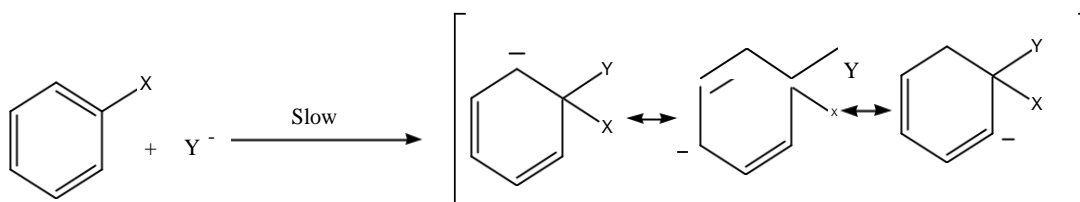
Addition/elimination mechanism

Elimination /addition mechanism

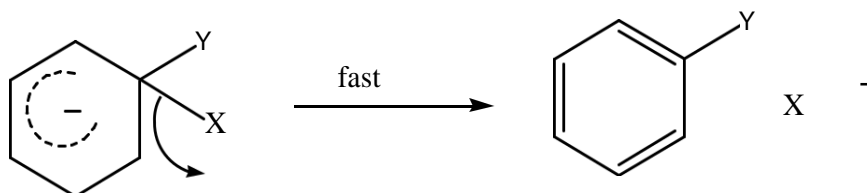
Addition /elimination mechanism

General schematic representation for addition elimination reaction: It is two step reaction.

Step I: In this step incoming nucleophile attacks at the same position where the leaving group is attached. Such attack is known as ipso attack.



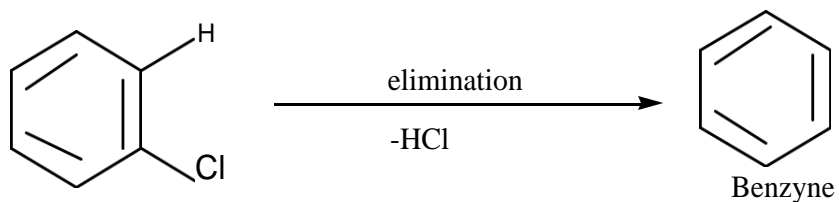
Step II: In second step the leaving group detached leading to regeneration of aromaticity in benzene ring.



Elimination/ Addition mechanism

Elimination/Addition mechanism is proceeding via benzyne mechanism. The benzyne intermediate has triple bond in benzene ring during the transition stage. Benzyne intermediate is highly reactive and they rapidly undergo nucleophilic substitution reaction. Aryl halides undergo substitution by the benzyne mechanism only in the presence of very strong bases such as alkali metal amide and organolithium reagents or somewhat weaker bases under vigorous conditions.

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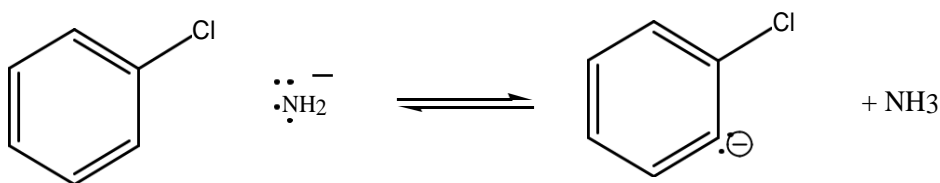


Benzyne mechanism involves two steps:

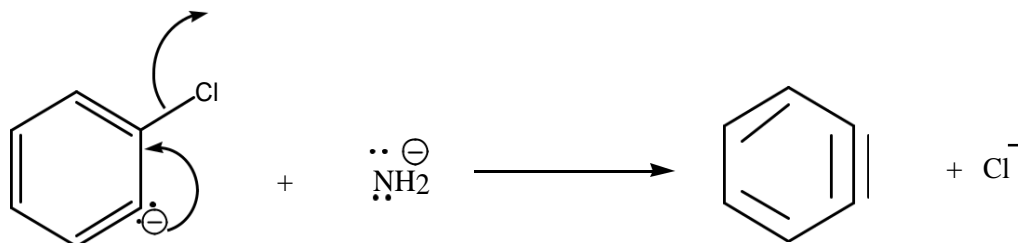
Elimination

In first step elimination of H and X (Halide) occurs to give benzyne. Elimination itself comprises of two steps.

Abstraction of a hydrogen ion by the strong base

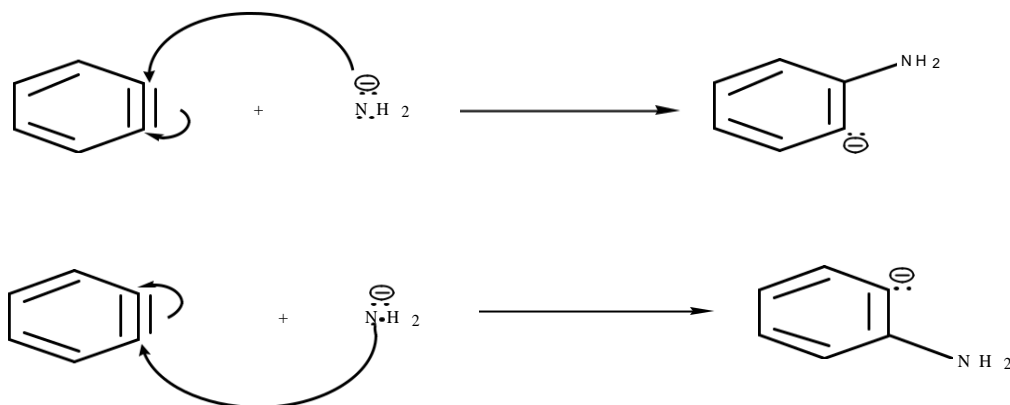


Loss of halide ion to form benzyne



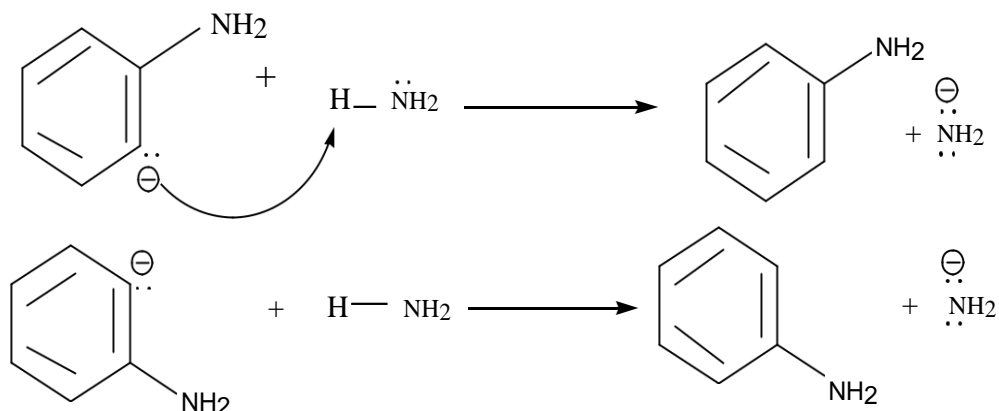
Addition

In second step addition of nucleophile and H occurs to give overall substitution product.



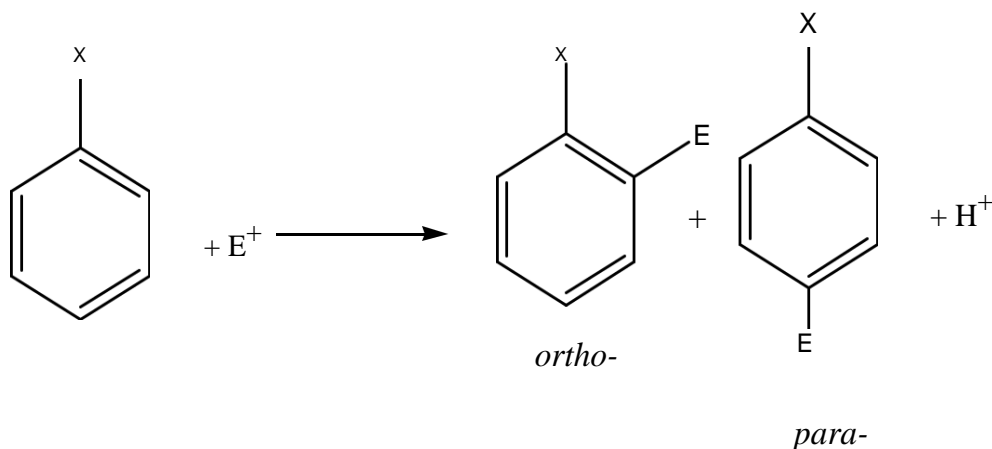
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Protonation of anion by reaction with acid, ammonia etc.



Electrophilic substitution reaction of Aryl halides

Aryl halides are reactive towards the electrophilic aromatic substitution but they are less reactive than benzene because halides are weak deactivators. The weak deactivation is due to the electronegativity of the halogen making the intermediate cations less stable than those produced when benzene undergoes substitution. Halides are *o*- or *p*- directing groups.

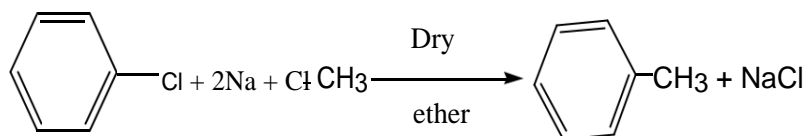


Electrophilic aromatic substitution reactions of chlorobenzene is given below.

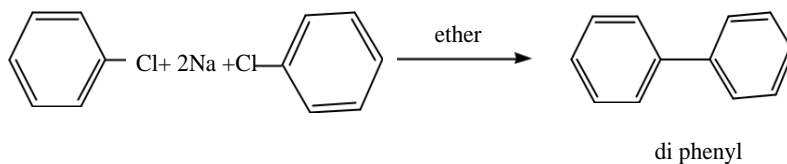
Other reactions

Wurtz- Fittig reaction- When aryl halide is treated with ethereal solution of alkyl halide, in the presence of sodium, we obtain an alkyl benzene.

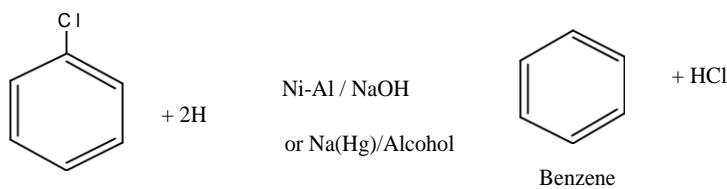
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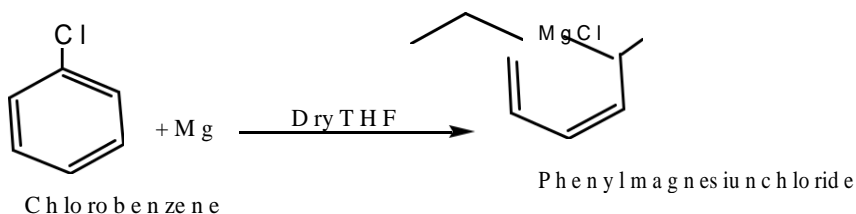
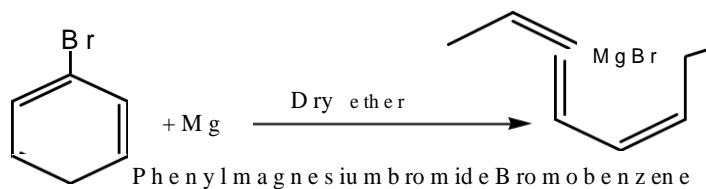
When only aryl halide is treated with sodium diaryl are produced, this reaction is called Fittig reaction.



Reduction – Aryl halides are reduced by Nickel-Aluminium alloy in alkali or sodium amalgam and aqueous alcohol in the presence of alkali.



Formation of Grignard reagent: When aryl halides and iodides are treated with magnesium turnings in dry ether they form Grignard reagent. Aryl chlorides form Grignard reagent only when the reaction is carried out in dry tetrahydrofuran (THF) as solvent.



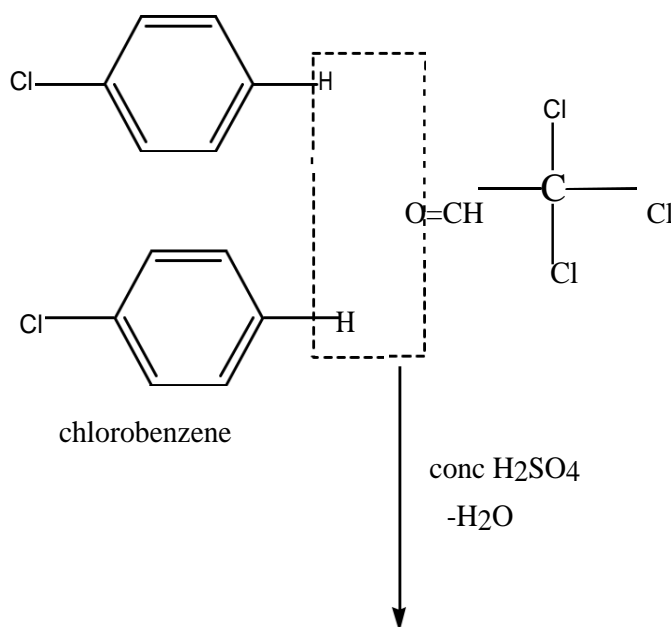
14.6 RELATIVE REACTIVITY OF ALKYL HALIDES vs ALLYL, VINYL AND ARYL HALIDES

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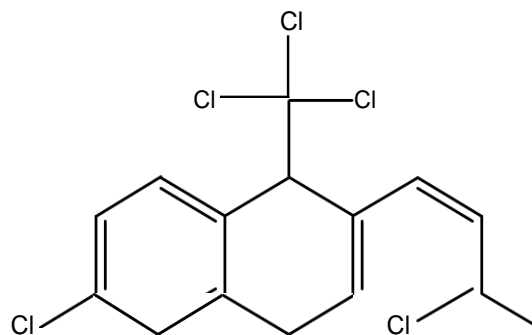
Aryl halide for example chlorobenzene has carbon atom in ring which has p-orbital available for overlapping with p-orbital of chlorine atom and thus the p-orbital carbon atom overlap with the p-orbital of attached Cl- atom. Hence the Cl-atom is firmly attached with the C-atom of benzene ring. Moreover the bond between the C-atom in the benzene ring has partial double bond character due to delocalization of electrons in the benzene ring. All these factors make it difficult for aryl halide to undergo SN1 or SN2 reactions and thus they are least reactive in nature. In case of vinyl halide also the side wise overlapping of the p-orbitals of carbon atom occurs with Cl- atom. Thus there is sidewise overlapping in the vinyl halide which makes it difficult to undergo SN1 or SN2 reactions and they are also less reactive.. However in case of alkyl halide carbon atom attached to halide atom does not have any unhybridised p-orbital to overlap with the p-orbital of the Cl-atom and Hence it is easy for them to undergo SN1 and SN2 substitution reactions. The allyl cation has delocalization which decreases the energy of the system. This makes it easier to remove a halide.

14.7 SYNTHESIS AND USES OF DDT and BHC

(i) Synthesis of 1, 1-Bis (4-Chlorophenyl)-2, 2, 2-Trichloroethane, (DDT)



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1,1-Bis (4-Chlorophenyl)-2,2,2-Trichloroethane

DDT is used as insecticide. DDT was initially used by the military in World War II to control malaria, typhus, body lice, and bubonic plague. DDT is still used today in South America, Africa, and Asia for this purpose. Farmers used DDT on a variety of food crops in the United States and worldwide. DDT was also used in buildings for pest control. DDT was so widely used was because it is effective, relatively inexpensive to manufacture, and lasts a long time in the environment. DDT is slightly to moderately acutely toxic to mammals, including people, if eaten. DDT is poorly absorbed through mammalian skin, but it is easily absorbed through an insect's outer covering known as an exoskeleton. People exposed to DDT while working with the chemical or by accidental exposure report a prickling sensation of the mouth, nausea, dizziness, confusion, headache, lethargy, in coordination, vomiting, fatigue, and tremors .

(ii) Benzene hexa chloride:

For benzene hexa chloride eight isomers are possible but only seven are known. One of these isomers is an insecticide called lindane, or Gammexane (γ - isomer). Gama Benzene Hexachloride is used for the treatment, control, prevention, & improvement of the contagious and itchy human head infection mites skin disease and lice skin disease. There are various side effect of BHC as insomnia, paresthesia, giddiness, dizziness, headache, nausea, vomiting, restlessness, skin irritation, contact dermatitis if used in excess quantity.

14.8 SUMMARY

Aryl halide, with electron withdrawing substituents at ortho and para position react by nucleophilic aromatic substitution reactions. These reactions 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

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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. Aryl halides can undergo many of the same electrophilic aromatic substitution reactions that benzene can including nitration, sulfonation, further halogenation and Friedel-Crafts alkylation or acylation reactions.

14.9 TERMINAL QUESTIONS

Short answer type questions

Q1. Write the structural formula for the following.

p- chlorotoulene

2,4- Dibromoanisole

2-Fluoro-1-chloro-4-nitrobenzene

p- chlorostyrene

Q2 Identify the major organic product of each of the following reactions.

(a) Bromobenzene + acetyl chloride $\xrightarrow{\text{AlCl}_3}$

(b) Iodobenzene + Lithium $\xrightarrow{\text{diethyl ether}}$

Q3 what are aryl halides? Give example.

Q4 Explain why aryl halides have low reactivity during nucleophilic substitution reaction.

Q5 Why aryl halide is less reactive than alkyl halide. Explain.

Q6 Describe the benzyne mechanism of nucleophilic aromatic substitution.

Multiple choice Questions

Aryl halides are less reactive towards nucleophilic substitution as compared to alkyl halide due to

- (a) Inductive effect (c) resonance stabilization (b) Electromeric effect
(d) stereoisomerism

Which of the following reagents can be used to distinguish between chlorobenzene and allyl chloride

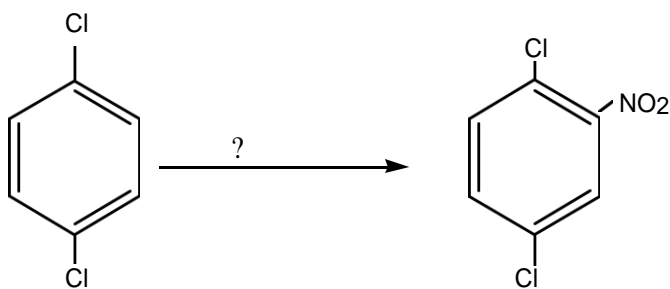
- (a) H_2/Ni (c) Zn/HCl
(b) Br_2 in CCl_4 (d) NH_2NH_2

3. Alkyl halides undergo

- (a) Electrophilic substitution reaction (c) Nucleophilic substitution reaction
(b) Electrophilic addition reaction (d) Nucleophilic addition reaction

4. which reagent can be used to carry out the following conversion

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- (a) $\text{HNO}_3 + \text{H}_2\text{SO}_4$ (b) NaNO_2
(c) H_2SO_4 (d) NO_3
5. DDT is prepared by the reaction of chlorobenzene with
- (a) Chloral + H_2SO_4 (c) Chlorine + H_2SO_4
(b) Chloroform (d) Carbon tetrachloride

Answers

- (c)
(b)
(c)
(a)
(a)

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