

## Chapter 1 - Bonding In Carbon Compounds

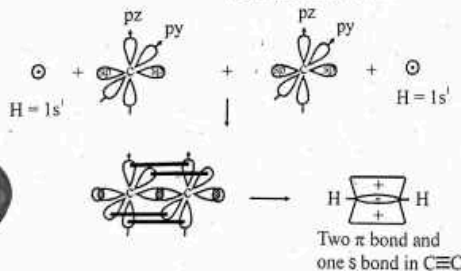
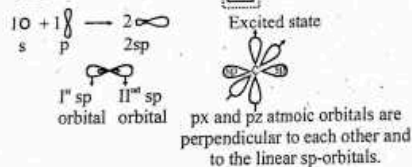
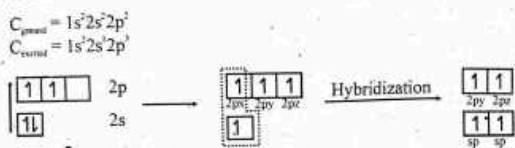
Q.1. What do you understand by the term 'hybridization'? Discuss  $sp$ ,  $sp^2$  and  $sp^3$  hybridization with suitable examples.

Ans. Hybridization:-

Linus Pauling introduced the concept of hybridization in 1931. The hybridization is a purely mathematical concept of mixing (Linear combination of atomic orbitals, LCAO) of atomic orbitals of dissimilar type (s, p, d, etc.) of nearly similar energy, for example 2s, 2p not 1s, 2p. In order to form a new set of orbitals which are of equivalent energy as well as in number with better overlapping power.

(1)  $sp$ -hybridization:-

In this type of hybridization one s and one p orbital of the valence shell of central atom of the given molecule combine to form two  $sp$  hybrid orbitals as follows.



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Let us take the formation of **acetylene**. In acetylene hybridization of carbon is  $sp$ . One 2s orbital blends with only one 2p-orbital to form two  $sp$ -hybrid orbitals. In this case two unhybridized orbitals remain, each with one electron.

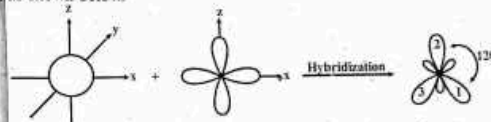
In , the two-carbon atoms are joined by an  $sp$ - $sp$  sigma bond. Each carbon atom is also bonded to a hydrogen atom by  $sp$ - $s$  sigma bond. The two p-orbitals of one carbon then overlap with the two p-orbitals of other carbon to form two pi bonds.

**Characteristic of  $sp$ -hybridization -**

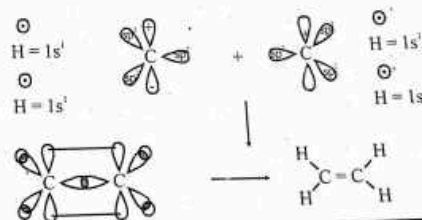
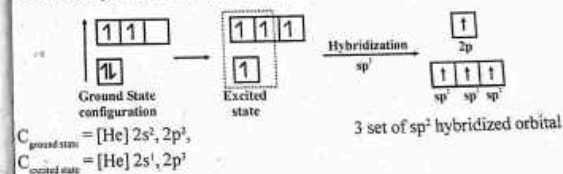
- (i) S-Character in  $sp$ -hybrid orbital is 50%.
- (ii) The angle between the hybrid orbital is  $180^\circ$ , i.e. They are linear in shape.
- (iii) Energy of  $sp$ -orbital is minimum.

(2)  $sp^2$  - hybridization:-

In this type of hybridization one s and two p orbitals of valence shell of central atom of the given molecule combine to form three  $sp^2$ -hybrid orbitals as shown below.



Let us take the formation of **ethylene**. To form  $sp^2$  bonding orbitals, carbon hybridizes its 2s orbital with only two of its 2p-orbitals, one p-orbital remains unhybridized on the carbon atom.



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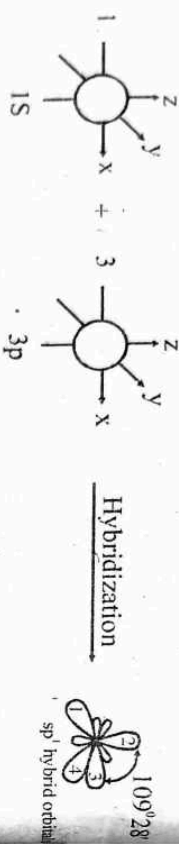
In ethylene two  $sp^2$  carbon are joined by a sigma bond formation by the overlap of one  $sp^2$  orbital from each carbon atom. Both carbon atom have also unhybridized p-orbitals, which can be oriented parallel to each other and there by overlap. Both lobes of the p-orbitals merge above and below the overlap sideways and forming a  $\pi$ -bond.

### Characteristics of $sp^2$ -hybridization:-

- S-character in  $sp^2$ -hybrid orbital is 33%.
- The angle between the hybrid orbital is  $120^\circ$ , i.e. they are trigonal planar shape.
- Energy of  $sp^2$ -orbital is more than  $sp$ -orbital.

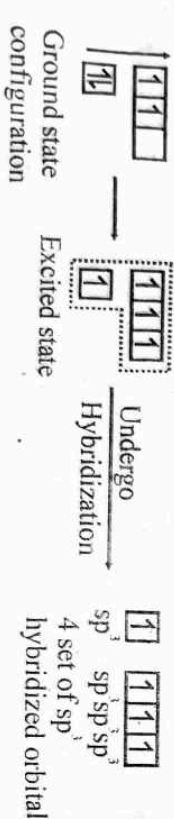
### (3) $sp^3$ -hybridization:-

In this type of hybridization one s and three p-orbital of valence shell of central atom of the given molecule combine to form four  $sp^3$  hybrid orbitals of equal energy.



There are  $109^\circ 28'$  angle between any two- $sp^3$  hybrids orbital. They result in tetrahedral structure.

Examples are methane ( $CH_4$ ).



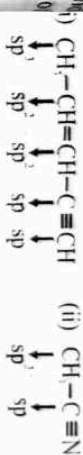
### Note:-

Some important points about hybrid orbitals.

- Increasing order of energy.  
 $sp < sp^2 < sp^3$
- Increasing order of bond length.  
 $sp-s < sp^2-s < sp^3-s$
- Increasing order of size of orbitals.

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$sp < sp^2 < sp^3$



### 2.2. Define and explain the following?

- Bond length
- Bond angle
- Bond energy. (Imp.)

### Ans. (a) Bond length:-

The distance between the nuclei of two bonded atoms are known as the bond length. Bond lengths of some important covalent bonds are given below:-

| Bond         | Bond length (Å) |
|--------------|-----------------|
| H-H          | 0.74            |
| C-C          | 1.54            |
| C=C          | 1.34            |
| C $\equiv$ C | 1.20            |
| C-H          | 1.10            |
| C-O          | 1.41            |

### (b) Bond angle:-

The angle between the directions of two covalent bonds is known as the bond angle. Hybrid orbital have directional preferences.

| Hybridization | Bond angle      |
|---------------|-----------------|
| $sp$          | $180^\circ$     |
| $sp^2$        | $120^\circ$     |
| $sp^3$        | $109^\circ 28'$ |

### (c) Bond Energy:-

Bond energy is defined as the energy need to break to the that particular bond of one mole molecule. The greater the bond energy, the stronger is the bond.

### Factor affecting the hybridization:-

Order of s character

| Hybridization or Hybrid orbital | % s character | % p character |
|---------------------------------|---------------|---------------|
| $sp^3$                          | 25.0%         | 76.0%         |
| $sp^2$                          | 33.3%         | 66.6%         |
| $sp$                            | 50.0%         | 50.0%         |

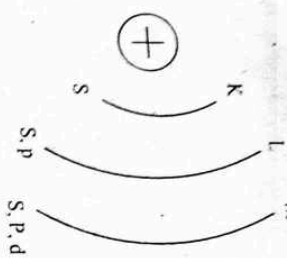
### Decreasing order of s character

$sp > sp^2 > sp^3$

Hence greater the % character of an orbital smaller will be size

$sp^3 > sp^2 > sp$

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Bond length: -

| Hybridization | Type of carbon | Bond length (Å) |
|---------------|----------------|-----------------|
| $sp^3$        | C - C          | 1.54            |
| $sp^2$        | C = C          | 1.34            |
| $sp$          | C $\equiv$ C   | 1.20            |

Hence  $sp$  hybridization has shortest bond length

Bond energy: - Shorter the bond length greater will be the strength of bond

| Hybridization | Bond energy (kcal/mol) |
|---------------|------------------------|
| $sp^3 - sp^3$ | 80.0                   |
| $sp^2 - sp^2$ | 122.0-145.0            |
| $sp - sp$     | 123.0-199.0            |

Electro-negativity:-

$s$ -orbital are more attractive towards the nucleus than  $p$ -orbitals and orbital will be more attractive than  $d$ -orbital. So greater the  $s$ -character greater will be electronegative tendency of the atom. Hence the electronegativity order will be

$$sp > sp^2 > sp^3$$

Q.3 Explain the term resonance.

(2007, 2008)

Ans. In the phenomenon, the two or more Lewis structure can be written the true structure of a molecule, but none of them can be said to represent uniquely, is referred to as resonance or mesomerism. The true structure of molecule is said to be a resonance hybrid of the various possible alternative structure which themselves are known as resonating structure or canonical structure. Every two adjacent resonating structure are represented by inserting a double-headed arrow between them. Thus the actual structure of the benzene may be represented in the following two ways.



Necessary Condition For Resonance:-

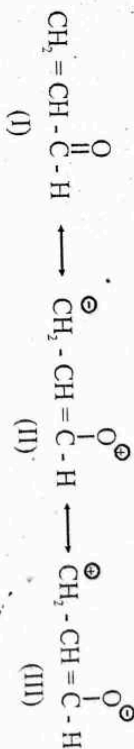
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- For resonance compound should have conjugation.
- All the conical form must be bonafide Lewis structure.
- The position of nuclei must be the same in all the structure.
- All conical form must have the same number of unpaired electron.
- Resonating structure must be planar.

Resonance energy: -

The resonance hybrid is more stable than any contributing canonical structure. The resonance energy is measure of extra stability of the resonance hybrid. It is defined as the difference in energy between the actual structure of species and the most stable canonical structure.

Q.4 Arrange the following resonating structure of Acrolein in decreasing order of stability. (2010)



Ans. (I) > (III) > (II)

Q.5 What is hyperconjugation and explain with example? (2004, 2008)

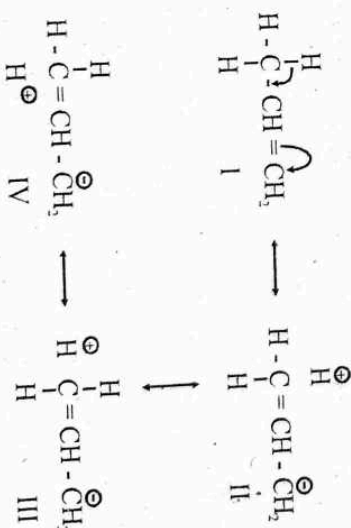
Related Questions:-

Q. Give the suitable example describe the delocalization involving  $\pi$  and  $p$  conjugation. (2006)

Q. Write short note on Hyperconjugation. (2015, 19)

Q. Write notes on Hyperconjugation Resonance. (2018)

Ans. This is a one type of delocalization of electron, for delocalization, molecule should have conjugate position however, hyperconjugation involve  $\sigma$ - $\pi$  overlap. This effect also called Baker Nathan effect who discovered the hyperconjugation. It is also called as no bond resonance. It involves the delocalization of sigma ( $\sigma$ ) electrons with  $\pi$ -electrons of a multiple bond when they are in conjugation. This phenomena is called hyperconjugation.



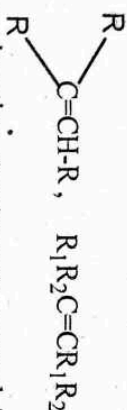
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This phenomena also called no bond resonance. Grater the no. of hyperconjugative structure, grater will be stability of the compound.

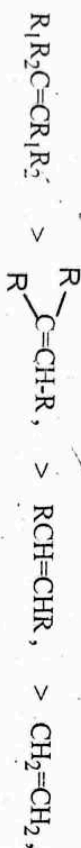
Condition for hyperconjugation:

- (1) If a compound having  $sp^3$  hybrid carbon such as arene, carbocation alkene etc.
- (2) With respect to  $sp^2$  hybrid carbon, adjacent carbon (termed as  $\alpha$  carbon) have at least on hydrogen and hybridization of  $\alpha$  carbon should be  $sp^3$ .
- (3) Grater the number of  $\alpha$  carbon hydrogen grater will be stability.

**Q.6 Explain the order of stability of the following alkenes. (2008)**



**Ans.** On the basis of number hyperconjugative structure we can explain the stability.



**Q.7. Explain inductive effect. Why does this effect decreases as the length of carbon chain decreases? What is meant by +I and -I symbols?**

**Related Questions -**

**Q. What is inductive effect? Explain its importance. (Imp)**

**Q. Write short note on Inductive effect. (2016)**

**Ans: Inductive Effect:-**

Displacement of electrons along a chain of atoms due to the presence of a polar bond is known as Inductive effect. This effect is a permanent effect. Hydrogen is chosen as a reference for the measurement of relative inductive effect.

Some important characteristics of inductive effect are :

- (i) If an electronegative atom is attached to one end of the carbon chain, the flow of electrons is visible throughout the chain.



- (ii) The electrons never leave their original molecular orbital.

- (iii) The polarisation of electrons is always in a single direction throughout the molecule, developing a permanent dipole moment.

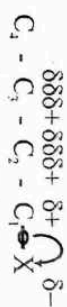
- (iv) Since the effect is transmitted through the carbon atoms, it decreases rapidly as the distance from the source (e.g., Cl) increases. In practice, it is ignored after the second carbon atom.

- (v) Atoms or groups which are more electronegative than hydrogen, exert negative inductive effect (-I), they pull electrons towards themselves.

On the other hand, if the atom or group is less electronegative than hydrogen, it exerts a positive inductive effect (+I), i.e., they repel or release electrons away from themselves.

This is a permanent effect, which gets introduced in the carbon atom chain when an atom/group (X) of different electronegativity is attached to its one end. As a result of this effect, the electron pairs of chain get displaced either towards (X) (if more electronegative) or away from X (if less electronegative) and a polarity get introduced in the chain permanently.

**Explanation:-**



Let us consider a carbon atom chain with group X having electronegativity slightly more than the carbon attached to one end.

X being more electronegative attracts shared pairs of electrons towards itself and acquires a partial negative charge on the other hand acquires a partial positive charge. The  $C_1 - X$  bond thus becomes a polar bond. The group X will also influence other carbon atoms in the chain ( $C_2, C_3, C_4$  etc) but as their distance from X increases the displacement of electron density towards X also decreases.

$$\text{i.e., Inductive effect} \propto \frac{1}{\text{Distance from X}}$$

This infer that inductive effect is distance depending.

**Phenomena:-**

Thus "The permanent displacement of electron pair density along the chain due to atom of different electronegativity is called as Inductive effect or Transmission effect".

**Type of Inductive Effect:-**

It is of two types -

(i) - I effect

(ii) + I effect

**(i) - I Effect:-**

The different atom/group have been arranged in decreasing order of inductive effect with hydrogen as the standard. If the inductive effect of an atom or group is more than that of hydrogen atom, it is called - I effect. The atom/group with - I effect are electron attracting in nature.

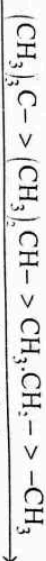
**Example:-**



- I effect decreases.

**(ii) + I Effect:-**

In case the inductive effect of an atom or group is lesser than that of hydrogen atom, it is called + I effect. The atom/group + effect are electron releasing in nature.



Decreasing order of + I effect

**Q.8** Explain the term Hydrogen bond with examples.

**Related Questions:-**

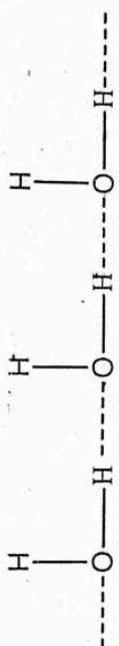
**Q.** What do you mean by hydrogen bonding? How does it effect the boiling point and water solubility of organic compounds?

**Ans. Hydrogen Bonding:-**

The linking of two atoms via a hydrogen atom is known as hydrogen bonding and this hydrogen bridge is form in between an hydrogen and electronegative atom for e.g. - F, Cl, O, & N hydrogen bond are in two types.

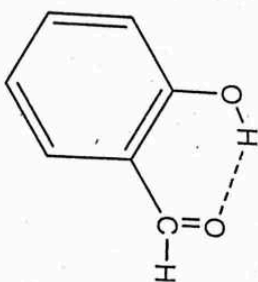
**(i) Intermolecular Hydrogen Bonding:-**

This type of hydrogen bonding occurs in between the molecules of a compound e.g.  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{HF}$  etc.



**(ii) Intramolecular Hydrogen Bonding:-**

This type of hydrogen bonding occur between the atoms in same molecule or within the molecule.



**Effect of Hydrogen Bonding:-**

**(a) On Boiling Point:-**

**(i)** Intermolecular hydrogen bonding will increase. Surface area of the compound hence increases boiling point of the substance.

**(ii)** Intramolecular hydrogen bonding: Decrease the surface area of the compound hence decrease the boiling point.

**(b) On Melting Point:-**

**(i)** Intermolecular hydrogen bonding: - It increases surface area of the compound, hence increases melting point of a compound.

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**(ii)** Intramolecular hydrogen bonding: - It decreases surface area of the compound hence decreases melting point of the compound.

**(c) On solubility:-**

**(i)** Intermolecular hydrogen bonding: - If solute forms hydrogen bonding with solvent will be soluble in the solvent.

**(ii)** Intermolecular hydrogen bonding: - Intermolecular hydrogen bonding decreases solubility of a compound.

**Q.9** Boiling point of 1-Buanol is greater than diethyl ether although both have same molecular formula. (2010)

**Ans.** In case of 1-Buanol, the formation of intramolecular hydrogen bonding is possible while in case diethyl ether not form hydrogen bonding. For more detail Please see the above question.

**Q.10.** Define the term aromaticity. Account for the aromaticity of cyclopentadienyl anion and cycloheptatrienyl cation. (2013)

**Related Questions:-**

**Q.** Describe Huckel rule. (2014)

**Ans. Aromaticity:-** It is clear that benzene is an especially stable molecule.

A number of other compounds have a similar special stability, which is called aromaticity. To be aromatic a compound must conform to all the following criteria:

(1) The molecule should be cyclic.

(2) There should be a p-orbital on every atom of an aromatic ring, i.e. cyclic molecule must be fully conjugated.

(3) Aromatic rings are planar. This planarity allows the p-orbitals on every atom to overlap.

(4) The cyclic arrangement of p-orbitals in an aromatic compound must contain  $(4n + 2)$   $\pi$ -electrons, where n is an integer (0, 1, 2, 3, ....). In other words, aromatic compounds have 2, 6, 10, 14, 18, ....,  $\pi$  electrons.

These criteria for aromatic behaviour were first recognised in 1931 by Erich Huckel. They are often called collectively the Huckel  $4n + 2$  rule or simply the  $4n + 2$  rule.

Huckel rule is also use for annulenes. Annulene is a general name for monocyclic hydrocarbons with alternating single and double bonds. The ring size of an annulene is indicated by a number in bracket, since the carbon atoms occur as doubly bonded pairs, an annulene must have an even number of carbons. Thus benzene is [6] annulene, cyclooctatetraene is [8] annulene. The general formula of annulenes is  $(\text{CH})_{2n}$ .

Benzene conforms to the  $(4n + 2)$  rule because it follows all four criteria.

The alkene 1, 3, 5-hexatriene is not aromatic.

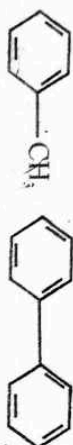


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## 1,3,5-hexatriene

This compound has six  $\pi$ -electrons and all p-orbitals are parallel. However, this compound is not aromatic because the six  $\pi$ -electrons are not present in a cyclic arrangement, this compound does not meet the criteria for aromaticity.

Toluene and biphenyl are both aromatic.

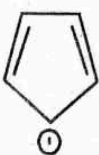


Toluene

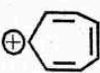
Biphenyl

The benzene ring in toluene meets all of the criteria for aromaticity. The methyl group is a substituent group and is not part of the aromatic system of  $\pi$ -electrons. Each ring of biphenyl is a separate aromatic  $\pi$ -electron system. We do not count the number of  $\pi$ -electrons in both rings together because all of them are not part of one continuous cycle.

Huckel  $4n + 2$  rule of aromaticity can also be applied to fused polynuclear compounds. This rule can also be applicable to cyclic, planar conjugated ions (cations as well as anions).



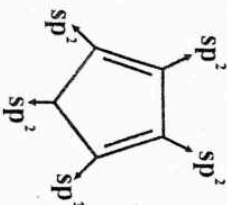
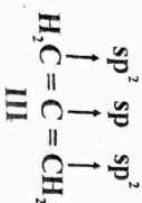
Cyclopentadienyl anion,  
more stable aromatic

Cycloheptatrienyl cation,  
6 $\pi$  electrons aromatic

**Q.11.** Indicate the hybrid state of each carbon of the following species.



*Ans.*

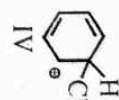
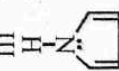
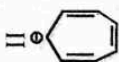
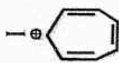


**Ans.**  $II > I > III$



(2017)

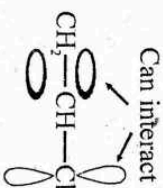
**Q.13.** Characterise the following species as aromatic, antiaromatic or nonaromatic. (2015)



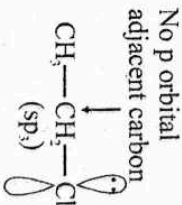
**Ans.** I - Aromatic, II - Antiaromatic, III - aromatic, IV - Antiaromatic,

Q.14. Length of C-Cl bond in  $\text{CH}_2=\text{CH}-\text{Cl}$  is shorter than in  $\text{CH}_3-\text{CH}_2-\text{Cl}$ .

**Ans.** It is clear from figure, vinyl halides can form partial double bond of the carbon-halide. This can be explained in terms that the p orbital of the halides can overlapped with the p orbital of carbon and thus giving the C-halide bond a partial double bond character. While in case of ethyl chloride such overlapping is not possible. Therefore, length of C-Cl bond in  $\text{CH}_2=\text{CH}-\text{Cl}$  is shorter than in  $\text{CH}_3-\text{CH}_2-\text{Cl}$ .



## Vinyl chloride



Ethyle chloride

## Chapter 2 - Mechanism Of Organic Reactions

### Arrow notation:-

In organic reaction movement of electron or flow of electron represent by a curved arrow. The direction of curved arrow show the direction of flow of electron.



Full arrow show transfer of two electron, where as half arrow show transfer of one electron.



Q.1. Describe homolytic and heterolytic bond fission of covalent bond.

Ans. Fission of covalent bonds:-

Bond fission is two types -

(i) Homolytic bond fission or homolysis:-

If a covalent bond is broken in such a way that each bonded group or atom takes one bonding electron then the breaking of bond is called homolysis.



As a result of homolysis free radicals are formed. Homolysis is favoured by heat, sunlight and peroxide.

(ii) Heterolytic bond fission or heterolysis:-

If a covalent bond is broken in such a way that one bonded group or atom takes both bonding electron then the breaking of bond is called Heterolysis.



As a result of heterolysis cations and anions are formed.

Q.2. Define nucleophiles and electrophiles, and classify the following accordingly -

- (i)  $\text{CH}_3\text{CH}^{\ominus}\text{CH}_3$ , (ii)  $\text{CH}_3\text{CH}^{\oplus}\text{CH}_3$ , (iii)  $\text{NH}_3$ , (iv)  $\text{AlCl}_3$

Ans. Classification of electrophilic reagents:-

1. Electrophiles or electrophilic reagents (Electro = electron, phile = love) -

They are electron deficient species. They have a tendency to accept electron pair from another molecule. In a reaction, an electrophile attacks at the point of maximum electron density. They are generated by heterolysis. All

electrophiles are Lewis acids. They may be neutral or positively charged.

(i) Neutral electrophiles:-



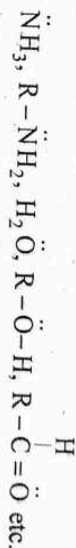
(ii) Charged electrophiles:-



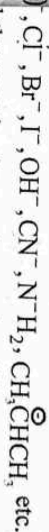
Nucleophiles or Nucleophilic reagents (Nucleo = Nucleus, phile = love):-

They are electron rich species. They have a tendency to donate electron pair. In a reaction, a nucleophile attacks at the point of minimum electron density. They are also generated by heterolysis. All nucleophiles are Lewis base. They may be neutral or negatively charged.

(i) Neutral Nucleophiles:-



(ii) Charged Nucleophiles:-

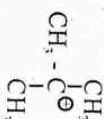


In the negative ions act as nucleophiles.

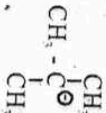
Reaction Intermediates:- Reaction Intermediates:-

The short lived species which formed by heterolysis or homolysis during reaction are called as reaction intermediates.

Carbene eg:-



(ii) Carbanion eg:-



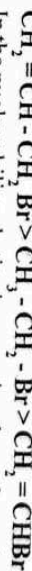
(iv) Carbene eg:-



Benzene eg:-



Explain the order of reactivity in the nucleophilic substitution reaction.



(2010)

In the nucleophilic substitution reaction the carbocation is an intermediate. Hence the stability of carbocation will govern the reactivity order.

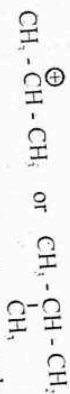
1. A tertiary Carbocation is stable but a tertiary Carboanion is unstable.

(2004)

Related Questions:-

In each of the following which ion is more stable and why? (2012)

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Ans. In tertiary carbocation, there are three electron releasing methyl groups which stabilize the positive charge on tertiary carbon. While in case of secondary carbocation the all three methyl group destabilize the negative charge on it and methyl tertiary carbocation already carry larger electron density via inductive effect that methyl group give another amount of electron density via inductive effect that makes the tertiary carbocation unstable.

Q.5 Discuss the stability of Carbocations.

(2007, 20)

Related Questions -

Q. Explain the stability order of primary, secondary and tertiary carbocations. (20)

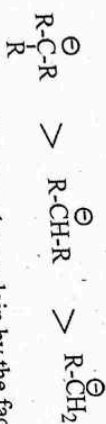
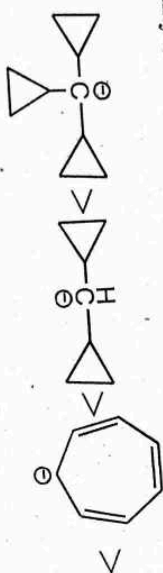
Q. What are carbocations? Discuss their structure. (20)

Q. Write notes on stability of Carbocations.

Ans. Carbocation:-

Reaction intermediates in which positively charged carbon atom is  $\text{sp}^2$  hybridized, present, are called as carbocation. Positively charged carbon is  $\text{sp}^2$  hybridized and have six electron. Carbocation act as a electrophile.

Stability of carbocation:-



The above stability can be explain by the fact that

(i) Inductive effect stability of alkyl carbocation or carbonium  $\propto$  -I power of alkyl group

$\propto$  + I power of group.

(ii) Number of resonating structure, greater the number of resonating structure greater will be the stability.

(iii) Hyper conjugation: greater the number of hyperconjugating structure greater will be stability.

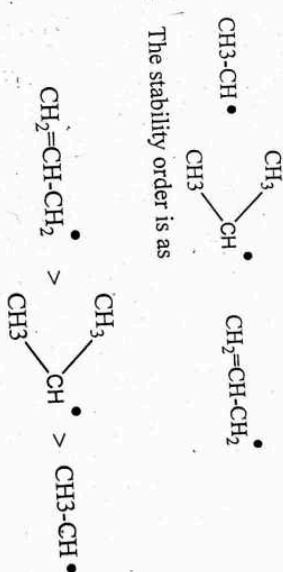
Structure of carbocations:- The carbon atom of carbocation is  $\text{sp}^2$  hybridized.

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in which the p orbital is devoid of any electron. The three bonding orbitals form three s bonds, the remaining p orbital is vacant. This vacant p orbital makes the carbon atom electron deficient and gives it a positive charge. The carbocation thus has a planar (flat) structure having all the three s bonds in one plane with the bond angles of  $120^\circ$  between them.



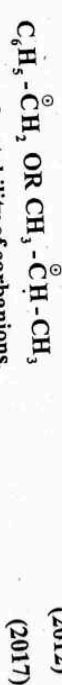
Q.6 Arrange the following free radicals in decreasing order of their stability. (2008)



Q.7 What is carbanions? Discuss the stability.

Related Questions:-

In each of the following which ion is more stable and why? (2012)

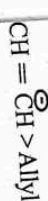
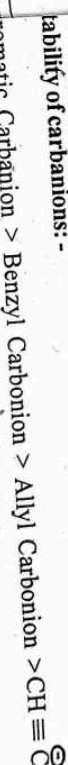


Discuss the stability of carbanions.

Ans. Carbanions:-

Reaction intermediates in which negatively charged carbon atom is present, are called as carbanions. Negatively charged carbon atom is  $\text{sp}^3$  hybridized and carries eight electrons. Carbanions act as a nucleophile.

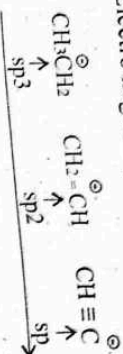
Stability of carbanions:-



Stability can be explain by following way.

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(a) Electro negativity of carbanion carbon:-  
Stability  $\propto$  Electro negativity of carbanionic carbon



% s character of carbanionic carbon order

(i) % s-character in increasing order. (ii) Stability in increasing order.

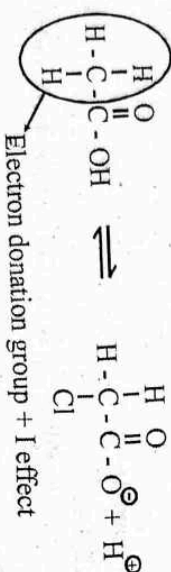
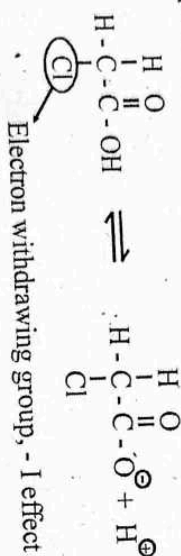
Q.8 Monochloro acetic acid is stronger than acetic acid.

Related Questions:-

(2011)

Q. Chloroacetic acid is stronger than acetic acid.

Ans. Monochloro acetic acid is more acidic because of -I effect present while in case acetic acid the +I effect present. Hence the formation of  $\text{H}^+$  is more facile in case of monochloro acetic acid due to the bond breaking i.e.  $\text{C}-\text{H}$  is easier compared to acetic acid.



Q.9 Explain with example the characteristics, structure and stability of free radicals.

Ans: General Characteristics of Free Radicals:-

(a) Free radicals are electrically neutral species containing one or more unpaired electron. This definition includes atoms of elements and stable molecules  $\text{NO}$  and  $\text{NO}_2$ .

Example:-

$\text{CH}_3$  (Methyl radicals)  $\cdot\text{C}(\text{Ph})_3$  (Triphenyl methyl radicals)  $\cdot\text{Cl}$  (Chlorine radicals)

(b) Free radicals are formed by homolytic cleavage



and  $\text{B}^{\cdot}$  are free radicals.

(c) Free radicals are very reactive

(d) They may be broadly classified into long lived and short-lived free radicals.

(e) Radicals may undergo substitution, addition rearrangement, elimination and fragmentation process.

(f) A radical produced in a reaction is capable of generating more such radicals generally through three major steps are known in radical reactions. They are initiation (initiation), generation of new radicals (propagations) and return to stable molecular species (termination).

(2011)

the decreasing order of stability of alkyl free radical is

the order of stability has been explained in terms of hyper conjugation. As we know greater the number of resonating structure and hyper conjugation greater will be stability

Triphenyl methyl > Diphenyl methyl > Benzyl > Allyl > 3<sup>o</sup> Allyl > 2<sup>o</sup>

Allyl > 1<sup>o</sup> Allyl > Tertiary > Secondary > Primary

his order can be explained with the help of resonance and hyper conjugation, we know greater the number of resonating structure and hyper conjugation greater will be stability.

10 What are singlet and triplet carbenes? Discuss their stability and geometry. (2005, 2008)

Related Questions:-

Discuss structure and stability of carbenes

What are Carbenes? How many types of carbenes are there? Give a method of synthesis for each. (2012, 15, 16)

Write short note on the Carbenes.

What are carbenes? Explain why triplet carbenes are more stable than singlet carbenes. (2013)

Ans. Carbene:-

Carbenes are neutral, highly reactive carbon intermediates represented by  $\text{:C:}$ .



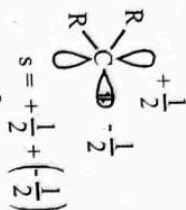
(i) Carbenes are related to carbanions through the  $\alpha$ -elimination reaction.

(ii) The simplest carbene is which known as methylene  $\text{CH}_2$ .

(iii) Substituted carbenes are simply named as derivative of carbenes. For example,  $\text{H}_3\text{C}-\ddot{\text{C}}\text{H}$  Phenyl Carbene,  $\text{R}-\ddot{\text{C}}-\text{R}$  Dialkyl Carbene,  $\ddot{\text{C}}\text{Cl}$  Dichloro carbene.

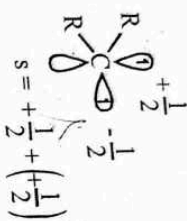


- (v) Hybridization of the divalent carbon of carbene may be  $sp^2$  as well  $sp$ .  
 (vi)  $sp^2$ -hybrid carbene is of two type  $sp^2$  singlet carbon and  $sp^2$  triplet.  
 (vii) Triplet carbene means the spin multiplicity  $2s + 1$  is 3, where  $s =$  number of spin electron. Hence triplet carbene has two unpaired electron. In the same way singlet means spin



$$\begin{aligned} s &= 0 \\ \text{Spin multiplicity} &= 2s + 1 \\ &= 2 \times 0 + 1 \\ &= 1 \end{aligned}$$

$sp^2$  singlet carbene



$$\begin{aligned} s &= 1 \\ \text{Spin multiplicity} &= 2s + 1 \\ &= 2 \times 1 + 1 \\ &= 3 \end{aligned}$$

$sp$  Triplet carbene

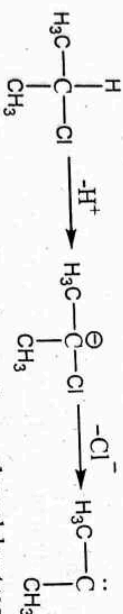
multiplicity ( $2s + 1$ ) is 1. The one possible when  $s = 0$  i.e. means paired electron.

(viii)  $sp$ -hybrid carbene is always triplet carbene.

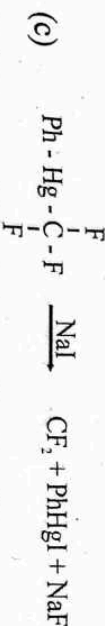
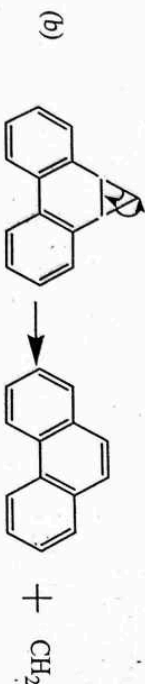
(ix) Carbenes are neutral electrophiles.

Generation:-

(1) In  $\alpha$  elimination step the carbon loses a group without its electron pair, usually a proton, and subsequently a group with its pair, usually a halide ion.



The generation of dichlorocarbene is mostly employed by treatment chloroform with a base, however, other examples are also known which are

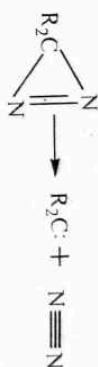
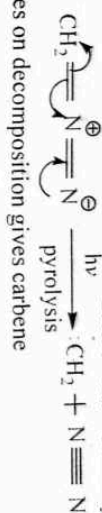


(2) The two most important ways of forming  $\text{:CH}_2$  are examples: the photolysis of ketene

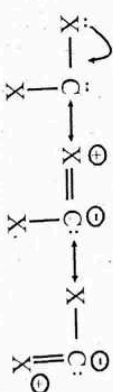


and its isoelectronic decomposition of diazomethane.

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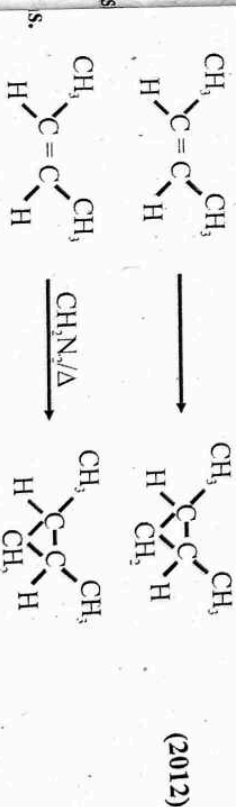


**ability of carbenes:-** Generally, a triplet carbene (e.g.  $\text{:CH}_2$ ) is 7.7 - 10 Kcal/mole more stable than the singlet carbene ( $\text{:CH}_2$ ). The triplet carbene has a lower energy because with two electrons in different orbitals there is less electron-electron repulsion than that when both are in the same orbital. However, the nature of substituents has an important effect on the stability of carbenes. For example, as the substituents on the carbene carbon become better pi electron donors, the stability of the singlet state increases and the singlet state carbene becomes more stable than the triplet state carbene. Thus carbenes are more stable in the singlet state than in the triplet state. This is because a p-orbital of the hydrogen (X) with a lone pair of electrons can overlap generally with the vacant p-orbital of the singlet carbene, thereby stabilising the singlet state. This stabilisation is not possible in the triplet state whose p-orbitals are not vacant. The resonating structures are:



Amongst diallocarbenes, the most stable is the singlet difluorocarbene. This can be explained as: Since fluorine and carbon are in the same period, their p-orbitals are of about the same size permitting more efficient overlapping. Furthermore, of the C—X bonds, the C—F bond length is the shortest which again provides far more extensive overlap of the respective p-orbitals. On this basis it can be concluded that the singlet  $\text{:CF}_2$  is more stable than  $\text{:CCl}_2$ , which is more stable than  $\text{:CBr}_2$ .

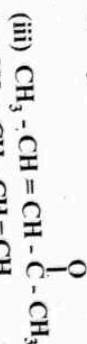
II How to converge following.



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Q.12 Which one of the following compound has inductive, mesomeric hyperconjugative effect.



Ans: (i) Inductive effect (ii) Hyperconjugative effect

(iii) Mesomeric (iv) Mesomeric

Remark:

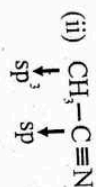
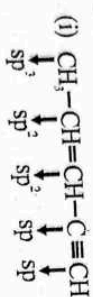
For carbon hybridization first of all count the number of  $\sigma$ -bonds present on that particular carbon atom.

If Number of  $\sigma$  bond

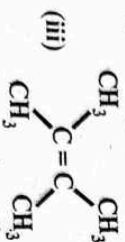
Zero  $\text{sp}^3$   
One  $\text{sp}^2$   
Two  $\text{sp}$

Types of hybridization

Examples:-



Q.13 Arrange the following alkenes in sequence of decreasing order carbon-carbon double bond length.



Ans: decreasing order of carbon-carbon double bond length  $i > ii > iii$

Q.14 Why 1,3-Pentadiene is more stable than 1,4-Pentadiene? (1m)

Ans. 1,3-Pentadiene is more stable than 1,4-Pentadiene due to in 1,3-Pentadiene has a conjugate position and it stabilize through resonance while the 1,4-Pentadiene not have conjugate position.

Q.15 Explain "Electromeric Effect" with example. (2m)

Ans: The effect that develops polarity in multiple bonded compounds the approach of a reagent is known as electromeric effect.

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Property:-

(i) It is temporary effect.

(ii) It takes place presence of a reagent.

(iii) It involves the complete transfer of  $\pi$  electron and  $\delta^+$  &  $\delta^-$  charge develops.

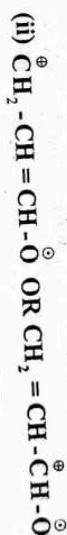
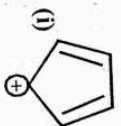
(iv) It involves  $\pi$  electron only so it takes place multiple bond.

For e.g.  $\text{>C=O} + \text{CH}_3\text{MgBr} \xrightarrow{\text{H}_2\text{O/H}} \text{>C(OH)CH}_3$

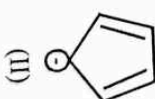
(v) This effect takes place in the direction of more electronegative atom and show by curved ( $\curvearrowright$ ) arrow, e.g.



Q.16. In each of the following parts of ions, which ion is more stable and why? (2012)



(1)



(11)

Carbocation I is less stable compare to II anion because of II structure ion  $6\pi e^-$  and it become aromatic compound.



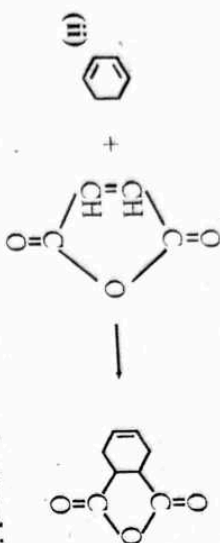
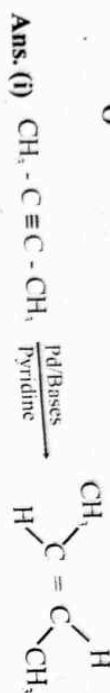
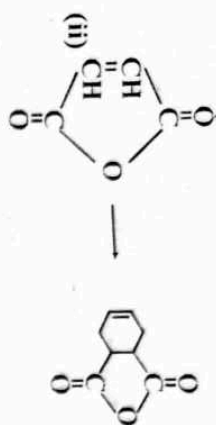
(1)

I structure is more stable compare to II structure.

Q.17. How will you bring about the following transformations? (2012)



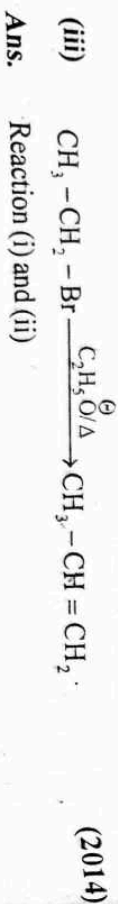
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Q.18. Which of the following are electrophile? (2014)



Q.19. Indicate the reaction(s) in which product formation takes place via formation of carbocation as reactive intermediate. (2014)



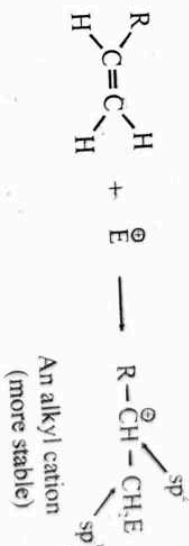
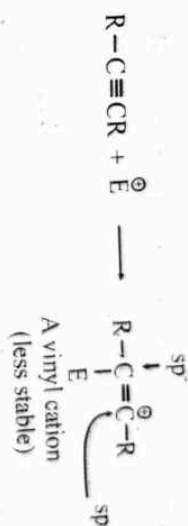
Ans. Reaction (i) and (ii)

Q.20. Why alkene is more reactive than alkyne for electrophilic addition reactions. (2014, 17)

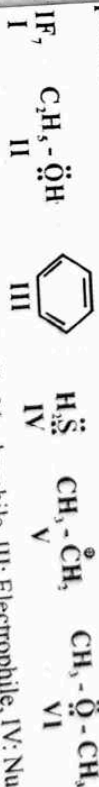
Ans. Since alkynes are more unsaturated than alkenes, it somehow seems wrong for them to be less reactive than alkenes. This apparent anomaly is rationalised by examining the intermediates that are formed when alkynes and alkenes react with an electrophile  $\text{E}^+$ .

The carbocation produced from an alkyne is a vinyl cation with a more electronegative  $\text{sp}$  hybridised carbon which is less tolerant of the positive charge than the alkyl cation with  $\text{sp}^3$  carbon produced from alkene. Thus addition of electrophile to an alkyne forms a much less stable intermediate than that in the case of an alkene.

We know that reactivity of a substance depends on the stability of reaction intermediate. Higher is the stability of reaction intermediate, more will be the reactivity of the substrate. Therefore, alkenes are more reactive than alkynes in electrophilic addition reactions.

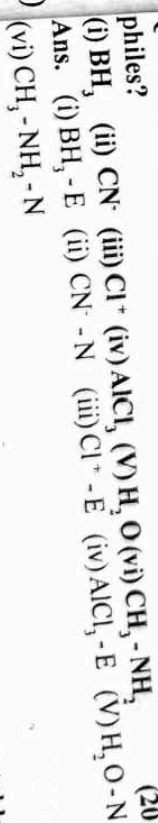


Q.21. Which among the following are electrophiles and which are nucleophiles? (2015)



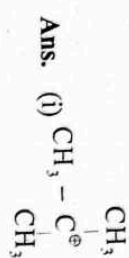
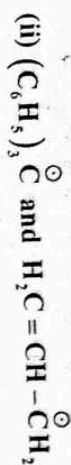
Ans. I - Neutral electrophile, II - Nucleophile, III: Electrophile, IV: Nucleophile, V - Electrophile, VI - Nucleophile.

Q.22. Which among the following are electrophiles and which are nucleophiles? (2016)



Q.23. In each of the following pairs of species which one is more stable?

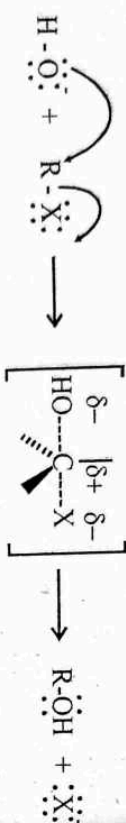




Q.24. Explain the given order of reactivity for nucleophilic substitution action.



Ans.

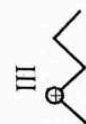
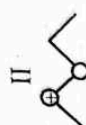
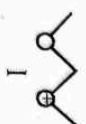


Bimolecular

Transition state

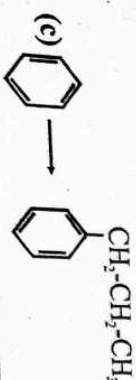
Since there is only one bimolecular step in this mechanism, the rate reaction will depend on the concentration of both  $R-X$  and  $OH^-$ . This mechanism is referred to as  $S_N2$ , and it involves transition state and given order follow the same order of alkyl cation stability.

Q.25. Arrange following carbocations in decreasing order of their stability.

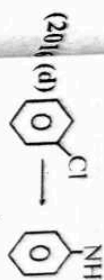


Ans. II > I > III

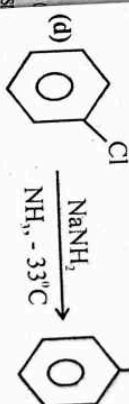
Q.26. Suggest suitable reagent(s) for the following chemical transformations. (2018)



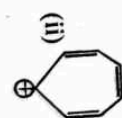
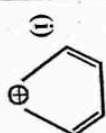
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(c) Go through Q.34(d) page No. 88.



Q.27. Arrange given carbocations in decreasing order of their stability. Give your answer with suitable reason(s):



(2019)

Ans. (ii) > (iii) > (i)

Q.28. Explain why  $\dot{C}F_2$  is more stable than  $\dot{C}Cl_2$ ?

Ans. Since fluorine and carbon are in the same period, their p-orbitals are

of about the same size permitting more efficient overlapping. Furthermore, the C-F bond length is the shortest which again provides for more extensive overlapping of the respective p-orbitals. On the basis of this we can infer that  $\dot{C}F_2$  is more stable than  $\dot{C}Cl_2$ .

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## Chapter 3 - Stereochemistry Of Organic Compounds

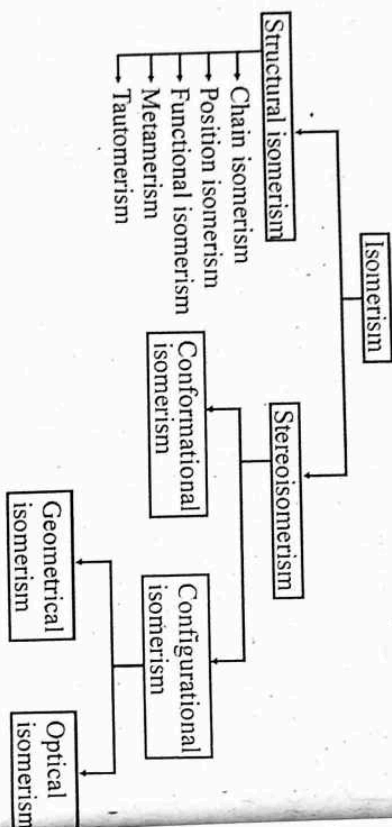
### Alkanes & Cycloalkanes

Compounds that have same molecular formula but different atomic arrangement are called isomers and such phenomenon is called as isomerism. e.g.



Both compounds have same molecular formula but they are not identical. One of two, one is alcohol and other one is ether.

There are following types of isomerism.



**Q.1.** What is stereoisomerism? Discuss the optical isomerism of lactic acid.

**Other Related Questions-**

**Q.** Mention necessary condition for an organic compounds to be optically active.

**Ans.** Discuss the condition for optical activity.

**Stereoisomerism:-**

The compound which have the same molecular and structural formula but differ in the arrangement of atoms or groups in space within their molecules are called stereoisomers. This phenomenon is known as stereoisomerism.

**Condition for optical activity:-**

The necessary and sufficient condition for optical activity is that the molecule should be dissymmetric i.e. should have no element of symmetry.

- Chiral carbon or chiral center. Those carbons are chiral carbon which have four different group or substituent e.g.
- Molecule should not have plane of

symmetry. That means molecule should not be divisible into two equal halves.

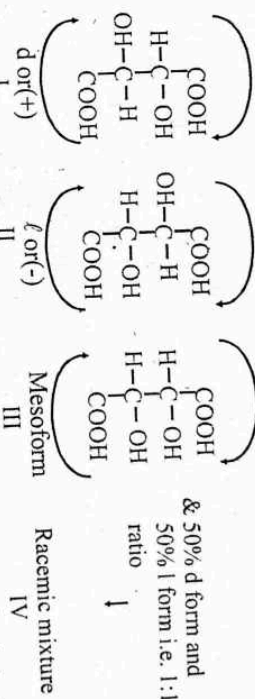
(iii) Molecule should not have center of symmetry.

(iv) Molecule should not have alternate axis of symmetry.

Tartaric acid has two chiral carbon or asymmetric carbon.



It exists in four different isomers.



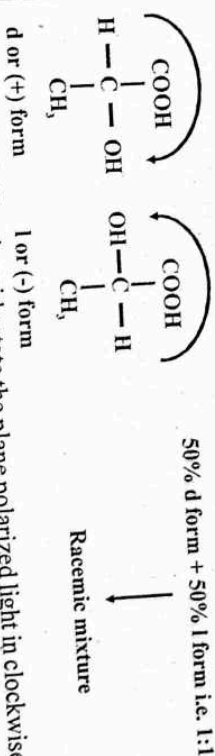
- d or (+) tartaric acid:- Structure I will rotate the plane of polarized light to the right
- l or (-) tartaric acid:- structure II will rotate the plane of polarized light to the left.

(iii) **Meso form:-** The structure III will be optically inactive. Since the rotatory power of the upper half of the molecule is balanced by that of the lower half.

Such type of optically inactivity is due to internal compensation.

(iv) **Recemic Mixture (dl) or  $\pm$  form-** Recemic mixture are optically inactive, it is due to external compensation.

Lactic acid exists in three-stereoisomer form.



+ or d form = (+) lactic acid rotate the plane polarized light in clockwise.  
- or l form = (-) lactic acid rotate the plane polarized light in anticlockwise.

Racemic mixture = this is optically active due to external Compensation.

**Q.2.**

Write short notes on

(i) Chirality

(2015)

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## (200)

(2) If the two group atom or subsequent atom have the same atomic number. The atomic number of second atoms determines the order (i.e. consider one by one atom).

$\text{ClCH}_2$ 
 $\begin{array}{c} \diagup \\ \text{C} = \text{C} \\ \diagdown \end{array}$ 
 $\begin{array}{c} \text{CH}_2\text{-CH}_3 \\ \diagdown \end{array}$

Both group have same atom  
hence we move to next atom

$$\begin{array}{c} \text{CH}_3-\text{CH}_2-\overset{*}{\underset{\text{Br}}{\text{C}}}-\text{CH}_3 \\ \text{CH}_3-\text{C}-\text{F} \\ \text{Br} \end{array}$$

Actual spatial arrangement of atoms or groups are called absolute configuration. R,S nomenclature based on absolute configuration. This system of nomenclature is also called as Cahn-Ingold-Prelog nomenclature. The R,S nomenclature system involves two steps.

(ii) After numbering the ligands, the molecule is imagined to be oriented so that the group of highest number (lowest priority) is directed away from the observer (in Fischer projection placed on top or bottom). Now the remaining three groups are viewed in the increasing order of number (i.e. in decreasing order of priority). If eye travel in clockwise direction the configuration is specified 'R', while if eye travel in anticlockwise direction, the configuration is specified 'S'.

The priority of the four ligands attached to a chiral centre at decided by applying the following sequence rules.

$$\begin{array}{c} \text{1 Br} \\ | \\ \text{2 H} \text{---} \text{C} = \text{C} \text{---} \text{Cl} \text{1} \\ | \\ \text{CH}_3 \text{2} \end{array} \quad \begin{array}{c} \text{3 COOH} \\ | \\ \text{1} \text{---} \text{C} \text{---} \text{Br} \text{2} \\ | \\ \text{H} \text{1} \end{array}$$

### S configuration

Always move  $1 \rightarrow 2 \rightarrow 3$  not  $1 \rightarrow 3 \rightarrow 2$  (x)

(3) Double and triple bond are counted as if they were split into two or three single bonds, respectively, for e.g.

$$\begin{array}{c} \text{H} \\ | \\ -\text{C}=\text{O} \\ \\ -\text{C}\equiv\text{CH} \\ \\ -\text{CH}=\text{CH}_2 \end{array}$$

Note: - In simple way we can consider double or triple bonded atom as twice or thrise respectively. [same rule apply in RS system]

4) In the case of Isotopes, the mass number is used to determine their relative priorities.

2.4. State the necessary conditions for a compound to show geometrical isomerism. Illustrate your answer with example. (2007)

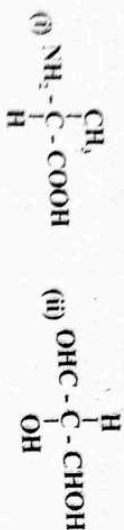
The following two conditions are necessary for geometrical isomerism

i) Compound should have at least one  $C = C$  double bond

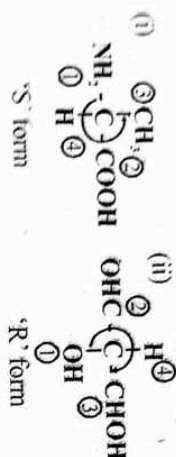
ii) Both double bounded carbon must have different atoms or groups

e.g. Cab = Cab, Cab = Ccd, Cab = Cbc show geometrical isomerism.  
Caa = Cbc does not show geometrical isomerism.

2.5. Give the configuration symbols R and S to the following compound.



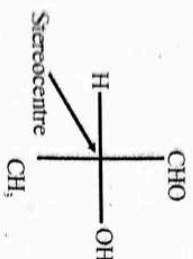
Ans.



Q.6. What is a stereocentre? How is a stereocentre related to a chiral centre?

Ans. Stereocentre:-

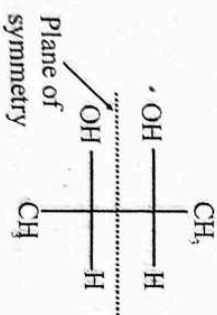
A carbon bonded to four different atoms or groups is called a stereocentre. It is also called as chiral centre. Present time stereocentre is defined as an atom on which an interchange of any two atoms or groups results in a new stereoisomer. When the new stereoisomer is an enantiomer, the stereocentre is called a chiral centre.



Q.7. Define the plane and the centre of symmetry with suitable examples.

Ans. Plane of symmetry:-

The plane within the molecule which divides the molecule into two equal halves which are related as mirror images is known as plane of symmetry, e.g.

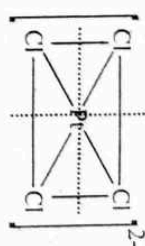


Centre of symmetry:-

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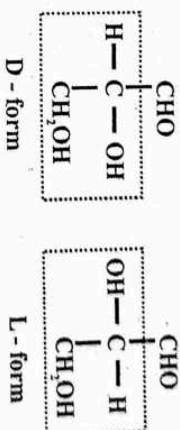
It is a point in a molecule from which if lines are drawn on one side and on the other side, at equal distance on the other side, will meet the same atoms or groups.



8. Write short notes on D and L nomenclature.

D and L nomenclature:-

Glyceraldehyde was selected as standard compound for D and L terminology of the optical isomers. The conversion is OH-group on the right and H on the left side in a two-dimensional plane paper, called D forms. This is happening on asymmetric carbon atom or chiral carbon, this is preferred next to primary alcoholic group. For L form vice-versa is true.



Define Enantiomer and Diastereomer and its property.

Taking suitable examples, discuss Diastereomers and Enantiomers.

(2015)

Enantiomer:-

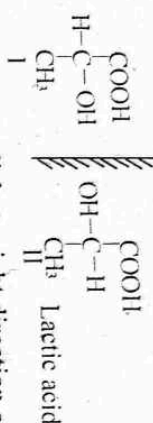
Any molecule having one asymmetric carbon atom exist in two configurations, which are non-superimposable, mirror image.

I and II have same molecular formula, same structure but different configurations hence I and II are known as configurational isomers. I and II are non-superimposable mirror image, hence (I) and (II) are optical isomers. Configurational isomers, which are non-superimposable mirror image, are known as enantiomers. Thus I and II are enantiomers. Pair of I and II is known as enantiomeric pair.

Properties:-

Enantiomers are the mirror image. Mirror images are not superimposable. They have identical physical properties M.P., B.P., density, refractive index. They have identical chemical properties except toward optically active reagent.

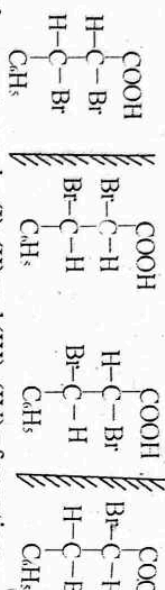
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(v) One enantiomer rotates the light to right direction and other rotates light by an equal magnitude to the left direction.

#### Diastereomers:-

Let us consider a di-bromocinnamic acid exist in the following optically active forms.



Thus there are two pairs (I), (II) and (III), (IV) of enantiomers. For more equimolar mixture of I and II will give one racemic mixture. Similarly equimolar mixture of III and IV will give other racemic mixture.

Now let us examine the relationship between the structures I and II and III, IV and I. These are configurational isomer but not mirror images. Configurational isomers, which are not mirror images, are known as diastereomers.

Thus I & III, I & IV, II & III and II & IV are diastereomers.

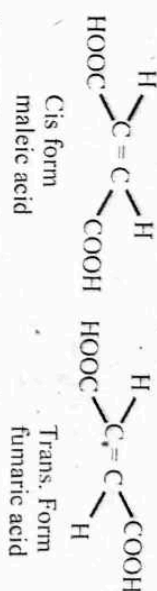
#### Properties:-

Enantiomers (also known as optical isomers) have similar physical and chemical properties while diastereomers shows different physical and chemical behavior. Thus their mixture can separate diastereomers either by the use of physical properties or by the use of chemical properties or both.

**Q.10. What is the case of geometrical isomerism? Discuss the geometrical isomerism of maleic acid and fumaric acid.**

**Ans. Geometrical isomerism:-**

The rotation about a carbon-carbon double bond is not free because of the carbon atom of the double bond with respect to each other. Due to hindered rotation, the relative position of atom or group attached to the carbon atoms of the double bonds get fixed. For example, Ha and Hb in fig (1) cannot exchange their position by rotation with respect to C<sub>1</sub> and C<sub>2</sub> without breaking the  $\pi$  bond.



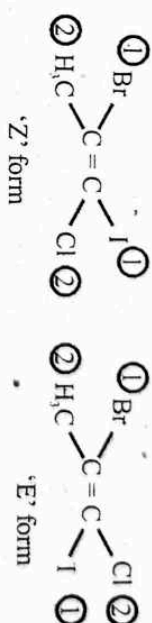
As a result, many substituted alkenes can exist in two distinct isomers, which differ from each other only in the relative positions of atoms or groups in space around the double bond, for example maleic acid and fumaric acid.

#### 11. Discuss about E, Z-system of nomenclature.

##### Other Related Questions:-

Describe the Z, E configuration of Geometrical isomers. (2017)

Ans. E, Z- Nomenclature system:-

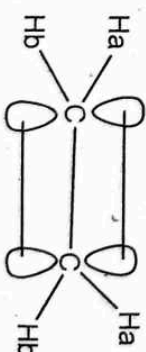


This nomenclature system is based on Cahn-Ingold-Prelog system. The E, Z system, first we identify the group of highest priority by sequence on each double bonded carbon atom. If the highest priority groups are on the same side of the double bond, the conformation is 'Z', and if they are on opposite sides, the conformation is 'E'.

**12. In short write down necessary and sufficient condition for compounds to exhibit geometrical isomerism. Discuss cis-trans isomerism of maleic acid and fumaric acid. (2007)**

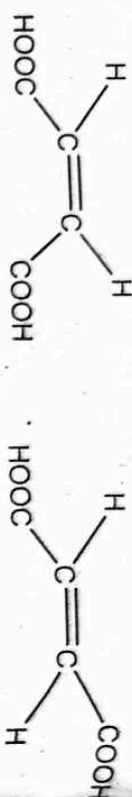
Ans. Geometrical isomerism:-

The rotation about a carbon-carbon double bond is not free because of the carbon atom of the double bond with respect to each other. Due to hindered rotation, the relative position of atom or group attached to the carbon atoms of the double bonds get fixed. For example, Ha and Hb in fig (1) cannot exchange their position by rotation with respect to C<sub>1</sub> and C<sub>2</sub> without breaking the  $\pi$  bond.



Due to this hindered rotation, the relative position of atom or group attached to the carbon atoms of the double bonds get fixed. For example, Ha and Hb in fig (1) cannot exchange their position by rotation with respect to C<sub>1</sub> and C<sub>2</sub> without breaking the  $\pi$  bond.

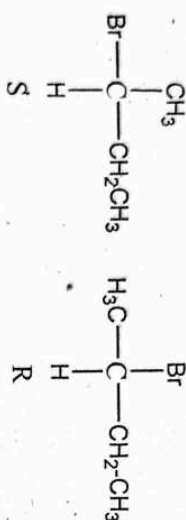
As a result, many substituted alkenes can exist in two distinct isomers which differ from each other only in the relative positions of atoms or groups in space around the double bond. For example maleic and fumaric acid.



Cis form  
Maleic acid

trans form  
Fumaric acid

Q.13. Draw the configuration and R and S enantiomers of 2-bromooctane.



Q.14. Taking suitable examples, discuss inversion, retention and racemization.

Related Questions -

Q. Write short notes on racemisation.

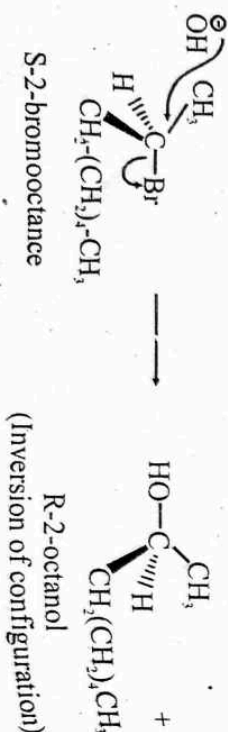
Q. Define the following terms with suitable examples:

(i) inversion in configuration (ii) Retention in configuration

(iii) Racemisation.

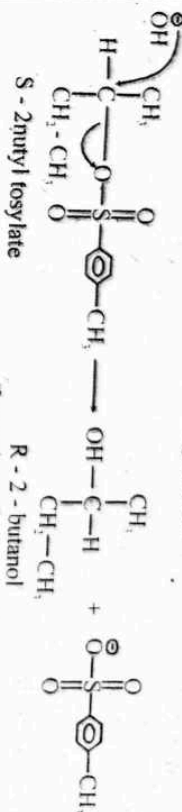
Ans. Inversion of Configuration:-

When a reaction takes place at a chiral carbon atom, change the configuration of the chiral carbon. For example, the  $S_N2$  mechanism involves an inversion of configuration of the carbon atom under attack nucleophile. An inversion of the configuration gives a product stereochemistry is opposite to that of the reactant. The reaction of hydroxide ion with optically active 2-bromooctane proceeds with inversion configuration.



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Similarly, the reaction of hydroxide ion with optically active 2-butyl tosylate proceeds with inversion of configuration:

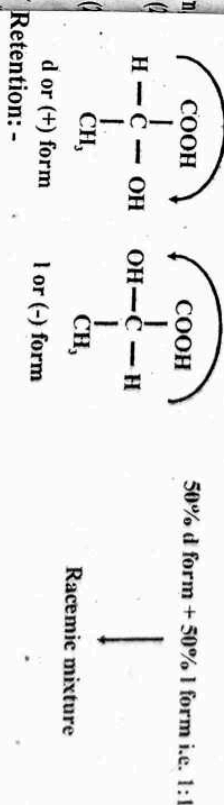


(Inversion of configuration)

P. Walden first proved that a substitution reaction had inverted configuration of a chiral carbon. In his honour, a substitution that inverts the configuration at a chiral carbon is called a Walden inversion. The  $S_N2$  family of reactions are common examples of Walden inversions since the backside attack of the nucleophile inverts the configuration of the electrophilic carbon atom.

Racemisation:-

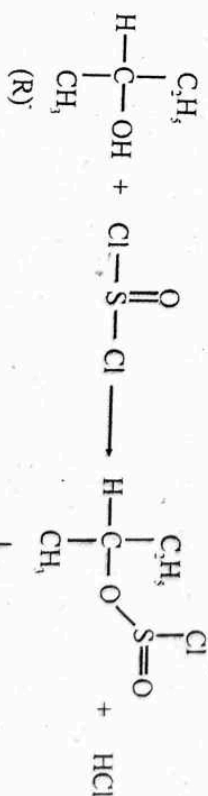
When a mixture of d and l form exist as 1:1 ratio in a solution, called racemic mixture. In a real sense the rotation of plane polarized light is nullified in such a way that one isomer is rotating clockwise and other isomer rotating plane polarized light in same magnitude so the resultant or net movement of plane polarized light is zero.



Racemic mixture

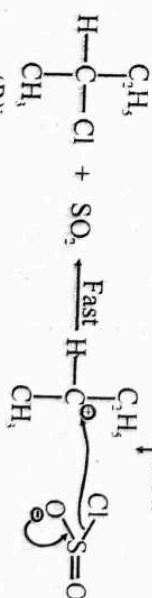
d or (+) form

l or (-) form



Retention of configuration

(Ion pair)



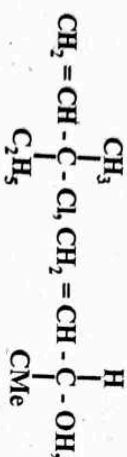
Inversion of configuration and racemization are the most common stereochemical results of reactions that take place at a chiral carbon atom. A

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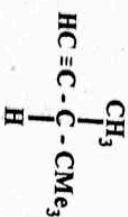
few reactions at chiral carbon atoms give products that have the configuration as the starting material; this result is called retention of configuration. An example is the reaction of an alcohol with thionyl chloride. This reaction provides a method for converting alcohols to alkyl chlorides with retention of configuration.

The product formation takes place via the formation of ion-pair. The pair formation in  $S_N1$  reaction gives racemic mixture. Then the question arises why do not we get a racemised product as we do in the standard  $S_N1$  reaction? The difference lies in the source of the nucleophile. In the  $S_N1$  reaction, the nucleophile is randomly distributed throughout the solution. In the thionyl chloride reaction of nucleophile is a part of the leaving group. The carbocation and the leaving group form a closely associated ion-pair, and the chloride ion immediately attacks the nearby face of the carbocation.

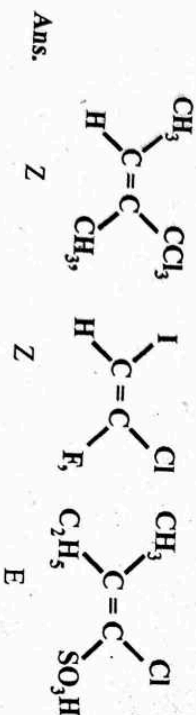
Q.15. Assign (R)/(S) nomenclature to each of the following compounds.



Ans.



Q.16. Assign (E)/(Z) nomenclature to the following compounds.



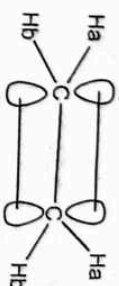
Q.17. In short write down necessary and sufficient condition for compounds to exhibit geometrical isomerism. Discuss cis-trans isomerism of maleic acid and fumaric acid.

Ans. Geometrical isomerism:-

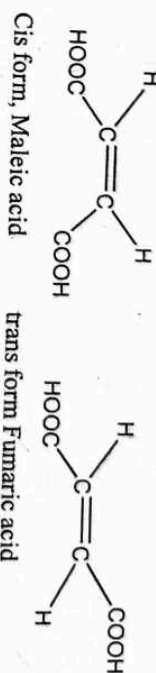
The rotation about a carbon-carbon double bond is not free because of the carbon atom of the double bond with respect to each other. Due to this, the rotation is hindered or restricted. In other words a  $\pi$  bond prevents free rotation of the carbon atom of the double bond with respect to each other. Due to this, the rotation is hindered or restricted.

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ordered rotation, the relative position of atom or group attached to the carbon atoms of the double bonds get fixed. For example, Ha and Hb in fig (1) cannot exchange their position by rotation with respect to  $C_1$  and  $C_2$  without breaking the  $\pi$  bond.



As a result, many substituted alkenes can exist in two distinct isomers, which differ from each other only in the relative positions of atoms or groups in space around the double bond. For example maleic acid and fumaric acid.



Q.18. Explain difference between configuration and conformation. What do you understand by terms 'Configuration' and 'Conformation'?

Write short note on the Conformation of n-butane. (2007) (2012, 19)

Draw the different conformations of n-Butane and discuss their stabilities. (2015)

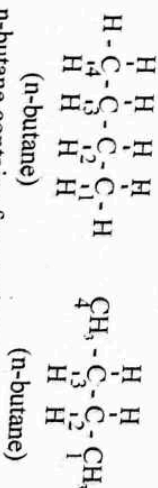
Ans. Configuration:-

The different spatial arrangements of atoms in a molecule which are not interconvertible in each other only by rotation along the C-C single bond, are called configuration and isomerism is called configurational isomerism. They can be separated easily.

Conformation:-

The different spatial arrangements of atoms in a molecule which are readily interconvertible by rotation about single bonds are called conformations and isomerism is called conformational isomerism. They cannot be separated easily.

Conformational isomers of n-butane:-



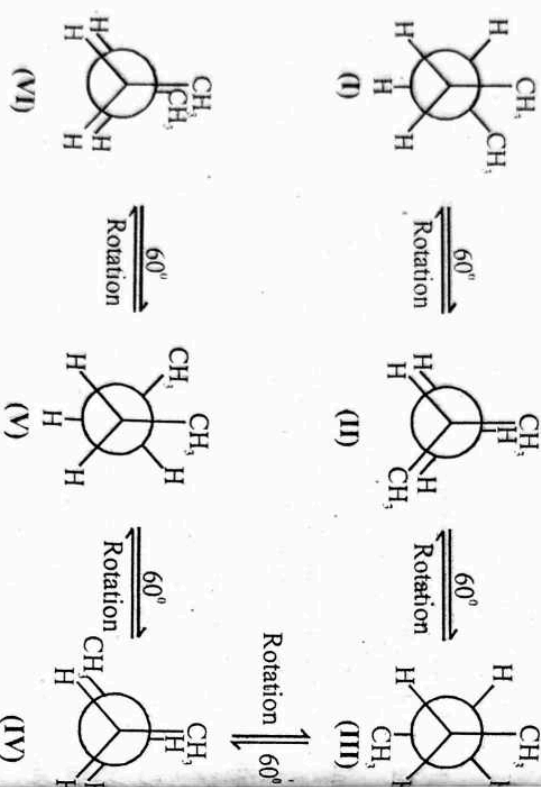
n-butane contains four carbon atoms in a straight chain and can be derived from ethane by replacing on hydrogen atom attached to one carbon with a methyl group.

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It contains three C-C single bond, around which the rotation can take place, but if we consider the rotation about the carbon-carbon bond in center ( $C_2-C_3$ ) the following eclipsed and staggered conformations are possible. They may be complete or partial as follows.



Butane has three staggered conformers (I, III and IV), conformer III, in which the two methyl groups are as far apart as possible is more stable than the other two staggered conformers I and V. The most stable of the staggered conformer (III) is called the *anti conformer* and the other two staggered conformers (I and V) are called *gauche conformers* (anti is Greek for "opposite of", gauche is French for "left").



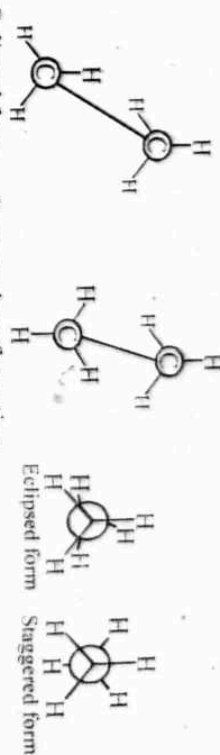
These conformations can be obtained by rotating the molecule  $60^\circ$ . Due to energy barrier in different conformations the anti conformation would be the most and fully eclipsed conformation is least stable conformation of n-butane.

**Q.19. Give the concept of conformation of ethane.** (2006)

**Ans. Conformation of ethane:-**

Ethane molecule contains a C-C single bond and each carbon atom is attached to three hydrogen atoms. If one of the carbon atoms is permitted to rotate about the C-C bond and other carbon remains stationary, an infinite number of arrangements of the hydrogen atoms of one carbon with respect to the

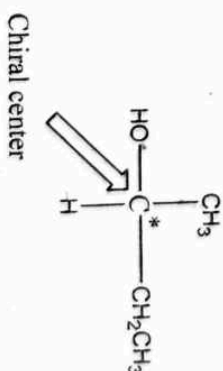
of other carbon atom can be obtained. In all these conformations in ethane molecule the bond angle and the bond length remain the same out of infinite number of conformations of ethane molecule, two conformations with respect to extreme, can be drawn as follows.



These conformations can be represented by more popular Newman's projection formula as. In eclipsed conformations, the hydrogen atoms are crowded together and eclipsed each other where as in staggered conformations; hydrogens are as far apart as possible. The infinite numbers of possible intermediate conformations are known as skew conformations. Both the conformations in ethane are interconvertible into each other but due to minimum potential energy, the staggered conformation is the dominant conformation of ethane molecule.

**Q.20. What is chiral molecule?** (2006)

**Ans.** A carbon bonded to four different atoms or groups is called a stereocenter. It is also called a chiral center. In other words a molecule does not have a plane of symmetry as well as a center of symmetry.



**Q.21. Give the relative order of stability of the conformers of n-butane.** (2016)

**Explain.**

**Related Question:-**

**Q. Discuss conformation of n-butane.** (2017)

**Ans. Conformations of n-Butane:-**

Butane has three carbon-carbon single bonds and the molecule can rotate about each of them. If the rotation will be about  $C_2$  and  $C_3$  bond

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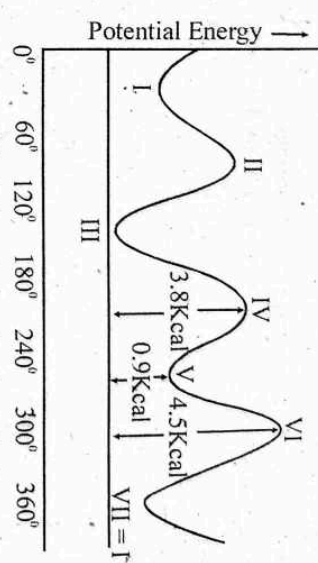
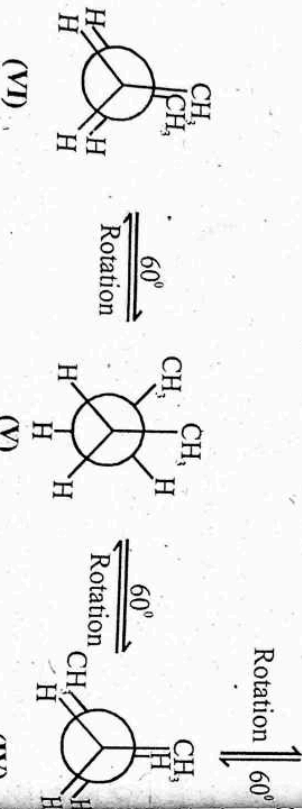
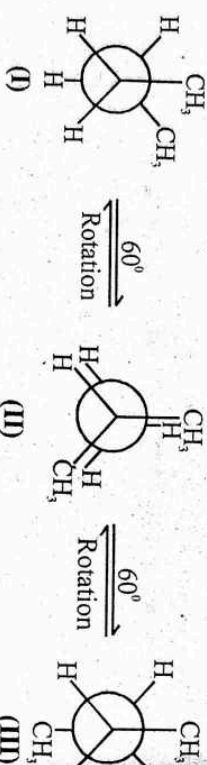
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then conformations will be symmetrical. For conformational analysis butane is due to bond-bond repulsion and steric strain is due to closeness of the eclipsing groups. In general, steric strain in the molecule is directly proportional to the size of the eclipsing groups. Eclipsed conformer VI is called the fully eclipsed conformer, while II and IV are called eclipsed conformers. The energy diagram for rotation about the  $\text{C}_2 - \text{C}_3$  bond of butane is shown in figure.

Butane has three staggered conformers (I, III and IV). Conformer II, which the two methyl group are as far apart as possible is more stable than other two staggered conformers I and V. The most stable of the staggered conformers (III) is called anti conformers and the other two staggered conformers (I and IV) are called are called gauche conformers (anti is Greek for "opposite of", gauche is French for "left").

In the anti conformer the largest substituents are opposite to each other in the gauche conformer, they are adjacent. The two gauche conformers have the same energy but each is 0.9 kcal/mole less stable than the anti conformer. Anti and gauche conformer do not have the same energy because of steric strain. Steric strain or steric hindrance is the strain put on a molecule when its atoms or groups are large in size and due to this they are too close each other, which causes repulsion between the electrons of atoms or groups. There is more steric strain in the gauche conformer than in the anti conformer. Two methyl groups are closed together in the gauche conformer. Steric strain in gauche conformer is called gauche interaction.



Thus, relative stabilities of the six conformers of n-butane is decreasing in the following order:

- Anti > gauche > eclipsed > fully eclipsed  
 III > I and V > II and IV > VI

Molecules with carbon-carbon single bonds have many interconvertible conformers. Conformer cannot be separated because they rapidly interconvert.

**Q.22. Give a comparison between configuration and conformation.**

**Ans. Configuration:-**  
 The different spatial arrangements of atoms in a molecule which are not interconvertible in each other only by rotation along the single bond, are called configuration and isomerism is called configurational isomerism. They can be separated easily.

**Conformation:-**

The different spatial arrangements of atoms in a molecule which are readily interconvertible by rotation about single bonds are called conformation and isomerism is called conformational isomerism. They cannot be separated easily.

**Q.23. Outlines the methods of different three, four, five, six membered cyclic alkanes.**

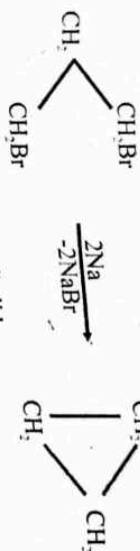
**Related Questions:-**  
 1. Write short note on Dieckmann reaction. (2012, 17)

**2. Formation of Cyclopropane:-**  
 Dehalogenation of  $\alpha, \omega$  dihalides using Na or Zn (Int. Wurtz Reaction)

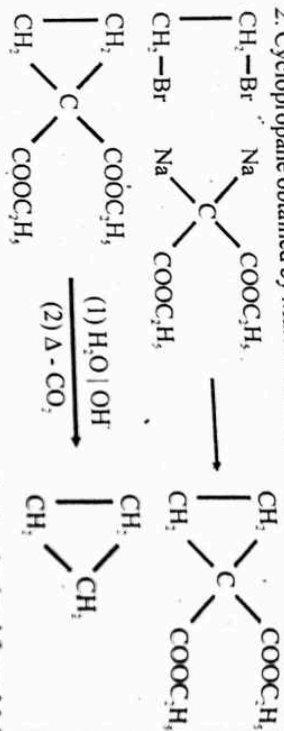
The eclipsed conformer in which the two methyl groups are closed (VI) is less stable than the other eclipsed conformers (II and IV). All these eclipsed conformers have both torsional and steric strain. Torsional

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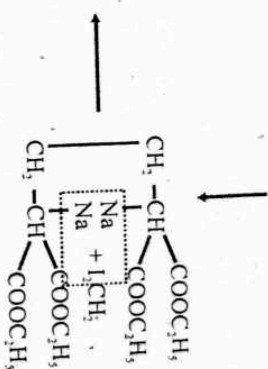
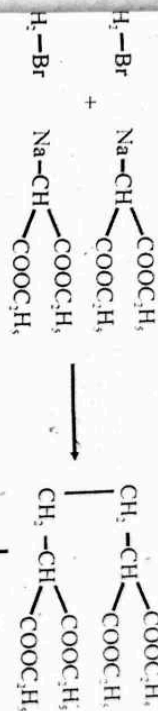
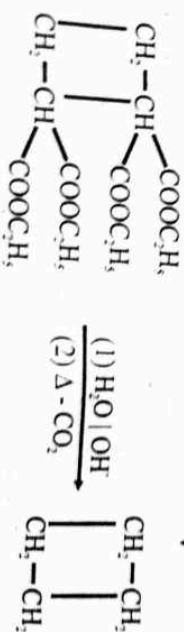
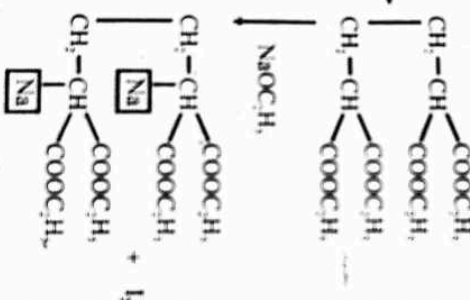
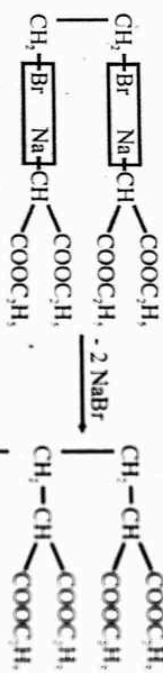
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 $\alpha, \omega$  dihalide or Terminal dihalide  
 used for larger rings.

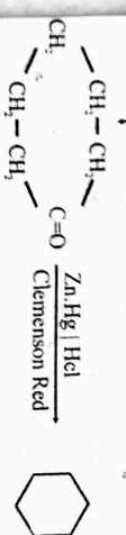
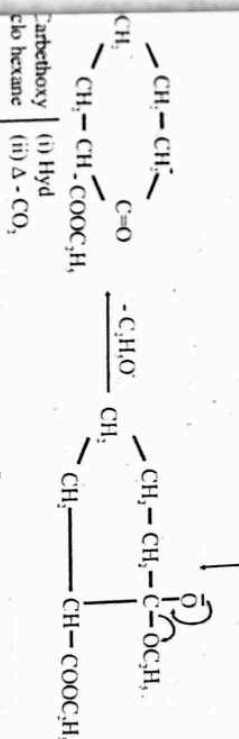
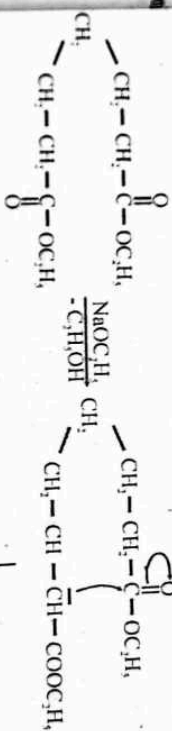
**Note:** - Method can not be widely used for the synthesis of malonic esters in the following sequence:



Formation of Cyclobutane & cyclopentane can also be obtained from Malonate ester synthesis.



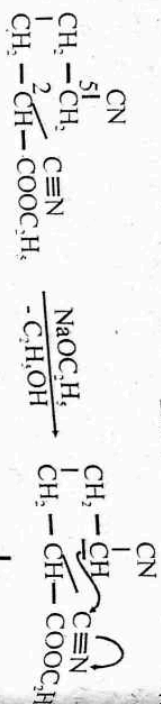
formation Of Cyclohexane takes place by the Dieckmann Condensation: -



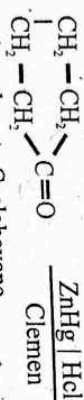
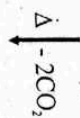
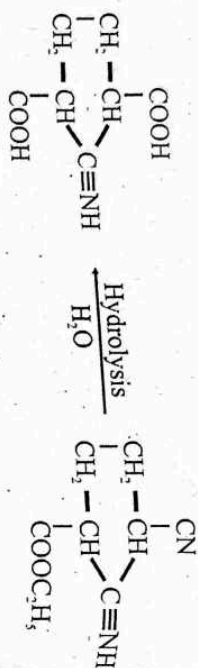
**24** Write notes on Thrope Zeigler reaction.

15. **Thorpe Zeigler Reaction:-**

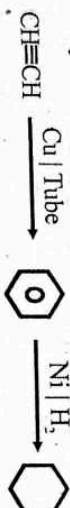
It involves an internal condensation of dicycno ester derivatives.



2. 5 Ethyl Pentanoate



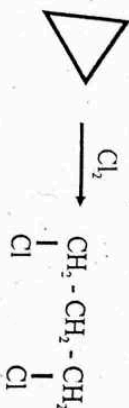
Convert Acetylene to Cyclohexane



Convert hexane 1,6 dinitrile to Cyclopentane.



Properties:-

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Cyclopropane is most reactive Cycloalkane and easily undergoes opening reactions as size of ring increases reactivity decrease. As larger ring are difficult to prepare there chemical reactivities are known.

25. Discuss in brief Baeyer's strain theory and its limitation.  
Solved Questions:-

What is Baeyer's strain theory? Show why this theory fails for rings larger than four membered? (2013)

Write note on Baeyer strain theory or carbenes. (2017, 19)

Baeyer strain theory:-

From analysis of cyclo-alkanes we come to the following conclusions

Cyclo-propane and cyclo-butane under go ring opening reactions more easily than cyclopentane and cyclo-hexane.

Rings larger than cyclo-hexane are not easy to obtain.

From the above two facts we can assume that rings larger or smaller than cyclo-hexane are less stable.

Adolf Van Baeyer in 1885 tried to explain the above facts by the help of Baeyer Strain theory, which includes the following points.

The structure of cyclo-alkane is flat and planar. Therefore the bond angles may be deviated from the normal bond angles of  $109.5^\circ$ .

The normal bond angle if deviated, cause to angle strain calculated as

$$= \frac{1}{2} (109.5^\circ - \text{bond angle})$$

Compounds

Bond angle

Angle strain



60°

$$\frac{1}{2} (109.5^\circ - 90^\circ) = 24.75^\circ$$



90°

$$\frac{1}{2} (109.5^\circ - 90^\circ) = 9.75^\circ$$



108°

$$\frac{1}{2} (109.5^\circ - 108^\circ) = 0.75^\circ$$



120°

$$\frac{1}{2} (109.5^\circ - 120^\circ) = -5.25^\circ$$

Cycloheptane

128°

$$\frac{1}{2} (109.5^\circ - 128^\circ) = -9.25^\circ$$

Form the above calculations it is clear that cyclopropane has under maximum angle strain, which is the cause of its reactivity and less stability.

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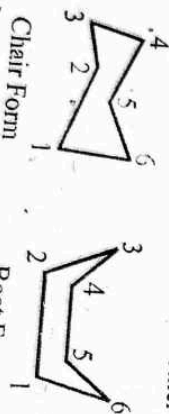
The same reason can be applied to cyclobutane. Ring larger than cyclo-hexane also show strain and are therefore easily formed.

| Compounds                                                                           | $\Delta H$ combustion              |
|-------------------------------------------------------------------------------------|------------------------------------|
| <chem>-CH4</chem>                                                                   | 157.4 kcal/mol — strain less value |
|  | 166.6 kcal/mol                     |
|  | 184.6 kcal/mol                     |
|  | 158.6 kcal/mol                     |
|  | 157.4 kcal/mol                     |

(c) From heat of combustion data as shown above we find that H comp. for cyclo-propane is maximum indicating that cyclo-propane has less energy and therefore lesser stability as told by Bayer, the same stability as told by Bayer.

Further cyclo-pentane has nearly the same value and it is the same as told by Bayer. But beyond cyclo-pentane cyclo-alkanes show little deviation from expected value; in fact cyclo-hexane shows the exact and should therefore be strain less contrary to Bayer Strain theory (Bayer Strain theory may explain the activities of smaller rings completely fails for larger rings).

**Limitations:-**  
(a) Bayer therefore made a mistake by suggesting flat and planar structure for all rings. Where actually larger rings are strainless as they have non-planar structure also called PUCKERED structure where the bond angle lies between the carbon bonds.  
(b) Larger rings are difficult to prepare by de halogenations of  $\alpha, \omega$  dihalides as the halogen atoms remain far apart, decreases ring closure. There are other conformations of cyclohexane one is chair form and other is boat form.

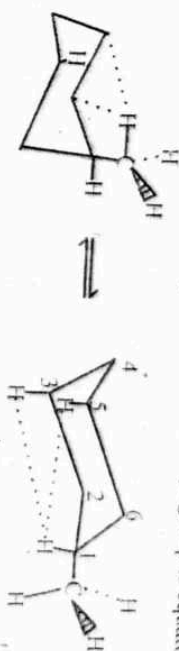


### Conformation of substituted cyclo-hexanes:-

A methyl group is bulkier than a hydrogen atom. When the methyl group is in the axial position, the methyl group and axial hydrogen of the ring are in close proximity. These interactions are called axial-axial interaction. When the methyl group is in the equatorial position, the methyl group and equatorial hydrogens are in close proximity. These interactions are called equatorial-equatorial interaction.

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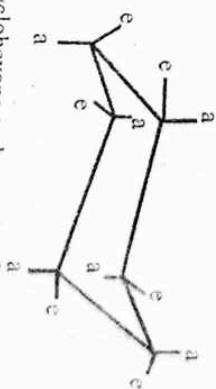
B.Sc. Year - Chemistry II Paper - 48  
The methyl group is in the equatorial position, the repulsion is minimum and also energy is lower. Hence at room temperature, about 95% methyl cyclohexane molecules are in the conformation in which the methyl group is equatorial.



2.26. What do you mean by the term conformation? What is axial and equatorial hydrogen? Discuss the conformation of cyclohexane. (2006)

2.27. Draw different conformation of cyclohexane and discuss their stability. (2015) (2018)

The stereoisomers, which are non-superimposable but easily interconvertible by rotation about single bonds, are known as conformational isomers and different arrangement are called as conformation.



The chair form of cyclohexane carbon atoms form a plane. If we place the chair form of the cyclohexane model on a plane, we find that six C-H bonds are perpendicular to the plane. These hydrogens are called axial (a) hydrogen. The remaining six C-H bonds point outward from the ring along the periphery. These hydrogens are called equatorial (e) hydrogens.

### Conformation of cyclohexane:-

Sachs and Mohr pointed out that two forms are possible for cyclohexane. These two forms are chair and boat conformation of cyclohexane, which are free from angle strain. Both forms are inter-convertible into each other at room temperature. The energy barrier in this process is about 11 Kcal/mole. It is noted that chair form is more stable than boat form.



Chair conformation

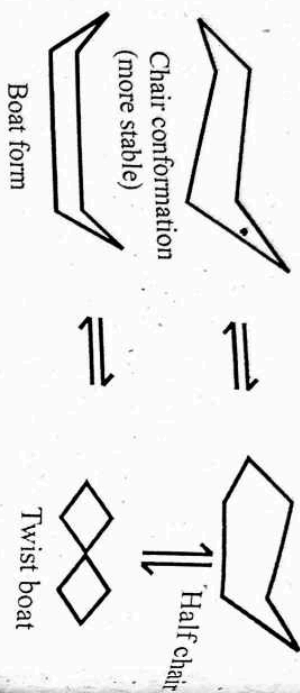
Boat conformation

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The factor, which makes the chair conformation more stable than the boat conformation, is the repulsion between hydrogen atoms, which are at the top of the boat. The distance between the flagpole hydrogens is only 1.83 Å, while the sum of the van der Waals radii of hydrogen atoms is 2.5 Å. This repulsion is called bow-sprit repulsion and contributes to increase the energy of the boat form.

The inter conversion of chair form in to boat form are shown below:



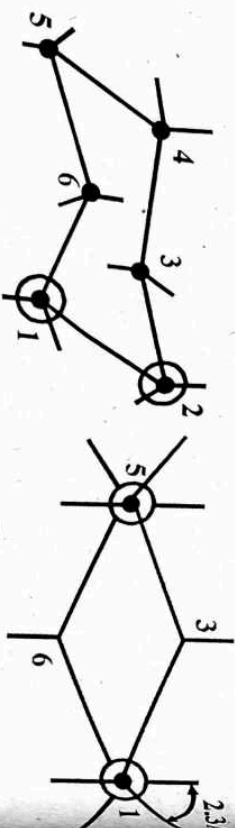
**Q.27** Explain why the chair conformation of cyclohexane is more stable than its boat conformation?

**Related Questions-**

**Q.** Explain which conformation of cyclohexane is more stable, chair conformation or Boat conformation and why?

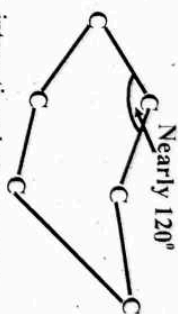
**Ans.** Straining less Ring- After Bayer strain theory completely failed, larger rings and Heat of combustion value of cyclohexane and staggered ethane was found to be same. It was concluded that cyclohexane is free from any type of angle strain.

**1. Chair form :-** The chair arrangement in cyclohexane has all carbon and C-H bond maintaining the tetrahedral bond angle as such arrangement is free from any type of angle strain. Form new man projection it is called that the C-H bonds between successive carbons are staggered and torsional strain is free from torsional strain. As the staggered hydride arrangement is free from torsional strain. As the staggered hydride arrangement is free from torsional strain.



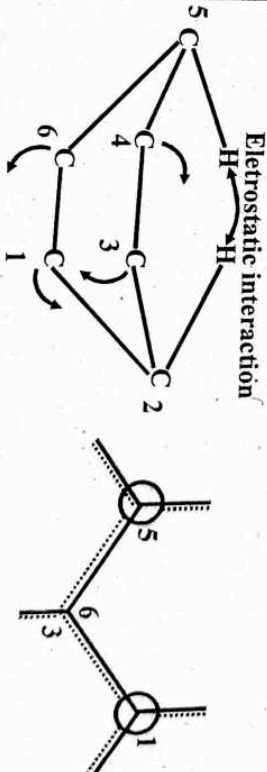
Newman Projection

caused by required distance 2.3 Å units. Further H-atoms are very small, there is no steric (Vander wall) strain therefore chair form is an ideal form. With the chair form :- Is obtained by elevating one of the end carbon atom (Flag pole C. Atom 2, 5) Such that it comes in nearly the same plane as the 4 central carbons. The elevation of the flag pole carbon causes a deviation from the tetrahedral bond angle giving rise to angle strain. This angle strain is nearly 120°.

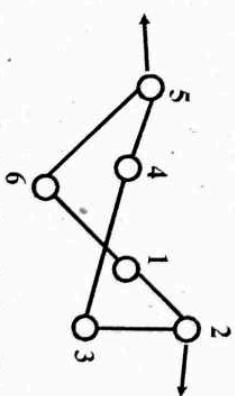


other cause electronic interactions between non-bonded hydrogen atoms give rise to torsional strain. This combined angle & torsional strain causes the half chair conformation to have 1.1 kcal more than chair form. It is therefore less stable and will be considered just a transition state & not a stable conformer (fig. 1).

**Twist Boat Form:-** It obtained by elevating the flag pole C-atom such that both are in the up direction. In the boat conformation the C-H bonds on successive carbons are in the eclipse arrangement giving rise to torsional strain. This torsional strain is further increased due to the electronic interactions between C-H bond of the flag pole carbons which are now close together. Due to this torsional strain the boat form has 7.1 kcal. more than chair form. It is also stable & is a transition state.



Twist Boat Form:



The twist boat is one step further than the boat form. In this conformation, the C-H bond has not tended but the flag pole C-atoms have been separated, due to which some amount of torsional strain has decreased making it more stable than the boat form.

is clear that the C-H bonds between successive carbons are staggered and torsional strain is free from torsional strain. As the staggered hydride arrangement is free from torsional strain. As the staggered hydride arrangement is free from torsional strain.

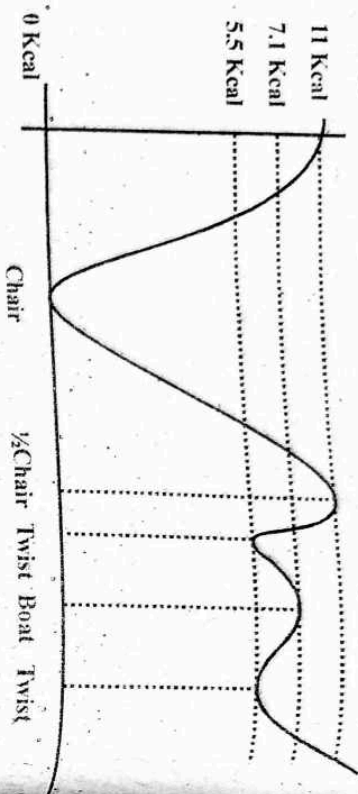
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twist boat arrangement more stable & it is only 5.5 Kcal more than the chair form.

**Conclusion:-**  
The chair form is most stable form the half chair & boat form transition state the twist boat form is the other stable form but less stable chair form.

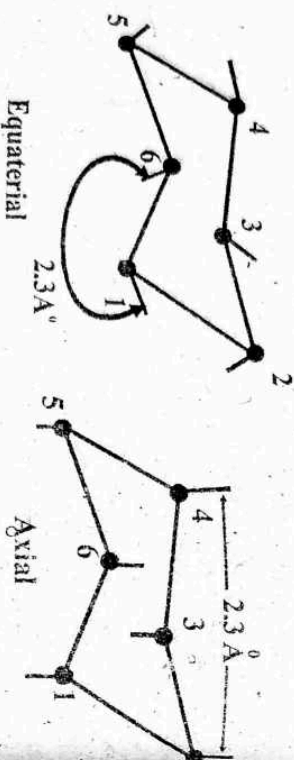
**Energy rotation Graph.**



**Q.28 Discuss 1,3 - diaxial interaction with an example.**

**Ans. Equatorial and Axial bond in cyclohexane**

The chair form of cyclohexane has each C-atom containing two types of bonds:  
1. All the equatorial bonds which lying the plane of the central carbon.  
2. All the axial bonds which lying perpendicular to the molecular plane.



3. on more methylation, the methyl group can come in (i) the equatorial position (ii) In the axial position

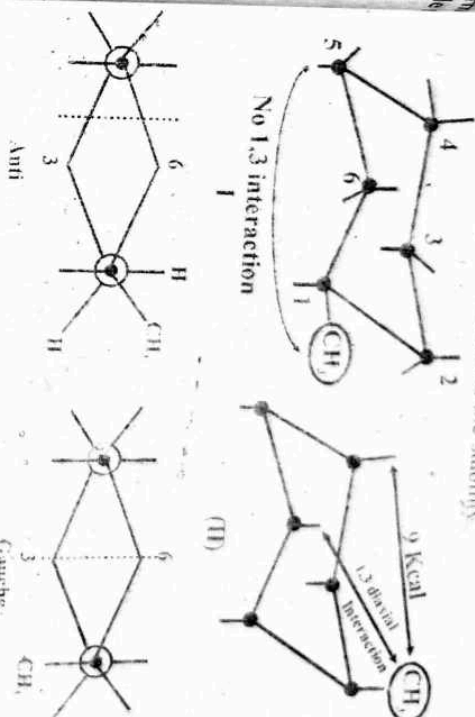
In the equatorial position the methyl group is in a less crowded arrangement is in a less crowded arrangement due to which interactions are less but axial position two 1,3 diaxial interaction can take place & increase the energy 1.8 kcal. We may therefore conclude that each 1,3 diaxial interaction has increased 0.9 kcal.

From Newman projection the points made above are more clear:-

When methyl group is in the equatorial position it is anti to carbon atom and is therefore subjected to less of interaction.

When the methyl group is in the Axial position it is in the syn-periplanar arrangement to position No. 3 result in 1,3 interaction. The Gauche arrangement to position No. 3 result in 1,3 interaction. The Gauche arrangement to position No. 3 result in 1,3 interaction. The Gauche arrangement to position No. 3 result in 1,3 interaction.

it increases the energy and decreases the stability.



**Conclusion:-**

Larger group are therefore are more compatible in equatorial position in axial position.

**Write note on E<sub>2</sub> reaction.**

(2017)

An elimination reaction is a type of organic reaction in which two substituents are removed from a molecule in either a one or two-step mechanism. The one-step mechanism is known as the E<sub>2</sub> reaction, and the two-step mechanism is known as the E<sub>1</sub> reaction. The numbers do not have to do with number of steps in the mechanism, but rather the kinetics of the reaction, molecular and unimolecular respectively. In rare cases, for molecules possessing particularly poor leaving groups, a third type of reaction, E<sub>1c</sub>, exists.

During the 1920s, Sir Christopher Ingold proposed a model to explain a similar type of chemical reaction: the E<sub>2</sub> mechanism. E<sub>2</sub> stands for bimolecular elimination. The reaction involves a one-step mechanism in which carbon-hydrogen and carbon-halogen bonds break to form a double bond (C=C) and a halide ion. The reaction is typically second order, because it is influenced by both the alkyl halide and the base (bimolecular).

Because the E<sub>2</sub> mechanism results in the formation of a pi bond, the two leaving groups (often a hydrogen and a halogen) need to be antiperiplanar. An antiperiplanar transition state has staggered conformation with lower energy.

- energy than a symperiplanar transition state which is in equilibrium with higher energy. The reaction mechanism involving this conformation is more favorable for E2 reactions (unlike E1 reactions  $E_2$  typically uses a strong base. It must be strong enough to remove weakly acidic hydrogen.
- In order for the pi bond to be created, the hybridization of carbon to be lowered from  $sp^3$  to  $sp^2$ .
- The C-H bond is weakened in the rate determining step and thus primary deuterium isotope effect much larger than 1 (commonly observed)
- E2 competes with the  $S_N2$  reaction mechanism if the base can also be nucleophilic (true for many common bases).

$$\begin{array}{c}
 \text{H}_3\text{C} \\
 | \\
 \text{H}_3\text{C}-\text{C}-\text{C}-\text{Br} \\
 | \quad | \\
 \text{H} \quad \text{H}
 \end{array}
 \xrightarrow[\text{K}^+]{\text{CH}_3\text{CH}_2-\text{O}-}
 \begin{array}{c}
 \text{H}_3\text{C} \\
 | \\
 \text{H}_3\text{C}-\text{C}=\text{C}-\text{H} \\
 | \quad | \\
 \text{H} \quad \text{H}
 \end{array}$$

An example of this type of reaction in scheme 1 is the reaction of isobutyl bromide with potassium ethoxide in ethanol. The reaction products are isobutylene, ethanol and potassium bromide.

**Q.30.** Draw the R configuration (Fischer projection) on the following compounds.

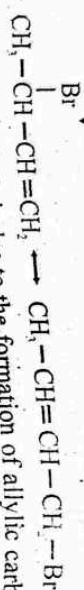
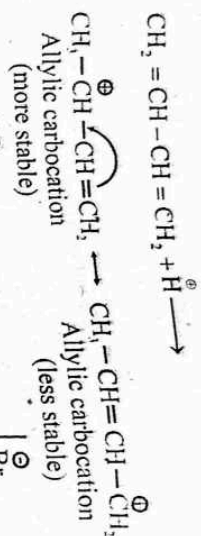
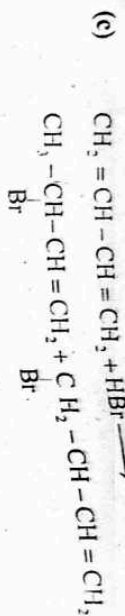
Q.31. Draw the E configuration of the following compounds.

(i)  $\text{OHCH}_2 - \text{CH} = \text{CHSH}$

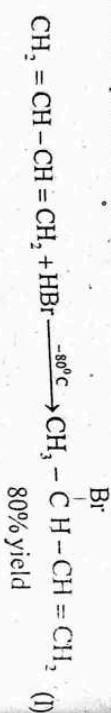
(ii)  $\text{C}_6\text{H}_5 - \text{CH} = \text{N} - \text{OH}$

(iii) 

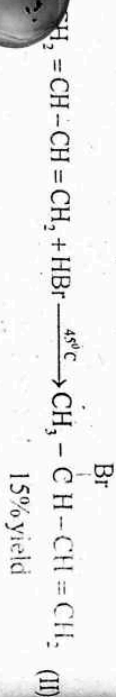
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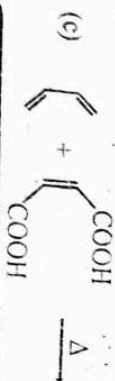
Formation of two products is due to the formation of allylic carbocation reaction intermediate. When reaction is carried out at low temperature, addition product is the major product.



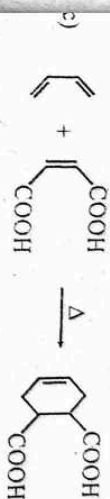
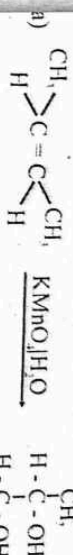
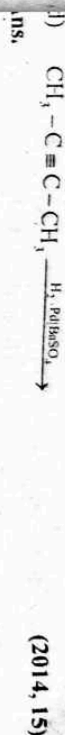
In contrast, when reaction is carried out at higher temperature, the major product is 1,4-addition product.



Q.34. Complete the following reactions showing the stereochemistry of the products:



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35. Difference between configuration and conformation. (2013)

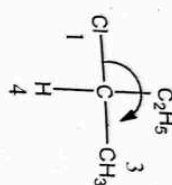
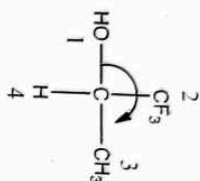
| Conformation                                                                                                                                                                 | Configuration                                                                                                                                                                                       |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| (i) Conformations of a molecule are the different spatial arrangements of its atoms and groups that arise due to the rotation of a part of the molecule about a single bond. | (i) Configuration of a molecule is the spatial arrangement of atoms and groups about a rigid part of the molecule, i.e., about a double bond or ring and about a dissymmetric part of the molecule. |
| (ii) Conformations have low energy barrier, which varies from 4.2 to 46 kJ per mole.                                                                                         | (ii) Difference of energy between two configurations is more than 84 kJ/mole.                                                                                                                       |
| (iii) Conformations are non-isolable.                                                                                                                                        | (iii) Configurations are isolable.                                                                                                                                                                  |
| (iv) Conformations are easily interconvertible, they get converted even at room temperature.                                                                                 | (iv) Configurations are not easily interconvertible.                                                                                                                                                |
| (v) Interconversions of conformations involve rotation of a part of a molecule about a single bond.                                                                          | (v) Interconversions of configurations involve bond breaking and bond reforming processes.                                                                                                          |
| (vi) A molecule could have an infinite number of conformations.                                                                                                              | (vi) A molecule can have only one configuration, i.e., a different configuration is a different molecule.                                                                                           |

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Q.36. Draw the R configuration of the following compounds.



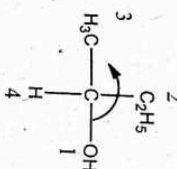
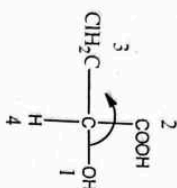
Ans. I



Q.37. Draw the S configuration of the following compounds

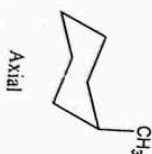


Ans. I



Q.38. Draw the preferred configuration of methylcyclohexane in the chair conformation.

Ans. Essentially, we are comparing the effects of the changing position of the methyl group. The methyl group is placed first in the axial position (approximately parallel to 3-fold axis) then in the equatorial position (approximately parallel to the next adjacent C-C bonds). The axial position gives a higher energy conformer. The difference between it and the equatorial conformer is about 1.8 kcal per mole, which can be interpreted as the change in energy involved in going from two "anti" to two "gauche" conformations. The equatorial conformer is more stable than that of axial conformer.

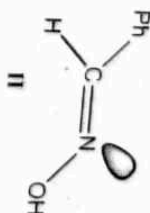
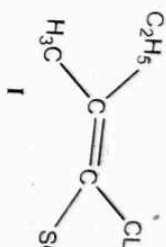


Q.39. Draw the (Z) configuration of compound (I) and (E) configuration of compound (II).

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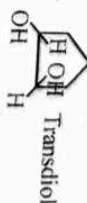
(2015)



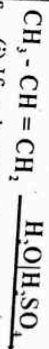
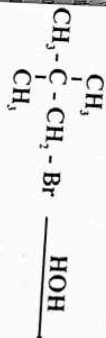
40. Complete the following reactions and indicate major product of the reaction.



(2015)

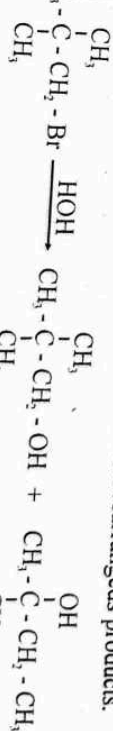


41. Complete the following reactions and give mechanism of any one of them.



(2016)

s. (i) If carbocation is primary or secondary having at least three carbons in rearrangement takes place in carbocation. This leads to the formation of more products, one is normal and others are rearranged products.



(Normal product)

Rearranged product (Major product)

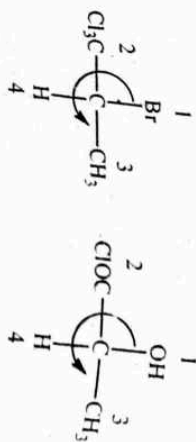


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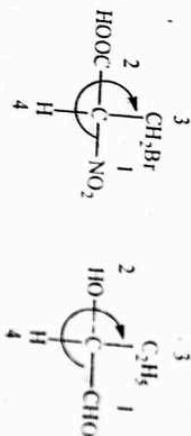
Based on Guidelines

FOR TEACH

Q.42. Draw 'S' configuration of following compounds.  
 (i)  $\text{CH}_3\text{-CHBr-CCl}_3$  (ii)  $\text{CH}_3\text{-CH(OH)-COCl}$   
 Ans.

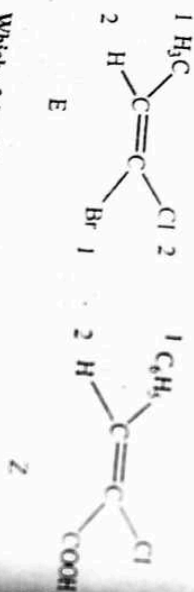


Q.43. Draw the 'R' configuration of the following compounds.  
 (i)  $\text{HOOC-CH(NO}_2\text{)CH}_3$ , Br (ii)  $\text{C}_2\text{H}_5\text{-CH(OH)-CHO}$   
 Ans.

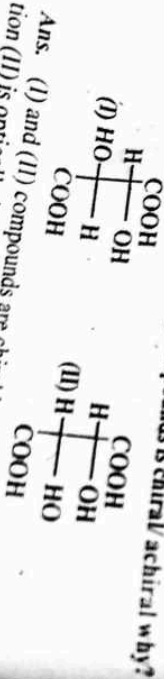


Q.44. Draw the (E) configuration of compound (i) and (Z) configuration compound (ii)

(i)  $\text{CH}_3\text{-CH=C(Cl)(Br)}$  (ii)  $\text{C}_6\text{H}_5\text{-CH=CH-C(=O)COOH}$   
 Ans.

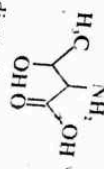


Q.45. Which of the following compounds is chiral/ achiral why?

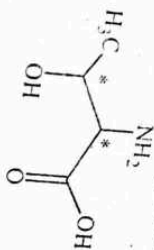


Q.46. Indicate the stereogenic centre(s) in the given compounds.

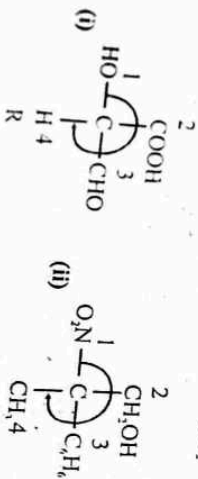
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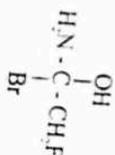
Ans. Indicate the stereogenic centre of the given molecule.



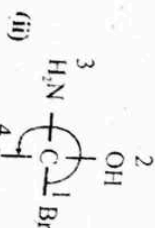
Q.47. Write 'R' configuration of following compounds.



Q.48. Draw 'S' configuration of the following compounds.  
 $\text{CH}_3\text{-CHCl-CH}_2\text{NO}_2$



(2017)



S

Q.49.

Draw structure of any two meso compounds.

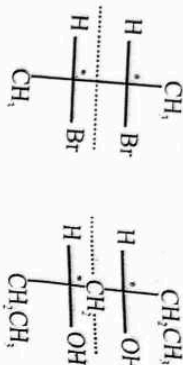
(2017)

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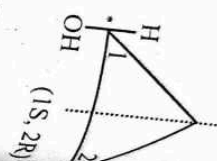
FOR TEACHERS

Ans. The compounds containing two or more chirality centres but possessing achiral molecular structure because of having plane of symmetry are called **meso compounds**.  
Some examples of meso compounds are given below:

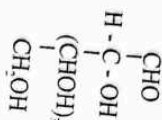


#### MESO compounds

Plane of symmetry is represented by dotted line .....



Q.50. Determine 'R' or 'S' configuration of C-2 asymmetric centre of D-glucose.



Ans. R' configuration of C-2 asymmetric centre.

Note: When deciding whether a stereocenter in a Fischer projection is R or S, realize that the hydrogen, in a horizontal bond, is pointing *towards you* - therefore, a counterclockwise circle means R, and a clockwise circle means S (the opposite of when the hydrogen is pointing away from you).

Q.51. Explain resolution of racemic modification.

Ans. The Racemic Modification:-

A mixture of equimolecular amounts of a pair of enantiomers is known as racemic modification. A racemic modification will be optically inactive, because the rotation caused by one half of the mixture is exactly cancelled by the opposite rotation displayed by the other half. A racemic mixture is denoted by the prefix dl- or (±).

The process of separation of Racemic Modification:-

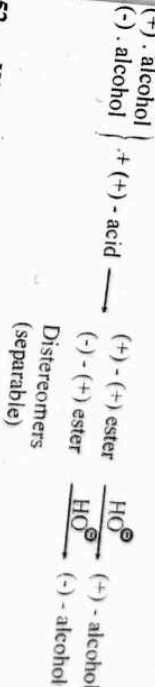
(i) Mechanical separation - It involves separation of two sets by hand picking applicable to those cases which give well defined crystals of crystalline that can be distinguished as enantiomers.

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i) Biochemical method - This method involves the use of micro-organisms such as penicillium glaucum which consumes only one type of enantiomer (D-tartaric acid) leaving behind tartaric acid. This method is not very satisfactory as one enantiomer is destroyed.

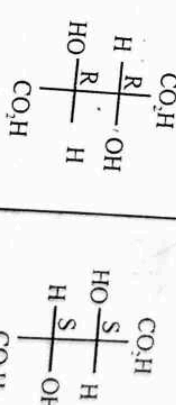
ii) Chemical method - In this method a racemic modification is reacted with an optically active reagent to give a pair of non-identical derivatives known as stereoisomers which differ in physical properties and hence can be separated by fractional distillation, crystallization etc.

For example, racemic alcohol can be separated as:



52. Write short note on Meso compounds.

Ans. Compounds that contain stereogenic centres but are themselves achiral are called meso compounds. This means that there is a plane of symmetry with R stereochemistry on one side and S stereochemistry on the other.

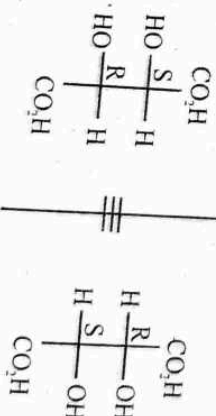


(+) - tartaric acid

(enantiomers)

Mirror

(-) - tartaric acid



Meso - tartaric acid (meso compound)

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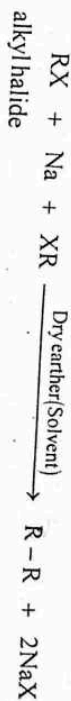
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## Chapter 4 - Alkanes And Cycloalkanes

Wurtz reaction:-

(2016)

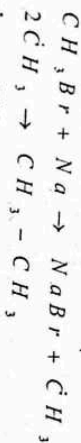
Higher alkanes are produced by heating an alkyl halide (R-X) with sodium metal in dry ether solution. The result is joining of their two-alkyl groups to give alkane containing twice carbon atoms as the original halide molecule.



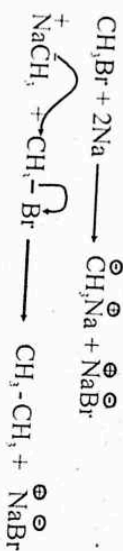
$CH_3 - Br + 2 Na + Br - CH_3 \xrightarrow{\text{Dry ether}} CH_3 - CH_3 + 2 NaBr$   
 Mechanism:- Two type of mechanism are possible for Wurtz-reaction.

Free radical reaction:-

This involves the attack of sodium atom on, methyl bromide to produce sodium bromide and methyl free radical. Two methyl free radicals then unite with each other to give ethane.



**Ionic Mechanism:-** This involves the intermediate formation of metal alkyls. Thus methyl bromide reacts with two atoms of sodium to produce methyl sodium ( $CH_3Na$ ) and sodium bromide. Methyl sodium then reacts with another molecule of methyl bromide.

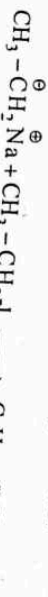


Give the mechanism of the reaction.

(2011)



The intermediate formation of organometallic compound operates when reaction is carried out in solution.



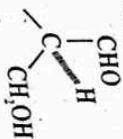
This mechanism also accounts for the presence of ethane and ethylene products.

(+) - Tartaric Acid: It rotate the plane of polarised light to the right (clockwise direction) and called dextrorotatory.

(-) - Tartaric Acid: It rotate the plane of polarised light to the left (anticlockwise direction) and called laevorotatory. (-) - Tartaric acid is the mirror image of the other.

Meso - Tartaric Acid: It possesses a plane of symmetry and consequently optically inactive. The optically inactive form is said to be internally compensated (Optical rotation of one asymmetric carbon is cancelled by the other).

Q.53. Assign R/S nomenclature to the compound

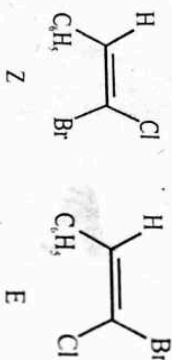


Ans. R

Q.54. Write (E) configuration and (Z) configuration of the given compound



Ans.



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## Chapter 5 - Alkenes, Dienes And Alkynes

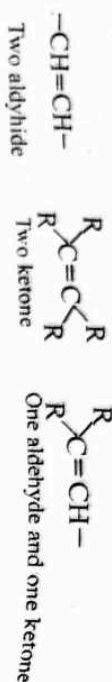
### Thermal Ozonolysis of Alkenes

**Q.1** Write short notes on ozonolysis.

**Ans:** When ozone is passed in an alkene an ozonide is formed, which on further treatment with a reducing agent like zinc and acetic acid, yields aldehyde or ketone or both are formed.

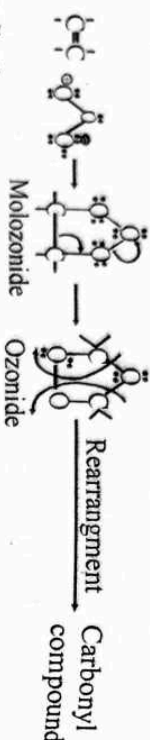
decomposing with water or reduction, also by ozonolysis. This result is used for the determination of the position of double bond in the molecule. The product

formed as



**Mechanism:-**

The formation of ozonide by the action of the ozone on alkenes takes place as:



**Application:** -

- (i) Determining the number of double bonds in alkenes.
- (ii) Determining the position of double bonds in alkenes.
- (iii) The distinction of alkenes.

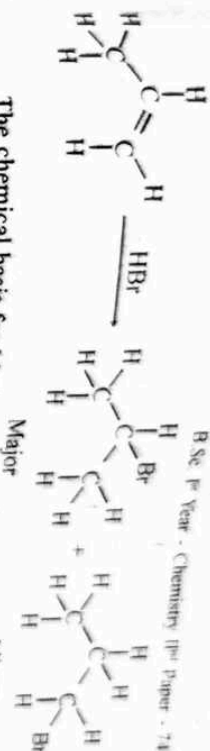
**Q.2.** Write a note on Markownikov's Rule.

ans. In organic chemistry, Markovnikov's rule or Markownikoff's rule describes the outcome of some addition reactions. The rule was formulated by Russian chemist Vladimir Vasilevich Markovnikov in 1870. The rule states that with

It states that with the addition of a protic acid HX to an asymmetric alkene, the acid hydrogen (H) becomes attached to the carbon with fewer alkyl substituents, and the halide (X) group becomes attached to the carbon with more alkyl substituents. Alternatively, the rule can be stated that the hydrogen atom is added to the carbon with the greatest number of hydrogen atoms while the X component is added to the carbon with the least number of hydrogen atoms.

The same is true when an alkene reacts with water in an addition reaction to form an alcohol which involve formation of carbocations. The hydroxyl group (OH) bonds to the carbon that has the greater number of carbon-carbon bonds, while the hydrogen bonds to the carbon on the other end of the double bond, that has more carbon-hydrogen bonds.

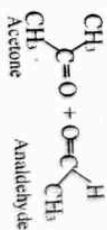
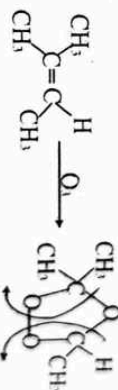
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The chemical basis for Markovnikov's Rule is the formation of the most stable carbocation during the addition process. The addition of the hydrogen ion to one carbon atom in the alkene creates a positive charge on the other carbon, forming a carbocation intermediate. The more substituted the carbocation, the more stable it is, due to induction and hyperconjugation. The major product of the addition reaction will be the one formed from the more stable intermediate. Therefore, the major product of the addition of HX (where X is some atom more electronegative than H) to an alkene has the hydrogen atom in the less substituted position and X in the more substituted position. But the other less substituted, less stable carbocation will still be formed at some concentration, and will proceed to be the minor product with the opposite, conjugate attachment of X.

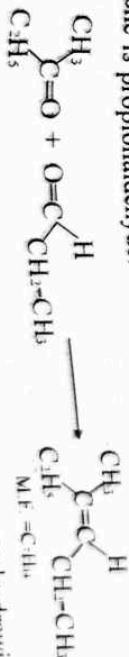
Q.3 Ozonolysis of 2methyl-2butene. (Imp.)

**Ans:**



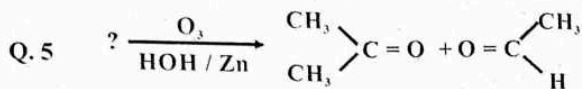
**Q.4** Write down the structural formula of an alkene whose molecular formula is  $C_7H_{14}$ , and on ozonolysis give a molecule of methyl ethyl ketone and one molecule of propionaldehyde. (Imp.)

**Ans:** According to the question one fragment is methyl cation, another one is propionaldehyde.

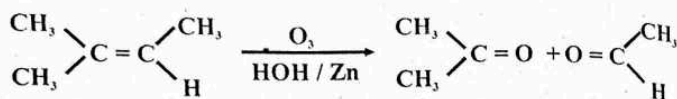


**Note:** - Such type of problem can be solved in very easy way by drawing both the fragment in such a way that both oxygen lie face to face, and then disappearing both oxygen atom and join the both carbon by double bond.

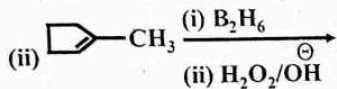
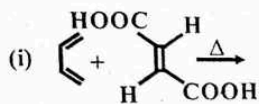
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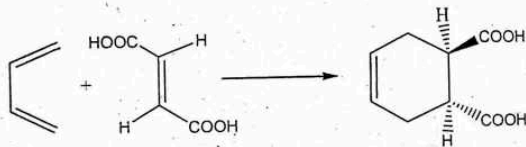
Ans:



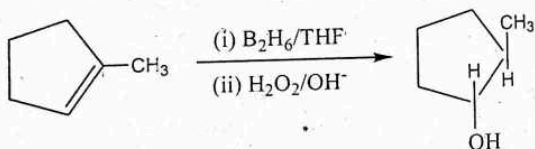
Q. 6 Complete the following reaction.



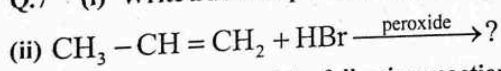
Ans. (i)



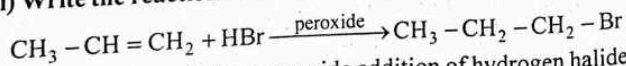
(ii)



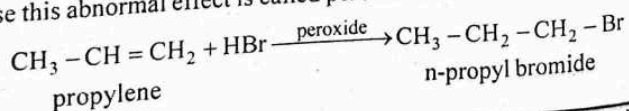
Q. 7 (i) Write a note on peroxide effect.



(iii) Write the reaction of the following reaction.



Ans: In presence of air or peroxide addition of hydrogen halide is abnormal and it takes place against Markownikoff's rule. The action of peroxide cause this abnormal effect is called peroxide effect.



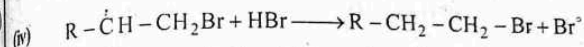
The mechanism of peroxide effect is based on free radical chain reaction. It is represented as



peroxide free radical



(2008)

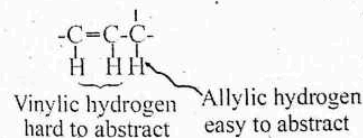


It is a chain reaction in which reactions (i) and (ii) are the chain initiation step while (iii) and (iv) are chain propagation step. Due to lesser concentration bromine atoms obtained (ii) do not react with each other instead add to the double bond of alkene whose concentration is high.

Q. 8 Give mechanism of free radical allylic substitution in alkene.

Ans: The alkenes under go substitution by halogen exactly in same way as alkanes. Further more, just as the alkyl group effect the reactivity of double bond towards addition, so the double bond effects the reactivity of the alkyl group towards substitution.

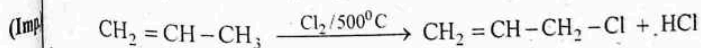
Examination of the reaction shows that abstraction of vinylic hydrogen is more difficult than that of allylic hydrogen.



Since the ease of formation of free radical is in the order

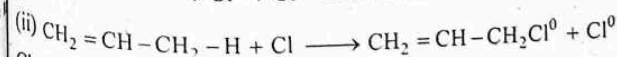
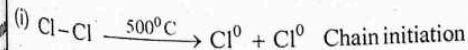
Allyl > tert > sec > prim > CH<sub>3</sub> > vinylic

(Imp) The ease of abstraction of hydrogen will also be in the above order.

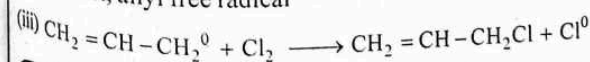


Mechanism: -

It is free radical chain reaction



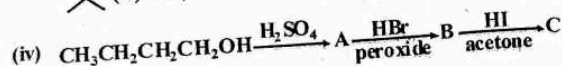
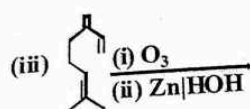
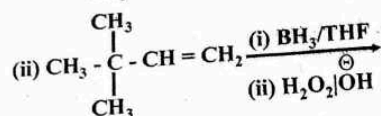
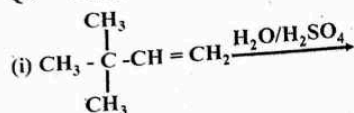
Chain start, allyl free radical



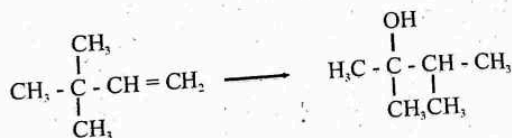
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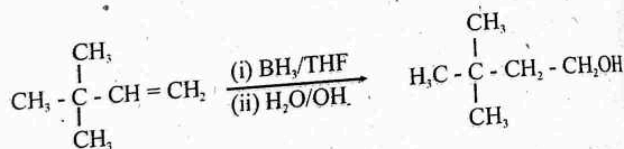
Q.9 Complete the following



Ans. (i)



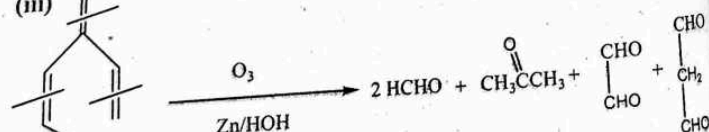
(ii)



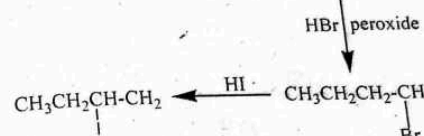
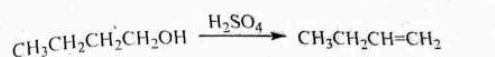
Remark:

Because carbocation intermediate are not formed in the hydroboration reaction so carbocation rearrangement do not occur.

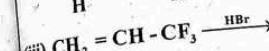
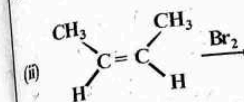
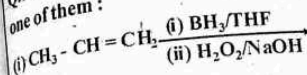
(iii)



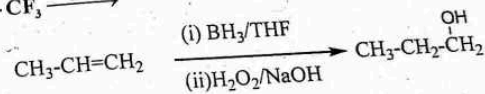
(iv)



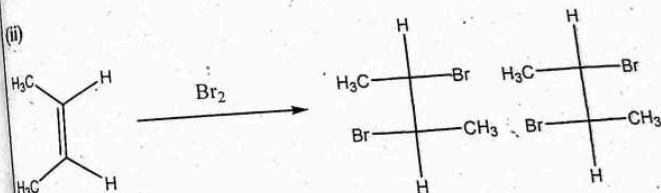
Q.10 Complete the following reactions &amp; write down the mechanism of any one of them: (2010)



Ans. (i)

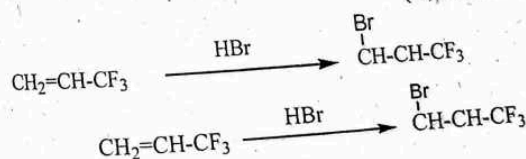


(ii)

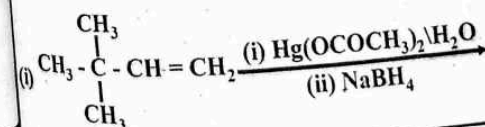


(dl), mixture

(iii)



Q.11 Complete the following reactions:



(2008, 14)

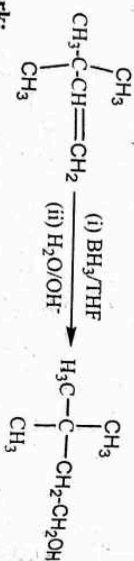
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Ans (i)

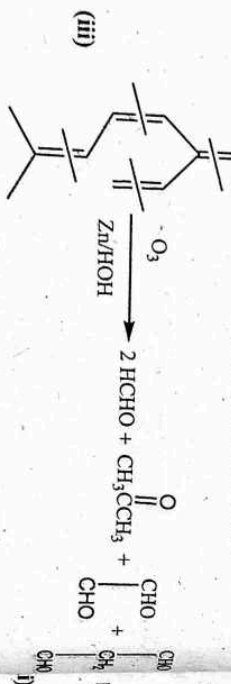


(ii)



Remark:

Because carbocation intermediate are not formed in the hydroboration reaction so carbocation rearrangement do not occur.



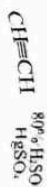
Q.15. Identify compounds A, B' and C in the sequence and give the mechanism of formation of A.



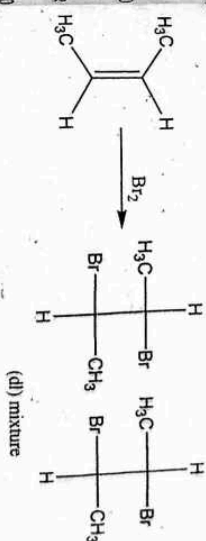
Ans:



HBr peroxide



17. Complete the following reactions & write down the mechanism of any one of them



18. Explain the acidity of hydrogen atom in  $\equiv \text{CH}$  group taking an example of acetylene. (Imp.)

Related Questions -

Why are terminal alkynes more acidic than alkenes or alkanes?

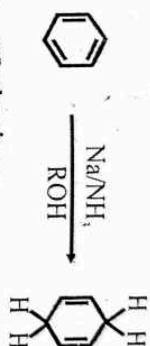
Why are acetylide anions more stable than vinylic or alkyl anions?

Ans: When a terminal alkyne is treated with a strong base, such as sodium amide  $\text{NaNH}_2$ , the terminal hydrogen is removed and acetylide anion is formed.



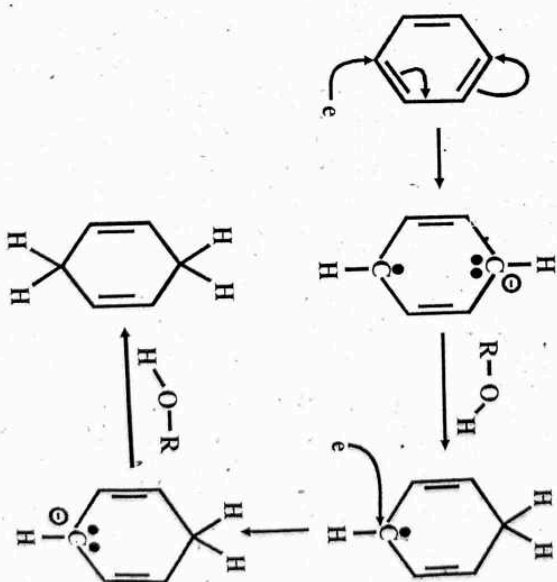
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**The Birch reduction** is the organic reduction of aromatic rings with sodium and an alcohol in liquid ammonia to form 1,4-cyclohexadienes. The reaction was reported by the Australian chemist Arthur John Birch. This reaction provides an alternative to catalytic hydrogenation, which usually reduces the aromatic ring all the way to a cyclohexane (after the initial reduction to a cyclohexadiene, catalytic reduction of the remaining (nonaromatic) double bonds is easier than the first reduction).



A solution of sodium in liquid ammonia consists of the electric salt

not acidic enough.



### Related Questions -

**Ans. Diel's-Alder Reaction:-**

**Mechanism: -**



Q.

Give the major organic product of the following reactions



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**Ans.** The reaction of bromine with dienes can proceed under two different conditions used. If the reaction is carried out under mild conditions, the product is a 1,4-addition product. If the reaction is carried out under harsh conditions, the product is a 1,2-addition product.

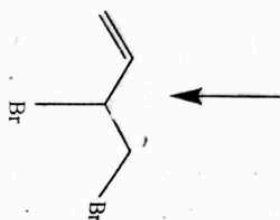
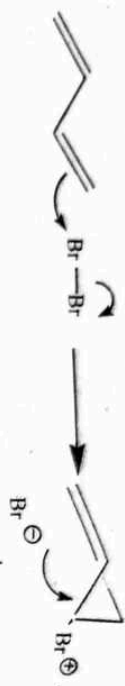
bonds to give a 1,2-dibromide. This is the mechanism for the addition of bromine to alkenes. The first step is the attack of the alkene on the bromine molecule, which is the rate-determining step. The second step is the attack of the bromide ion on the carbocation intermediate.

The 1,4-dibromide is only formed from the thermodynamic product. The mechanism is the electrophilic

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diene to give a bromonium ion, which bromide opens to give the dibromide. 1,2-dibromide can then react further because it can undergo nucleophilic substitution.

#### Low Temperature - Kinetic Product



1,2-dibromide

#### High Temperature - Thermodynamic Product



1,2-dibromide



1,4-dibromide

Q.22 3° Alkyl halide gives SN1 reaction whereas 1° alkyl halide gives SN2 reaction.

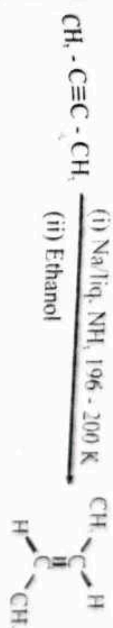
Ans. In SN1 reaction the reaction proceeds through carbocation and the carbocation stability order is  $3^\circ > 2^\circ > 1^\circ$ . While in SN2 reaction is one process and there is no intermediate involved. The carbon atom having a positive charge due to bond dipole of C-X any factor which minimize the positive charge that can favour the SN2 in case of 1° alkyl halide gives only one Me group while 3° Alkyl halide having three Me group which

deactivate the central c for SN2. Hence 3° Alkyl halide gives SN1 reaction whereas 1° alkyl halide gives SN2 reaction.

Q.23 How will you bring the following conversions.

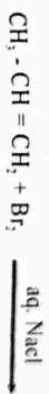


(2011)



Q.24 Give the mechanism of the reaction.

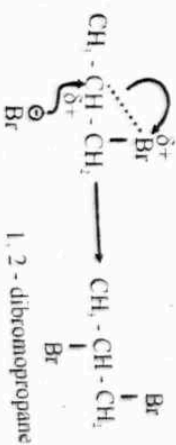
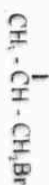
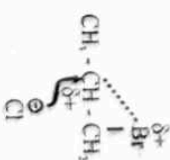
(2011)



Ans. Step I  $\text{CH}_3 - \text{CH} = \text{CH}_2 + \text{Br}_2 + \text{Cl}^- \longrightarrow \text{CH}_3 - \text{CH} - \text{CH}_2\text{Br}$

But not  $\text{CH}_3 - \text{CH} - \text{CH}_2\text{Cl}$

Step II



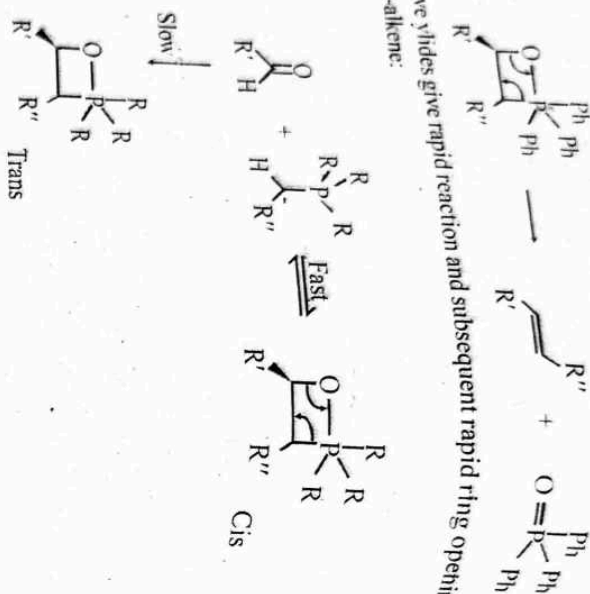
1,2-dibromopropane

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Reactive ylides give rapid reaction and subsequent rapid ring opening to give the (Z)-alkene:



Q.29. Write short on Corey House synthesis.

Ans. The Corey House synthesis is an organic reaction that involves the reaction of a lithium dialkyl cuprate with an alkyl halide to form a new alkane, an organo copper compound and a lithium halide.



Reaction mechanism:-

This reaction occurs in two steps. The alkyl halide is treated with lithium metal, and solvated in ether, which converts the alkyl halide into an alkyl lithium compound, R-Li. The starting R-X can be primary, secondary or tertiary alkyl halide:



The second step requires the alkyl lithium compound to be treated with cuprous iodide (CuI). This creates a lithium dialkyl cuprate compound. These compounds were first synthesized by Henry Gilman of Iowa State University, and are usually called Gilman reagents in honor of his contributions. The lithium dialkyl cuprate is then treated with the second alkyl halide, which couples to the compound:

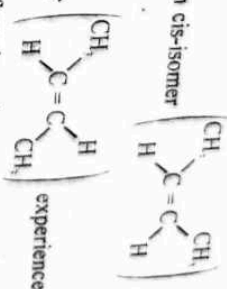


If second alkyl halide is not the same as the first, then cross-products are formed.

It is important to note that for this reaction to work successfully, the second alkyl halide must be a methyl halide, benzyl halide, primary alkyl halide or a secondary cyclo alkyl halide. The relative simplicity of this reaction makes it a useful technique for synthesizing organic compounds.

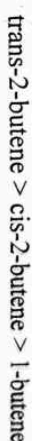
Q.31. Explain why 2-butene is more stable than 1-butene. (2016)

Ans. In 1-butene ( $CH_3 - CH_2CH=CH_2$ ) the steric repulsion is practically absent. In 2-butenes, the two methyl groups in cis-isomer



being closer together than in trans-isomer greater repulsion and consequently the cis-form is under greater strain than trans form. The steric effect destabilises a molecule. Thus trans-2-butene is more stable than cis-2-butene.

On the otherhand hyperconjugation stabilises the molecule and is smallest in 1-butene but much larger in 2-butenes. Since hyperconjugation has greater stabilising effect than steric destabilising effect, 1-butene is the least stable. The order of stability is as



Q.32. Write short note on Dehydration of Alcohols. (2012)

Ans. Dehydration of Alcohols:-

A process in which alcohols undergo E1 or E2 mechanisms to lose water and form a double bond. This dehydration proceeds by heating alcohols in the presence of a strong acid, such as sulfuric or phosphoric acid, at high temperature.



Primary alcohols undergo bimolecular elimination (E2 mechanism) while secondary and tertiary alcohols undergo unimolecular elimination (E1 mechanism). The relative reactivity of alcohols in dehydration reaction is ranked as the following

Methanol < primary < secondary < tertiary

Primary alcohol dehydrates through the E2 mechanism

Oxygen donates two electrons to a proton from sulfuric acid  $H_2SO_4$ , forming an alkyloxonium ion. Then the nucleophile  $HSO_4^-$  back-side attacks one adjacent hydrogen and the alkyloxonium ion leaves in a concerted process, making a double bond.

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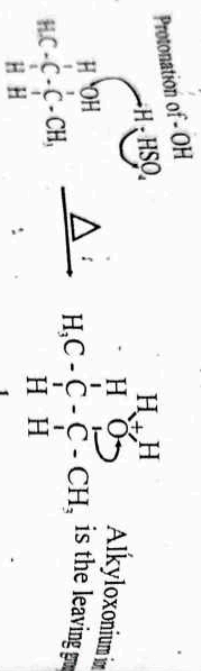


Secondary and tertiary alcohols dehydrate through the  $\text{E}_1$  mechanism.

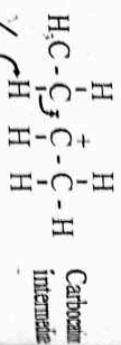
**mechanism**

Similarly to the reaction above, secondary and tertiary  $-\text{OH}$  protonates from alkylxonium ions. However, in this case the ion leaves first and forms a carbocation as the reaction intermediate. The nucleophile  $\text{H}_2\text{O}$  then takes one hydrogen from the carbon next to the carbocation, forming a double bond.

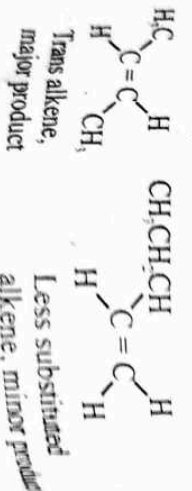
**Dehydration reaction of secondary alcohol:-**



Q. A. B. C. D. E. F. G. H. I. J. K. L. M. N. O. P. Q. R. S. T. U. V. W. X. Y. Z.



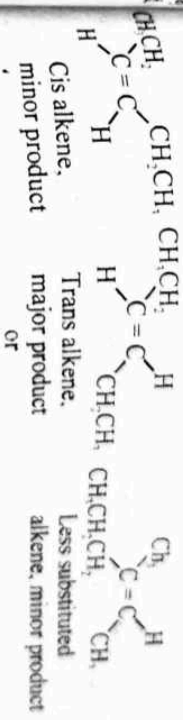
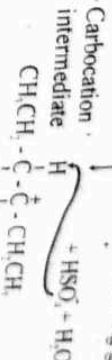
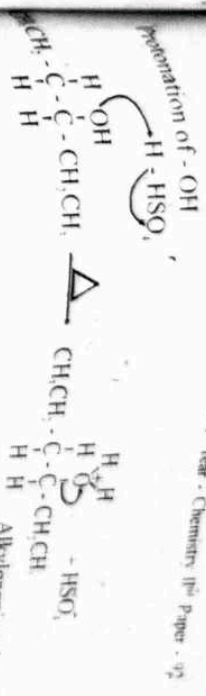
$\text{HSO}_4^- + \text{H}_2\text{O}$



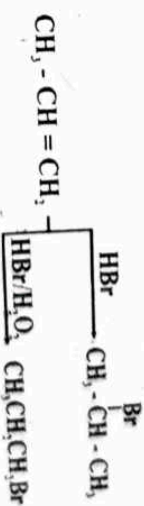
are for

**Dehydration reaction of tertiary alcohol:-**

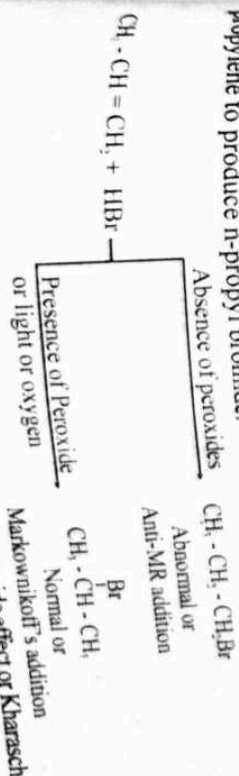
When more than one alkene product are possible, the favored one is usually the thermodynamically most stable alkene. More-substituted alkenes are favored over less-substituted ones; and trans-substituted alkenes are favored over cis-substituted ones.



Q33. Give suitable explanation for following observation. (2016)



**Ans.** Addition of  $\text{HCl}$  and  $\text{HI}$  to unsymmetrical alkenes takes place according to Markovnikov's rule but the addition of  $\text{HBr}$  for long time was quite confusing. In the absence of metallic salts, organic peroxides and oxygen and in the presence of polar media,  $\text{HBr}$  undergoes a slow addition to propylene to produce only isopropyl bromide in complete accordance to Markovnikov's rule. However, in the presence of peroxides, oxygen or light  $\text{HBr}$  reacts with propylene to produce n-propyl bromide.

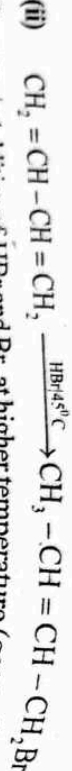
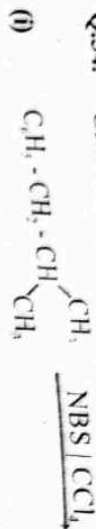


This abnormal addition of  $\text{HBr}$  to propene is called as peroxide effect or Kharasch effect.

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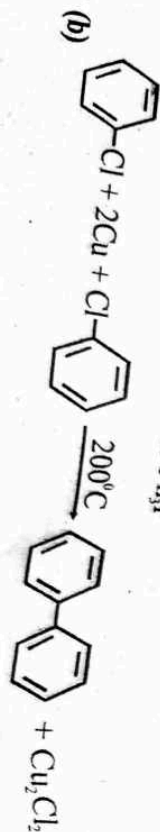
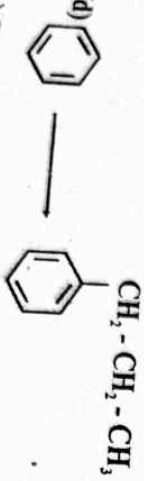
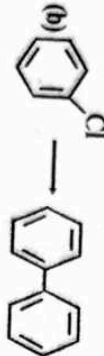
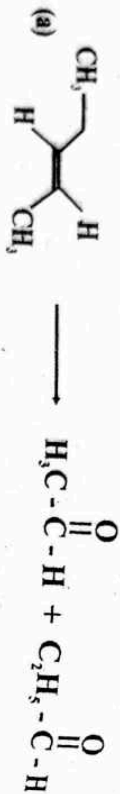
effect as it is brought about by the presence of peroxide.

Q.34. Give the major product of the following reaction



Comment: Addition of HBr and Br<sub>2</sub> at higher temperature (generally 40-60°C). The 1,4-addition product predominate.

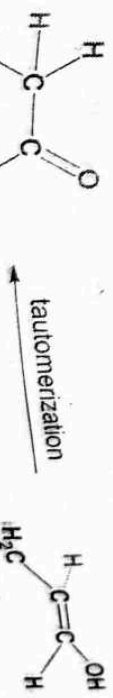
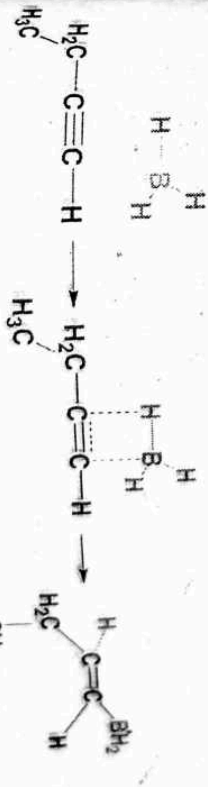
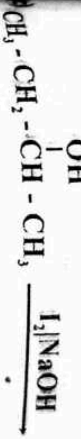
Q.35. How the following conversions can be achieved?



through Q. 12 page no. 100

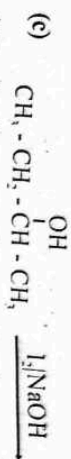


Complete the following reactions and indicate major products of the

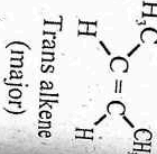
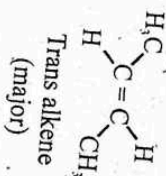
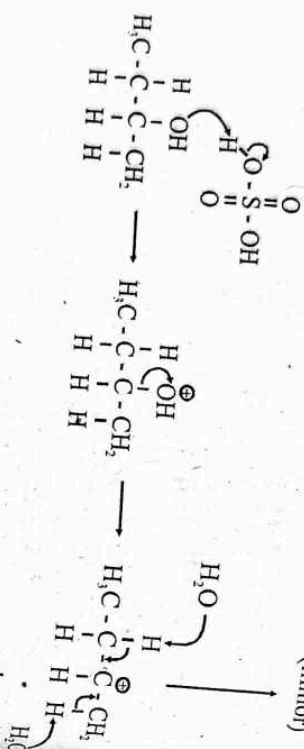
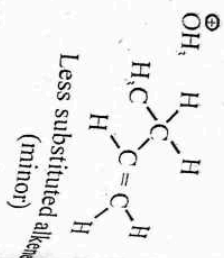


aldehyde

enol



Ans. Analogous to given mechanism, you may draw the products.



Q.37.

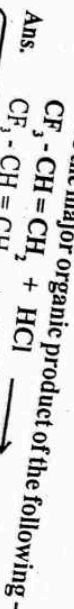
$\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{Cl}$  is more reactive than  $\text{CH}_3 - \text{CH} = \text{CH} - \text{Cl}$  in  $\text{S}_\text{N}1$  reaction.

Ans. In  $\text{S}_\text{N}1$  reaction, the reaction intermediate is carbocation. In case  $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{Cl}$ , it generates allylic carbocation, while  $\text{CH}_3 - \text{CH} = \text{CH} - \text{Cl}$ , it generates vinyl carbocation. Due to allylic carbocation stabilization by resonance,  $\text{CH}_2 = \text{CH} - \text{Cl}$  is more reactive than  $\text{CH}_3 - \text{CH} = \text{CH} - \text{Cl}$  in  $\text{S}_\text{N}1$  reaction.



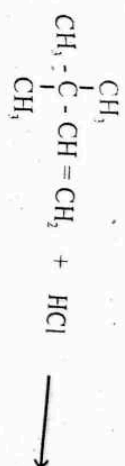
Q.38.

Give the major organic product of the following -

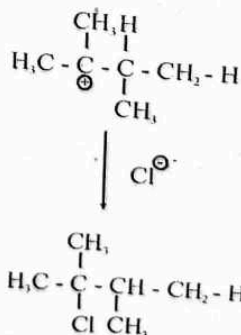


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Complete the following reactions and write mechanism of formation products in each.

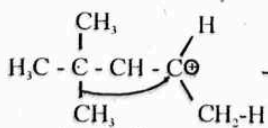


Ans. The formation of carbocations is sometimes accompanied by a structural rearrangement. Such rearrangements take place by a shift of a neighboring alkyl group or hydrogen, and are favored when the rearranged carbocation is more stable than the initial cation.

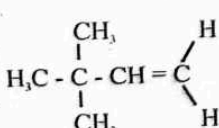


2-chloro-2, 3-dimethylbutane

The addition of HCl to 3,3-dimethyl-1-butene, for example, leads to an unexpected product, 2-chloro-2,3-dimethylbutane, in somewhat greater yield than 3-chloro-2,2-dimethylbutane, the expected Markovnikov product. This surprising result may be explained by a carbocation rearrangement of the initially formed 2° carbocation to a 3° carbocation by a 1,2-shift of a methyl group.



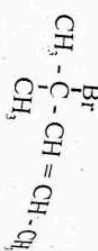
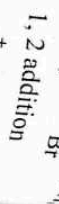
3-chloro-2, 2-dimethylbutane



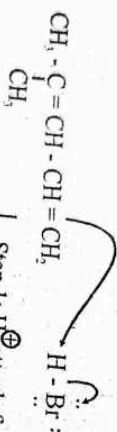
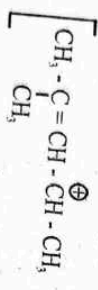
Q.40. Complete the following reaction and give its mechanism.



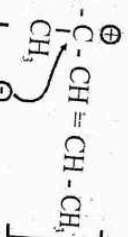
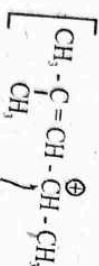
Ans.



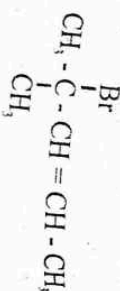
Mechanism :

Step 1: H<sup>+</sup> attack from allylic carbocation

This carbocation rearrange to a more stable carbocation.



1, 2 - addition



1, 4 - addition

(Exclusive product)

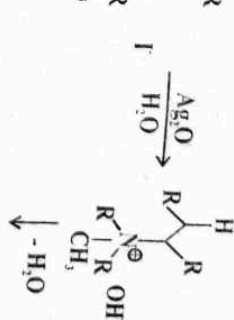
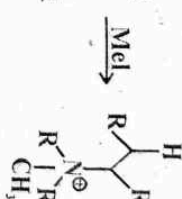
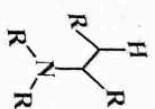
Q.41.

Write short note on Hofmann elimination.

Ans. Hofmann elimination, also known as exhaustive methylation, is a process where a quaternary ammonium reacts to create a tertiary amine and an alkene.

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by treatment with excess methyl iodide followed by treatment with aqueous alkali, water, and heat.

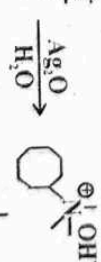
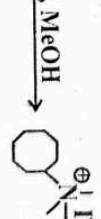
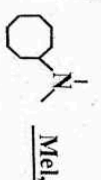


After the first step, a quaternary ammonium iodide salt is created. After replacement of iodine by a hydroxyl anion, an elimination reaction takes place to form the alkene.

With asymmetrical amines, the major alkene product is the least substituted and generally the least stable, an observation known as the Hofmann rule. This is in direct contrast to normal elimination reactions where the more substituted, stable product is dominant (Zaitsev's rule).

The reaction is named after its discoverer, August Wilhelm von Hofmann.

An example is the synthesis of trans-cyclooctene:



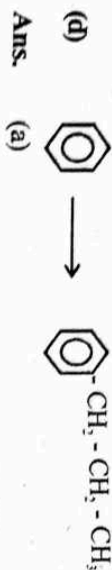
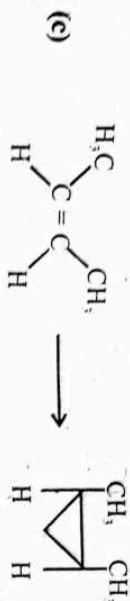
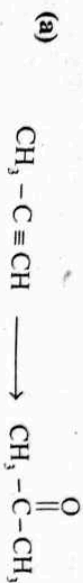
trans : cis = 60 : 40

In a related chemical test called Herzig - Meyer alkamide group determination a tertiary amine with at least one methyl group and lacking a beta-hydrogen is allowed to react with hydrogen iodide to the quaternary ammonium salt which when heated degrades to iodomethane and the secondary amine.

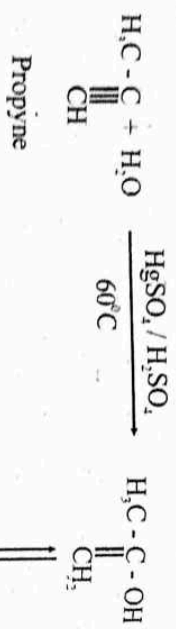
Q.42.

How will you bring following chemical transformations? (2017)

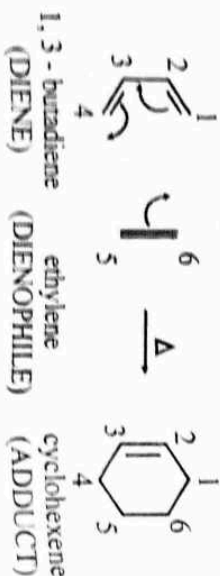
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Ans.



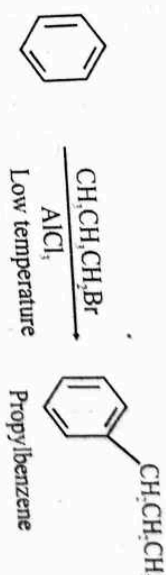
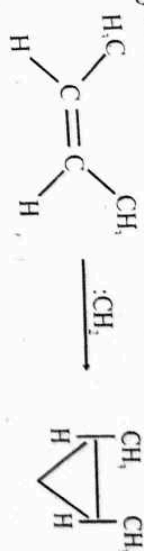
(b) The Diels-Alder reaction combines a *diene* (a molecule with two alternating double bonds) and a *dienophile* (an alkene) to make rings and bicyclic compounds. The three double bonds in the two starting materials are converted into two new single bonds and one new double bond. Since this reaction forms two new carbon-carbon bonds in a single step, it is a very useful and powerful reaction.



(c) One of the most synthetically important chelotropic reactions is the addition of a singlet carbene to an alkene to make a cyclopropane (see figure 11.11). A carbene is a neutral molecule containing a divalent carbon atom.

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carbons in its valence shell. Due to this, carbenes are highly reactive intermediates and generated as reaction intermediates. A singlet carbene contains an empty *p* orbital and a roughly *sp*<sup>2</sup> hybrid orbital that has two electrons. Singlet carbenes add stereospecifically to alkenes, and alkene stereochemistry is retained in the cyclopropane product.

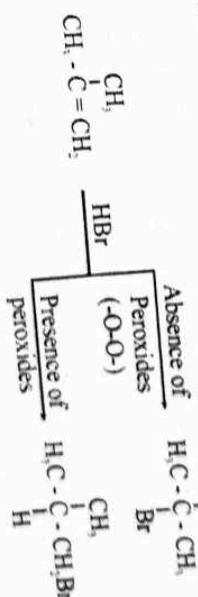


### Write short note on Peroxide Effect.

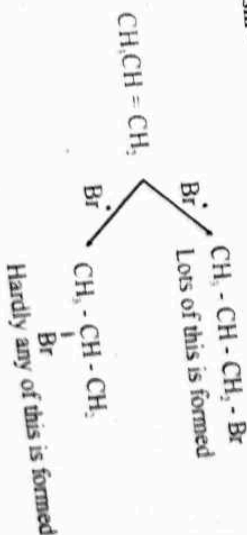
(2018)

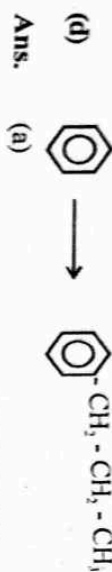
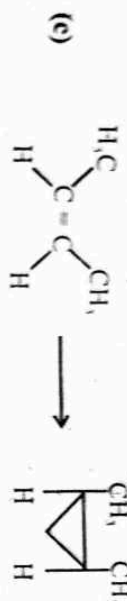
When an unsymmetrical reagent is treated with unsymmetrical alkene in presence of peroxide, then addition takes place against the Markownikoff's rule i.e. negative part of reagent adds to that carbon of carbon-carbon double bond which carries more number of hydrogen atoms. This is known as peroxide effect.

For example, when isobutylene is treated with HBr in presence of peroxide, addition takes place to form isobutyl bromide (1-bromo-2-methylpropane).

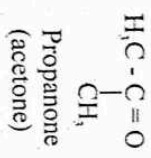
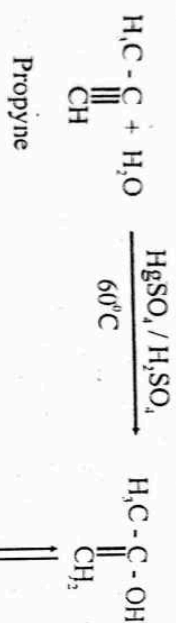


### Mechanism -

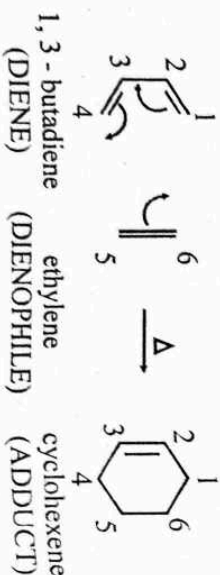




Ans.

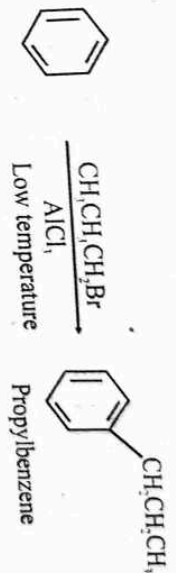
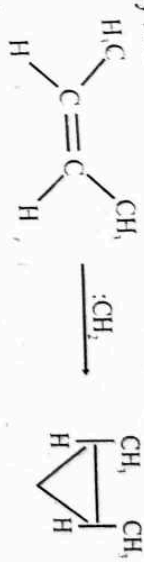


(b) The Diels-Alder reaction combines a *diene* (a molecule with two alternating double bonds) and a *dienophile* (an alkene) to make rings and bicyclic compounds. The three double bonds in the two starting materials are converted into two new single bonds and one new double bond. Since this reaction forms two new carbon-carbon bonds in a single step, it is a very useful and powerful reaction.



(c) One of the most synthetically important cheletropic reactions is the addition of a singlet carbene to an alkene to make a cyclopropane (see figure on left). A carbene is a neutral molecule containing a divalent carbon with two unpaired electrons in its valence shell.

Due to this, carbenes are highly reactive intermediates. A singlet carbene contains an empty *p* orbital and a roughly *sp*<sup>2</sup> hybrid orbital that has two electrons. Singlet carbenes add stereospecifically to alkenes, and alkene stereochemistry is retained in the cyclopropane product.

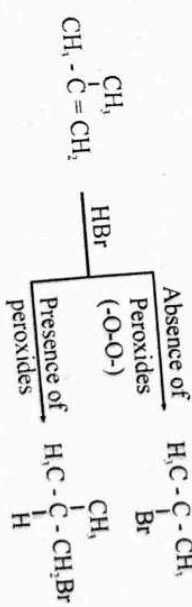


### Write short note on Peroxide Effect.

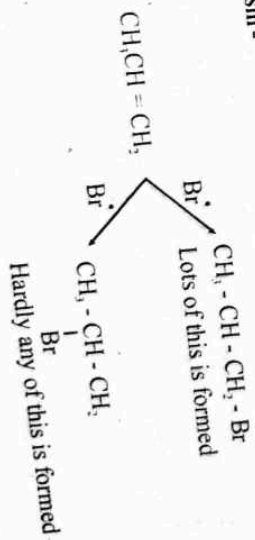
(2018)

When an unsymmetrical reagent is treated with unsymmetrical alkene in presence of peroxide, then addition takes place against the Markownikoff's rule i.e. negative part of reagent adds to that carbon of carbon-carbon double bond which carries more number of hydrogen atoms. This is known as peroxide effect.

For example, when isobutylene is treated with HBr in presence of peroxide, addition takes place to form isobutyl bromide (1-bromo-2-methylpropane).

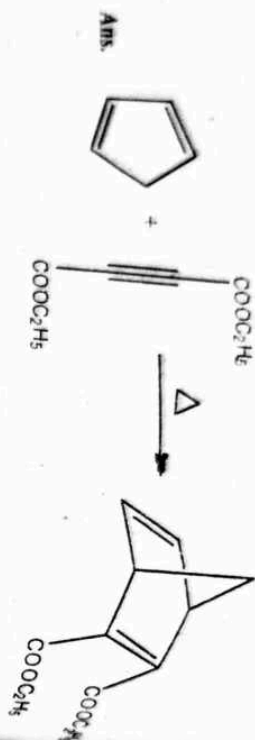


### Mechanism -



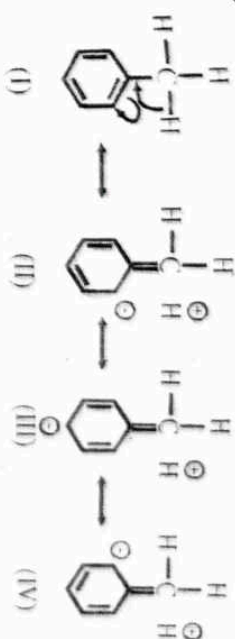
ides is weaker. Hence they decompose to form free radicals which attack on alkyl bromide to form Bromine free radicals. These bromine free radicals attack on alkyl bromide to give alkyl free radicals, which attack on next mole of HBr to form alkyl bromide.

Q.44. Complete the following reaction -



Discuss the directive influence of -CH<sub>3</sub> and -CN groups in aromatic electrophilic substitution reactions.

O - P Directing:-

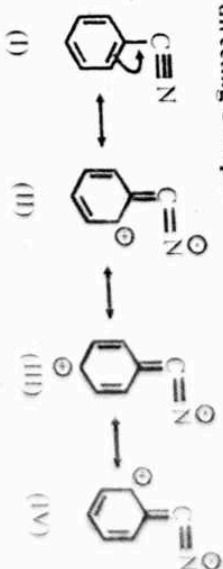


When the alkyl group has at least one alpha hydrogen (i.e. alkyl group may be 1° or 2° but not 3°). Such type of alkyl group are o-p directing groups because of the hyperconjugation.

In the hyperconjugation forms (II - IV) the ortho and para positions have a greater electron density than the meta position. Thus the electrophilic

(E) would naturally attack at these positions.

Meta-directing Groups:-



Q.2. Arrange given compounds in order of decreasing reactivity for A<sub>SE</sub> reactions:

- (i) C<sub>6</sub>H<sub>5</sub>-OCH<sub>3</sub>, (2019)  
(ii) C<sub>6</sub>H<sub>5</sub>-CH<sub>3</sub>  
(iii) C<sub>6</sub>H<sub>5</sub>-NO<sub>2</sub>, (iv) C<sub>6</sub>H<sub>5</sub>-CHO

Ans. (i) > (ii) > (iv) > (iii)

Q.3. On the basis of the stability of sigma complex, explain why nitro-group is meta directing whereas methoxy group is ortho and para directing? (2005, 2006, 2008)

Related Questions:-

Q. On the basis of s - complex stability, explain why -NO<sub>2</sub> group is meta director for aromatic electrophilic substitution reaction? (2012, 14)

Q. Explain the following with suitable reasons that

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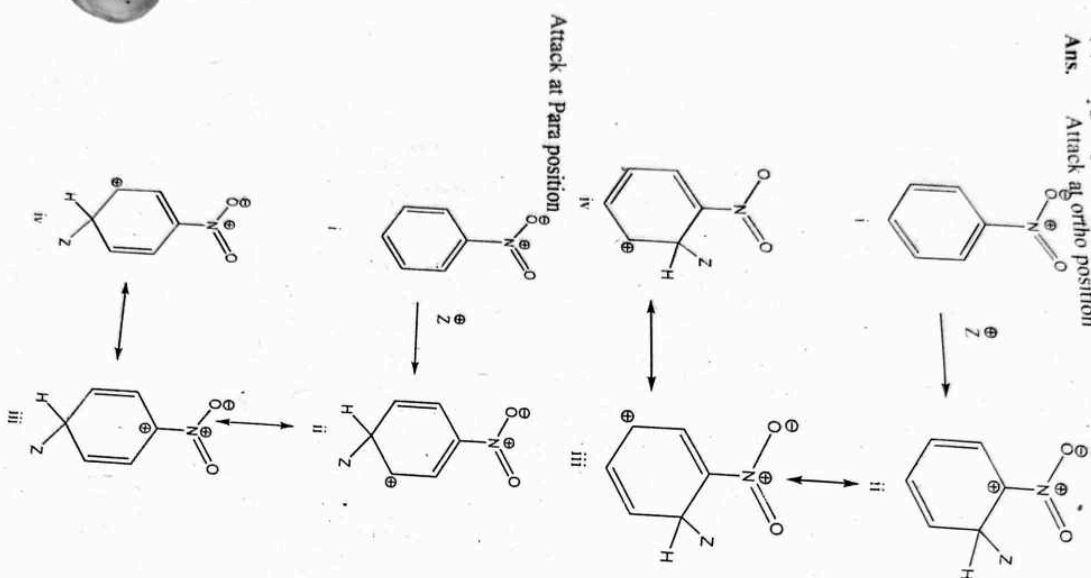
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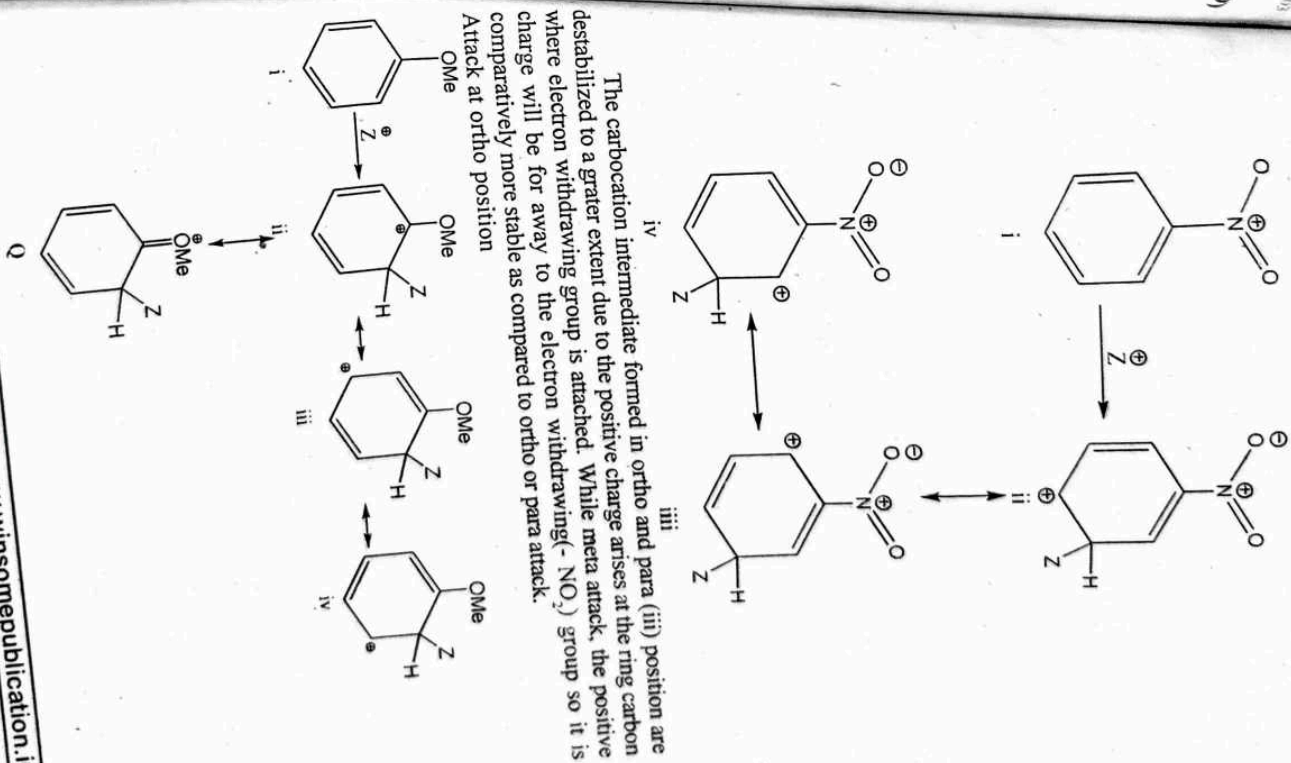
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- (a)  $\text{CH}_3$  group is o- and p-directing group.  
 (b)  $\text{NO}_2$  group is meta directing group.  
 Ans. Attack at ortho position

(20/9)



Attack at meta position



discuss the mechanism of the Friedel-Crafts reaction. (2006, 08)

Write short notes on Friedel-Crafts alkylation. (2013, 14)

Write short note on Friedel-Craft Alkylation's and acylation. (2016)

Write short note on Friedel-Craft Reaction. (2018)

**Friedel-Craft Reactions:-**

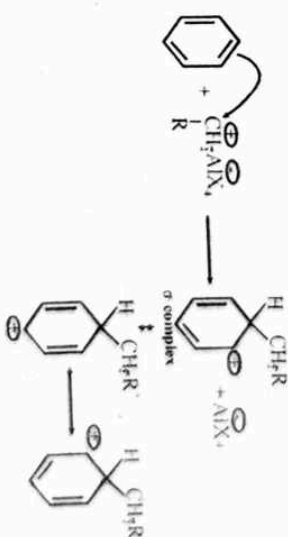
Alkylation of aromatic compound with aliphatic compound like alkanes, alcohols, esters, ethers, alkenes, aldehydes, and ketones in the presence of Lewis acid or proton acid as catalyst is known as Friedel-Crafts alkylation. This reaction is an example of aromatic electrophilic substitution reaction. If alkylating agent is halide, alcohol, ester or ether then catalyst is Lewis acid, but when alkylating agent is alkene, aldehyde and ketone, catalyst is proton acid.

**Mechanism:-**

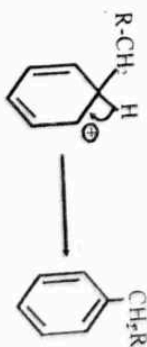
Step I:-



Step II:-



Step III:-



Step IV



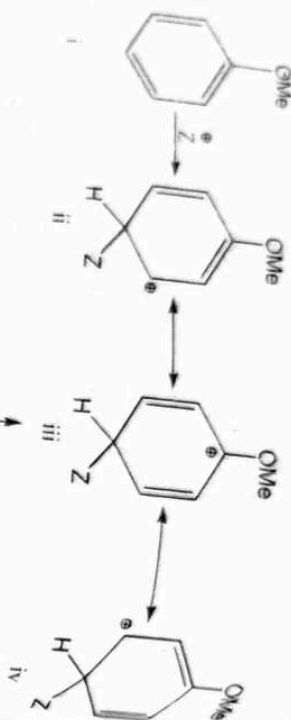
If the alkyl halide is secondary and tertiary, then reaction starts with the formation of carbocation and this carbocation acts as the electrophile.

**Friedel-Craft's Acylation:-** (Imp)

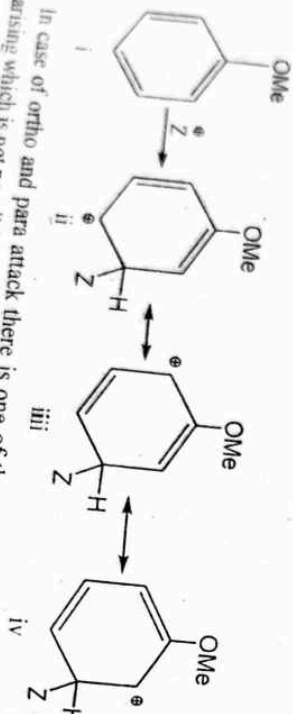
The group is called an acyl group and a reaction where by an acyl group is introduced into a compound is called acylated reaction. Acylation

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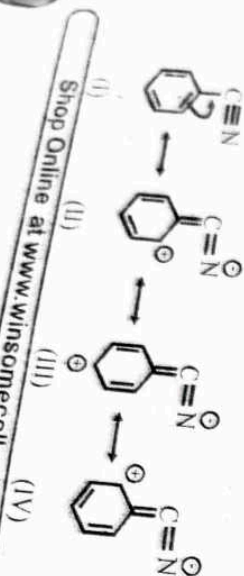
Attack at Para position



Attack at meta position



In case of ortho and para attack there is one of the extra resonance form arising which is not possible with the meta attack that is Q which stabilize the carbocation or in other way the positive charge is get stabilize hence the Meta-directing Groups:-



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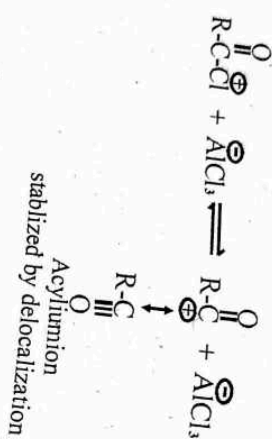
of aromatic compounds takes place in the presence of excess amount of Lewis acid because the product of the reaction is ketone, which forms complex with Lewis acid.



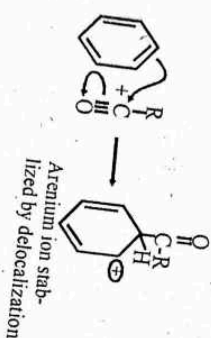
Step I:-



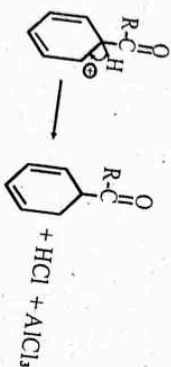
Step II:-



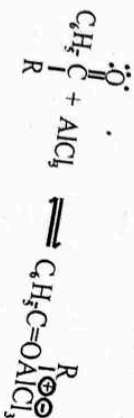
Step III:-



Step IV:-



Step V:-



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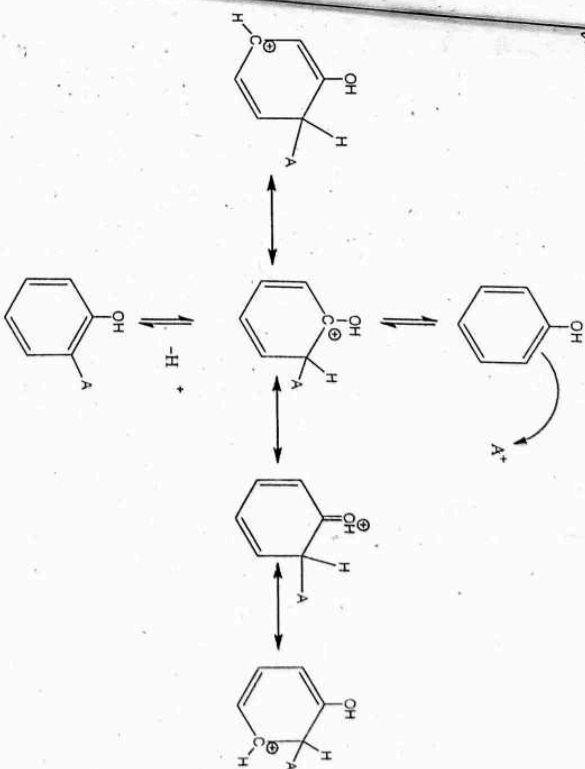
Explain why -OH group is ortho, para director and activator whereas -NO<sub>2</sub> group is meta director and deactivator for aromatic electrophilic substitution reaction.

Please see the Q ans no 26 for why -NO<sub>2</sub> meta direction group. (2010)

OH group is as follows:

Groups with unshared pairs of electrons, such as the OH group, is strongly activating and ortho/para-directing. Such activating groups donate those unshared electrons to the pi system.

Ortho Attack:



When the electrophile attacks the ortho and para positions, the oxygen atom can donate electron density to the pi system giving four resonance structures. This substantially enhances the stability of the cationic intermediate.

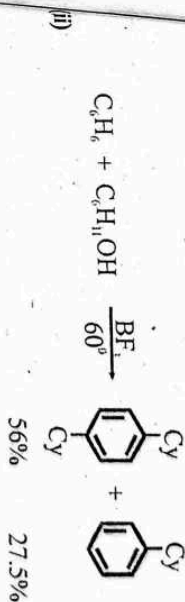
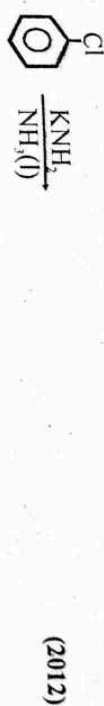
Para Attack:

Compare this with the case when the electrophile attacks the meta position. In that case, the nitrogen atom cannot donate electron density to the pi system, giving only three resonance contributors. For this reason, the meta-substituted product is produced in much smaller proportion to the ortho and para products.

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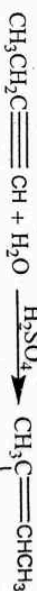
substituents, such as the alkyl and aryl substituents, may also donate electron density to the  $\pi$  system; however, since they lack an available lone pair of electrons, their ability to do this is rather limited. Thus they weakly activate the ring and do not strongly disfavor the *meta* position.

Give the major product of following reaction

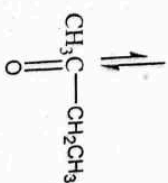


Q.7. Write note on Hydration of alkynes. (2009)

Ans. Alkynes undergo acid catalyzed addition of water. The product of the reaction is an enol. The enol immediately rearrange to a ketone.



an enol



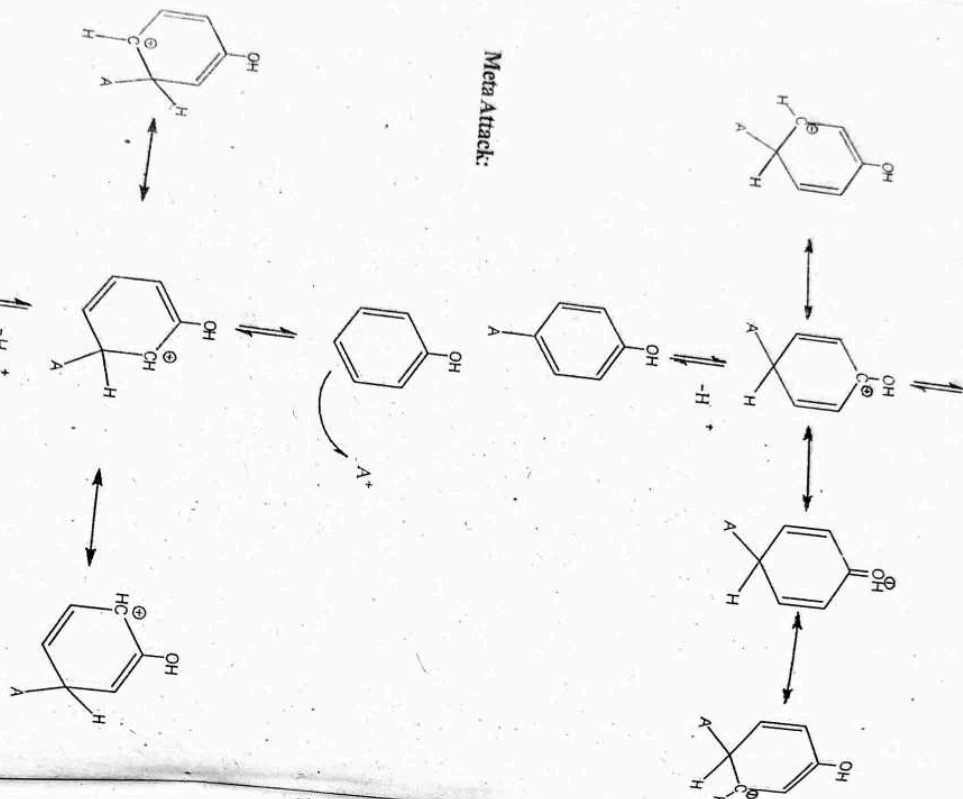
a ketone

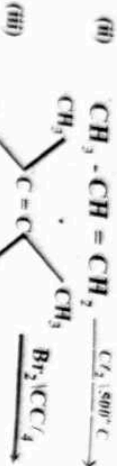
Q.8 Complete the following reactions and indicate the major product.



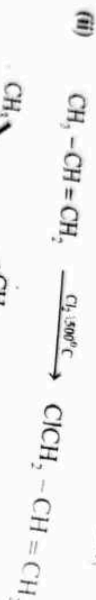
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Meta Attack:





Ans.



Q.9.

Complete the following reactions and outline the mechanism of the action.



(2012, 16)

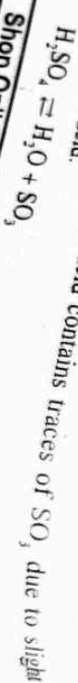
p.3:



The product is benzenesulphonic acid. The electrophile is actually sulphur trioxide,  $\text{SO}_3$ , and you may find the equation for the sulphonation reaction written:



The sulphur trioxide electrophile arises in one of two ways depending on which sort of acid you are using. Concentrated sulphuric acid contains traces of  $\text{SO}_3$  due to slight dissociation of the acid.

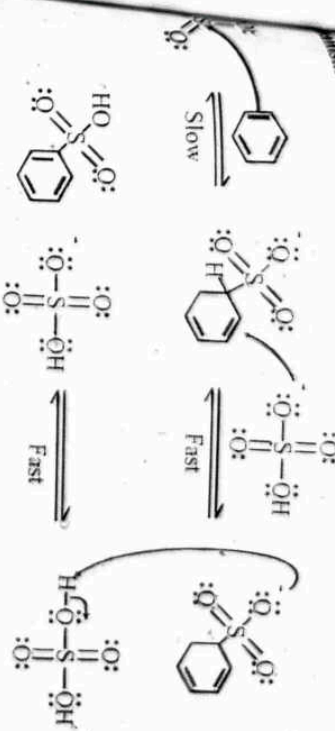


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forming sulphuric acid.  $\text{H}_2\text{SO}_4$  can be thought of as a solution of sulphur trioxide - and so is a much richer source of the  $\text{SO}_3$ . sulphur trioxide is an electrophile because it is a highly polar molecule with a large amount of positive charge on the sulphur atom. It is this which is attracted to the ring electrons.

(2014)

p.1:



p.2:

The p electrons of the aromatic  $\text{C}=\text{C}$  act as a nucleophile, attacking electrophilic S, pushing charge out onto an electronegative O atom. This forms the arenium ion intermediate.

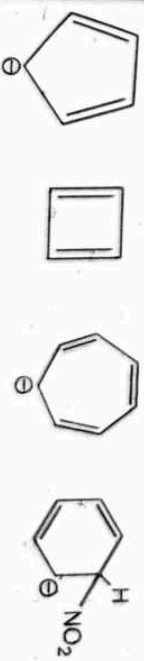
Loss of the proton from the  $\text{sp}^3$  C bearing the sulfonyl- group reforms  $\text{C}=\text{C}$  and the aromatic system.

Protonation of the conjugate base of the sulfonic acid by sulfuric acid produces the sulfonic acid.

10. Identify the following as aromatic/non-aromatic or antiaromatic:

Ans:

(2008)



Aromatic Antiaromatic Antiaromatic nonaromatic

Q.11. What is Chiral molecule?

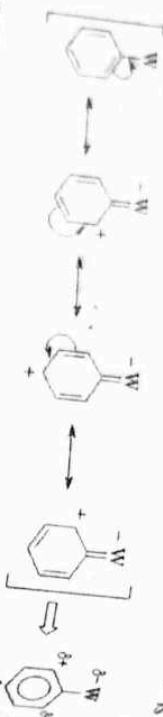
(2006)

Ans. A carbon bonded to four different atoms or groups is called a stereocentre. It is also called a chiral centre. In a other word a molecule donot have plane of symmetry as well as center of

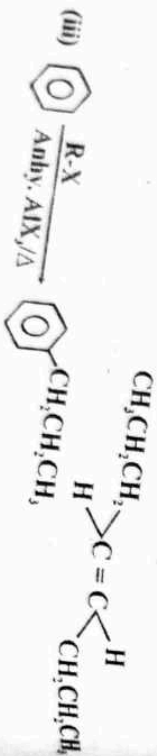
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Q.12. Explain.  $-NR_2$  group is meta directing for electrophilic aromatic substitution reaction.

Ans. Adjacent to the p system deactivate the aromatic ring by decreasing the electron density on the ring through a resonance withdrawing effect as  $-NR_2$ ,  $-NO_2$ . The resonance only decreases the electron density at ortho- and para-positions. Hence these sites are less nucleophilic, and the system tends to react with electrophiles at the meta sites. Let W is  $-NR_2$  group. Resonating structure are as :



Q.13. How the following conversions can be achieved?



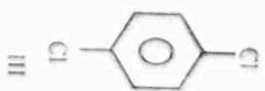
Q.14. Characterise the following species as aromatic, antiaromatic or nonaromatic.



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Q.15. Arrange following compounds in decreasing order of their dipole moment. (2017)



Ans. II > I > III

Q.16. Indicate the ortho, meta, para-directing effect of the following groups and also mention whether activating/deactivating in nature. (2016)



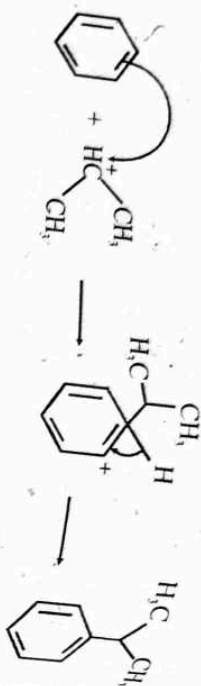
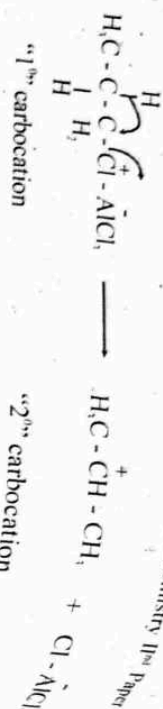
Ans. (i)  $-NH_2$  is ortho and para, activating in nature  
(ii)  $-OCH_3$  is activating group and it is a ortho, para directing group.  
(iii)  $-Br$  ortho and para, deactivating in nature  
(iv)  $-COOH$  Meta, deactivating in nature.

Q.17. Complete the following reactions and write mechanism of formation of products in each. (2017, 19)



Mechanism:

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Q.18. Characterise the following species as aromatic, antiaromatic or nonaromatic.



Ans.

II, IV are aromatic and I, III are antiaromatic.

Q.19.

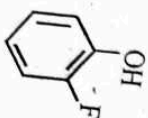
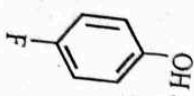
Explain water solubility of o-nitro phenol is less than p-nitro phenol.

Ans. Ortho-Nitrophenol is less soluble in water than p- and m-Nitrophenols because: (1) o-Nitrophenol is more volatile in stream than those of m- and p-isomers (2) o-Nitrophenol shows intramolecular H-bonding (3) o-Nitrophenol shows Intermolecular H-bonding (4) Melting point of o-Nitrophenol is lower than those of m- and p-isomers.

Q.20.

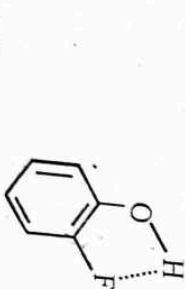
Explain p-fluorophenol is more acidic than o-fluorophenol.

Ans. In case of p-fluorophenol +R-effect and -I-effect of F almost balance each other due to almost identical sizes of 2p-orbitals of C and F and hence it is almost as acidic as phenol itself. In case of o-fluorophenol is the weakest acid due to strong intramolecular H-bonding.



p-fluorophenol

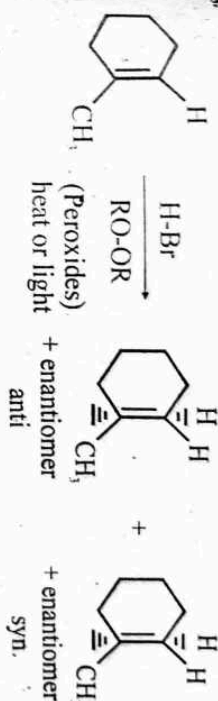
o-fluorophenol



o-fluorophenol (intramolecular hydrogen bonding)

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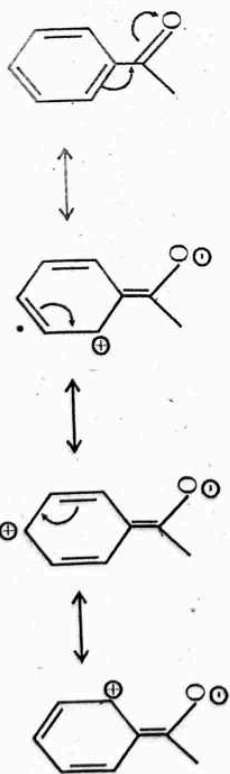
Give the major organic product of the following -



Regiochemistry : anti-Markovnikov  
Stereochemistry : syn + anti

Q.22. Explain with suitable reason that -CHO is a meta directing group.

Ans. Thus, these groups make the aromatic ring very electron poor relative to benzene and, therefore, they strongly deactivate the ring i.e. reactions proceed much slower in rings bearing these groups compared to those reactions in benzene. We see that the resonance contribution in the starting material places positive charges at the *ortho* and *para* positions and these will deter attack at those positions by electrophiles i.e. these groups are *meta* (m) directing.



Q.23. Explain with suitable reason that -NH<sub>2</sub> group is o-, p-directing group.

Ans. NH<sub>2</sub> group in aniline is ortho and para directing group because they can release electrons towards ring due to resonance and at the same time they withdraw electrons towards themselves from aromatic ring due to +I effect. The resonating structure of aniline shows negative charge develops in ortho and para positions and electron deficient electrophiles attack ortho and para positions.

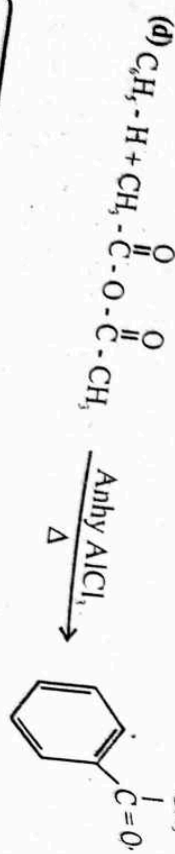
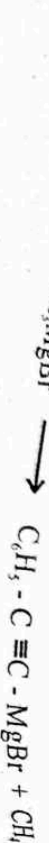
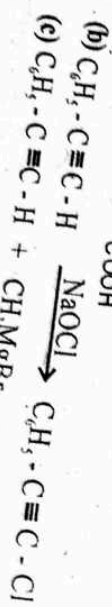
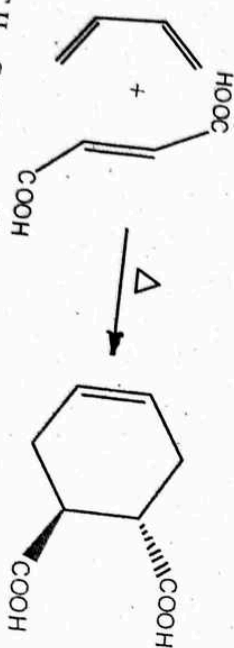
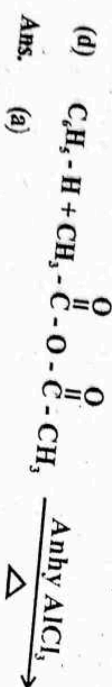
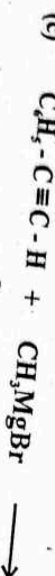
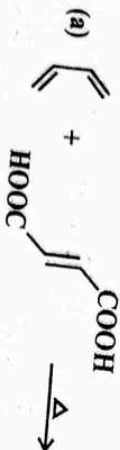
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Ans. (i) = Antiaromatic



Q.25. Complete the following reactions:



(2018)

Write note on  $S_N1$  Reaction.

Write short note on  $S_N1$  reaction.

(2018)

The  $S_N1$  reaction is a substitution reaction in organic chemistry. "SN" stands for nucleophilic substitution and the "1" represents the fact that the rate-determining step is unimolecular. Thus, the rate equation is often shown as having first-order dependence on electrophile and zero-order dependence on nucleophile. This relationship holds for situations where the amount of nucleophile is much greater than that of the carbocation intermediate. Instead, the rate equation may be more accurately described using steady-state kinetics. The reaction involves a carbocation intermediate and is commonly seen in reactions of secondary or tertiary alkyl halides under strongly basic conditions or, under strongly acidic conditions, with secondary or tertiary alcohols. With primary and secondary alkyl halides, the alternative  $S_N2$  reaction occurs. In inorganic chemistry, the  $S_N1$  reaction is often known as the dissociative mechanism. This dissociation pathway is well-described by the cis effect. A reaction mechanism was first proposed by Christopher Ingold et al. in 1940. This reaction does not depend much on the strength of the nucleophile unlike the  $S_N2$  mechanism.

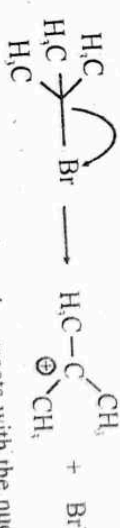
Mechanism:-

An example of a reaction taking place with an  $S_N1$  reaction mechanism is the hydrolysis of tert-butyl bromide with water forming tert-butanol:



reaction tert-butylbromide water overall

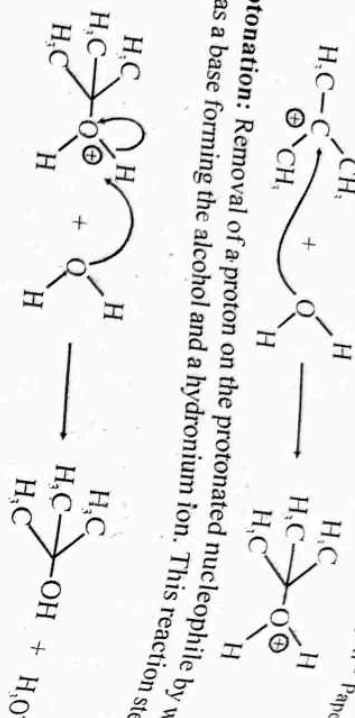
This  $S_N1$  reaction takes place in three steps:  
Formation of a tert-butyl carbocation by separation of a leaving group (a bromide anion) from the carbon atom: this step is slow and reversible.



**Nucleophilic attack:** the carbocation reacts with the nucleophile. If the nucleophile is a neutral molecule (i.e. a solvent) a third step is required to complete the reaction. When the solvent is water, the intermediate is an oxonium ion. This reaction step is fast.



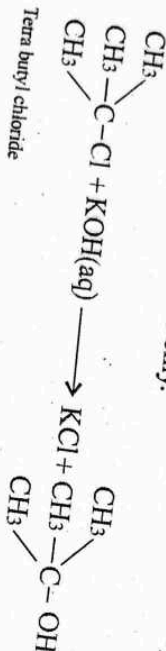
**Deprotonation:** Removal of a proton on the protonated nucleophile by water acting as a base forming the alcohol and a hydronium ion. This reaction step is fast.



**Q.2. Give the mechanism of SN1 reaction of alkyl halides.**

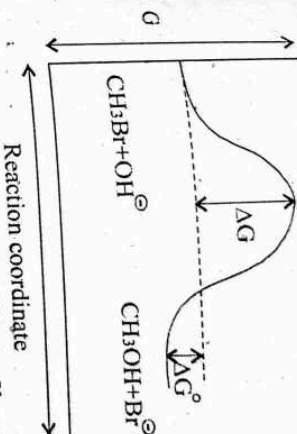
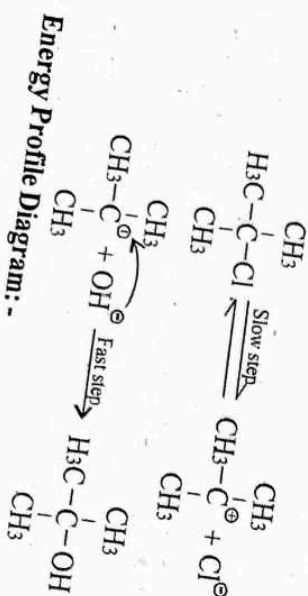
**Ans. Unimolecular Nucleophilic substitution (SN1):-**

The nucleophilic substitution reactions in which the rate of reaction depends upon the concentration of only one reactant are called unimolecular nucleophilic substitution reaction i.e. SN1 reaction e.g., in concentration of tetra butyl chloride only.



**Mechanism:-**

order = 1



Where  $b$  = breaking of bond  
 $f$  = forming of bond  
 $G$  = free energy

**Fig:- Reaction coordinate diagram for an SN1 reaction (2008)**

**(B) Bimolecular Nucleophilic Substitution (SN2):-**

The nucleophilic substitution reaction in which the rate of reaction depends upon the conc. of two reactants are called bimolecular nucleophilic substitution reaction.



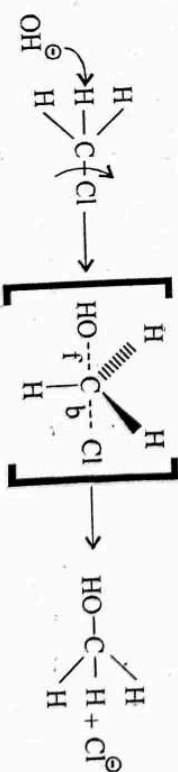
$$\text{Rate} = k [RX] [OH^-]$$

Order = 1 + 1 = 2



**Mechanism:-**

It involves concerted i.e. single step mechanism.



**Energy Profile Diagram:-**

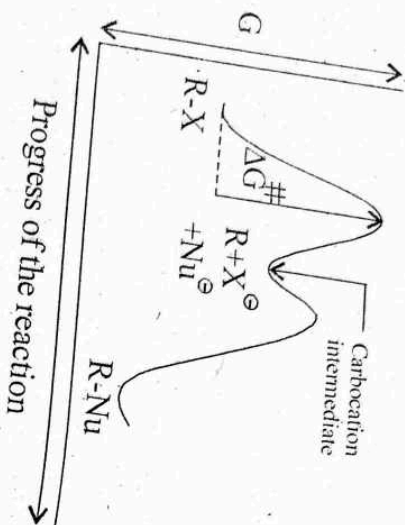


Fig. - Reaction coordinate diagram for an SN2 reaction

### Factor:-

**The Basicity of the Leaving Group:-** By comparing the relative SN2 reaction rates of compounds with atoms in the same periodic group (the halides, for example), results show that the ability as a leaving group during an SN2 reaction depends on its basicity. In general, the weaker the basicity of a group, the greater its leaving ability. For example, the iodide ion is a very weak base and because it is so, it is the most reactive. Weak bases do not share their electrons well because their electrons are farther away from the nucleus, making it easier for their bonds to be broken. In contrast, the fluoride ion is a stronger base than the other halides and, therefore, the least reactive. In fact, the fluoride ion is such a strong base that compounds involving them essentially do not undergo SN2 reaction. Looking at the periodic table, relative basicity decreases down a group.

**The Size of the Nucleophile:-** How readily a compound attacks an electron-deficient atom also affects an SN2 reaction. As a rule, a negatively charged species (e.g. OH<sup>-</sup>) are better nucleophiles than neutral species (e.g. H<sub>2</sub>O, water). There is a direct relationship between basicity and nucleophilicity: stronger bases are better nucleophiles. Acidity, the ability of an atom to give up a proton (H<sup>+</sup>), is comparatively relative when molecules whose attacking atoms are approximately the same in size, the weakest going toward the left side of the periodic table. If hydrogen were attached to second-row elements of the periodic table, the resulting compounds would have the following relative acidities:

Weaker Acid) NH<sub>3</sub> < H<sub>2</sub>O < HF (Stronger Acid)

If each of these acids were to give up a hydrogen, the result would be a conjugate base, and the relative strengths will reverse. The stronger base now moves toward the left side of the periodic table.

Stronger Base) NH<sub>2</sub><sup>-</sup> > OH<sup>-</sup> > F<sup>-</sup> (Weaker Base)  
Elements increase in size down the periodic table. Although basicity decreases down the periodic table, nucleophilicity increases as size increases depending on the solvent used.

**Solvent:-** If a reaction is carried out in a protic solvent, whose molecules have a hydrogen bonded to an oxygen or to a nitrogen, the larger atom is a better nucleophile in an SN2 reaction. In other words, the weaker base is the better nucleophile in a protic solvent. For example, the iodide ion is better than a fluoride ion as a nucleophile. However, if the reaction is carried out in an aprotic solvent, whose molecules do not have hydrogen bonded to an oxygen or to a nitrogen, then the stronger base is the better nucleophile. In this case, the fluoride ion is better than the iodide ion as a nucleophile.

**Sterics:-** Steric hindrance is any effect of a compound due to the size and/or arrangement of its substituent groups. Steric effects affect nucleophilicity but does not affect base strength. A bulky nucleophile, such as a tert-butoxide ion with its specific arrangement of methyl groups, is a poorer nucleophile than an ethoxide ion with a straighter chain of carbons, even though tert-butoxide is a stronger base.

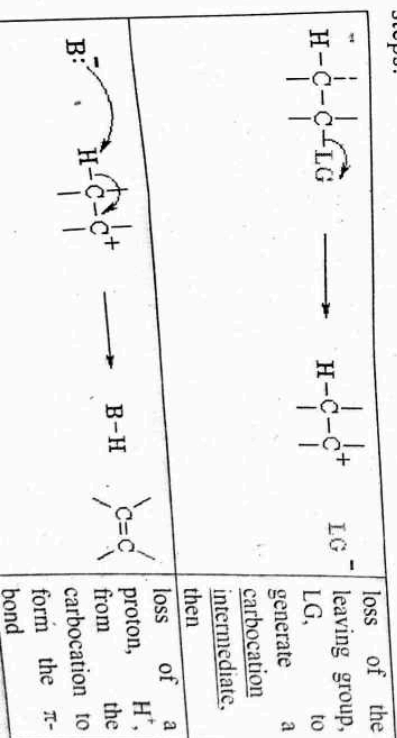
### Q.3 Write short notes on E1 reaction.

(2008)

Ans: E1 mechanism:-

E1 indicates a *elimination, unimolecular* reaction, rate of reaction = k [R-LG].

This implies that the rate determining step of the mechanism depends on the decomposition of a single molecular species. Overall, this pathway is a multi-step process with the following two critical steps:



Lets look at how the various components of the reaction influence the reaction pathway:

**R-group**

Reactivity order:  $(CH_3)_3C > (CH_3)_2CH > CH_3CH_2 > CH_3$

In an E1 reaction, the rate determining step is the loss of the leaving group to form the intermediate carbocation. The more stable the carbocation is, the easier it is to form, and the faster the E1 reaction of the carbocation will react fastest, but they are forgetting that it is the generation of the carbocation that is rate determining. Since carbocation intermediates are formed during an E1, there is always the possibility of rearrangements (e.g. 1,2-hydride or 1,2-alkyl shifts) to generate a more stable carbocation. This is usually indicated by a change in the position of the alkene or a change in the carbon skeleton of the product when compared to the starting material.

**Leaving group (LG):-**

The only event in the rate determining step of the E1 is breaking the C-LG bond. Therefore, there is a very strong dependence on the nature of the C-LG bond. In the acid catalysed reactions of alcohols, the -OH is protonated first to give an oxonium ion, providing the much better leaving group, a water molecule (see scheme below).

**Base:-**

Since the base is not involved in the rate determining step, the nature of the base is unimportant in an E1 reaction. However, the more reactive the base, the more likely an E2 reaction becomes.

**Selectivity:-**

- E1 reactions usually favour the more stable alkene as the major product
- This E1 mechanistic pathway is most common with:
  - good leaving groups
  - stable carbocations
  - weak bases.
- A typical example is the acid catalysed dehydration of 2° or 3° alcohols.

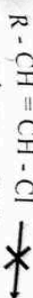
**Q.4 Explain why vinyl chloride is less reactive than ethyl chloride.**

**Related Questions:-**  
**Q. Vinyl halides are aliphatic halogen compound but they resemble with aryl halides in their reactivity. How do you account for this. (2003, 04)**

**Ans.**

Aryl halides and vinyl halides do not under go SN1 reaction. There are two reasons why vinyl halides do not under go SN1 reaction. (1) Vinyl and aryl cations are even unstable than primary alkyl carbocations and we know that alkyl halides do not under go SN1 reaction.

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carbocations are highly unstable to be form. Highly unstable because of hybridization of C<sup>+</sup> is sp.



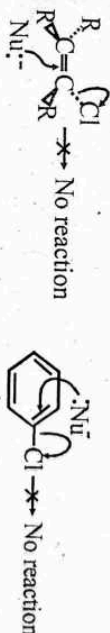
sp hybridization

phenyl cation is unstable to be formed because hybridization of C<sup>+</sup> is sp. Therefore vinyl and aryl halides do not undergo SN1 reaction.

sp<sup>2</sup>-hybrid carbon forms stronger C-X bond than sp<sup>2</sup>-hybrid carbon as a result it is harder to break the C-halogen bond when halogen is present on sp<sup>2</sup> carbon.

**reactivity of Vinyl Halide Towards Nucleophilic:-**

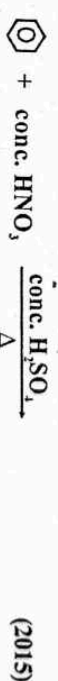
Vinyl Halides ( $R_2C=CRX$ ) and aryl halides are unreactive towards SN<sub>2</sub> reaction. This lack of reactivity is probably due to steric factors, because the incoming nucleophile would have to approach in the plane of the carbon-carbon double bond to carry out a backside displacement.



**Q.5 Give the mechanism of Nitration of benzene. (2010, 13)**

**Related Questions:-**

**Q. Complete the reaction**



**Ans. Nitration of Benzene**



Reaction type: Electrophilic Aromatic Substitution

Overall transformation: Ar-H to Ar-NO<sub>2</sub>

Reagent: for benzene, HNO<sub>3</sub> in H<sub>2</sub>SO<sub>4</sub> / heat

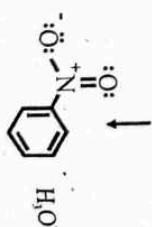
Electrophilic species: the nitronium ion (i.e. NO<sub>2</sub><sup>+</sup>) formed by the loss of water from the nitric acid.

**Mechanism For Nitration Of Benzene:-**

**Step 1:**

An acid/base reaction.

Protonation of the hydroxy group of the nitric acid. This provides a better leaving group.



**Step 2:**

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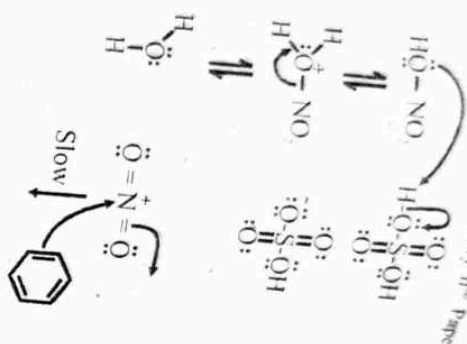
Loss of the leaving group, a water molecule provides the nitronium ion, the reactive electrophile.

Step 3:

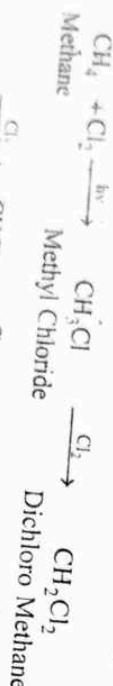
The electrophilic nitronium ion reacts with nucleophilic C=C of the arene. This is the rate determining step as it destroys the aromaticity of the arene.

Step 4:

Water functions as a base to remove the proton from the sp<sup>2</sup> C bearing the nitro-group and reforms the C=C and the aromatic system.



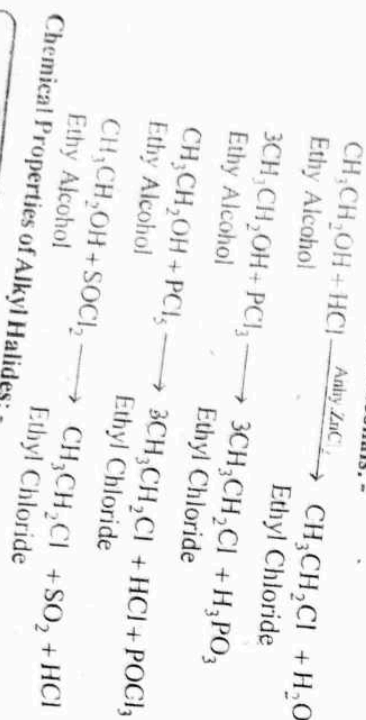
General methods of preparation of alkyl halides: -  
(i) By Halogenation of Alkane: -



(ii) By Addition of Hydrogen Halides to Alkene: -



(iii) By Substitution Reaction of Alcohols: -

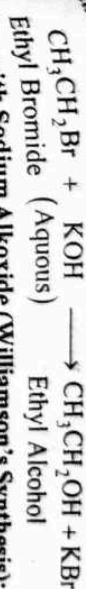


Chemical Properties of Alkyl Halides: -

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Alkyl halides mainly give nucleophilic substitution reaction.

Reaction with Aqueous KOH: -



Reaction with Sodium Alkoxide (Williamson's Synthesis): -



Reaction with KCN: -



Reaction with AgCN: -



Wurtz Reaction: -



Chloroform (CHCl<sub>3</sub>): -

Chemical Reactions of Chloroform: -

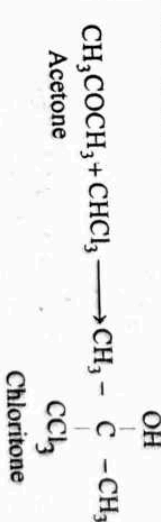
Reaction with Silver Powder: -



Reaction with Nitric Acid (Formation of Chloroform): -

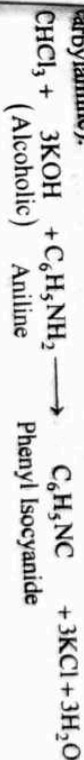


Reaction with Acetone: -



(iv) Carbylamine Reaction: -

This reaction is also called as Isocyanide test. In this reaction chloroform react with aniline and alcoholic KOH and form phenyl isocyanide (Phenyl carbylamine).



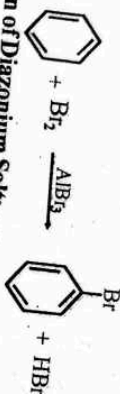
Q.6. Write methods of formation of aryl halides.

Ans. Method of Preparation: -

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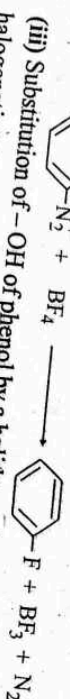
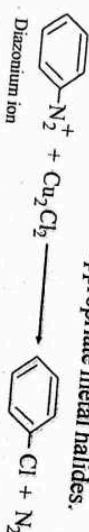
### (i) Direct Halogenation:-

Aryl Chlorides or Aryl Bromide are generally prepared by the direct halogenation of aromatic hydrocarbons in the presence of Lewis acid, which act as Catalyst for e.g.  $AlCl_3$ ,  $AlBr_3$  or  $FeCl_3$ .



### (ii) Decomposition of Diazonium Salt:-

Aryl halides are prepared most satisfactorily by the decomposition of diazonium salt in the presence of appropriate metal halides.



(iii) Substitution of  $-OH$  of phenol by a halide - when phenol is treated with halogenating agents such as  $PBr_3$  or  $SO_2$ , an aryl halide is produced.



Q.7.

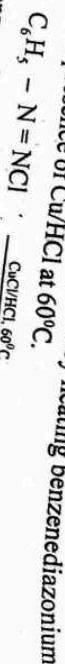
How is chlorobenzene prepared in laboratory? How will you distinguish between chlorobenzene and Benzyl chloride? Starting from chlorobenzene how will you obtain the following:

(i) Phenol

(ii) Aniline

(iii) Phenyl cyanide

In lab chlorobenzene is prepared by heating benzenediazonium chloride in the presence of  $Cu/HCl$  at  $60^\circ\text{C}$ .

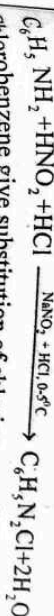


This reaction is called Sandmeyer reaction.

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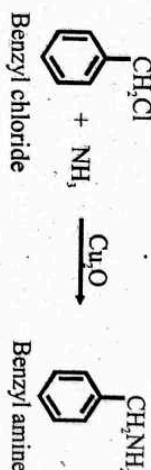
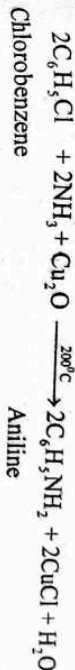
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Benzenediazonium chloride is obtained by action of cold sodium nitrate and hydrochloric acid on aniline at  $0-5^\circ\text{C}$ .

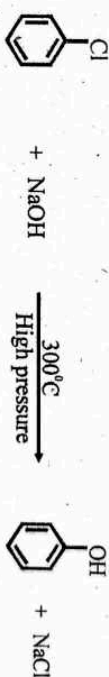


Chlorobenzene give substitution of chlorine very difficulty where as benzyl chloride easily give substitution of chlorine.

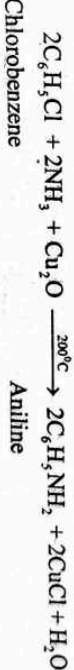
Chlorobenzene on reaction with ammonia give aniline where as Benzyl chloride give Benzyl amine.



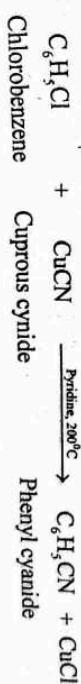
(i) Phenol:-



(ii) Aniline:-



(iii) Phenyl cyanide:-



Q.8.

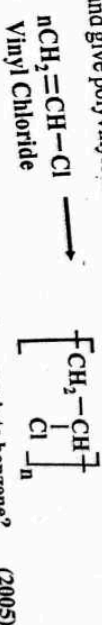
Give a brief account of vinyl polymerization.

(2009)

Ans.

Vinyl Polymerization:-

Vinyl halides polymerised and give polyvinyl polymer. For example vinyl chloride polymerise and give. For example vinyl chloride polymerize and give polyvinylchloride.



(2005)

Q.9.

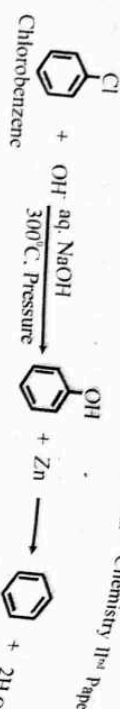
How will you convert the chlorobenzene into benzene?

Ans.

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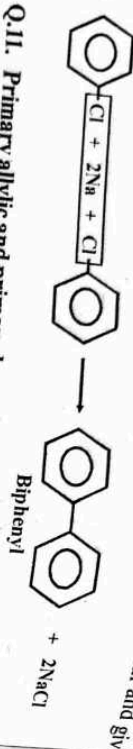
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**Q.10. How will you prepare biphenyl?**

Ans. Two molecule of benzyl chloride react with sodium metal and give biphenyl.



**Q.11. Primary allylic and primary benzylic halides show higher reactivity in  $\text{S}_\text{N}1$  reactions than other primary alkyl halides. Explain.**

Ans. In  $\text{S}_\text{N}1$  reaction the intermediate species is carbocation. The stability order of Primary allylic and primary benzylic cation greater than that of primary alkyl cation. Hence Primary allylic and primary benzylic halides show higher reactivity in  $\text{S}_\text{N}1$  reactions than other primary alkyl halides

**Q.12. Arrange the following halides in order of increasing  $\text{S}_\text{N}2$  reactivity:**

$\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3-\text{CH}_2-\text{Cl}$ ,  $(\text{CH}_3)_2\text{CH}_2\text{Cl}$

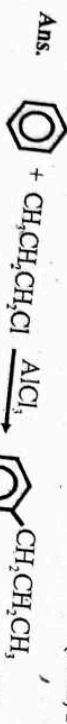
Ans: Increasing order of  $\text{S}_\text{N}2$  reactivity

$\text{CH}_3\text{Br} > \text{CH}_3\text{Cl} > \text{CH}_3-\text{CH}_2-\text{Cl} > (\text{CH}_3)_2\text{CH}_2\text{Cl}$

**Q.13. Give the major organic product of the reaction**



(2011, 14, 15)



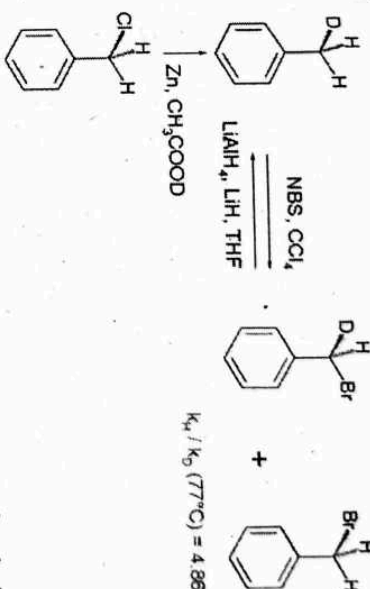
**Q.14. Write a short note on primary isotope effect in the determination of reaction mechanism.**

Ans. The kinetic isotope effect (KIE) is a dependence of the rate of a chemical reaction on the isotopic identity of an atom in a reactant. It is also called "isotope fractionation," although this term is somewhat broader in meaning. A KIE involving hydrogen and deuterium is represented as: with  $k_\text{H}$  and  $k_\text{D}$  reaction rate constants.

An isotopic substitution will greatly modify the reaction rate when the isotopic replacement is in a chemical bond that is broken or formed in the rate limiting step. In such a case, the change is termed a primary isotope effect.

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When the substitution is not involved in the bond that is breaking or forming, the rate change, termed a secondary isotope effect is observed. Thus, smaller rate change, the kinetic isotope effect can be used to elucidate the reaction mechanism. If other steps are partially rate-determining, the effect of isotopic substitution will be masked.



Reaction mechanisms are routinely elucidated using the kinetic isotope effect, e.g. the halogenation of toluene:

In this particular "intramolecular KIE" study the radical substitution of hydrogen by bromine is examined in the reaction involving *N*-bromosuccinimide as the brominating agent. With mono-deuterated toluene (obtained by organic reduction of benzyl chloride with zinc and deuterated acetic acid), it was found that hydrogen is replaced by bromine faster than deuterium, the reaction product gets enriched in deuterium. A KIE of 4.86 was determined. This finding is in accordance with the general accepted view of a radical substitution in which a hydrogen atom is removed by a bromine free radical species in the rate-determining step.

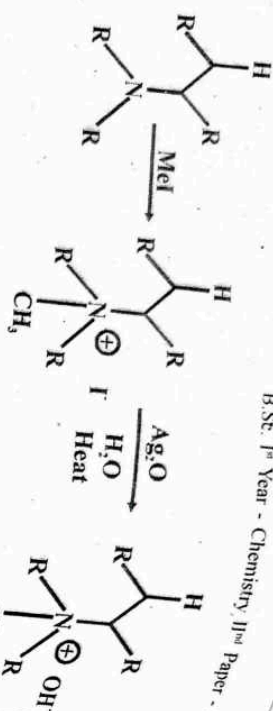
**Q.15. Explain the terms Hofmann elimination with examples.** (2007, 09)

**Related Questions:-**

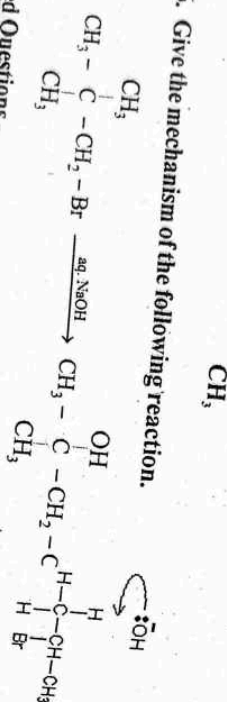
**Q. Write short note on Hoffmann elimination.** (2013, 14)

Ans. Hoffmann elimination (also known as *exhaustive methylation*) is a process where an amine is reacted to create a tertiary amine and an alkene by treatment with excess methyl iodide followed by treatment with silver oxide, water, and heat. After the first step, a quaternary ammonium iodide salt is created. After replacement of iodine by an hydroxyl anion, an elimination reaction takes place to the alkene. With unsymmetrical amines, the major alkene product is the least substituted and generally the least stable, an observation known as the Hoffmann rule. This is in direct contrast to normal elimination reactions where the more substituted, stable product is dominant (Zaitsev's rule).

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Q.16. Give the mechanism of the following reaction.

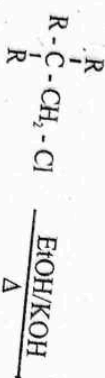


Related Questions:-

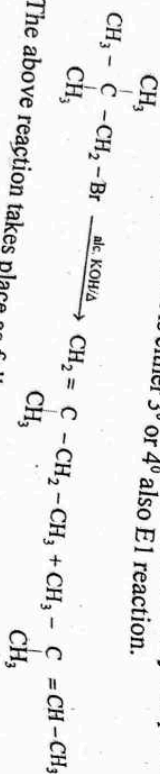
Q. Complete the reaction



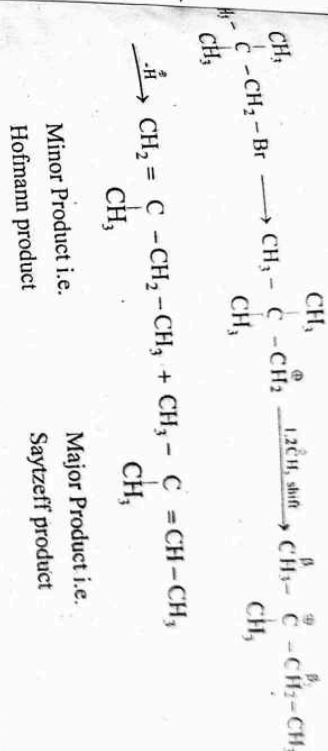
Q. Discuss the detailed mechanism of the reactions after completing the reactions. (2015)



Ans. Tertiary alkyl halides always give E1 reaction, secondary and primary alkyl halides whose  $\beta$ -carbon is either  $3^\circ$  or  $4^\circ$  also E1 reaction.

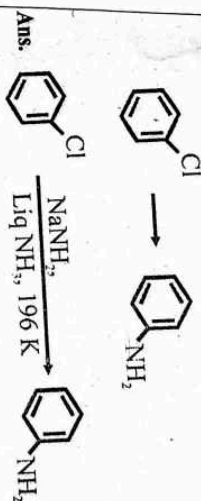


The above reaction takes place as follows:

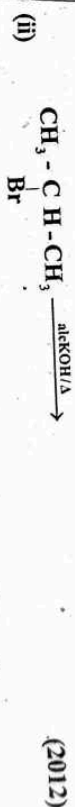
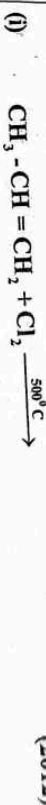


Q.17. How will you bring about the following conversions:

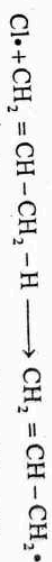
(2011)



Q.18. Complete the following reactions and outline the mechanism of reaction.

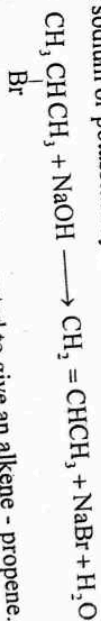


Reaction Mechanism:-



(ii) Elimination:-

Halogenoalkanes also undergo elimination reactions in the presence of sodium or potassium hydroxide.

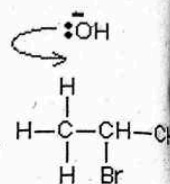


The 2-bromopropane has reacted to give an alkene - propene.

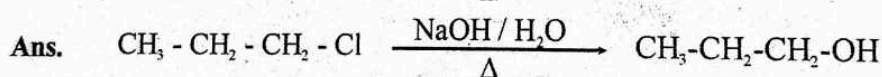
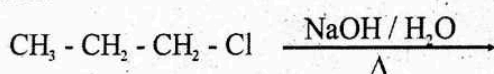
Notice that a hydrogen atom has been removed from one of the end carbon atoms together with the bromine from the centre one. In all simple elimination reactions the things being removed are on adjacent carbon atoms and a double bond is set up between those carbons.

**The role of the hydroxide ion in an elimination reaction -**

Hydroxide ions have a very strong tendency to combine with hydrogen ions to make water - in other words, the  $\text{OH}^-$  ion is a very strong base. In an elimination reaction, the hydroxide ion hits one of the hydrogen atoms in the  $\text{CH}_3$  group and pulls it off. This leads to a cascade of electron pair movements resulting in the formation of a carbon-carbon double bond, and the loss of the bromine as  $\text{Br}^-$ .



**Q.19. Discuss the detailed mechanism of the reactions after completing the reaction.** (2018)



**Mechanism -**

