

Chapter 1

Electromagnetic Spectrum : Absorption Spectra: -

Introduction -

In this chapter we will study about the two absorption spectroscopy i.e. ultraviolet absorption spectroscopy (UV - spectroscopy) and infrared absorption spectroscopy (IR - spectroscopy).

Electromagnetic Radiation and Electromagnetic Spectra: -

Electromagnetic radiation contains both the electric part as well as magnetic part and both are perpendicular to each other.

When this electromagnetic radiation incident on atoms/molecules then the transition of electron takes place from one quantised energy level to another quantised energy level. Due to this transition a spectra are arises which is known as **electromagnetic spectra**.

Cosmic ray	γ -ray	X-ray	UV	Visible	IR	Micro wave	Radio wave
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Energy decreases from L - R
 λ - increases

Energy of electromagnetic radiation is given by (Energy of one photon) -

$$E = h\nu$$

$$\left(\because \nu = \frac{c}{\lambda} \right) \text{ where } h = \text{Plank's constant}$$

$$E = \frac{hc}{\lambda}$$

λ = wavelength of electromagnetic radiation.

And Also $\bar{\nu} = \frac{1}{\lambda}$

$\bar{\nu}$ = wave number

Beer-Lambert's Law: -

This law states that decrease in the intensity of the incident beam is proportional to the concentration (C) and thickness (dx) of the medium.

$$-d\frac{I}{I} \propto C \cdot dx \quad \Rightarrow \quad -d\frac{I}{I} = \alpha \cdot C \cdot dx$$

On solving the above equation we find the relation

$$\log\left(\frac{I_0}{I}\right) = \epsilon \cdot Cx$$

Where I_0 = Initial intensity of beam, I = Final intensity of beam, ϵ = Molecular absorptivity coefficient or extinction coefficient.

Absorbance: -

$$A = \epsilon Cx$$

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Transmittance: -

$$T = \frac{I_t}{I_0}$$

Mathematically they are related -

$$T = 10^{-A} = 10^{-\epsilon c x}$$

$$(\because A = \epsilon c x)$$

Energy of a molecule: -

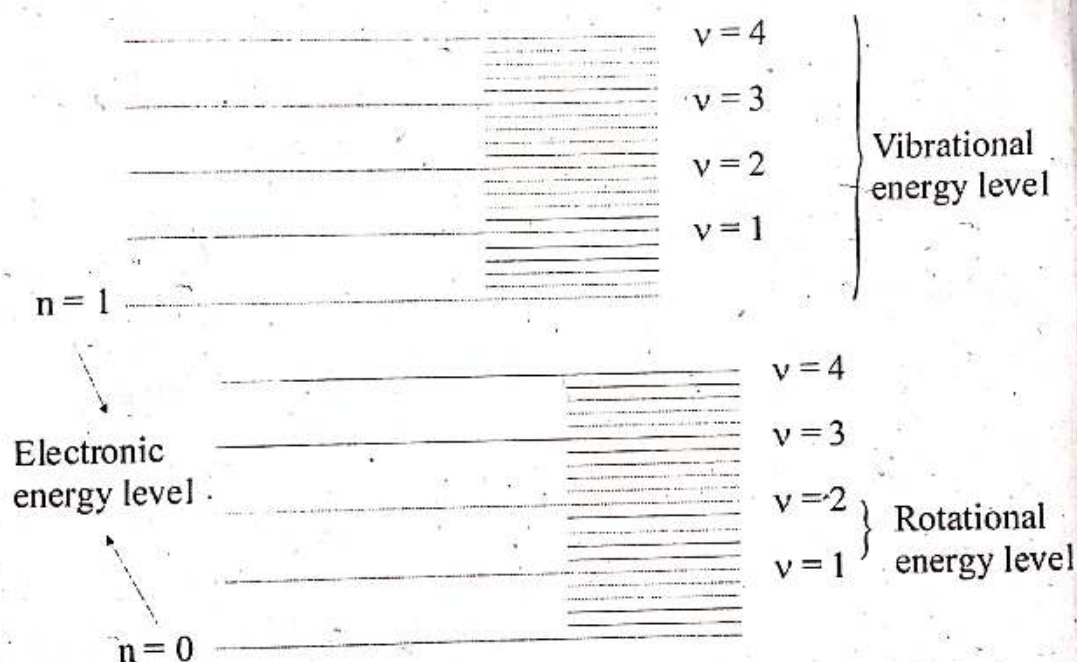
Any molecules contains different type of quantised energy level like translational energy level, electronic energy level, vibrational energy level, rotational energy level and nuclear energy level but in spectroscopy mainly three energy level are important.

(i) Electronic energy level

(ii) Vibrational energy level

(iii) Rotational energy level

Energy Order: -



From the above figure it is clear that the electronic level of a molecule constructed with many quantised vibrational energy level and quantised rotational energy level.

UV-Spectroscopy: -

When a molecule absorb UV-visible radiation then the electronic transition takes place. The spectrum arises due to electronic transition ($n=0 \rightarrow n=1$) are known as UV-spectra.

The UV-spectroscopy is an example of absorption spectroscopy therefore it is also known as UV - absorption spectroscopy. UV-spectroscopy gives information either molecule are conjugated or nonconjugated.

Type of electronic transition: -

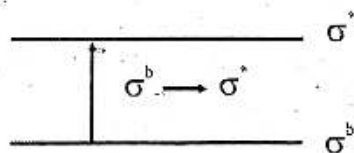
There are mainly four type of electronic transition -

(a) $\sigma \rightarrow \sigma^*$ transition: -

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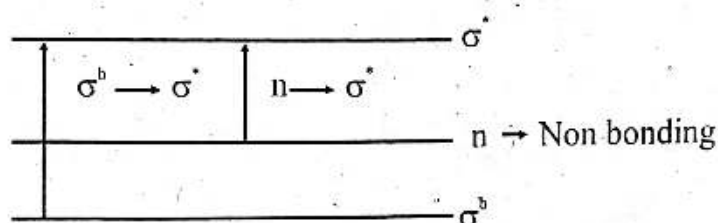
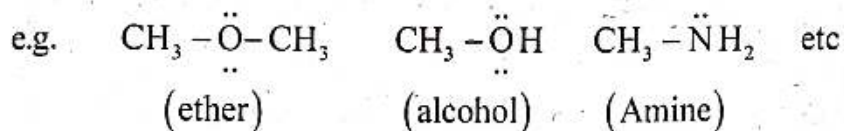
This type of transition occurs in alkanes. e.g. - CH_4 , $\text{CH}_3 - \text{CH}_3$, $\text{CH}_3 - \text{CH}_2 - \text{CH}_3$ etc.

Thus in other words we can say that the $\sigma - \sigma^*$ transition occurs in the saturated system.



(b) $n \rightarrow \sigma^*$ transition: -

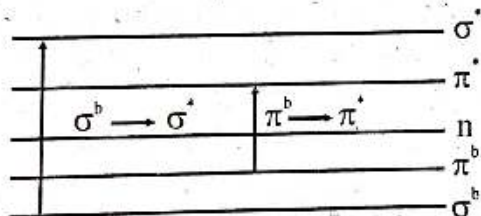
Saturated molecule having heteroatom shows $n \rightarrow \sigma^*$ transition transition as well as $\sigma \rightarrow \sigma^*$ transition.



(c) $\pi \rightarrow \pi^*$ transition: -

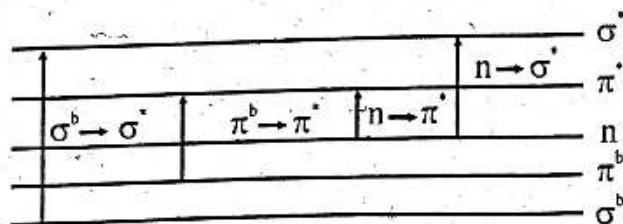
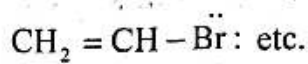
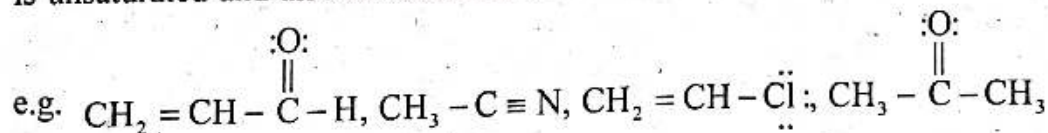
$\pi \rightarrow \pi^*$ transition occurs in unsaturated molecules.

e.g. $\text{CH}_2 = \text{CH}_2$, $\text{CH} \equiv \text{CH}$, $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$ etc.



(d) $n \rightarrow \pi^*$ transition: -

This type of electronic transition shows by those molecules which is unsaturated and also contained heteroatom.



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Decreasing order of energy: -

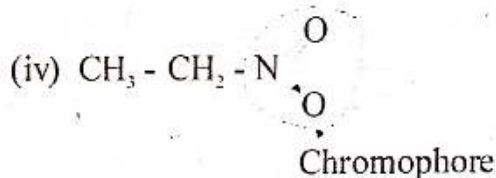
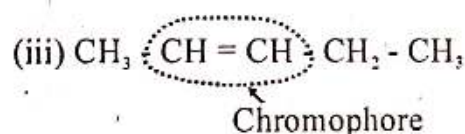
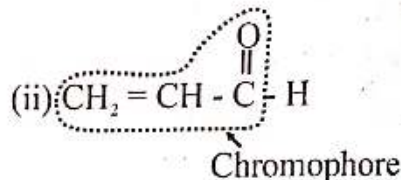
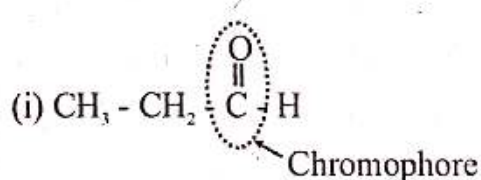
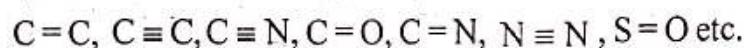


Q.1. Write the short notes on chromophore and auxochrome. (2019)

Ans. Chromophores: -

Chromophores are the groups or atoms which are responsible for the absorption of UV-visible light (UV-spectra) in molecules. Chromophores are the unsaturated groups.

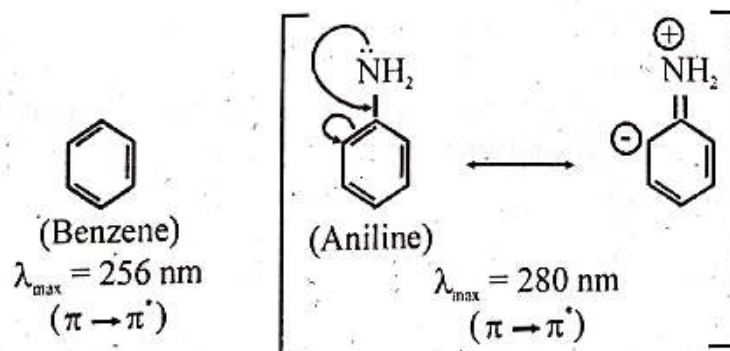
For example -



Auxochromes: -

Auxochromes are those groups or atoms which are not responsible for the absorption of UV - visible light but when they attached with the chromophores then the absorption position of an electronic transition shifted towards higher wavelength or lower wavelength.

e.g. -Cl, -Br, -I, -OH, -OCH₃, -NH₂, -NHMe, -SH etc.



Note -

Auxochromes shift the $\lambda_{\max}$ value of the molecules either by increasing conjugation or by decreasing conjugation. When auxochromes increase the conjugation the energy decrease and hence $\lambda_{\max}$ becomes increases.

$$\lambda_{\max} \propto \text{Extent of conjugation}$$

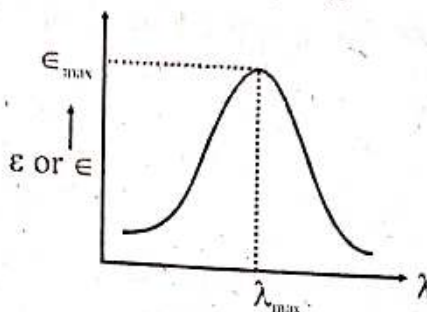
UV - Spectra graph plot: -

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UV-spectrum are plotted between molar absorptivity coefficient (ϵ) versus wavelength (λ) in which ϵ present on Y-axis and λ present on x-axis.

$$\epsilon \propto \frac{1}{\lambda} \Rightarrow \epsilon \propto A$$

A = absorbance

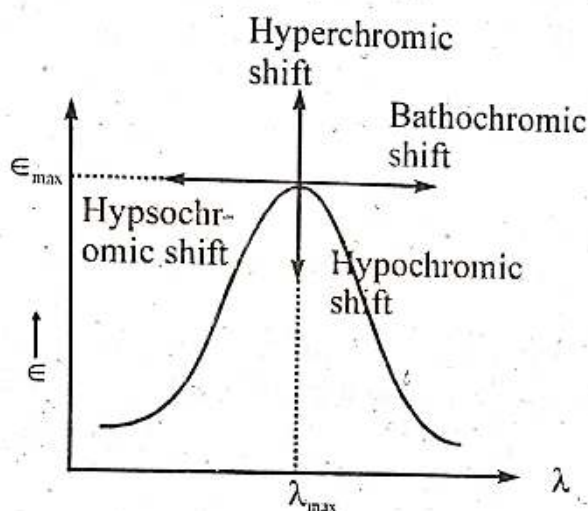


Shifts in UV-spectrum: -

There are four type of shifts in UV-spectra.

- (i) Bathochromic shift (Red Shift)
- (ii) Hypsochromic shift (Blue Shift)
- (iii) Hyperchromic shift
- (iv) Hypochromic shift

Since we well known that the UV-spectrum are plotted between molar absorptivity coefficient (ϵ) vurses wavelength (λ), as shown below -



Q.2. Write short note on Bathochromic shift.

(2014, 18)

Ans. Bathochromic Shift: -

The shifting of absorption position towards higher wavelength are called bathochromic shift. Bathochromic shift arises when the conjugation in the molecule increases. This shift is also known as the red shift.

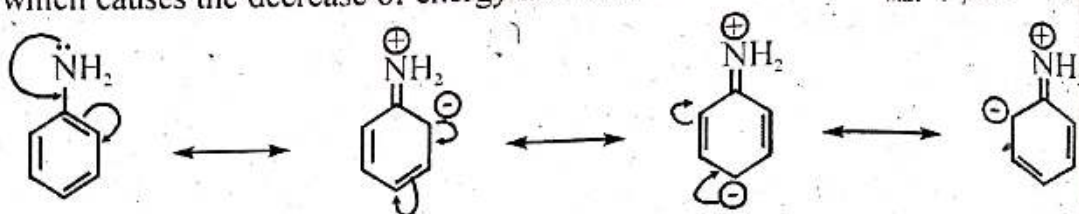
Ex. -



In the above example benzene shows the $\lambda_{max} = 256 \text{ nm}$ due to $\pi \rightarrow \pi^*$ transition. But in the case of Aniline the λ_{max} increases (i.e. $\lambda_{max} = 280 \text{ nm}$) due to the $n \rightarrow \pi^*$ transition. In the case of Aniline the extent of conjugation increases

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which causes the decrease of energy and thus increase in the $\lambda_{\max}$ value.

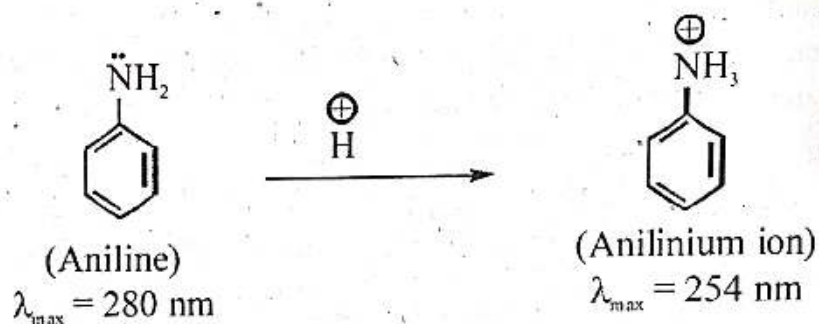


(2) Hypsochromic Shift: -

(2018)

The shifting of absorption position towards lower wavelength, are called hypsochromic shift. Hypsochromic shift are arises due decrease of conjugation. This shift is also known as blue shift.

Ex. -

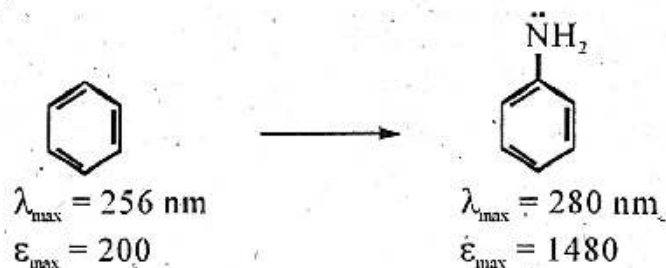


In the above example the extent of conjugation decrease in anilinium ion thus the energy increases and thus the $\lambda_{\max}$ decreases.

(3) Hyperchromic shift:-

The increase of $\epsilon_{\max}$ value of an absorption band are called hyperchromic shift. The $\epsilon_{\max}$ value also increase on increasing the conjugation.

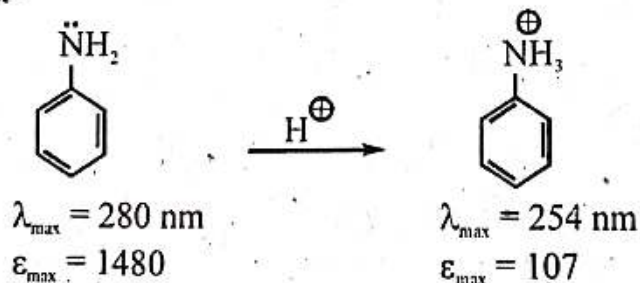
Example:-



(4) Hypochromic shift:-

The decrease of $\epsilon_{\max}$ value of an absorption band are called hypochromic shift.

Example:-



Q.3. Write note on factors on which $\lambda_{\max}$ depends. (2012, 14, 13, 17)

Ans. Factor affecting $\lambda_{\max}$ - value:-

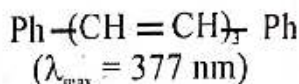
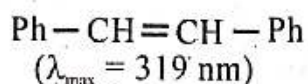
There are following factor which affect $\lambda_{\max}$ - value -

- (1) Resonance or Mesomeric effect (2) Hyperconjugation
(3) Steric effect (4) Hydrogen bonding (5) Solvent effect

(1) Resonance effect or Mesomeric effect:-

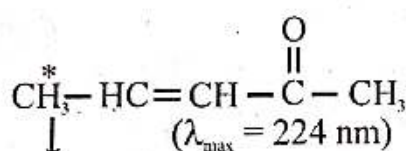
When the resonance increase then the extent of conjugation increases, thus the energy decrease and $\lambda_{\max}$ become increases. i.e. bathochromic shift.

Example:-

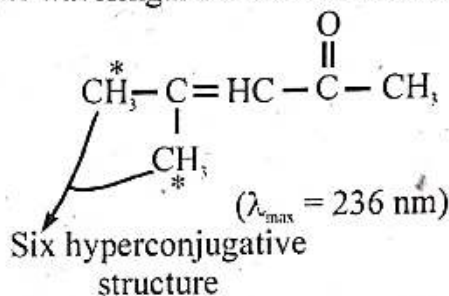


(2) Hyperconjugation:-

Hyperconjugation also increase the extent of conjugation in the molecules so the $\lambda_{\max}$ - value shifted towards higher wavelength i.e. bathochromic shift.



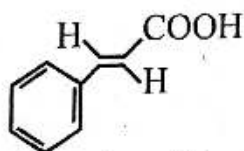
Three hyperconjugative structure



(3) Steric effect:-

Steric hindrance on the molecules decreases the extent of conjugation so the energy increases and $\lambda_{\max}$ become decreases.

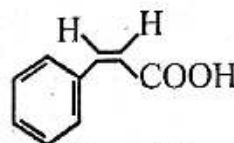
Example:-



(Trans cinnamic acid)

$$\lambda_{\max} = 272 \text{ nm}$$

$$\epsilon_{\max} = 15,900$$



(Cis cinnamic acid)

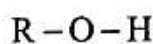
$$\lambda_{\max} = 268 \text{ nm}$$

$$\epsilon_{\max} = 10,700$$

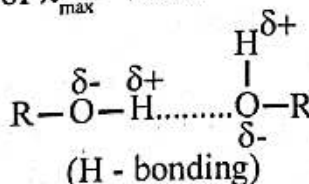
Cis cinnamic acid are more sterically hindered than the trans cinnamic acid.

(4) Hydrogen bonding:-

If hydrogen bonding in the molecules increases then electronegativity of the heteroatom increases which causes the decrease of polarity and increase of energy and thus decrease of $\lambda_{\max}$ - value.



(Isolated)



(5) Solvent effect:-

In general on increasing the solvent polarity the $\pi \rightarrow \pi^*$ transition

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shows bathochromic shift i.e. towards the higher wavelength, whereas $n \rightarrow \pi^*$ transition shows hypsochromic shift i.e. towards lower wavelength.

Woodward-Fieser rule for calculating the $\lambda_{\max}$ - value:-

(Imp.)

(A) For conjugated dienes:-

Base value for transoid or hetroannular diene = 214 nm

Base value for cisoid or homoannular diene = 253 nm

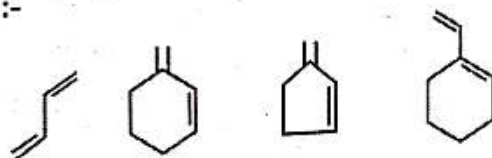
Add each substituent:-

Alkyl substituent or ring residue = 5 nm

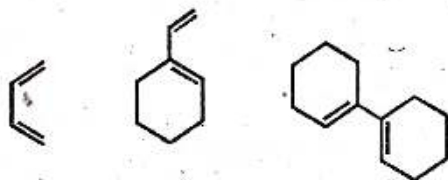
Exocyclic double bond = 5 nm

Extended double bond conjugation = 30 nm

Transoid:-

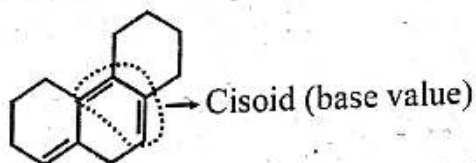


Cisoid:-

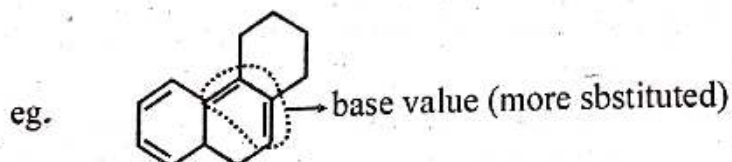


Base Value:-

1. Base value always contains two conjugated double bond.
2. Those conjugated diene treated as base value region which has largest $\lambda_{\max}$ value.
cisoid > transoid



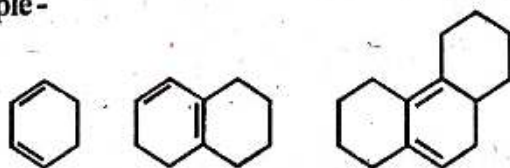
3. More substituted cisoid always treated as base value.



Homoannular and Hetroannular:-

When both conjugated double bond present in one ring are called homoannular.

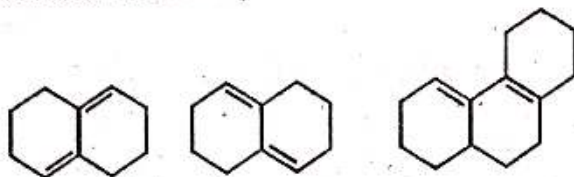
Example-



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when both conjugated double bond present in different ring are called heteroannular dienes.

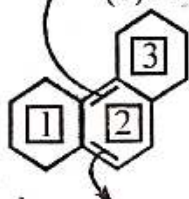
e.g.



Exocyclic double bond: -

Double bond which present on the terminal of the ring are called exocyclic double bond. Exocyclic double bond must be present in investigation region. e.g.

- (a) Exocyclic due to ring (1) and (3) (Because this double bond present on the terminal of both ring (1) and (3))



Exocyclic double bond due to ring (1) (Because double bond present on terminal of ring (1))

Thus total exocyclic double bond = 2 + 1 = 3.

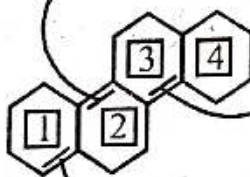
- (b) Exocyclic due to ring (1) (Because this double bond present on the terminal of ring (1)).



Exocyclic due to ring (2) (Because this double bond present on terminal of ring (2))

Total exocyclic double bond = 1 + 1 = 2

- (c) Exocyclic due to ring (1) and (3)

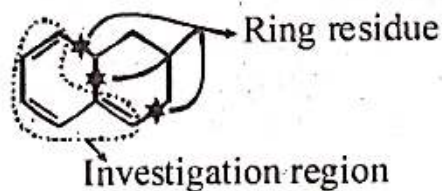
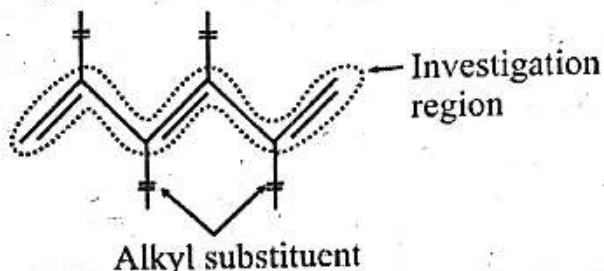


Exocyclic due to ring (2) and (4)

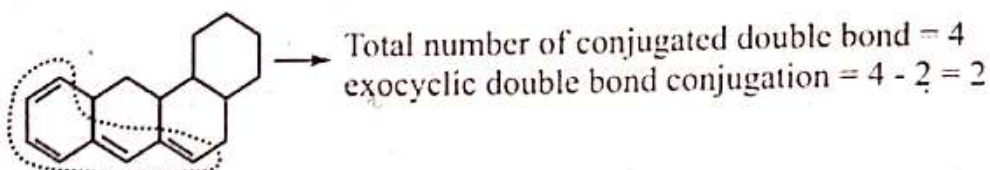
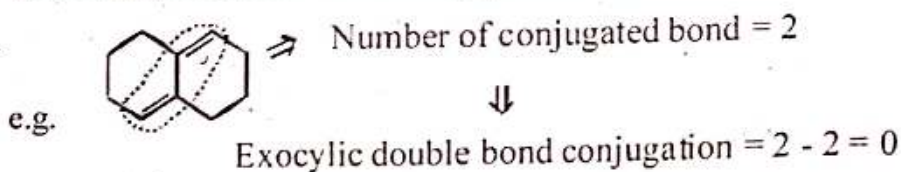
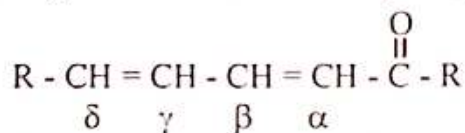
Exocyclic due to ring (2)

Total exocyclic double bond conjugation = 2 + 2 + 1 = 5

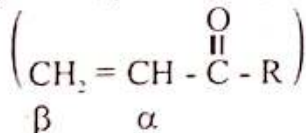
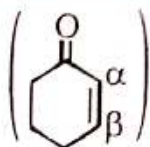
Alkyl substituent and ring residue: -



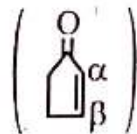
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Extended double bond conjugation:-If total number of conjugated double bond = n Then exocyclic double bond conjugation = $n - 2$ **(B) For α, β - unsaturated carbonyl compounds (Enones): -****Base value: -**

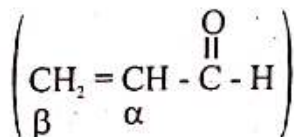
- Acyclic α, β - unsaturated ketone

Six membered α, β - unsaturated ketone } 215 nm

- Five membered cyclic α, β - unsaturated ketone = 202 nm



- α, β - unsaturated aldehyde = 207 nm

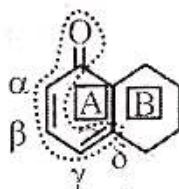
**Add to each: -**

- Alkyl substituent or ring residue at α - position = 10, β - position = 12, γ or higher = 18
- Exocyclic double bond = 5
- Extended double bond conjugation = 30

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- Homo annular dienes = 39

Example - Calculate the $\lambda_{\max}$ value of the following molecules



Sol. Base value for six member α, β - unsaturated ketone = 215 nm.

2 ring residue of δ - position = $18 \times 2 = 36$

1 - Exocyclic double bond due to ring (B) = 5

1 - extended double bond conjugation = 30

Homoannular diene = 39

Total $\lambda_{\max} = 215 + 36 + 5 + 30 + 39 = 325$ nm

Thus $\lambda_{\max}$ of above molecule = 325 nm.

R Spectroscopy (Infra-Red Spectroscopy)

When a molecule absorb IR (infra red) radiation then change in vibrational and rotational energy level takes place i.e. - The molecule become vibrated as well as rotated.

- IR-spectroscopy is an example of absorption spectroscopy.
- The IR-spectroscopy give the detail of structure of the compounds.
- IR-spectroscopy give information about the type of functional group present in the molecule. Because different functional group have different absorption in IR-frequency.
- IR-spectra are plotted between % of transmittance and wave number.

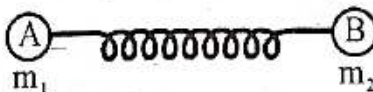
Vibrational frequency: -

The vibrational frequency of a bond can be calculated by Hook's law -

$$\nu = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$$

where K = force constant (bond strength), μ = reduce mass, ν = vibrational frequency

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$



Thus from above formula it is clear that the vibration frequency are depend upon following three factors -

1. Strength of bond (K): -

Vibrational frequency is directly proportional to strength of the bond (K).

i.e. $\nu \propto K$

2. Mass of the atom present in molecules: -

Vibrational frequency is inversely proportional to the reduced mass.

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i.e.
$$v \propto \frac{1}{\mu}$$

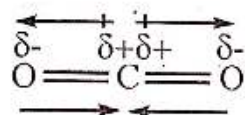
3. Arrangement of atom with in the molecules.

Selection rule: -

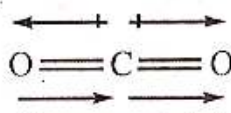
"IR-active molecules are those molecules which have a permanent dipole moment or change in dipole moment."

IR-radiation absorb by the molecules due to interaction of dipole of molecule and electric vector component of the IR-radiation. In other words only those vibrations are IR-active by which the dipole moment of the molecules become change.

For example, symmetrical stretching of CO₂ molecule is the IR-inactive because during stretching dipole moment does not change.



Symmetrical
stretching
(IR - inactive)



Unsymmetrical
stretching
(IR active because dipole moment
change during stretching)

Degree of freedom:-

The sum of the co-ordinate to locate the atom within the molecules in space are called degree of freedom. Each atom has three degree of freedom corresponds to three co-ordinate axes x, y and z.

Thus a molecule containing "n-atom" have total number of degree of freedom is "3n".

• For non-linear molecules:-

Translational degree of freedom = 3

Rotational degree of freedom = 3

Vibrational degree of freedom = 3n - 6

• For linear molecules:-

Translational degree of freedom = 3

Rotational degree of freedom = 2

Vibrational degree of freedom = 3n - 5

Molecular vibrations:-

Since we know that absorption of IR-radiation by molecules causes change in the vibrational as well as rotational energy levels.

Here two type of vibrations are possible-

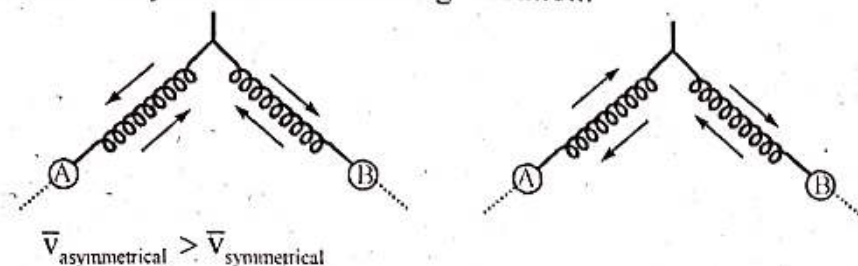
1. Stretching vibration
2. Bending vibration

1. Stretching vibration:-

In stretching vibration the motion of atom takes place along the bond axis. Thus during the stretching vibration the bond length of the molecule increases.

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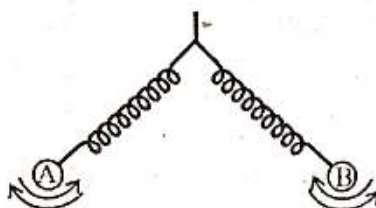
There are two type of stretching vibrations i.e. symmetrical stretching vibration and unsymmetrical stretching vibration:



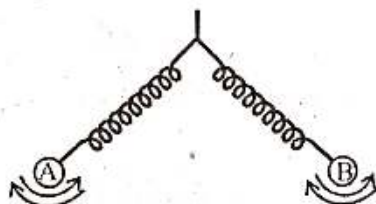
2. Bending vibration:-

In bending vibration, the position of an atom changes with respect to the original bond axis i.e. perpendicular to the bond axis. Here in this case no change in the bond length of molecules but the bond angle may be changes. Bending vibrations are of four type-

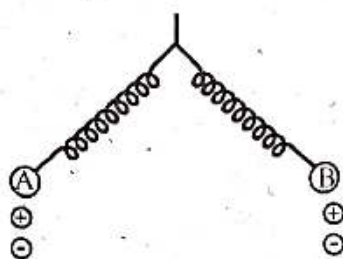
1. Scissoring:-



2. Rocking:-



3. Wagging:-

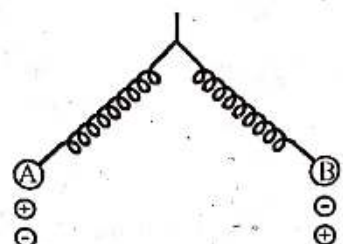


Where -

⊕ = Above the plane

⊖ = Below the plane

4. Twisting:-



Where -

⊕ = Above the plane

⊖ = Below the plane

Q.4. Write note on factors affecting Vibrational frequencies.

(2012, 15, 17, 19)

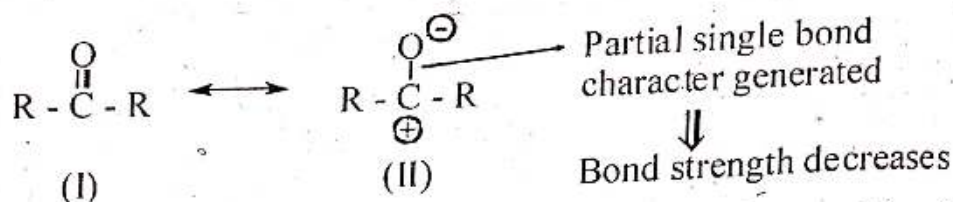
Ans. Factor affecting vibrational frequency:-

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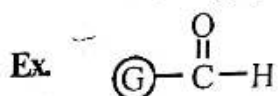
- (I) Inductive effect
(III) Hydrogen bonding
(V) Field effect

- (II) Mesomeric effect or Resonance effect
(IV) Steric effect
(VI) Size of ring

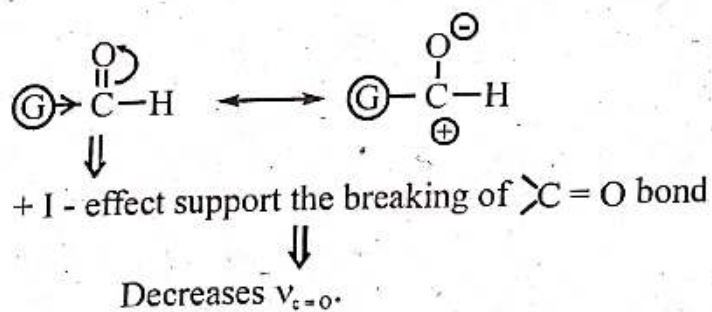
(I) Inductive effect:-



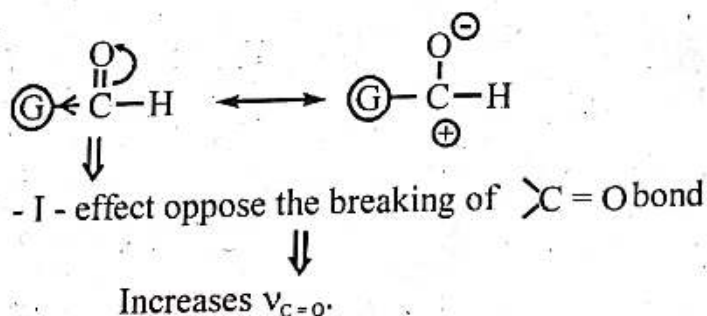
Carbonyl compound shows two type of resonating structure (I) and (II). Hence in this case the bond strength from (I) → (II) decreases therefore the (I) resonating structure contains more $\nu_{\text{C=O}}$ than the structure (II). In other words we can say that if any factor causes the breaking of >C=O double bond will decrease the $\nu_{\text{C=O}}$. Let us explain with some example.



Case (i) - When G is + I group.

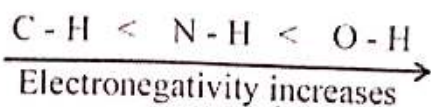


Case (ii) - When G is - I group.



Vibrational frequency also depends the electronegativity of the atom. The increase of electronegativity causes the increase of bond strength hence stretching frequency increases.

Ex -



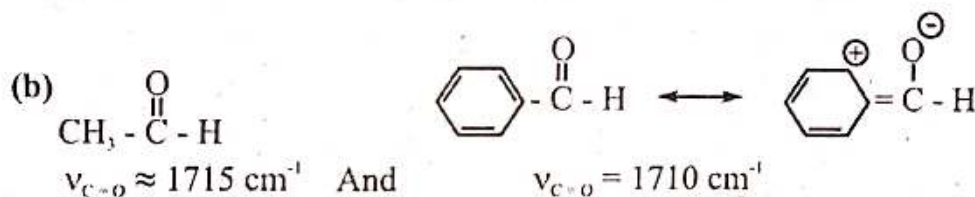
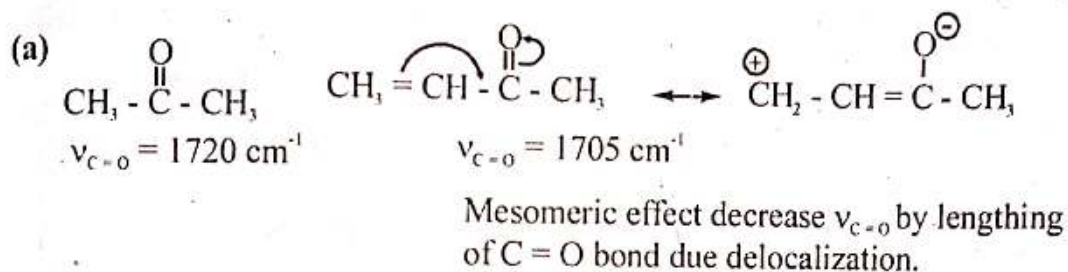
$\downarrow$
Bond strength also increases

$\downarrow$
Stretching frequency also increases

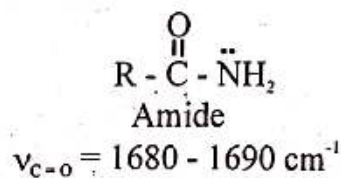
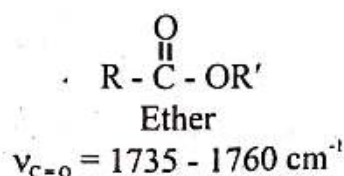
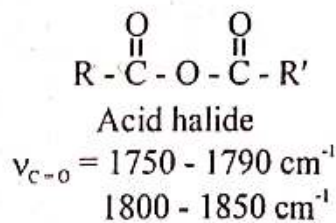
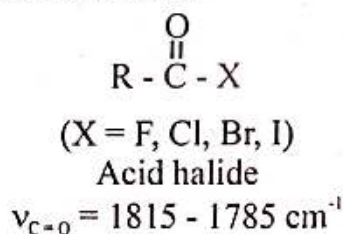
(II) Resonance or mesomeric effect: -

Mesomeric or resonance effect decrease the stretching frequency due to delocalization of multiple bond.

Ex. -



$\nu_{\text{C}=\text{O}}$ of acid derivative: -



(III) Hydrogen bonding: -

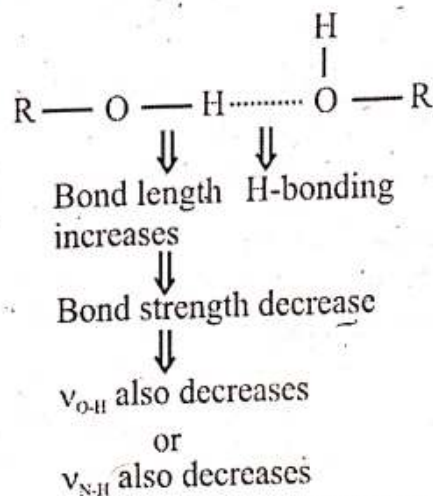
H-bonding also affect the stretching frequency of O-H and N-H bond. H-bonding increase the bond length of O-H and N-H bond and decreases the bond strength. Thus stretching frequency of O-H and N-H bond also decreases.

Note: -

- Stronger the H-bonding, greater is the lowering in vibrational frequency of O-H and N-H bond.

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- IR-technique is the best technique which explain intermolecular H-bonding and intramolecular H-bonding present in the molecules.



Free O-H group

$$\nu_{\text{O-H}} = 3350 - 3650 \text{ cm}^{-1}$$

Free N-H group

$$\nu_{\text{N-H}} = 3400 - 3500 \text{ cm}^{-1}$$

H-bonded N-H group

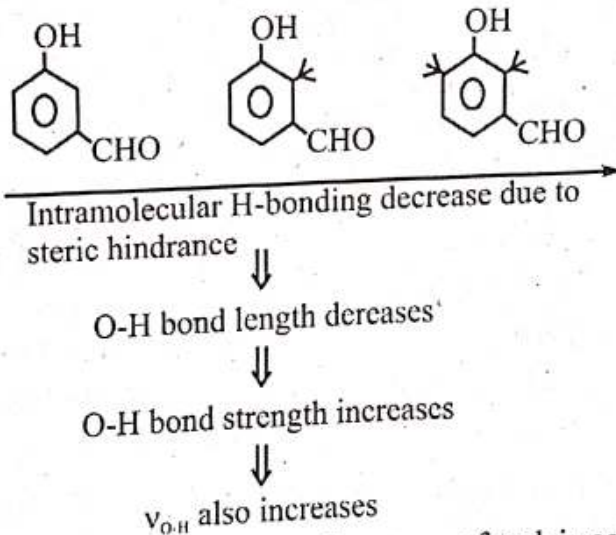
$$\nu_{\text{O-H}} = 3350 - 3500 \text{ cm}^{-1}$$

H-bonded N-H group

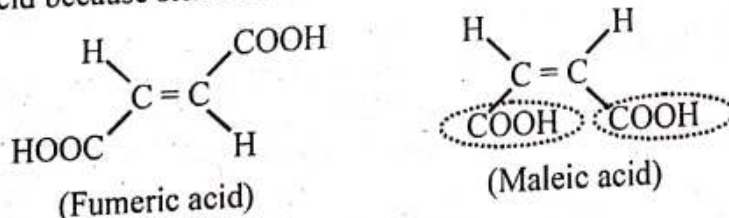
$$\nu_{\text{O-H}} = 3250 - 3400 \text{ cm}^{-1}$$

(IV) Steric effect: -

Steric effect also affect vibrational frequency either by decreasing H bonding or decreasing conjugation.

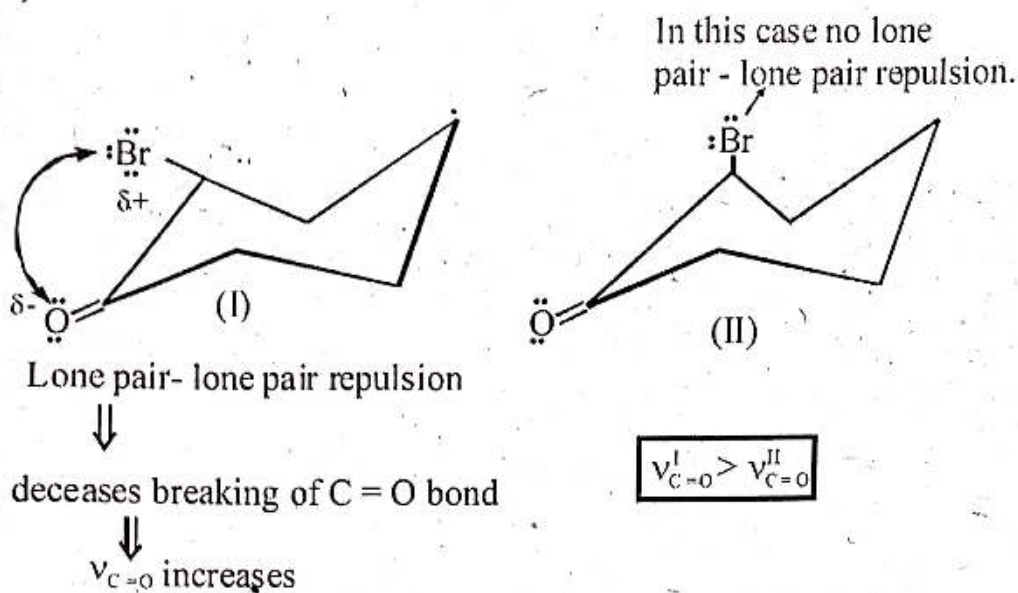


Ex. - C = C double bond strengthening frequency of maleic acid is more than fumaric acid because steric hindrance decrease $\nu_{\text{O-H}}$ frequency.



$$\nu_{\text{C}=\text{C}}^{\text{F}} < \nu_{\text{C}=\text{C}}^{\text{M}}$$

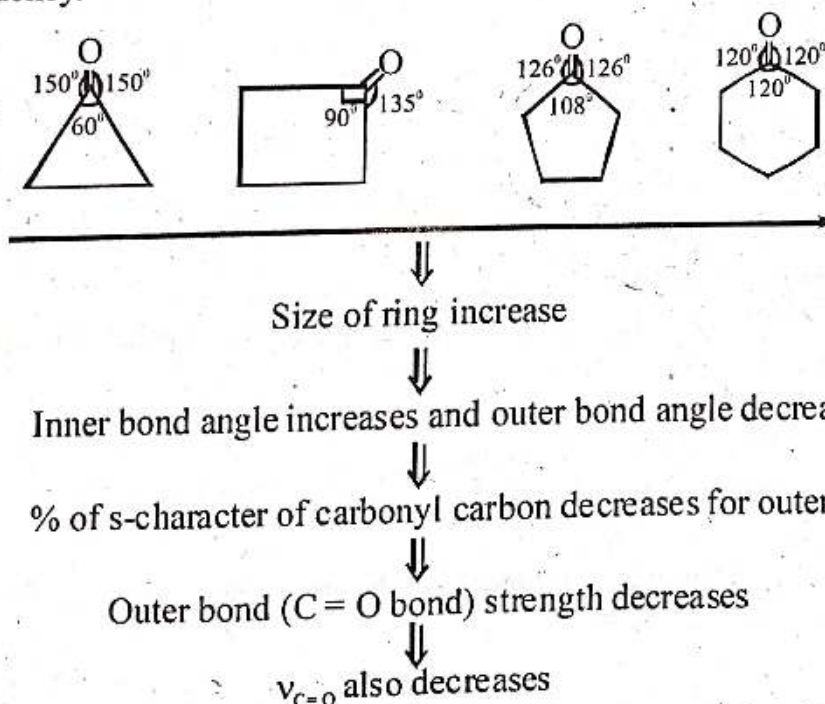
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(V) Field effect: -**(VI) Size of ring: -**

We well know that % of s-character is directly proportional to the bond angle.

$$\% \text{ of s - character} \propto \text{Bond angle}$$

Generally the decrease of ring size cause to the increase of $\nu_{C=O}$ stretching frequency.

**Examination of an IR-spectrum: -**

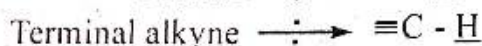
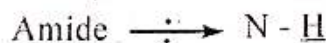
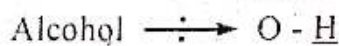
An IR-spectrum consist of two region -

- (1) Functional group region (4000 cm^{-1} - 1500 cm^{-1}).
- (2) The finger print region (1500 - 667 cm^{-1})

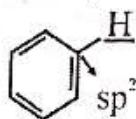
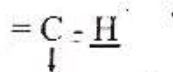
(1) Function group region: -

- (i) 3600 - 3200 cm^{-1} -

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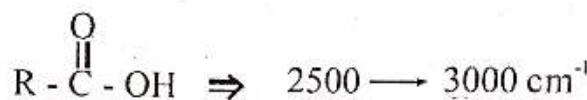
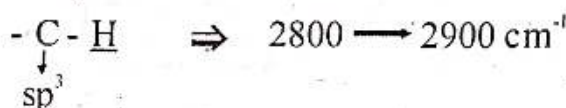


(ii) 3200 - 3000 cm^{-1} -

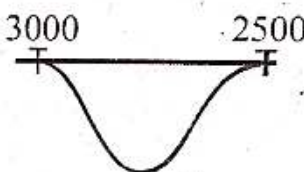


C-H stretching frequency

(iii) 3000 - 2500 cm^{-1} -

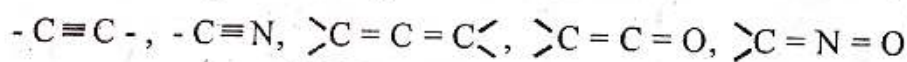


Carboxylic acid



(iv) 2300 - 2100 cm^{-1} -

This shows triple bond region



Cummulative system

(v) 1900 - 1680 cm^{-1} -

This region shows double bond region.

- All $\nu_{\text{C=O}}$ of aldehyde, ketone, ester, amide, anhydride, acid halide, lactone, lactam, carboxylic acid.

(vi) 1750 - 1500 cm^{-1} -

All $\nu_{\text{C=C}}$ of alkene and arynes.

- In this region all C = C stretching frequency of alkenes and arynes occurs.
- Some C = C stretching frequency of benzene region goes to fingerprint region (1460 - 1500 cm^{-1}).

(2) Fingerprint region: -

- Fingerprint region is not very important region because this is highly dense region.
 - The region between 1500 - 667 cm^{-1} is called fingerprint region because every compound has unique absorption pattern in this region.
- All single bond stretching frequency also occurs in this region (except C

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- H, N - H, Ph - H etc.)

(I) $1500 - 1350 \text{ cm}^{-1}$:-

tertiary butyl group = 1380, 1365

Gem dimethyl = 1380 cm^{-1} .

(II) $1300 - 100 \text{ cm}^{-1}$ - In this range C - C single bond and C - O single bond lies. For example the $\nu_{\text{C-O}}$ of alcohol, ether, ester, lactone, acid anhydride lies in this frequency range.

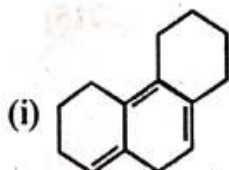
(III) Below 1000 cm^{-1} - This region is very useful in identifying the type of substitution on aromatic ring

(A) A strong band $770 - 730 \text{ cm}^{-1}$ shows monosubstitution.

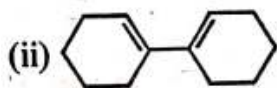
(B) Ortho and para disubstituted compounds show one band each ($735 - 700 \text{ cm}^{-1}$ ortho and $800 - 860 \text{ cm}^{-1}$ for para).

(C) Meta disubstituted compounds are recognised by two medium bands in the region of $850 - 710 \text{ cm}^{-1}$.

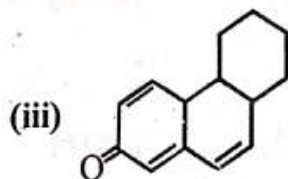
Q.5. Calculate λ_{max} of given compounds by the use of Woodward-Fieser rule:



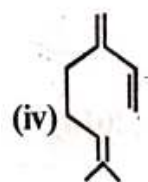
(2011, 14, 17)



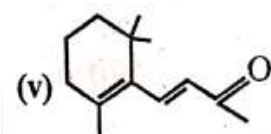
(2011)



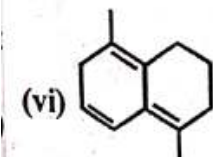
(2011, 12, 14, 17)



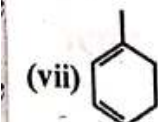
(2011)



(2012)

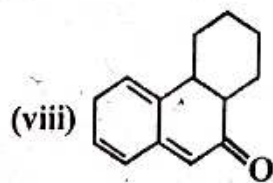


(2013)

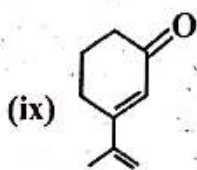


(2013)

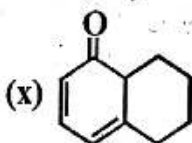
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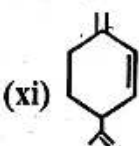
(2013)



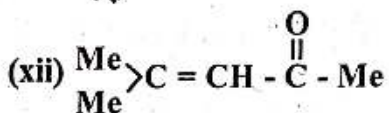
(2013)



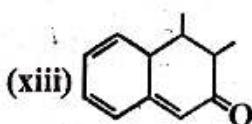
(2014)



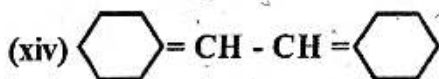
(2015)



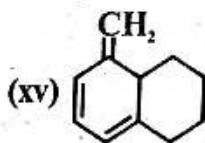
(2015)



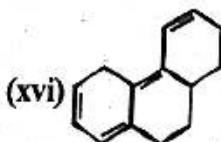
(2015)



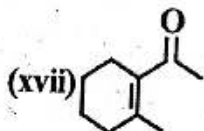
(2015)



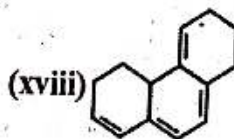
(2016)



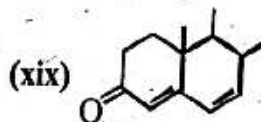
(2018)



(2018)



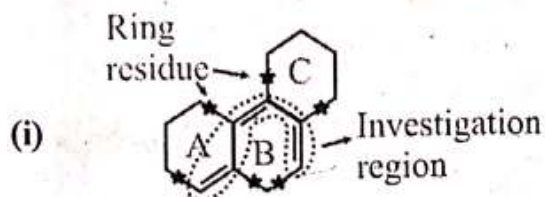
(2019)



(2019)

Ans.

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cisoid, base value = 253 nm.

six ring residue = $6 \times 5 = 30$

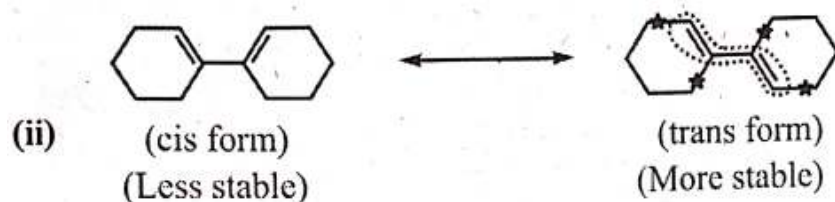
One exocyclic double bond to ring A = 5 nm

One exocyclic double bond to ring B = 5 nm

Two exocyclic double bond to ring C = $2 \times 5 = 10$ nm

One extended double bond conjugation = 30 nm.

$$\lambda_{\max} = 333 \text{ nm}$$



Transoid, Base value = 214 nm

four ring residue = $4 \times 5 = 20$ nm

$$\lambda_{\max} = 234 \text{ nm}$$

(iii)

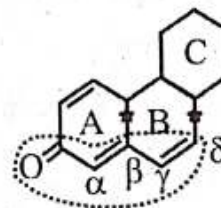
Six member enone, Base value = 215 nm.

one ring residue at β - position = 12 nm.

one ring residue at δ - position = 18 nm.

One exocyclic double bond to ring B = 5 nm.

One extended double bond conjugation = 30 nm.



$$\lambda_{\max} = 280 \text{ nm}$$

(iv)

Transoid, base value = 214 nm

one ring residue = 5 nm

$$\lambda_{\max} = 219 \text{ nm}$$

But observed $\lambda_{\max} = 224$ nm

(v) Acyclic α, β - unsaturated ketone, base value = 215 nm

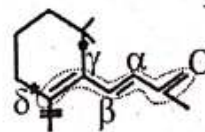
One ring residue at γ - position = 18 nm

One ring residue at δ - position = 36 nm

One alkyl substituent at δ - position = 18 nm

One extended double bond conjugation = 30 nm

$$\lambda_{\max} = 299 \text{ nm}$$



(vi) Transoid, base value = 214 nm

Two alkyl substituent = $2 \times 5 = 10$ nm.

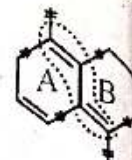
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Four ring residue = $4 \times 5 = 20$ nm.

One exocyclic double bond to ring A = 5 nm.

One exocyclic double bond to ring B = 5 nm.

$$\lambda_{\max} = 254 \text{ nm}$$



(vii) Cisoid, base value = 253 nm.

One alkyl substituent = 5 nm.

Two ring residue = $2 \times 5 = 10$ nm

$$\lambda_{\max} = 268 \text{ nm}$$



(viii) Six member enone, base value = 215 nm.

One ring residue at β -position = 12 nm

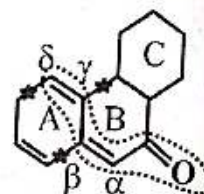
One ring residue at γ -position = 18 nm

One exocyclic double bond to ring A = 5 nm

One exocyclic double bond to ring B = 5 nm

One extended double bond conjugation = 30 nm

$$\lambda_{\max} = 303 \text{ nm}$$



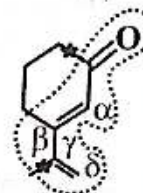
(ix) Six member enone, base value = 215 nm.

One ring residue at β -position = 12 nm.

One ring residue at γ -position = 18 nm

One exocyclic double bond conjugation = 30 nm

$$\lambda_{\max} = 275 \text{ nm}$$



(x) Six member α, β - unsaturated ketone (enone), base value = 215 nm

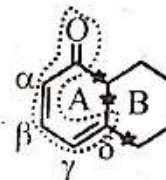
Two ring residue at δ -position = $2 \times 18 = 36$ nm.

Exocyclic double bond to ring n = 5 nm.

One extended double bond conjugation = 30 nm

Homoannular diene = 39

$$\lambda_{\max} = 325 \text{ nm}$$



(xi) Transoid, base value = 214 nm

Two ring residue = $2 \times 5 = 10$ nm

One exocyclic double bond = 5 nm

$$\lambda_{\max} = 229 \text{ nm}$$

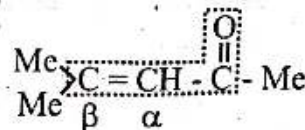


(xii) Acyclic α, β - unsaturated ketone,

base value = 215 nm

Two Alkyl substituent at β - position = 24 nm

$$\lambda_{\max} = 239 \text{ nm}$$

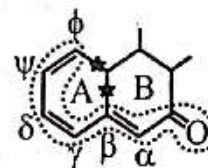


(xiii) Six member enone, base value = 215 nm

one ring residue at β - position = 12 nm

one ring residue at ϕ - position = 18 nm

one exocyclic double bond to ring A = 5 nm



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Two extended double

$$\text{bond conjugation} = 30 \times 2 = 60 \text{ nm}$$

$$\lambda_{\text{max}} = 310 \text{ nm}$$

(xiv) Transoid, base value = 214 nm

$$\text{Four ring residue} = 4 \times 5 = 20 \text{ nm}$$

Two exocyclic double bond at ring

$$\text{A and B} = 5 \times 2 = 10 \text{ nm}$$

$$\lambda_{\text{max}} = 244 \text{ nm}$$

(xv) Cisoid, base value = 253 nm

$$\text{Three ring residue} = 3 \times 5 = 15 \text{ nm}$$

One exocyclic double bond at ring B = 5 nm

One exocyclic double bond at ring A = 5 nm

One extended double bond conjugation = 30 nm

$$\lambda_{\text{max}} = 308 \text{ nm}$$

(xvi) Cisoid, base value = 253 nm

$$\text{five ring residue} = 5 \times 5 = 25 \text{ nm}$$

One exocyclic double bond to ring A = 5 nm

One exocyclic double bond to ring B = 5 nm

Two extended double bond conjugation = $2 \times 30 = 60 \text{ nm}$

$$\lambda_{\text{max}} = 348 \text{ nm}$$

(xvii) enone (ketone) base value = 215 nm

one ring residue at α - position = 10 nmOne ring residue at β position = 12 nmOne alkyl substituent at β -position = 12 nm

$$\lambda_{\text{max}} = 249 \text{ nm}$$

(xviii) Cisoid, base value = 253 nm

$$\text{five ring residue} = 5 \times 5 = 25 \text{ nm}$$

one exocyclic double bond to ring A = 5 nm

one exocyclic double bond to ring B = 5 nm

one exocyclic double bond to ring C = 5 nm

2 extended double bond conjugation = $2 \times 30 = 60 \text{ nm}$

$$\lambda_{\text{max}} = 353$$

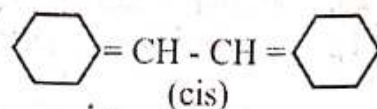
(xix) Six member enone (ketone) base value = 215 nm

One ring residue at β -position = 12 nmOne ring residue at δ -position = 18 nm

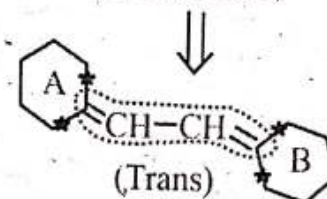
One exocyclic double bond to ring B = 5 nm

One extended double bond conjugation = 30 nm

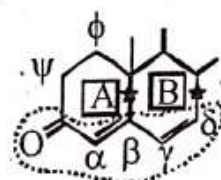
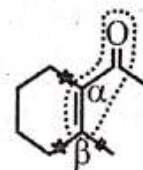
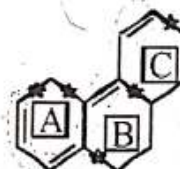
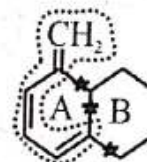
$$\lambda_{\text{max}} = 280 \text{ nm}$$



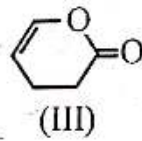
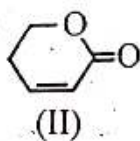
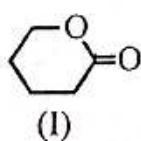
(Less stable)



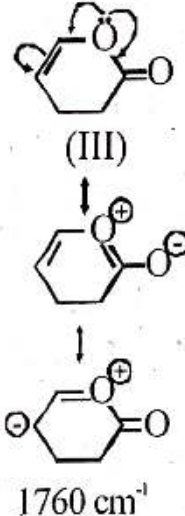
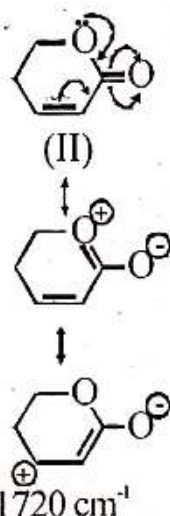
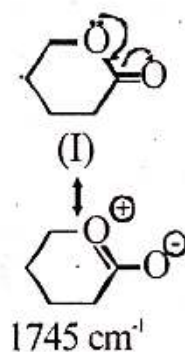
(More stable)



Q.6. The carbonyl stretching absorptions for the following lactones are 1720, 1745 and 1760 cm^{-1} . Match the absorption with appropriate structure and give reason for your choice. (2011, 14, 17)



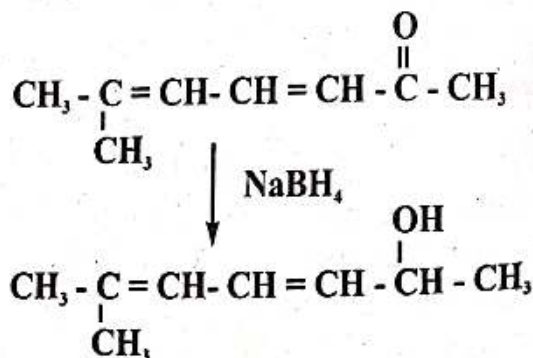
Ans.



Lactone (II) [cyclic ester] shows minimum $\nu_{\text{C=O}}$ stretching frequency because >C=O bond present in conjugation with both lone pair of oxygen atom and C=C double bond. Thus the bond order of >C=O become decreases.

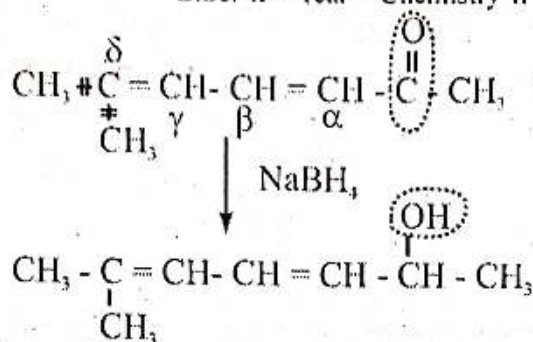
Lactone (III) shows maximum $\nu_{\text{C=O}}$ stretching frequency because out of three resonating structure, two resonating structure contains >C=O double bond and only one resonating structure contains >C-O single bond. Thus >C=O bond order in lactone (III) is maximum. Thus, $\nu_{\text{C=O}}$ stretching frequency order - (III) > (I) > (II)

Q.7. How can UV and IR spectroscopy be used to determine the completion of the following reaction - (2011, 14)



Ans.

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Explanation by UV - spectroscopy -

λ_{max} of reactant -

Acyclic α, β - unsaturated ketone, base value 215 nm

Two alkyl group on α - position = $2 \times 18 = 36$

one exocyclic double bond conjugation = 30 nm

$$\lambda_{\text{max}} = 281 \text{ nm}$$

λ_{max} of product: -

Base value = 214 nm

Three alkyl substituent = $3 \times 5 = 15 \text{ nm}$

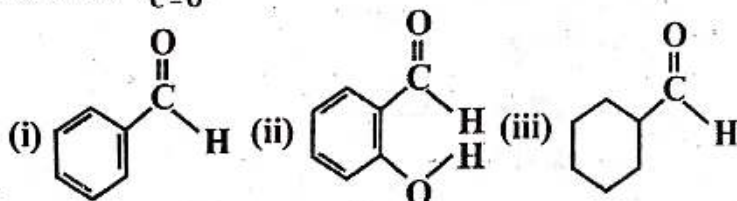
$$\lambda_{\text{max}} = 229 \text{ nm}$$

Thus during the reaction λ_{max} change from 281 nm to 229 nm.

Explanation by IR - spectroscopy: -

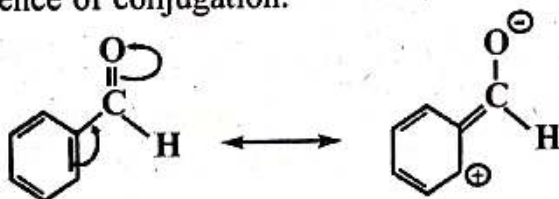
When carbonyl stretching frequency ($\nu_{\text{C=O}}$) become disappear and addition - OH stretching frequency ($\nu_{\text{O-H}}$) appears, this indicate the completion of reaction.

Q.8. Give reasons, arrange the following compound in decreasing order of their $\nu_{\text{C=O}}$. (2013, 17)

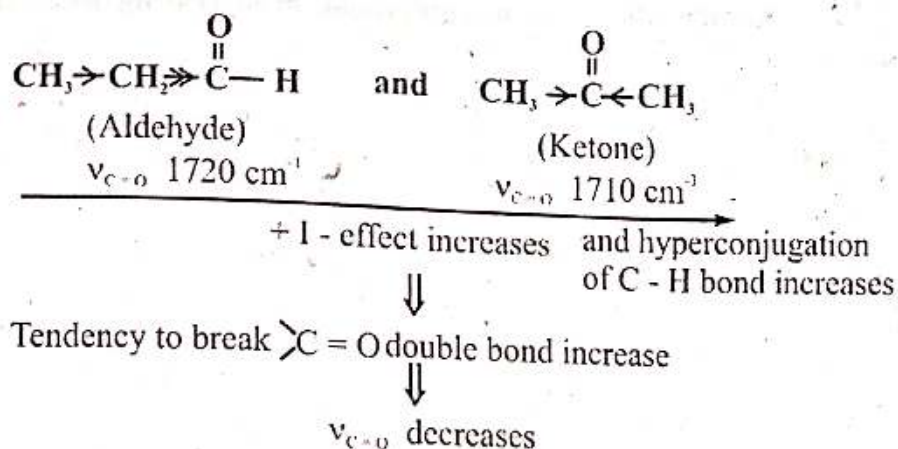


Ans. Decreasing order of $\nu_{\text{C=O}}$ -
(III) > (I) > (II)

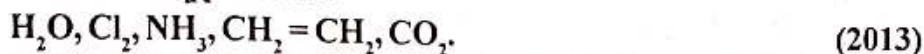
- Molecule (III) has more $\nu_{\text{C=O}}$ stretching frequency because there is no conjugation present in the molecule, so $\text{C}=\text{O}$ double bond character is more than other.
- Molecule (I) has less $\nu_{\text{C=O}}$ stretching frequency than molecule (III) due to presence of conjugation.



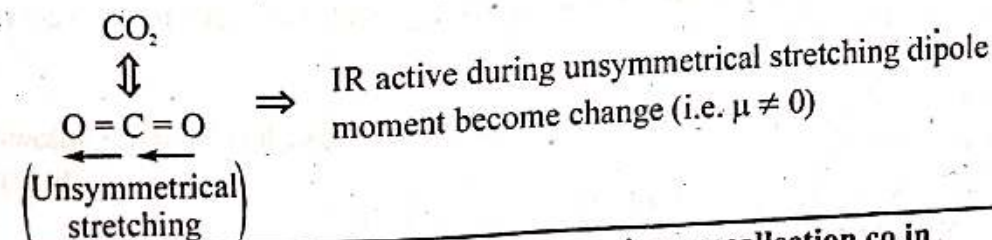
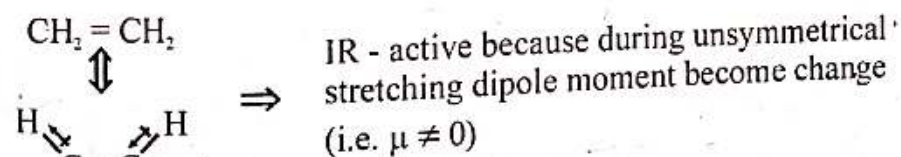
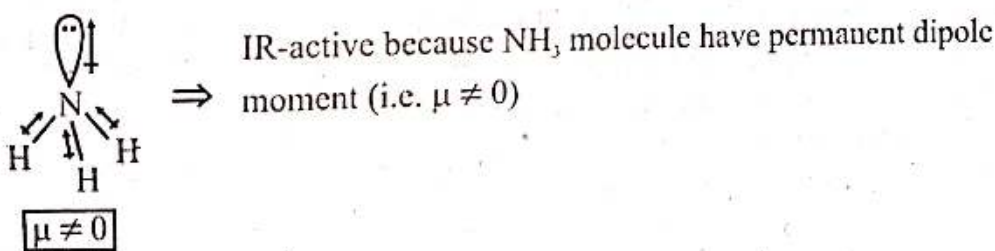
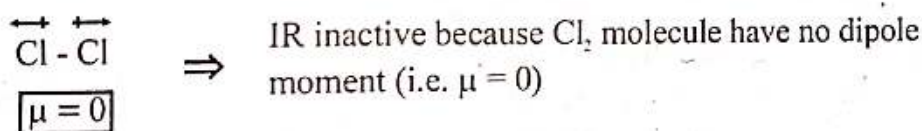
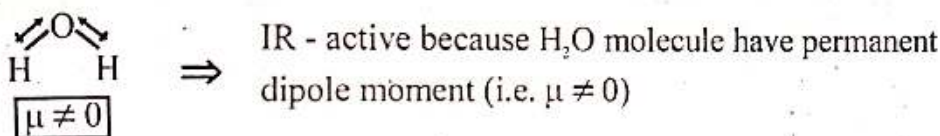
greater than that of ketone.



Q.11. Giving reasons, indicate which of the following molecules are IR active and which are IR inactive -

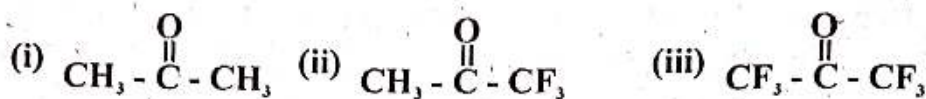


Ans. Those molecules which have permanent dipole moment are IR-active (i.e. $\mu \neq 0$).

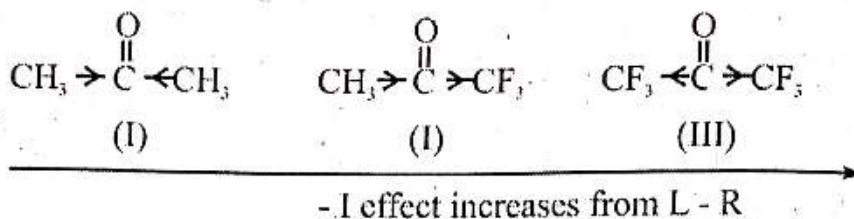


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Q.12. Arrange the following compounds in decreasing order of $\nu_{\text{max C=O}}$ frequency. (2014)



Ans.



$\Rightarrow$ double bond breaking tendency decreases.

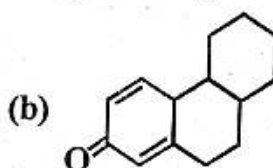
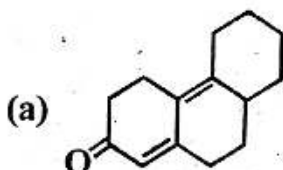
$\Rightarrow$ $\text{C}=\text{O}$ bond strength increases.

$\Rightarrow \nu_{\text{C=O}}$ increases.

Thus decreasing order of $\nu_{\text{C=O}}$ will be -

(III) > (II) > (I)

Q.13. Which of the following has a higher λ_{max} and why? (2015)



Ans. (a) Six member enone, base value = 215 nm.

one ring residue at β - position = 12 nm

one ring residue at γ - position = 18 nm

two ring residue at δ - position = $2 \times 18 = 36$ nm

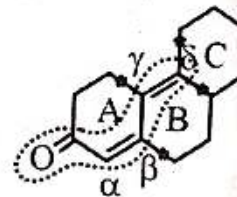
one exocyclic double bond at ring A = 5 nm

one exocyclic double bond at ring B = 5 nm

one exocyclic double bond at ring C = 5 nm

one extended double bond conjugation = 30 nm

$$\lambda_{\text{max}} = 326 \text{ nm}$$

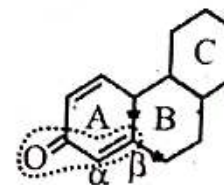


(b) Six member enone, base value = 215 nm

Two β -ring residue = $2 \times 12 = 24$ nm

One exocyclic double bond at ring B = 5 nm

$$\lambda_{\text{max}} = 244 \text{ nm}$$

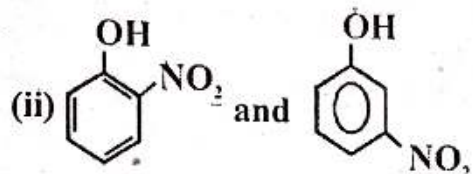


Thus the compound (a) has higher λ_{max} value (i.e. 326 nm) than compound (b) (i.e. 244 nm).

Q.14. Using IR spectroscopy, how will you distinguish each of the following pairs of compounds? (2015)



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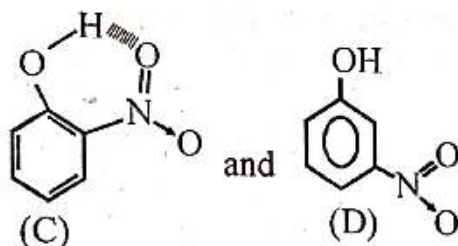


Ans. (i) $\text{CH}_3 - \text{CH}_2 - \text{C} \equiv \text{C} - \text{H}$ and $\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3$,
 (A) (B)

$$\nu_{\text{C-H}} \approx 3300 \text{ cm}^{-1}$$

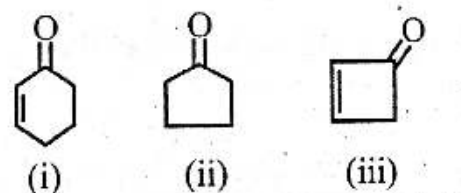
Alkyne (A) shows terminal $\equiv \text{C} - \text{H}$ stretching ($\nu_{\text{C-H}}$) frequency at 3300 cm^{-1} whereas this peak is absent in alkyne (B).

(ii) In molecule (C) - OH stretching frequency is less than the molecule (D) due to presence of intramolecular H-bonding.



Q.15. Which of the following compounds would give the lowest value of $\nu_{\text{C=O}}$ absorption frequency and why? (2018)

Ans.



Size of ring decreases from L - R

Inner bond angle decreases and outer bond angle increases

% of s-character of carbonyl carbon increases for outer bond

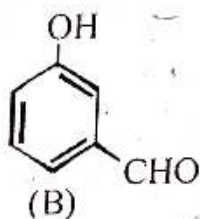
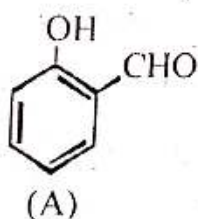
Outer bond ($\text{C} = \text{O}$ bond) stretching frequency increases

$\nu_{\text{C=O}}$ also increases

The compound (I) give lowest $\nu_{\text{C=O}}$ absorption frequency.

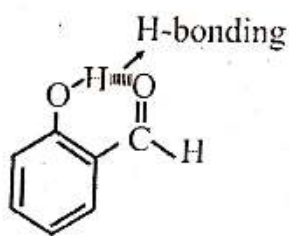
Q.16. How will you distinguish between compound (A) and (B) with the help of IR? (2018)

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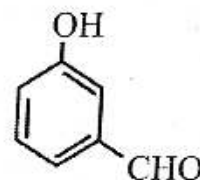


Ans. In Salicylaldehyde the IR absorption frequency of ν_{O-H} and $\nu_{C=O}$ shifted to lower frequency side because of intramolecular H-bonding. This change in the concentration does not cause any shift in ν_{O-H} and $\nu_{C=O}$ bands.

But in case of m-hydroxybenzaldehyde the intermolecular H-bonding is possible, so in this case also the IR absorption frequency of ν_{O-H} and $\nu_{C=O}$ shifted to lower frequency side but in this case on increasing the dilution the ν_{O-H} and $\nu_{C=O}$ band shifted to higher IR absorption frequency.

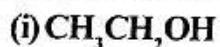


o - hydroxybenzaldehyde
(Salicylaldehyde)



m - hydroxybenzaldehyde

Q.17. How do you distinguish between the following pair of compounds on the basis of IR spectroscopy:



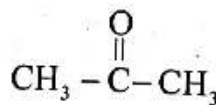
(2019)

Ans. In compound (I) IR absorption peak appears at 3600 cm^{-1} due to ν_{O-H} stretching frequency. But in compound (II) IR absorption peak appears at $1715-1725\text{ cm}^{-1}$ due to $\nu_{C=O}$ stretching frequency.



(I)

$(\nu_{O-H} = 3600\text{ cm}^{-1})$



(II)

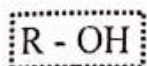
$(\nu_{C=O} = 1715-1725\text{ cm}^{-1})$

Chapter 2

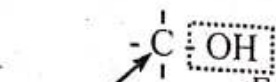
Alcohol

Introduction: -

Alcohols are those compounds which contains R-OH group, where R is an alkyl group or substituted alkyl group. The hydroxy group is attached through a saturated carbon.



General formula



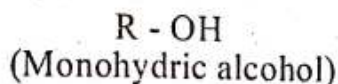
Saturated carbon

Functional group

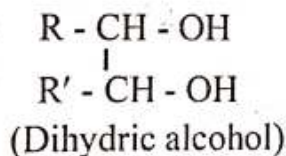
The hydroxy group (-OH) is the functional group of alcohols.

Classification of alcohols: -

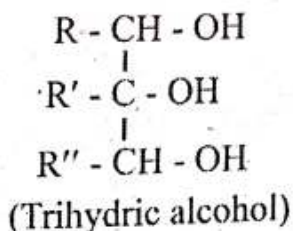
- Alcohols containing one hydroxyl group are called monohydric alcohols.
For example -



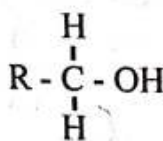
- Alcohol containing two hydroxyl group are called dihydric alcohols. For example -



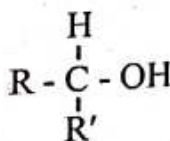
- Alcohol containing three hydroxyl group are called trihydric alcohols.



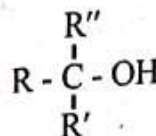
- Alcohol containing more than three hydroxyl group are called polyhydric alcohols.
- If carbon atom is designated in this manner that one, two or three substituent attached through it, then the alcohols are called as primary (1°), secondary (2°) or tertiary (3°) alcohols respectively.



Primary (1°) alcohol



Secondary (2°) alcohol



Tertiary (3°) alcohol

IUPAC Naming: -

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Prefix	+	root word	+	suffix - I	+	suffix II
Side chain		Number of carbon in main chain		Standard or unsaturated		Functional group

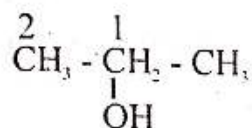
Alcohol, -OH	Suffix II, -O	Prefix hydroxy
--------------	---------------	----------------

→ Choose parent chain (larger, containing functional group)

→ Number of parent chain.

Preference order: - Suffix II > Suffix I > Prefix

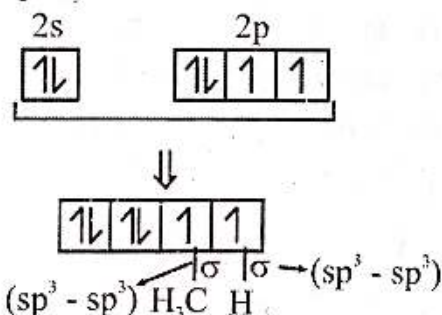
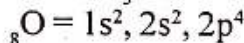
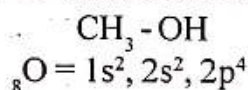
Example -



2- methyl, butanol - 1

Structure of alcohols: -

To understand the structure of alcohols, let us take an example -



The hybridization of oxygen atom in alcohol is sp^3 . The oxygen atom contains two bond pair and two lone pair of electron. Due to presence of lone pair of electron the shape of alcohol molecule is "Bent" or "V-shape."

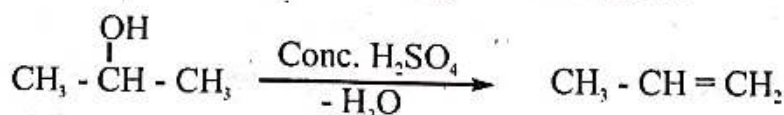


Q.1. Write short note on dehydration of alcohol.

(201)

Ans. Dehydration of Alcohol (Dehydration of monohydric alcohol): -

When alcohol treated with acid, gives alkene by elimination of water molecule. This reaction is known as dehydration reaction.



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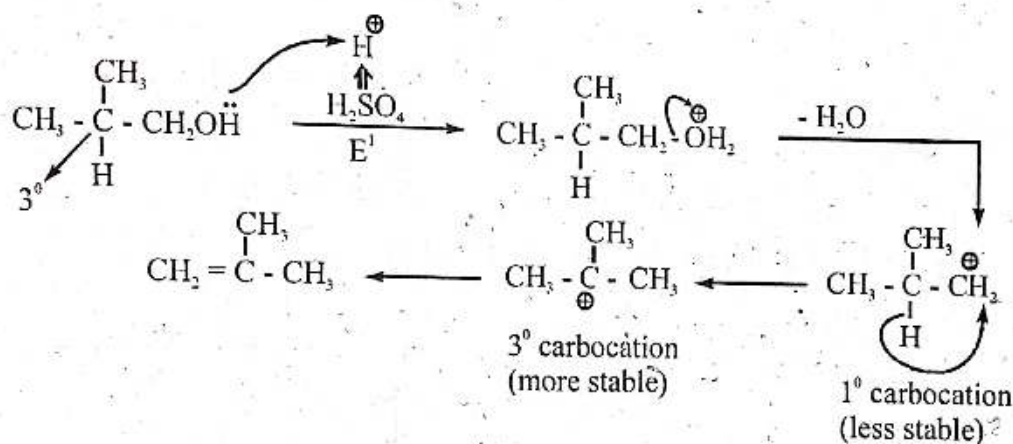
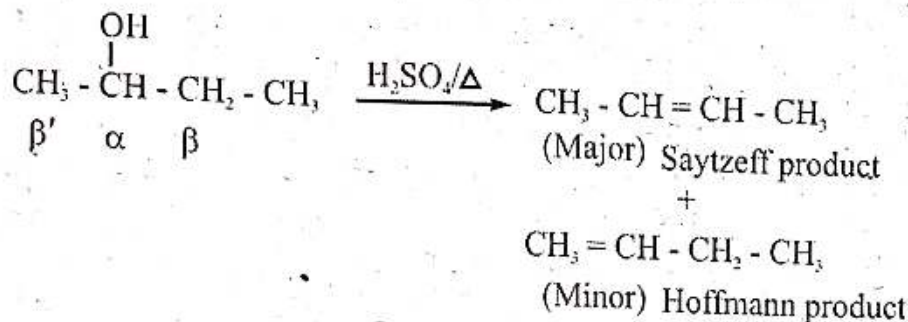
Alcohols undergoes elimination reaction either by E¹ - mechanism or E² - mechanism depending upon the structure of alcohols.

(1) All 2° and 3° - alcohols always gives E¹ - reaction.

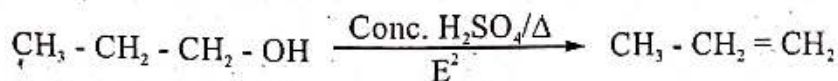
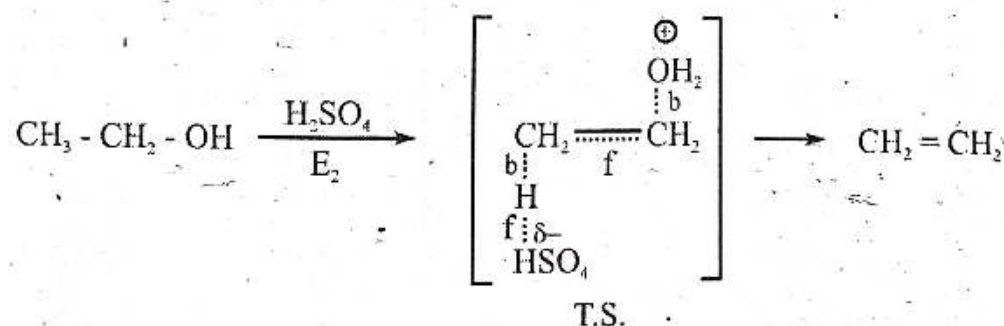
(2) All 1° - alcohol in which β-carbon is 3° or 4° also gives E¹-reaction.

Note -

When alcohol contains more than one type of β-hydrogen then Saytzeff product is formed as major product.



• 1° - alcohol of β - carbon is 1° or 2° gives E² - Rⁿ.

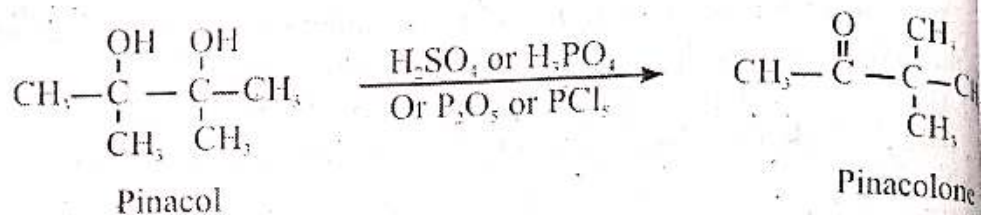
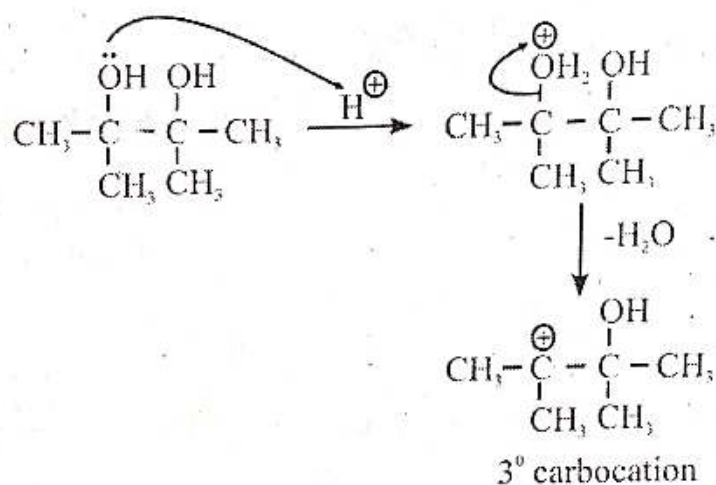
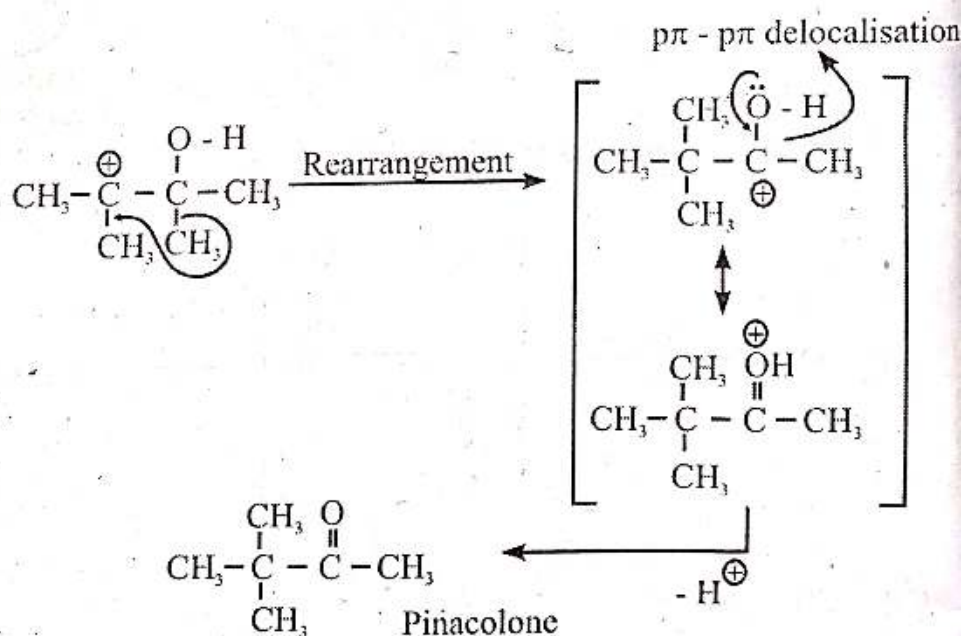


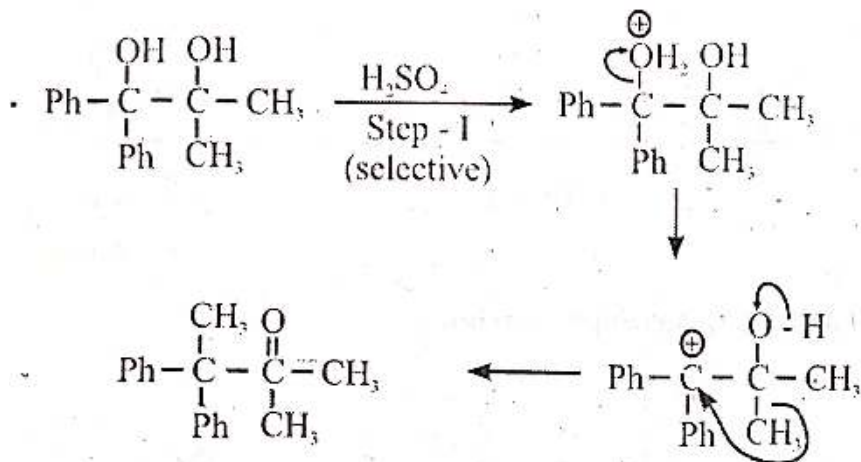
Reactivity order of alcohol towards dehydration: -
 $3^\circ > 2^\circ > 1^\circ$

Q.2. Write short note on Pinacol - Pinacolone rearrangement. (2017, 19)

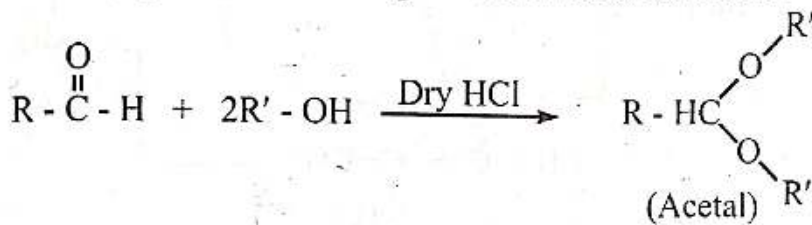
Ans. Pinacol - Pinacolone rearrangement:-

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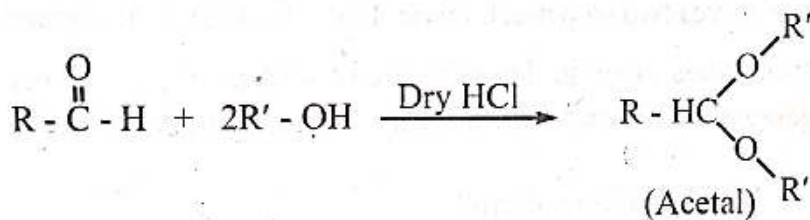
**Mechanism: -****Step I - Formation of stable carbocation.****Step II - Migration of group on cationic carbon.****Example -**



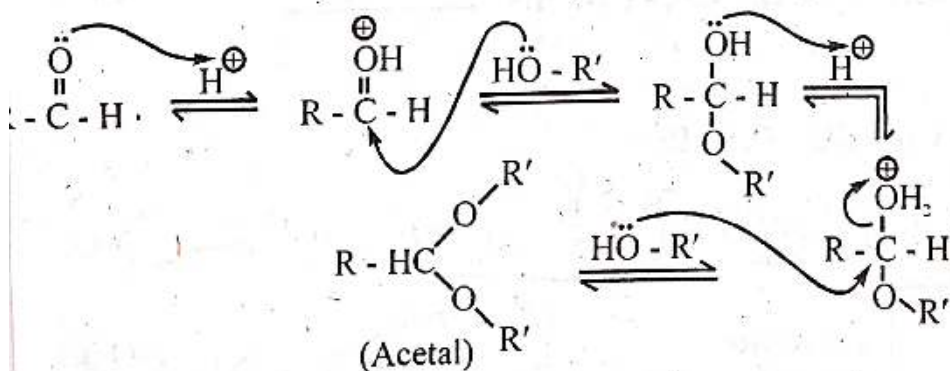
3. Complete the following reaction with mechanism? (2012)



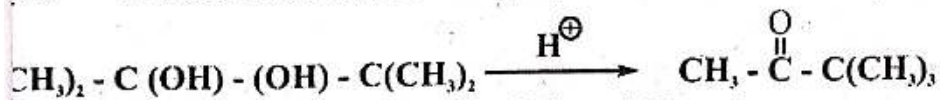
ns.



Mechanism: -

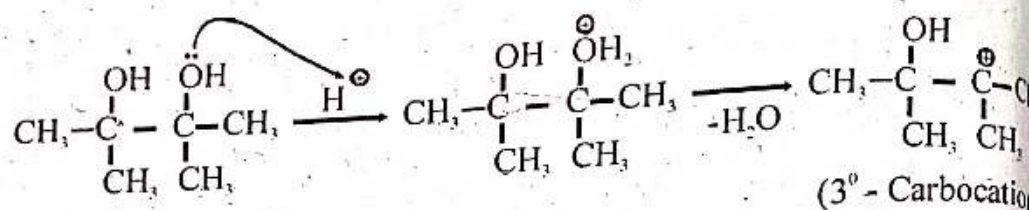


4. Give the mechanism of the given reaction: (2012, 14, 15)

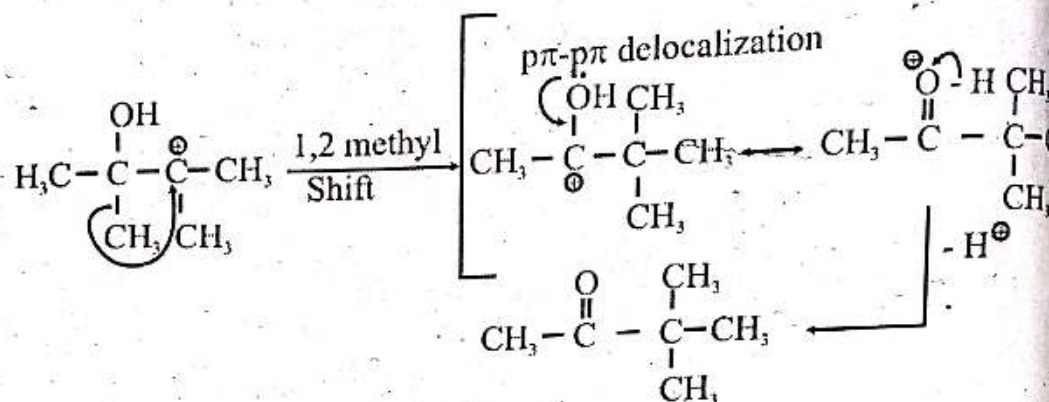


ns. This reaction is an example of Pinacol-Pinacolone rearrangement.

Step (I) Formation of stable carbonation -

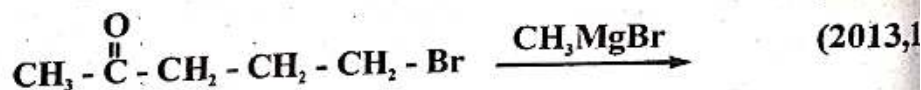


Step (II) Migration of group on cationic carbon -

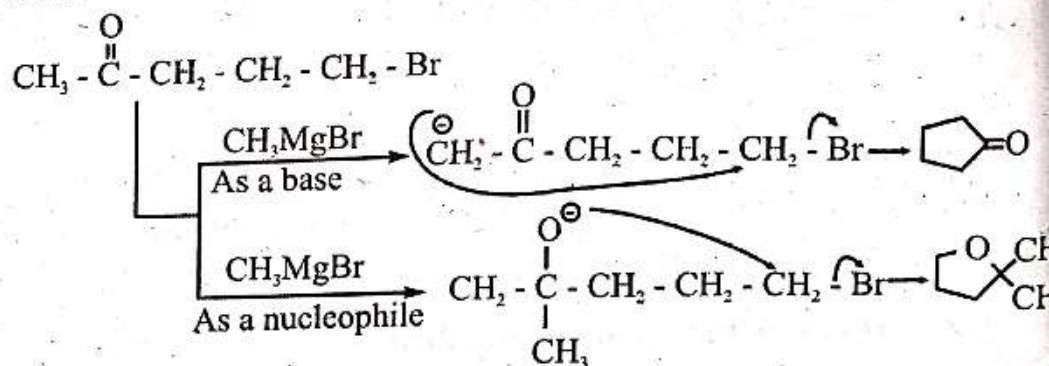


This reaction involves two step mechanism. In the first step, the formation of stable carbocation takes place in the presence of an acid (H^+). In second step, the rearrangement occurs and the formation of product takes place.

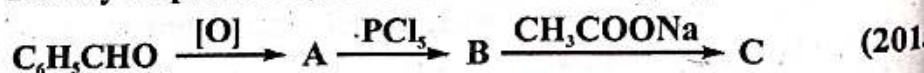
Q.5. Complete the following reaction -



Ans.

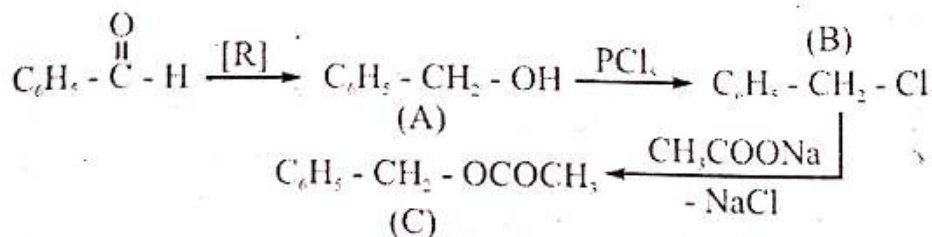


Q.6. Identify the product A, B and C in the following sequence of reaction

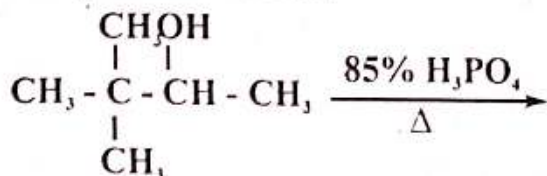


Ans.

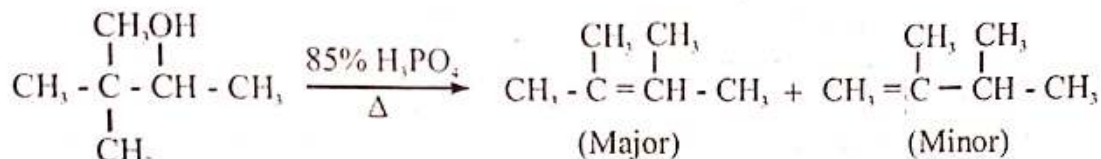
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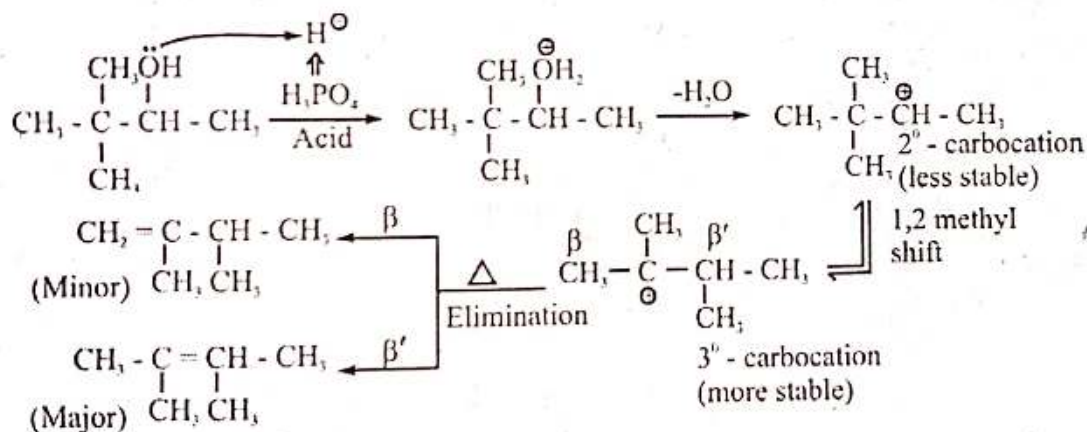
Q.7. Complete the reaction: (2015)



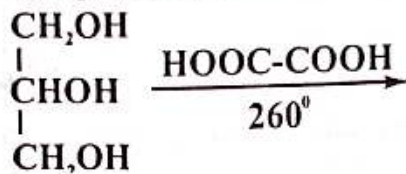
Ans.



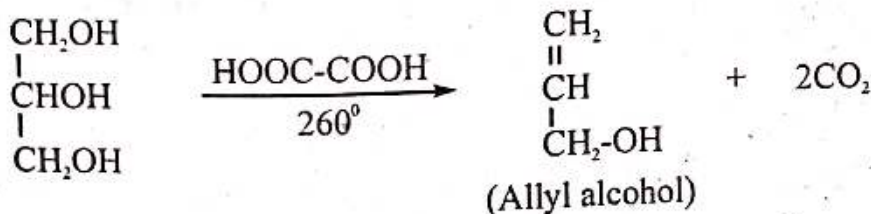
Mechanism: - In this reaction H_3PO_4 is act as an acid and after heating the elimination takes place.



Q.8. Complete the reaction: (2015)

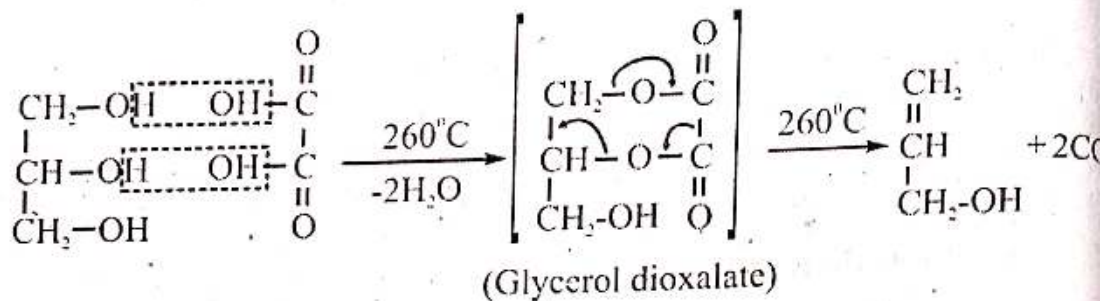


Ans.



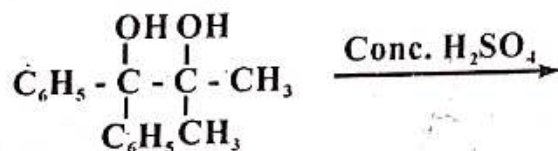
Mechanism:-

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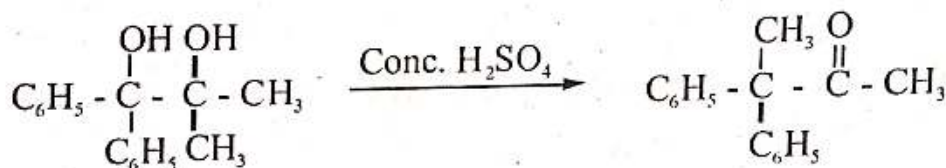


Q.9. Complete the following reaction:

(2016, 18)

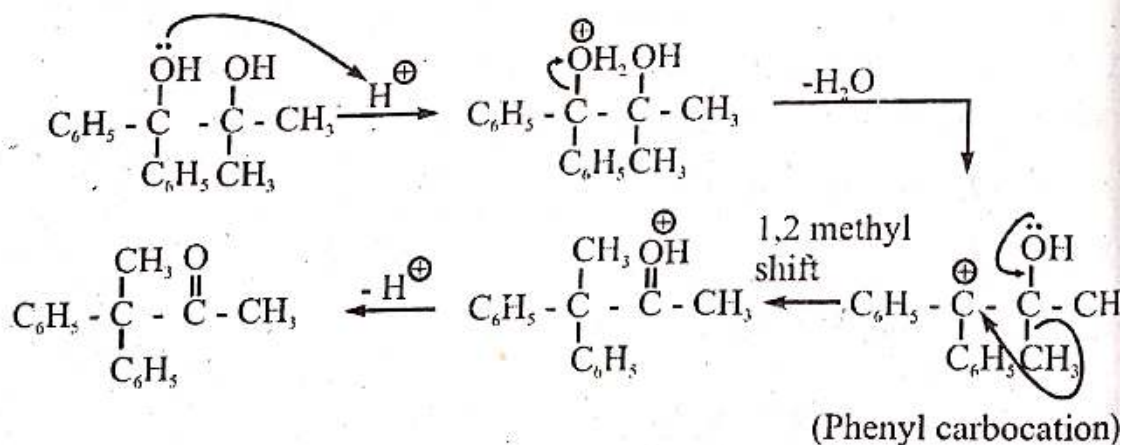


Ans.

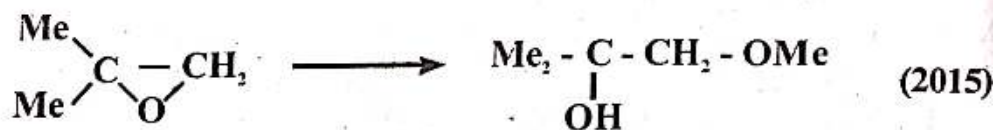


Mechanism:-

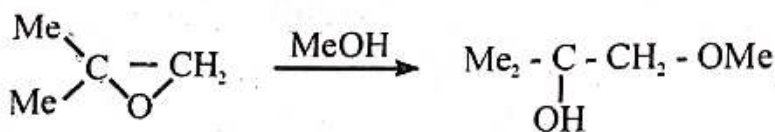
Phenyl carbocation are more stable than alkyl carbocation.



Q.10. How will you bring about following transformation? Give mechanism.

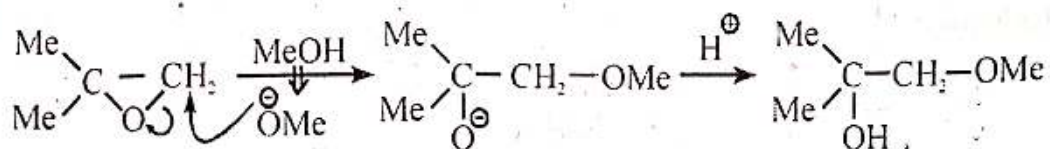


Ans.

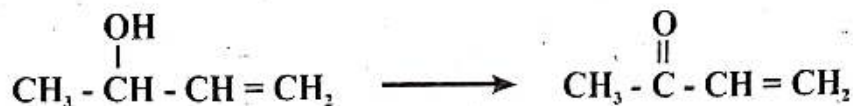


Mechanism:-

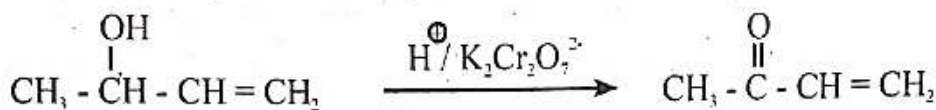
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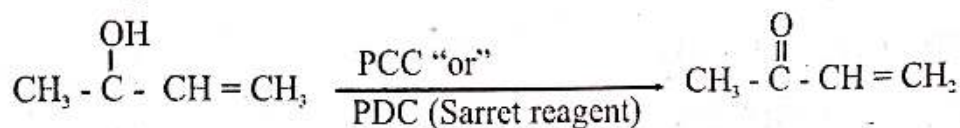
Q.11. How will you bring about the following transformation? (2016)



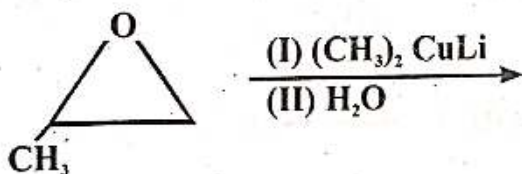
Ans. This example is an example of oxidation of alcohol.



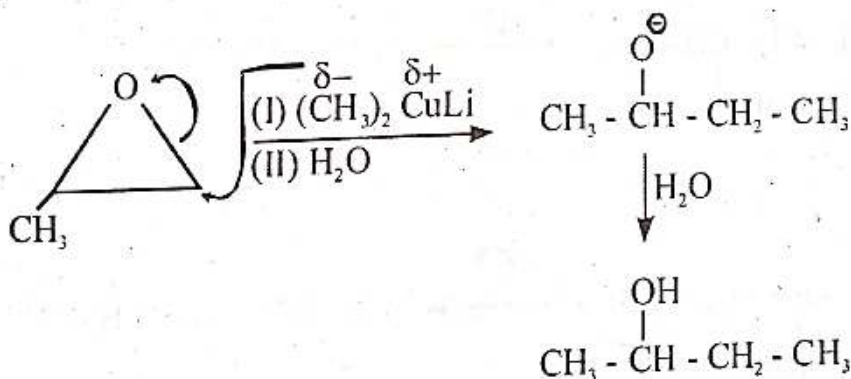
Alternating method:-



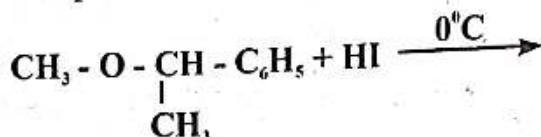
Q.12. Complete the following reaction: (2017)



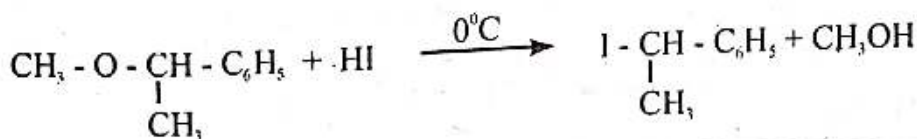
Ans.



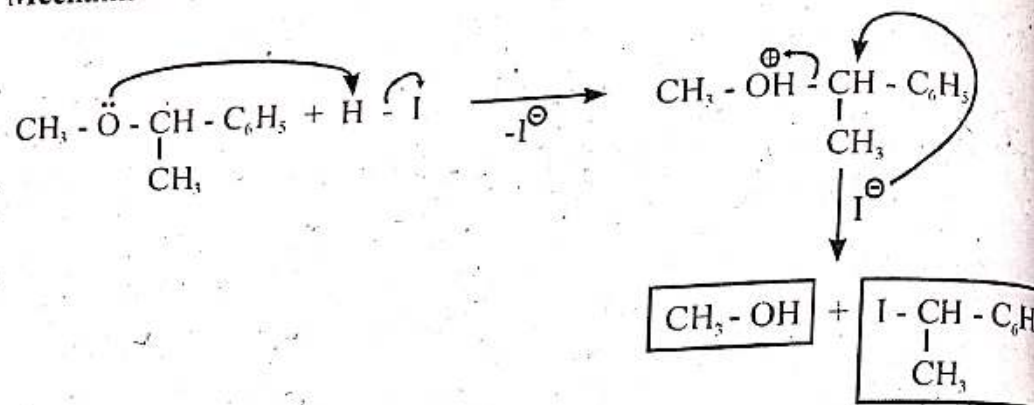
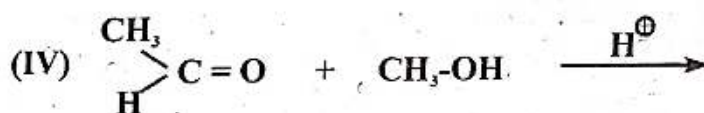
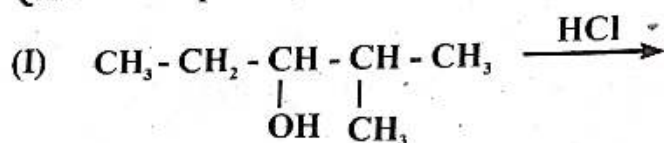
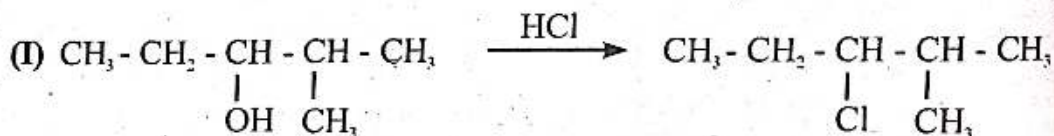
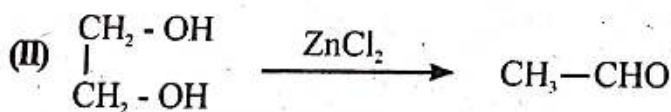
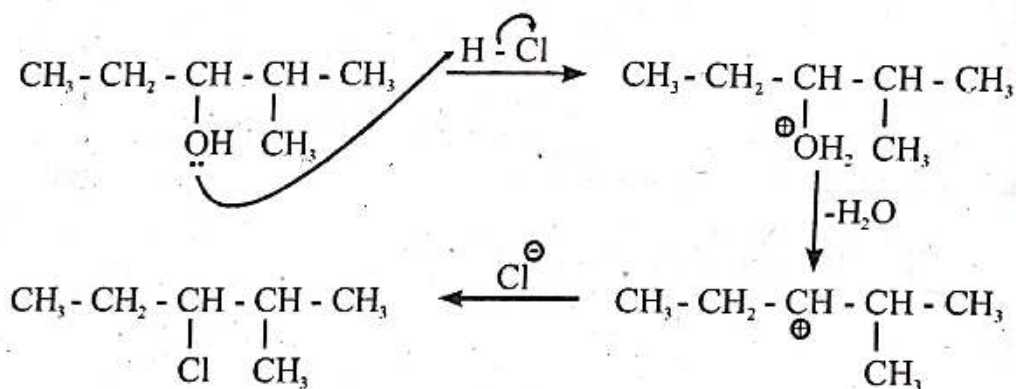
Q.13. Complete the following reaction: (2017)

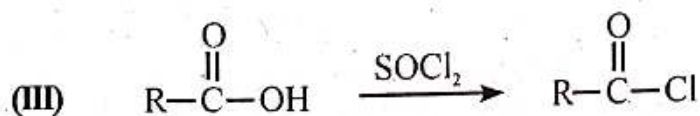
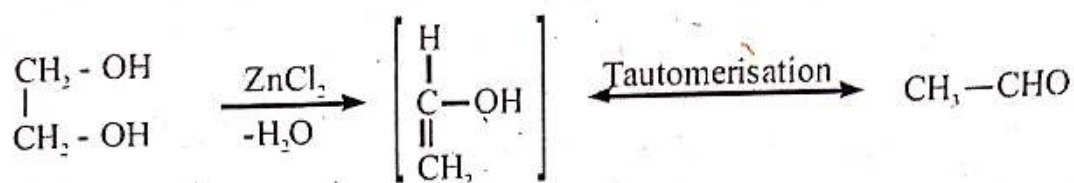
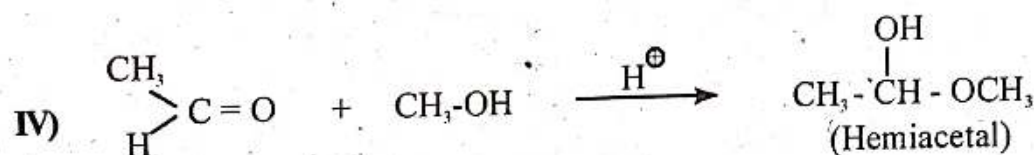
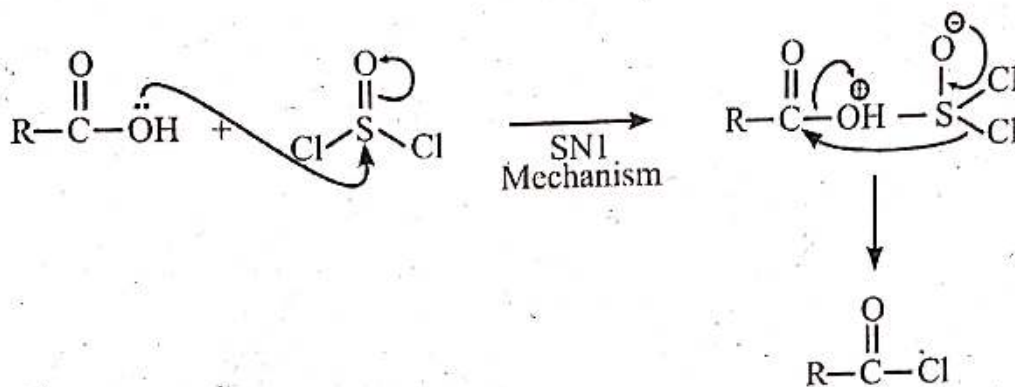
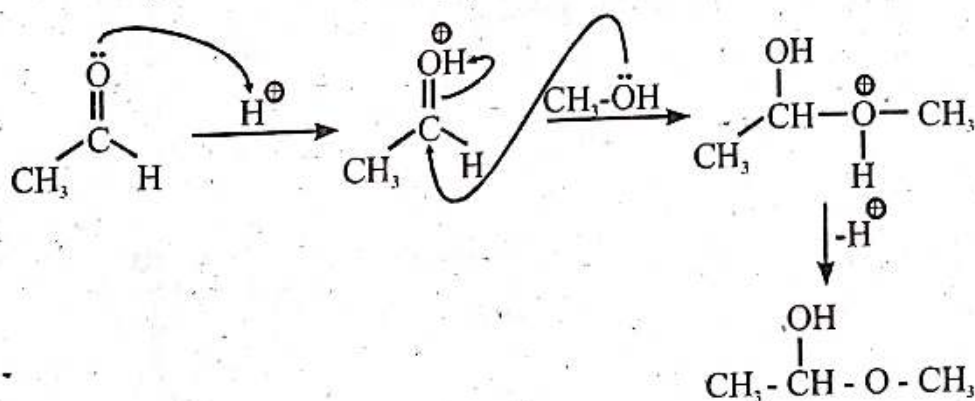
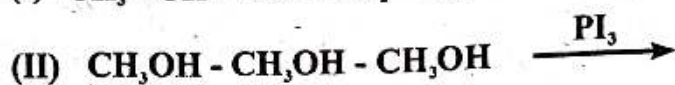
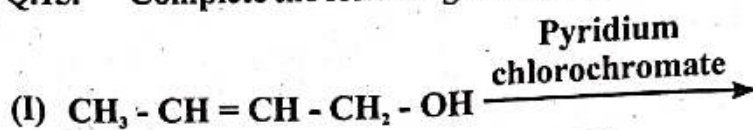


Ans.

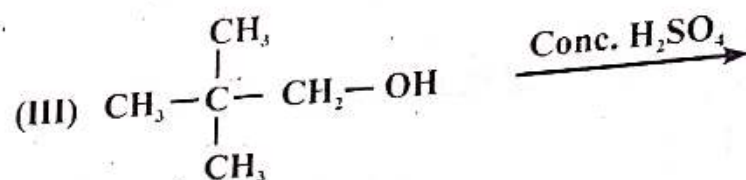


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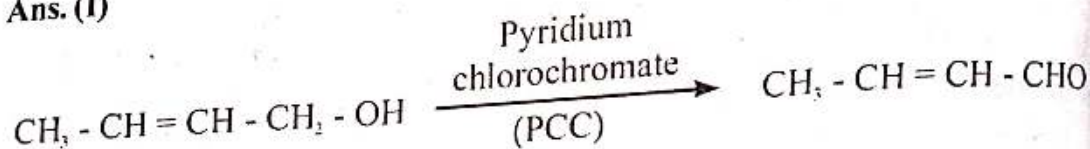
Mechanism:-**Q.14. Complete the following reactions and give their mechanism: (201)****Ans.****Mechanism:-**To shop our books visit at www.winsomecollection.co.in

Mechanism:-**Mechanism:-****Mechanism:-****Q.15. Complete the following reactions:****(2018)**

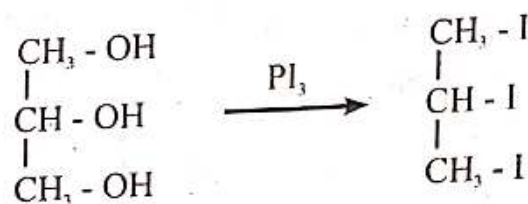
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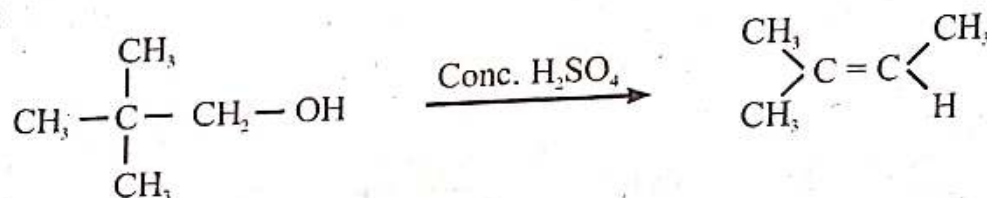
Ans. (I)



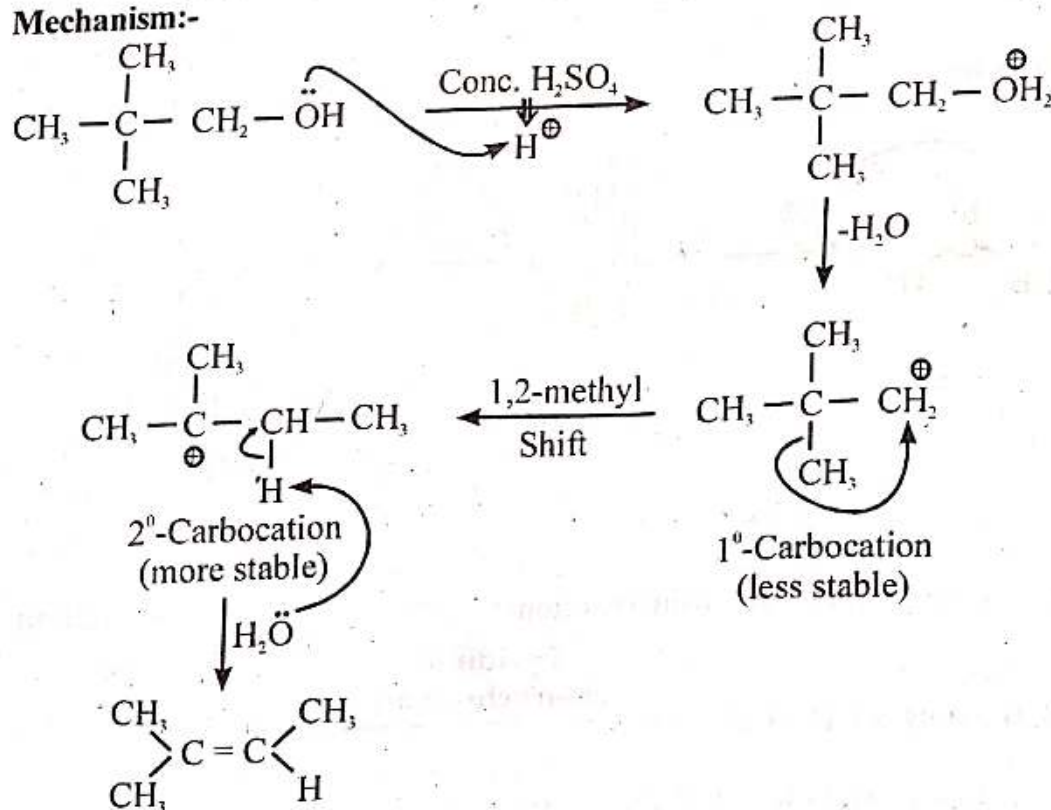
(II)



(III)



Mechanism:-

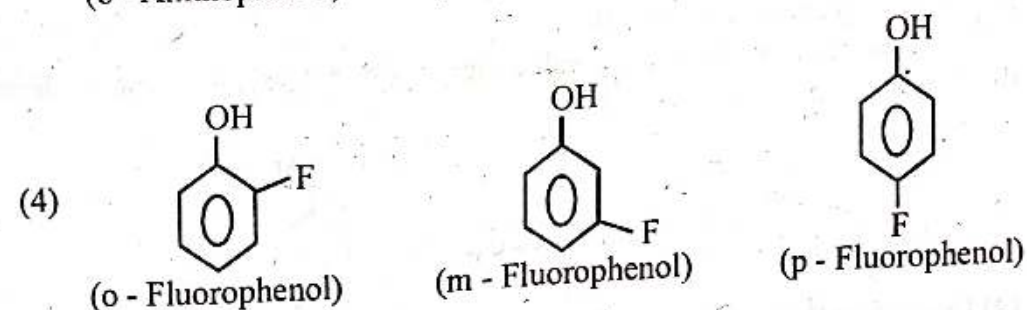
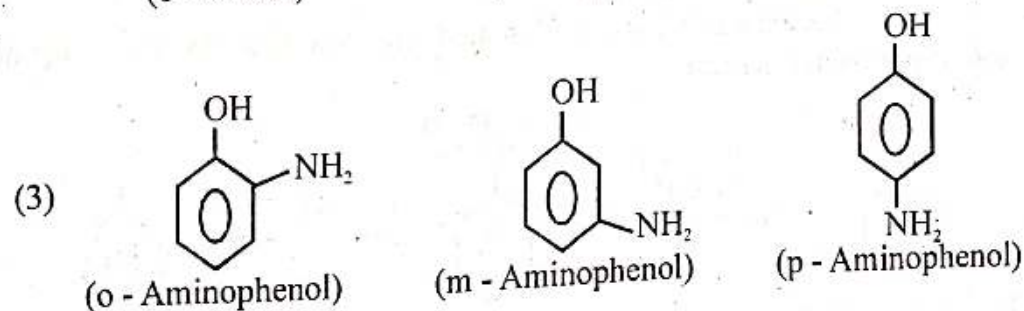
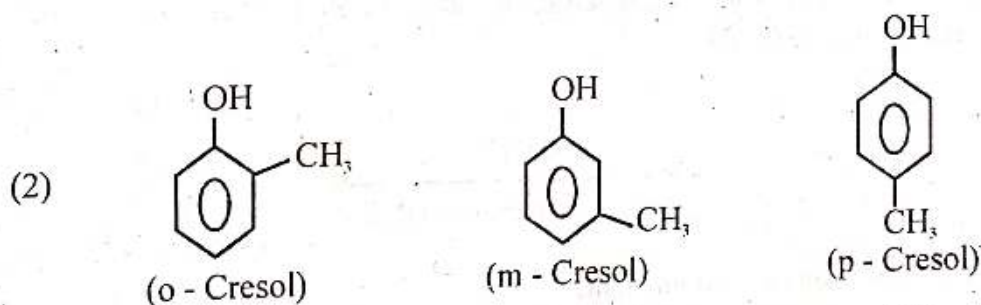
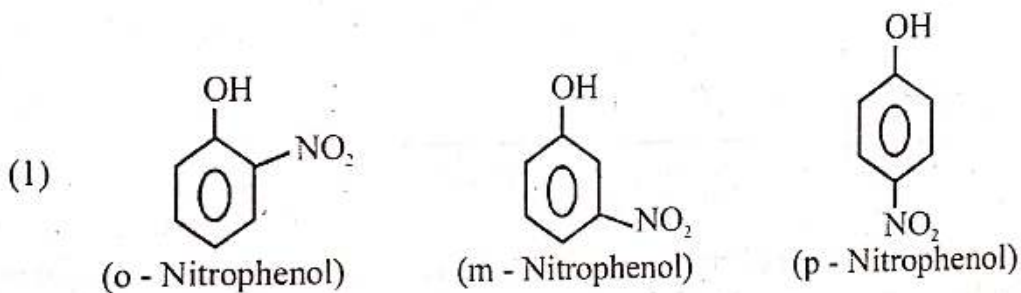
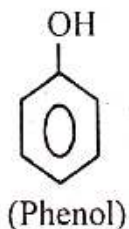


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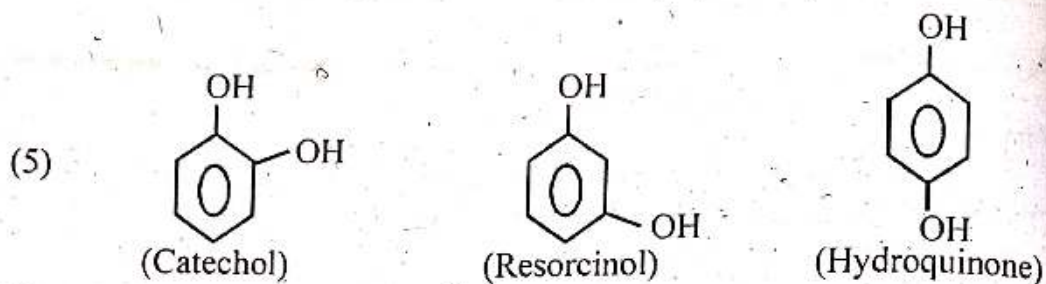
Chapter 3

Phenol:-

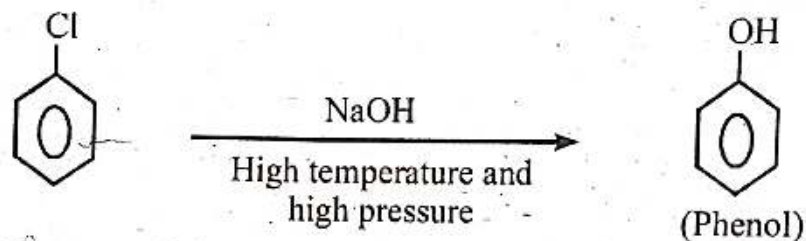
Phenols are those aromatic compounds containing hydroxyl group (-OH) directly attached to the aromatic ring. As-



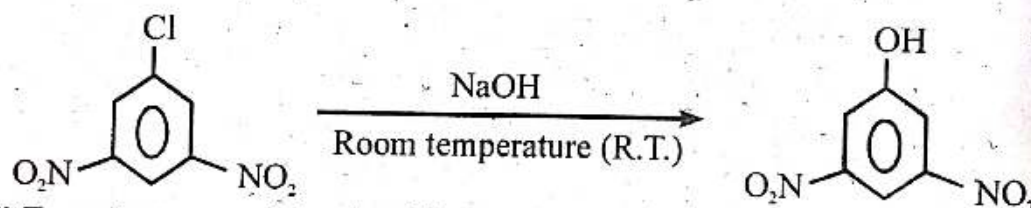
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**Method of Preparation:-****(1) From aryl halide:-**

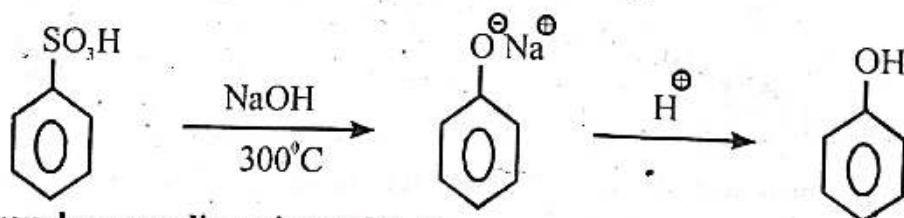
Aryl halide when treated with NaOH at high temperature and pressure, the formation of phenol takes place. This reaction is an example of aromatic nucleophilic substitution reaction.



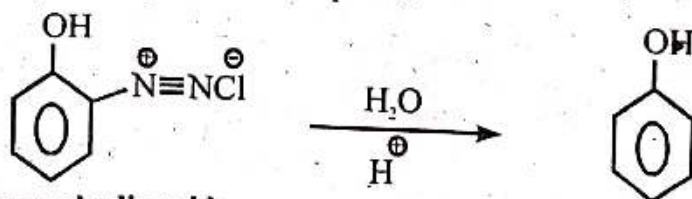
Presence of electron withdrawing group (EWG) on aromatic ring of aryl halide favour the aromatic nucleophilic substitution and reaction occurs at room temperature (R.T.).

**(2) From benzene sulphonic acid:-**

When benzene sulphonic acid treated with NaOH at 300°C, the formation of phenol takes place.

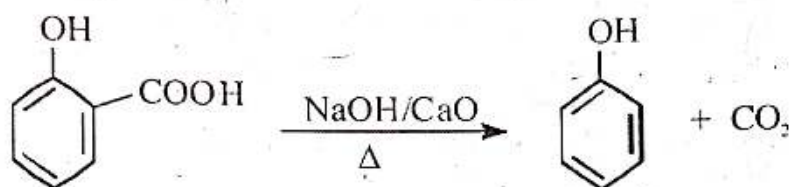
**(3) From benzene diazonium salt:-**

When benzene diazonium salt undergoes hydrolysis in acidic medium, the formation of phenol takes place.

**(4) From salicylic acid:-**

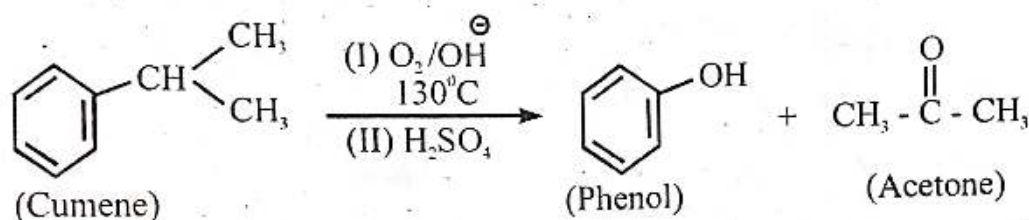
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When salicylic acid treated with soda lime (NaOH/CaO) the formation of phenol takes place.



(5) From isopropyl benzene (cumene):-

This is most important commercial method for the preparation of phenol and it is known as cumene-phenol process.

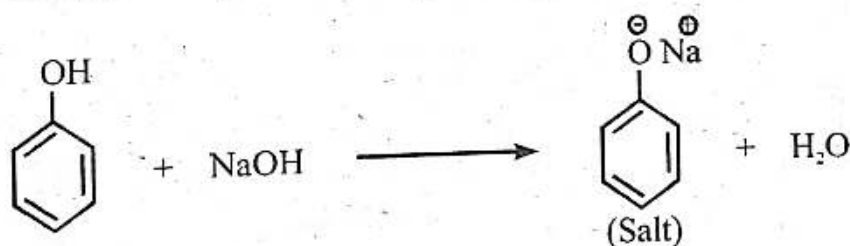


Chemical properties:-

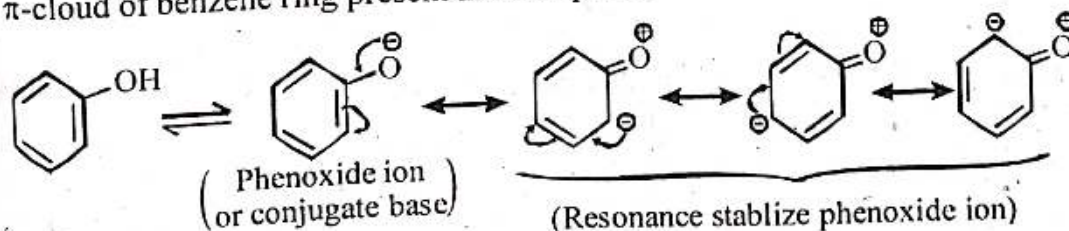
The reactivity of phenol is due to presence of benzene ring as well as presence of hydroxyl group (-OH group). Thus phenol shows two type of reactivity.

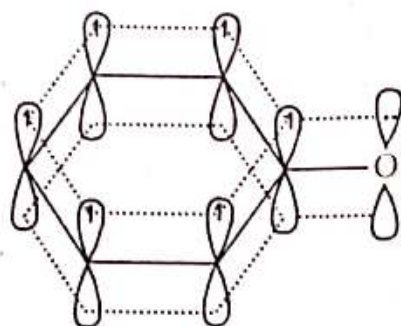
Acidic nature of phenol:-

Phenol shows acidic nature and give salt with NaOH as well as turns blue litmus paper into red.

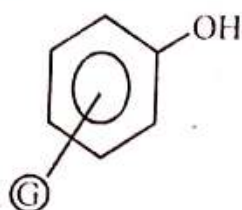


Phenol shows acidic nature more than alcohols because when H^+ remove from the phenol, the formation of phenoxide ion takes place. This phenoxide ion are well stable due to resonance effect and shows four resonating structure. This delocalisation takes place because the lone pair on O-atom and π -cloud of benzene ring present in same plane.





Effect of substituent on the acidity of phenol:-

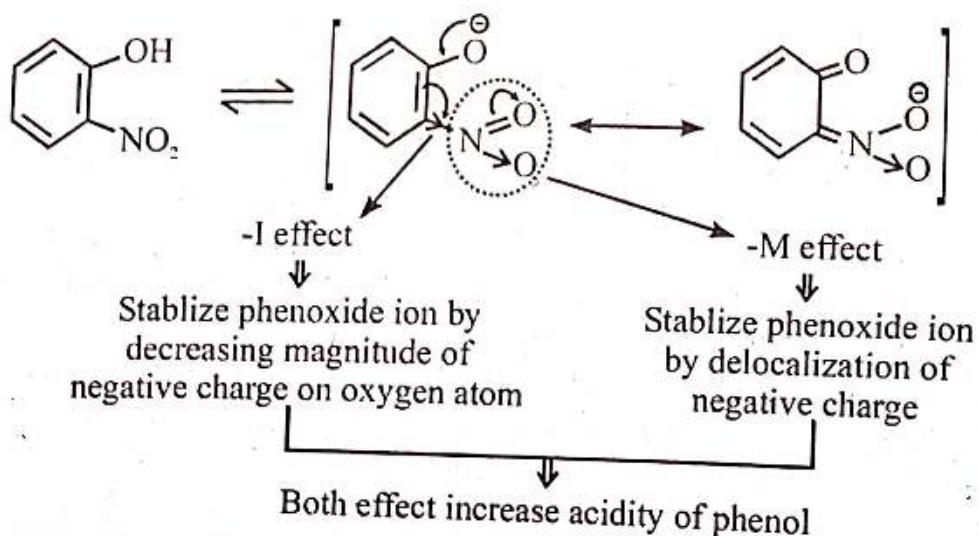


Case (I):- When (G) is -M group -

Ex.:- $-\text{NO}_2$, $-\text{CN}$, $-\text{C}(=\text{O})-\text{R}$, $-\text{SO}_3\text{H}$ etc.

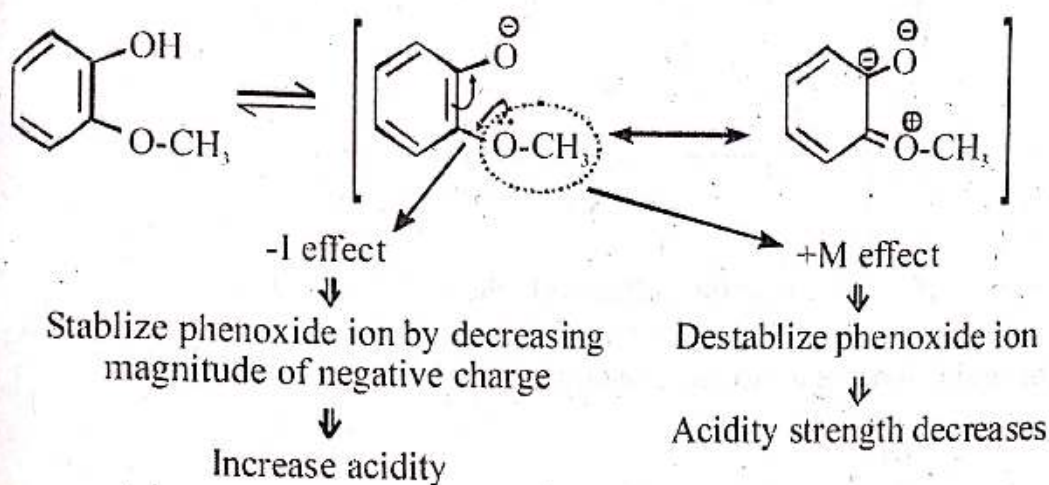
The acidic strength of phenol is directly proportional to the stability of phenoxide ion.

Thus electron withdrawing group (EWG) increase the acidity of phenol due to -M - effect as well as -I - effect.



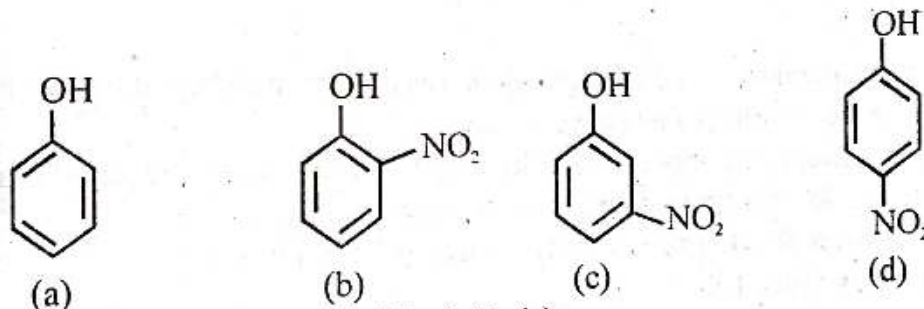
Case (II):- When "G" is +M - group -

Ex.:- $-\text{OH}$, $-\text{OMe}$, $-\text{Cl}$, $-\text{F}$ etc.



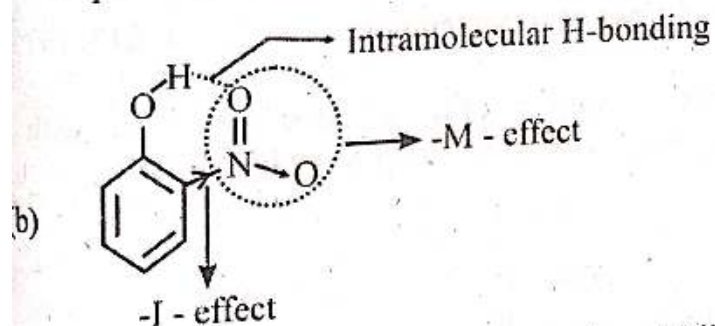
- Q.1. Arrange the following molecule in decreasing order of their acidity-
 (a) phenol (b) o-Nitrophenol
 (c) m-Nitrophenol (d) p-Nitrophenol (2011, 12, 15, 16, 18)

Ans.

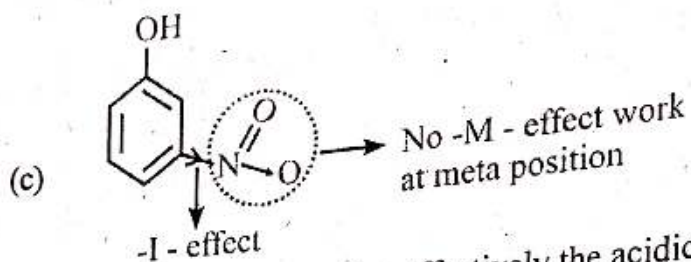


Acidic strength order:- (d) > (b) > (c) > (a)

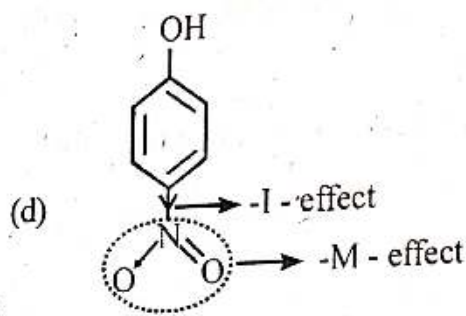
The explanation are as follows-



$\Rightarrow$ -M - effect increase acidity by increasing stability of phenoxide ion due to delocalization of negative charge.
 $\Rightarrow$ Strong -I - effect also increases acidity by increasing stability of phenoxide ion by decreasing the magnitude of negative charge.
 $\Rightarrow$ Intramolecular H-bonding decreases the acidity of phenol by engaging the H-atom.



⇒ -M - effect does not affect effectively the acidic strength.
⇒ Moderate -I - effect, increase acidity of phenol by increasing stability of phenoxide ion due to decrease the magnitude of negative charge.



⇒ -M - effect increase acidic strength by increasing the stability of phenoxide ion due to delocalization of negative charge.

⇒ Weak -I - effect also increase acidity of phenol by increasing stability of phenoxide ion decreasing magnitude of negative charge.

Thus from above discussion the acidity order will be-

(d) > (b) > (c) > (a)

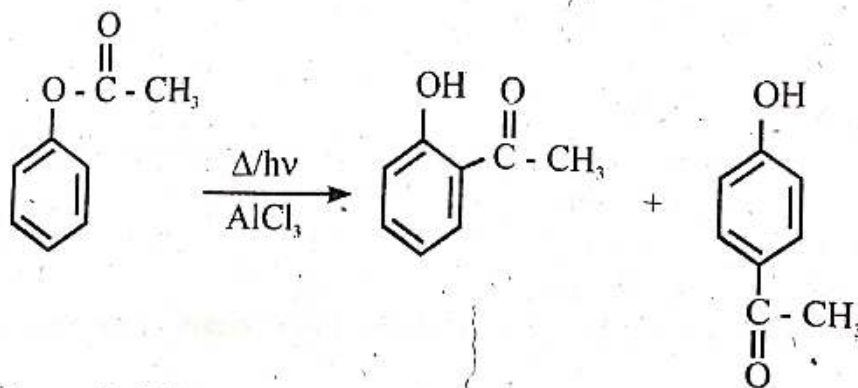
or p-Nitrophenol > o-Nitrophenol > m-Nitrophenol > phenol

Q.2. Give the mechanism of Fries rearrangement.

(2013, 19)

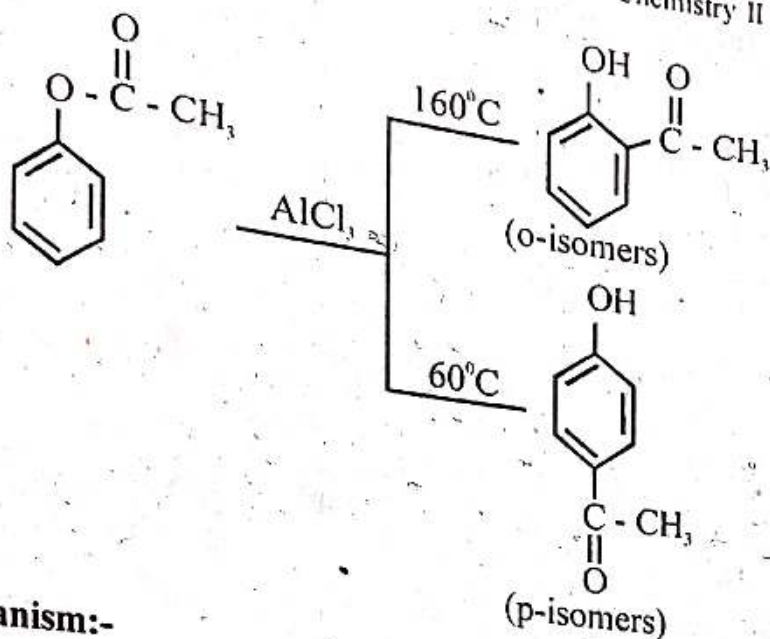
Fries rearrangement:-

Phenolic ester gives Fries rearrangement when heated by U.V. light with the anhydrous AlCl_3 and form mixture of ortho and para hydroxy ketone.

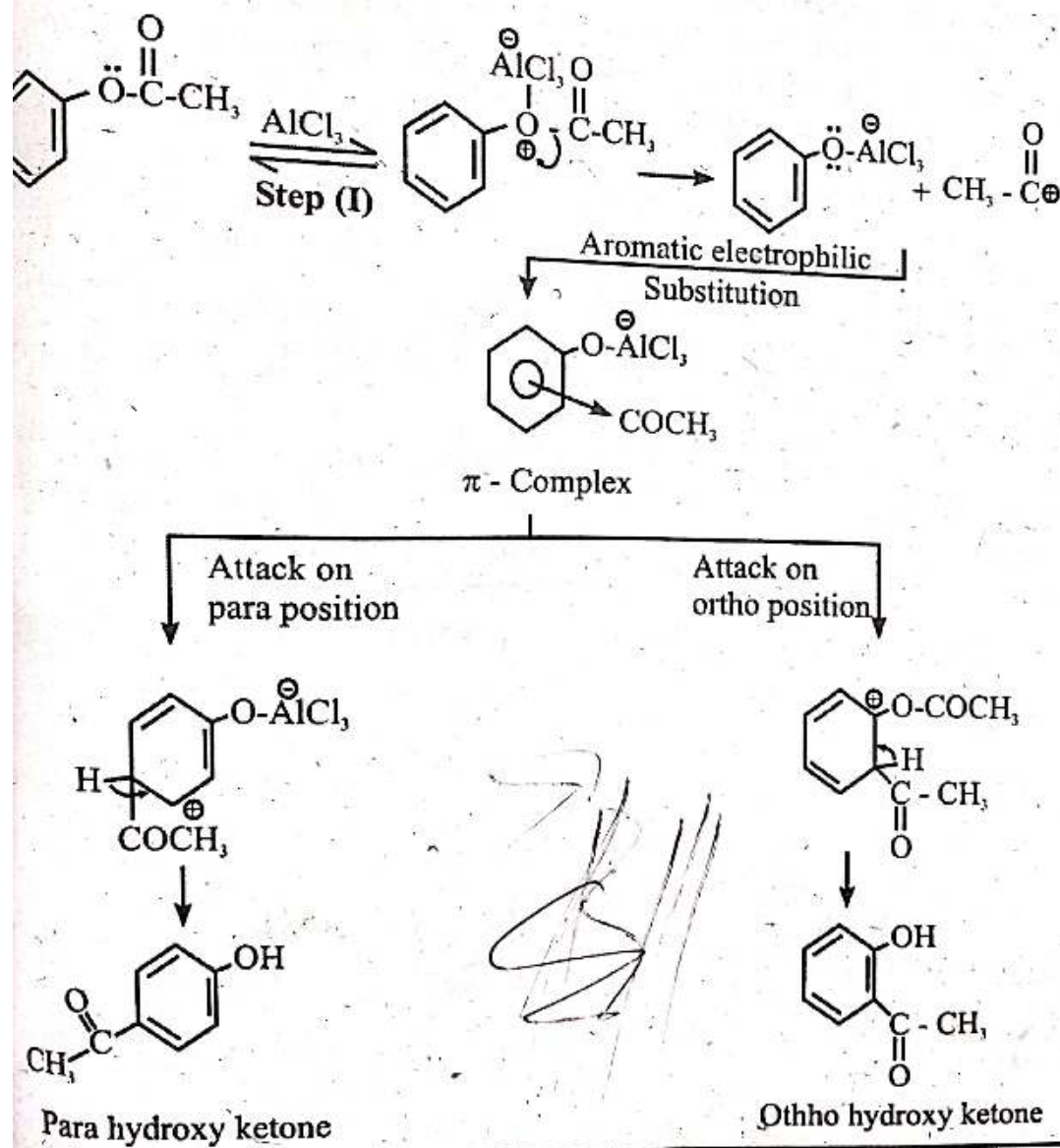


Generally high temperature favours ortho isomers and low temperature favours para isomers.

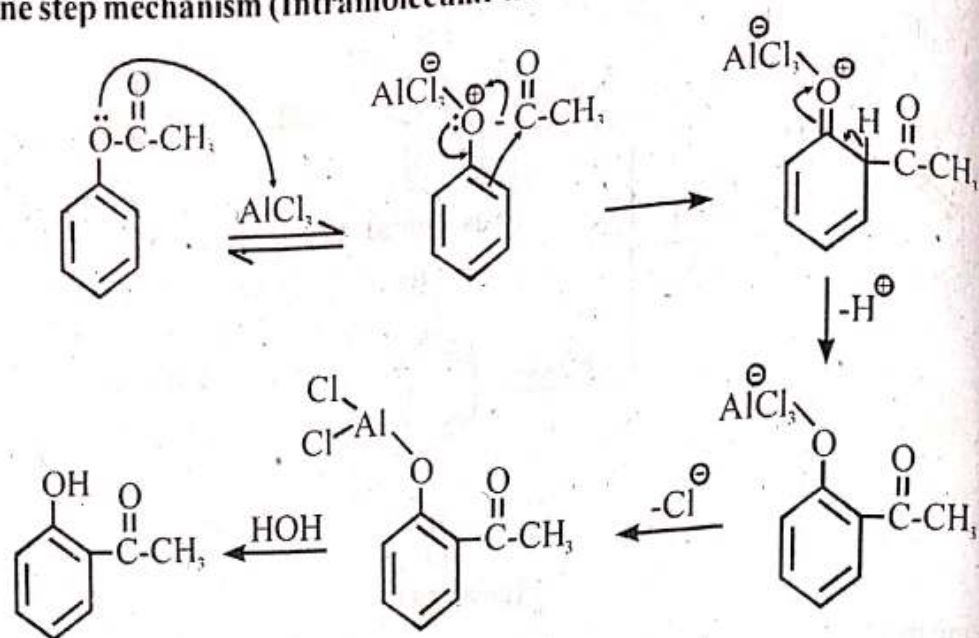
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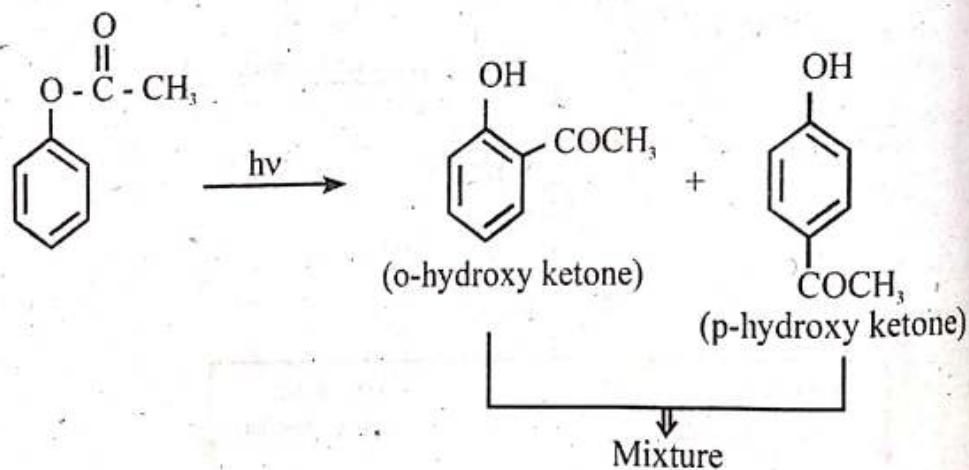
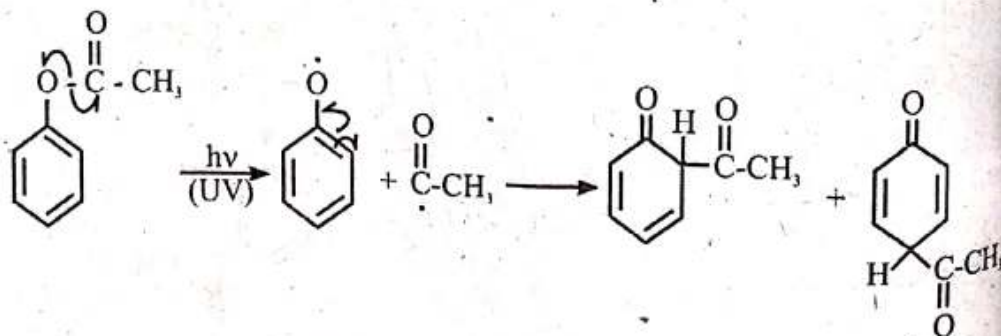
Mechanism:-

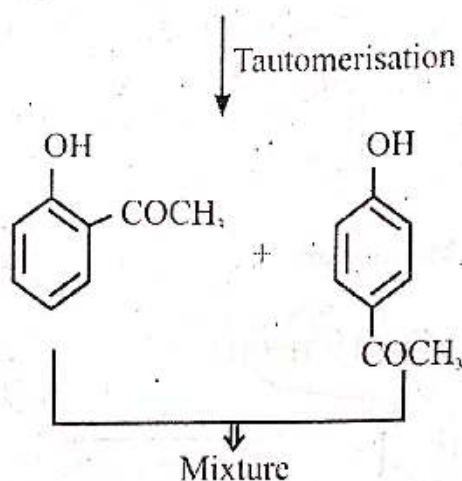


One step mechanism (Intramolecular mechanism) of Fries rearrangement

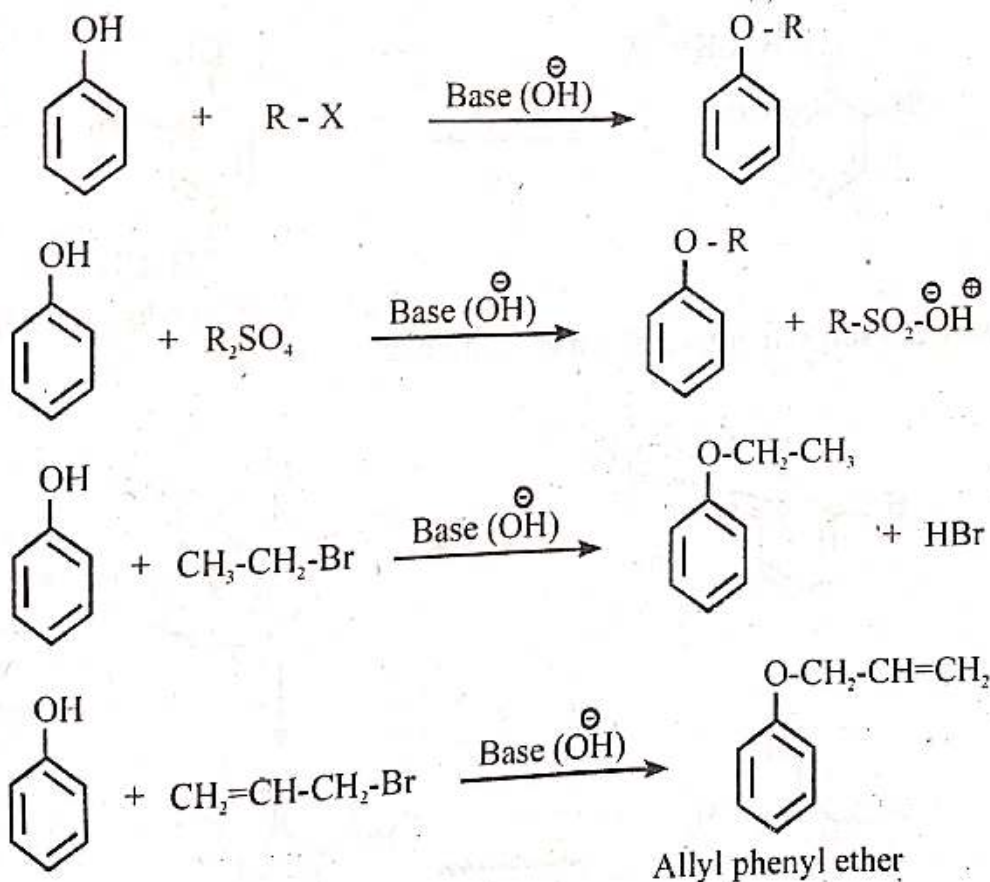
**Photo - Fries rearrangement:-**

If Fries rearrangement carried out in the presence of UV-light in the absence of a catalyst, then this is called photo-Fries rearrangement. In this reaction free radicals are formed.

**Mechanism:-**

**(2) Alkylation of phenol:-**

When phenol are treated with alkyl halides or alkyl sulphates in presence of base, then the formation of phenolic ester takes place. This reaction is catalysed by the base.



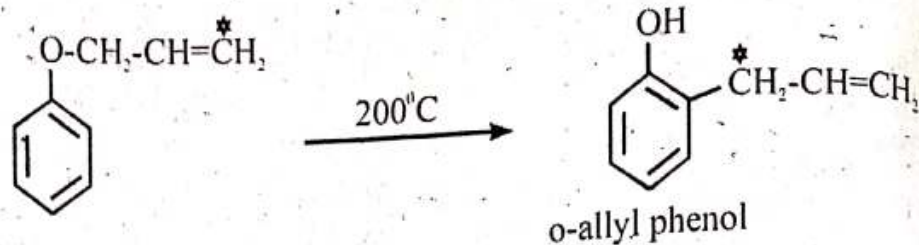
Q.3. Write the short note on Claisen rearrangement.

(2019)

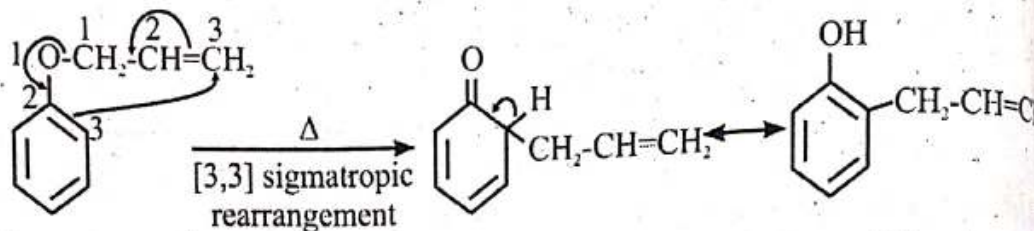
Claisen rearrangement:-

Allyl phenyl ether rearrange to o-allyl phenol when heated at 200°C, this rearrangement is called claisen rearrangement.

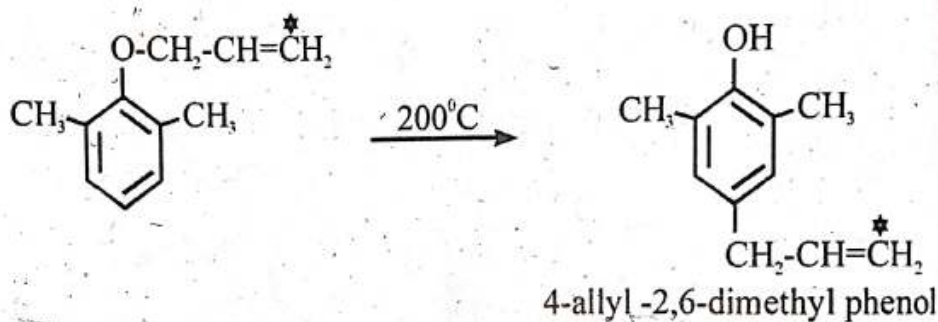
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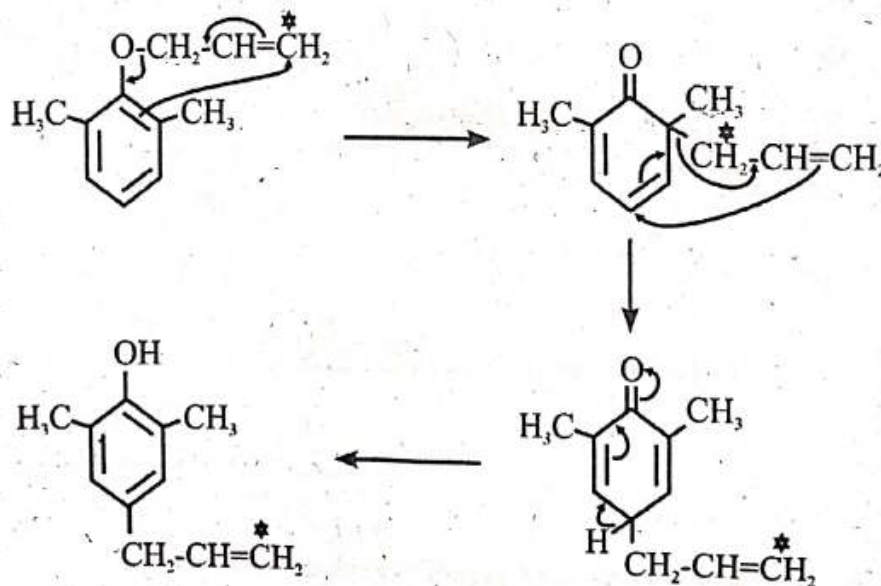
Mechanism:-



In this rearrangement if the ortho position is free then only ortho rearrangement occurs. If both ortho positions are substituted then rearrangement takes place at para position.



Mechanism: - (If ortho position is substituted).

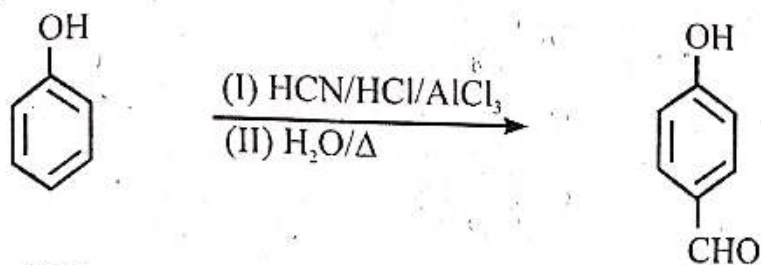


(3) Formylation (Gattermann reaction):-

When phenol is treated with the mixture of hydrogen cyanide (HCN) and

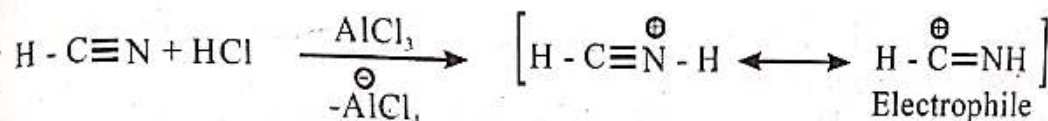
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hydrogen chloride (HCl) in the presence of aluminium chloride (AlCl_3), the formation of parahydroxy benzyl aldehyde takes place. This reaction is known as Gattermann reaction.

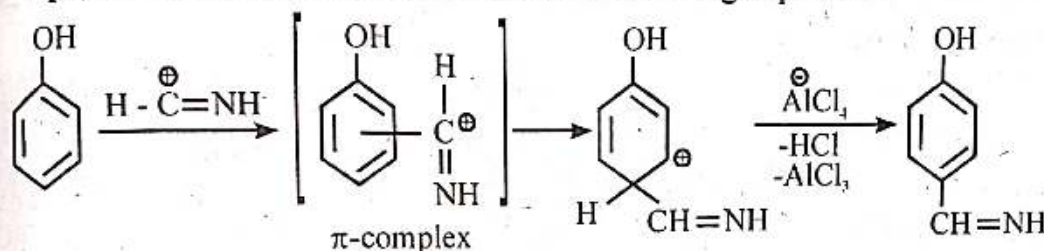


Mechanism:-

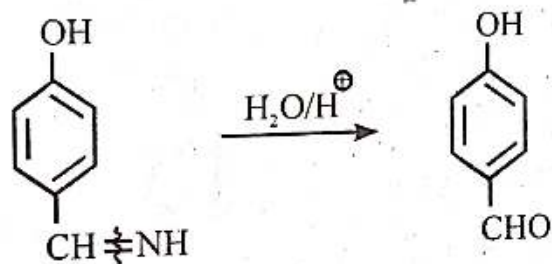
Step (I):- Formation of electrophile



Step (II):- Electrophilic substitution on benzene ring of phenol



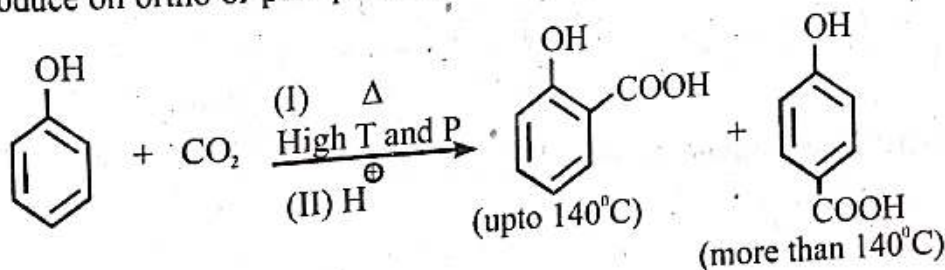
Step (III):-



(4) Kolbe-Schmitt reaction:-

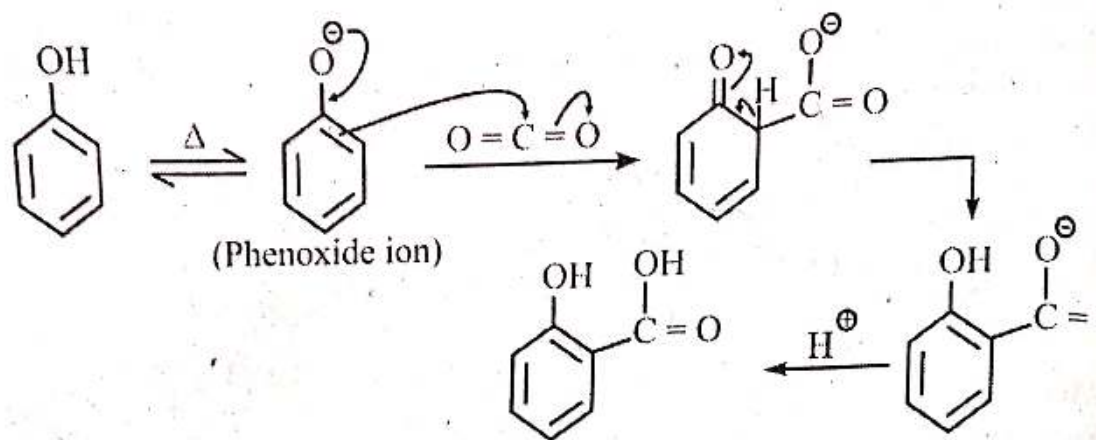
(2011, 15, 19)

The reaction of phenol with CO_2 under high temperature and pressure is known as Kolbe-Schmitt reaction. In this reaction carboxylic group ($-\text{COOH}$) introduce on ortho or para position.



Mechanism:-

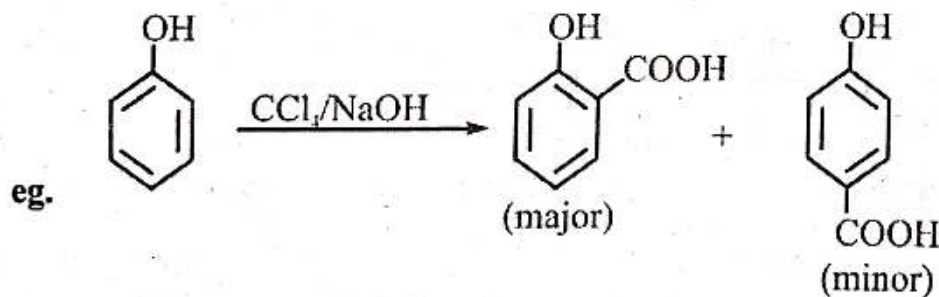
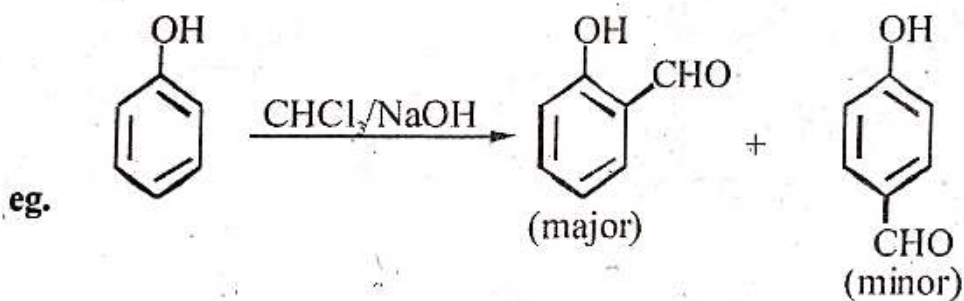
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Q.4. Discuss the mechanism of Reimer-Tiemann reaction. (2012, 14, 17)

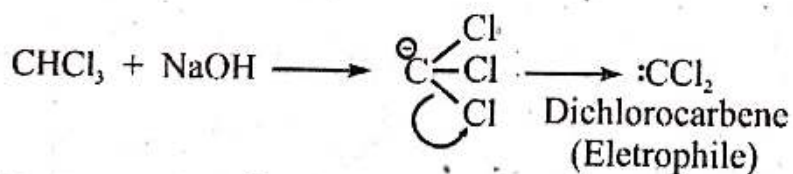
Reimer-Tiemann Reaction: -

When phenol reacts with chloroform in the presence of base, the ortho-hydroxy benzaldehyde is formed. In this reaction, para isomer also formed a minor product.

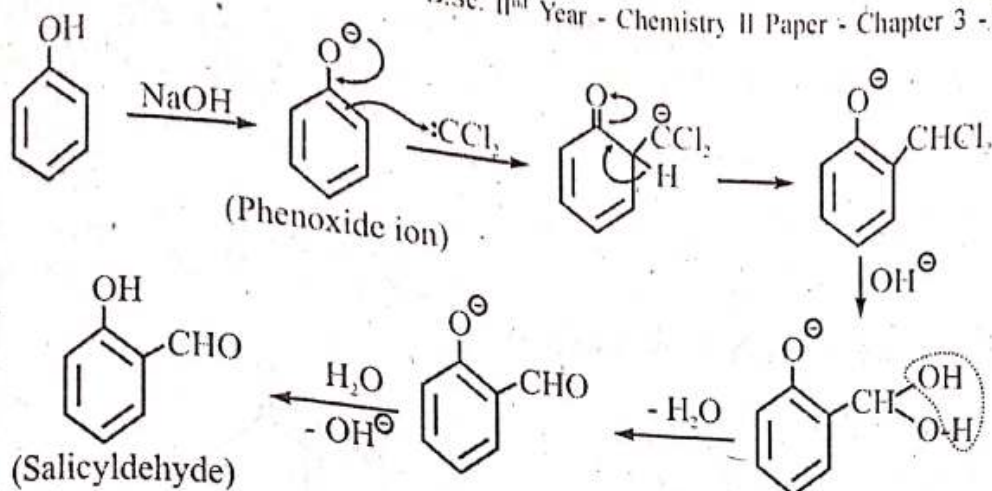


Mechanism: -

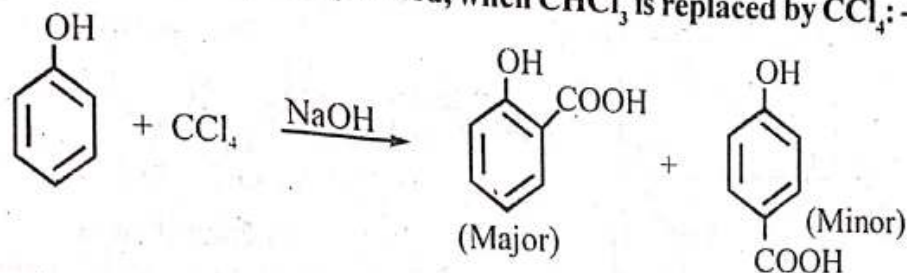
Step (I) - Formation of carbene intermediate -



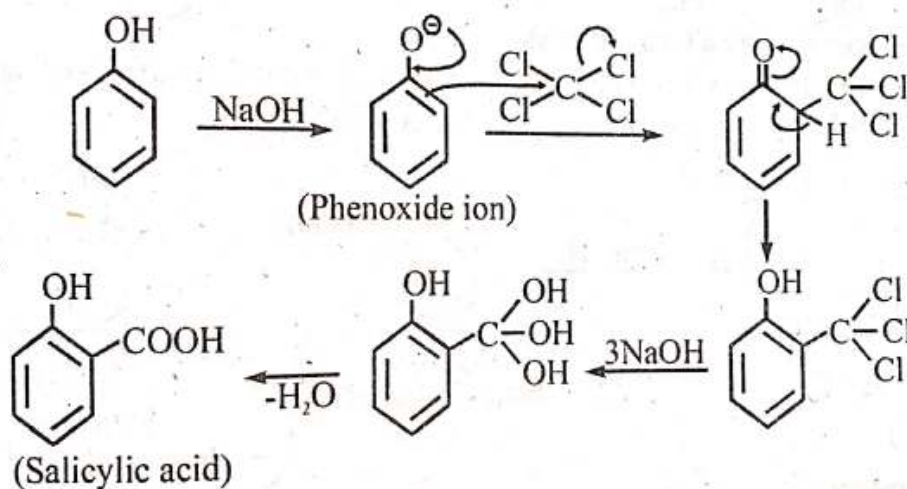
Step (II) - Electrophilic substitution on benzene -



Similarly the reaction is also proceed, when CHCl_3 is replaced by CCl_4 :-

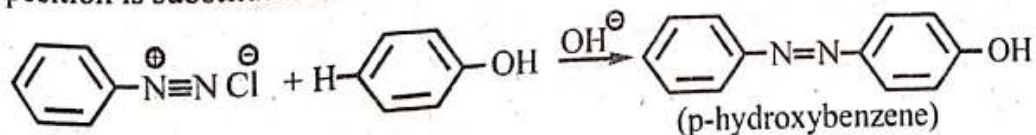


Mechanism:-



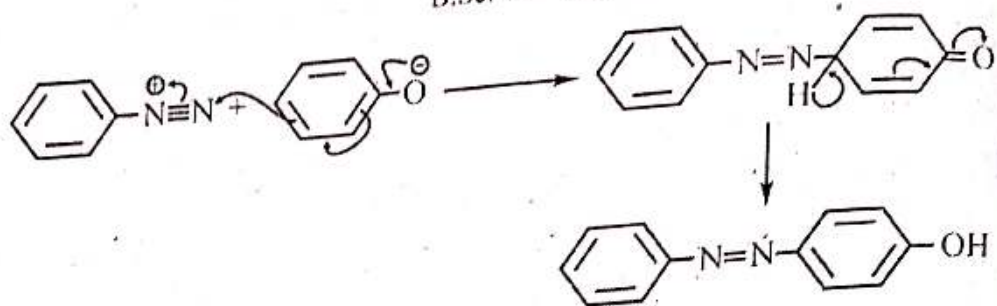
(6) Coupling with Diazonium salt:-

In alkaline solution, phenol couple with diazonium salt to form hydroxyazo compounds. Coupling reaction takes place at para position. If para position is substituted then the coupling may takes place at the ortho position.

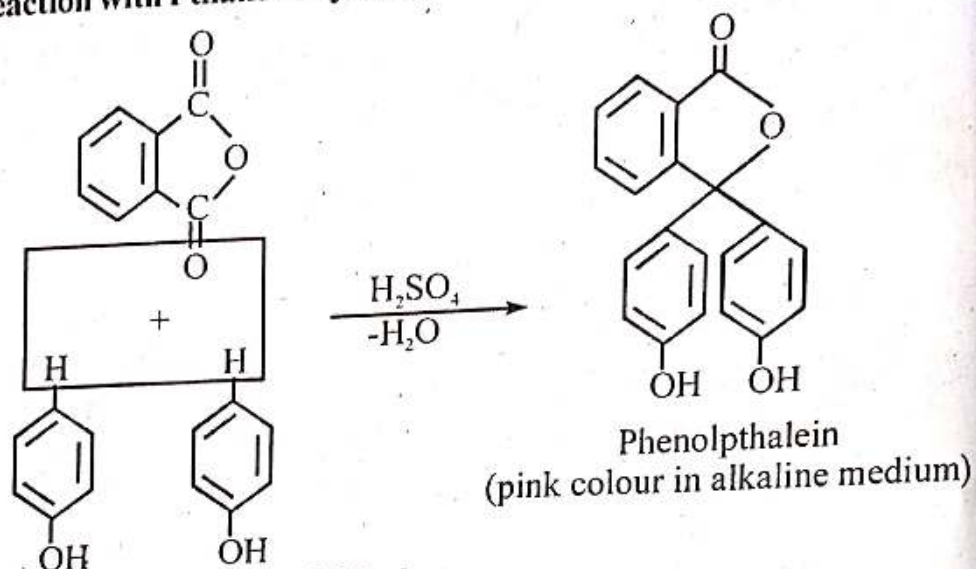


Mechanism:-

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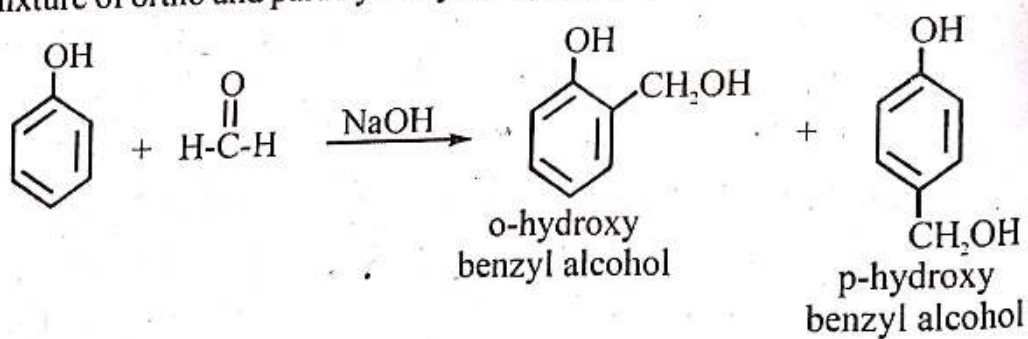


(7) Reaction with Phthalic anhydride:-

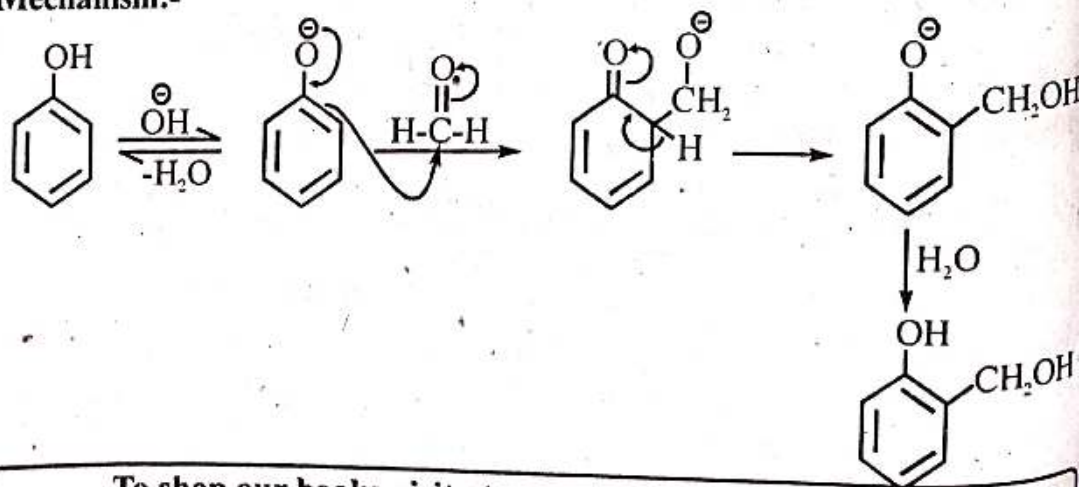


(8) Condensation with formaldehyde:-

When phenol reacts with formaldehyde in the presence of a base like NaOH , a mixture of ortho and para hydroxy benzyl alcohols forms.

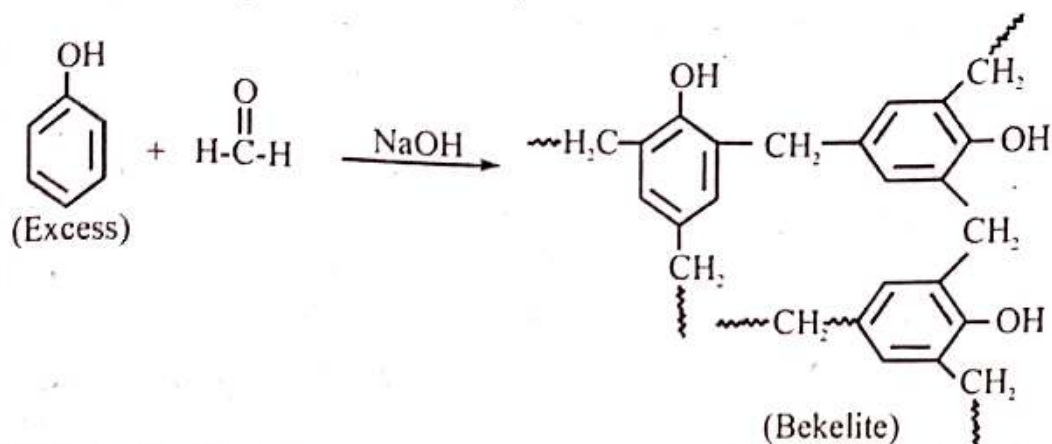


Mechanism:-



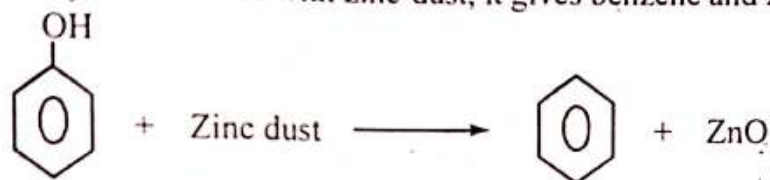
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When formaldehyde and phenol present in excess, the formation of "Bekelite" takes place.

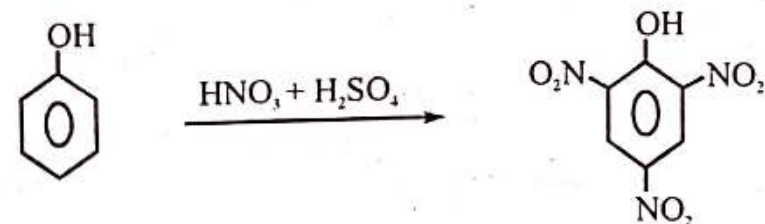
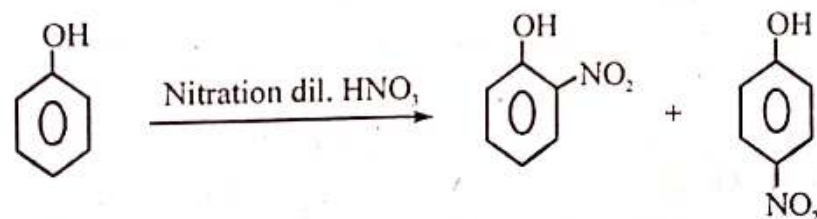
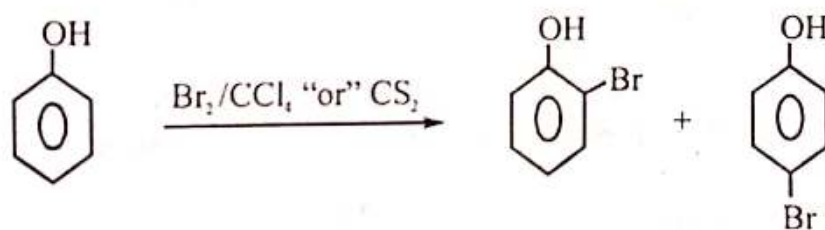
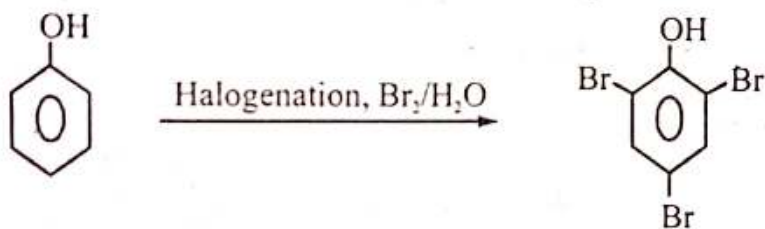


(9) Reduction of phenol:-

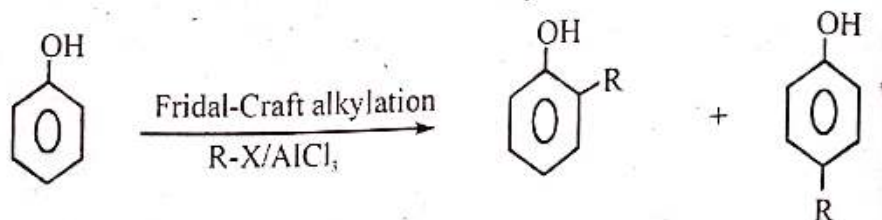
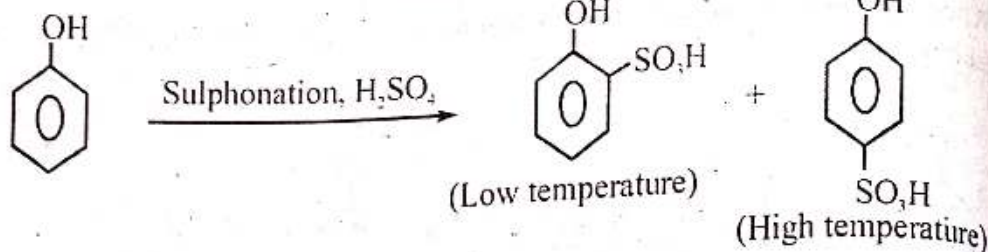
When phenol reduce with zinc-dust, it gives benzene and zinc oxide.



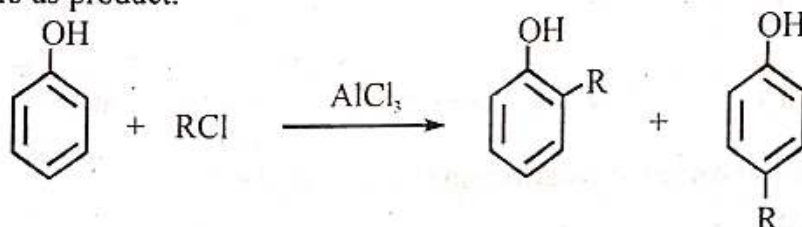
(10) Other electrophilic substitution reaction of phenol:-



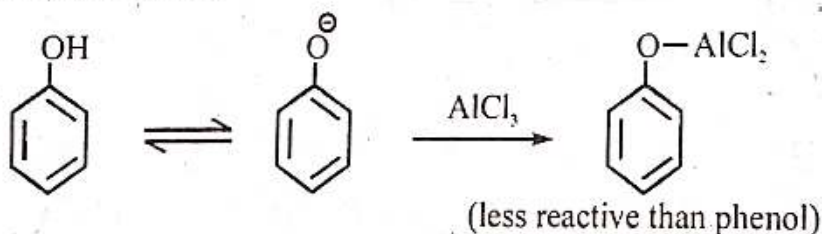
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**(II) Friedel-Craft alkylation:-**

Phenol undergoes Friedel-Craft alkylation to give the ortho and para isomers as product.



Phenol does not give better Friedel-Craft alkylation because phenol react with AlCl_3 to form salt.

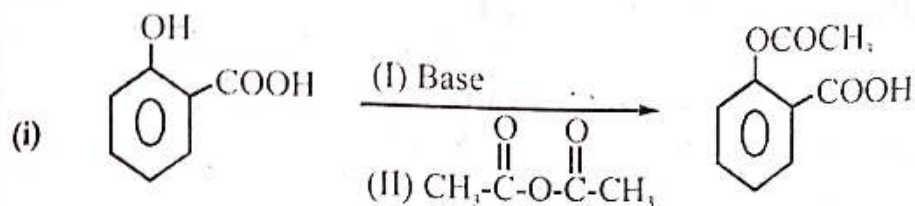


Q.5. How the following conversions can be done? Give answer.

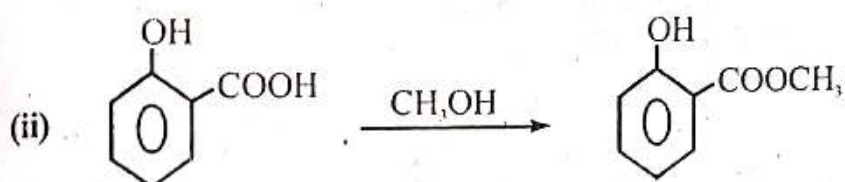
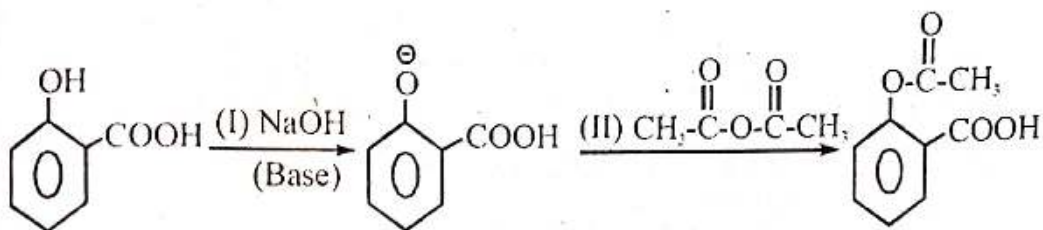


(2011,13)

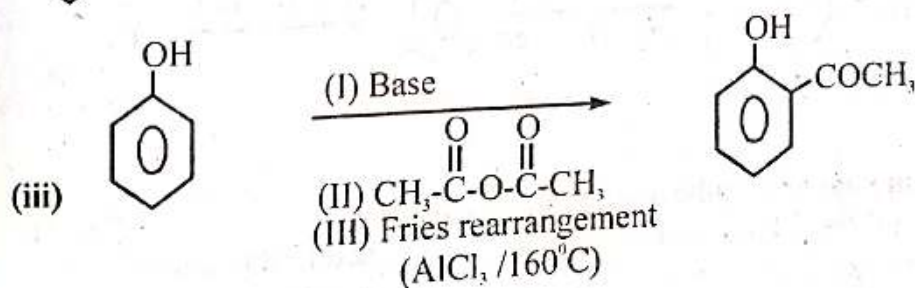
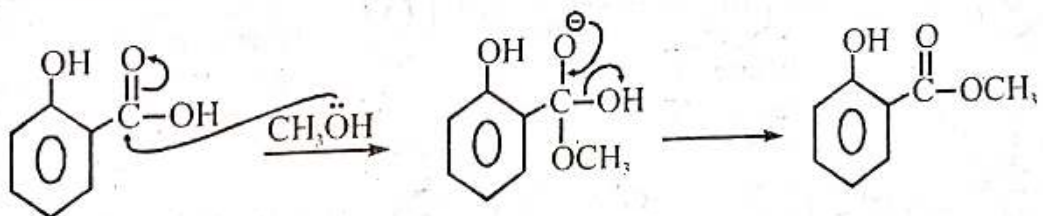
Ans.



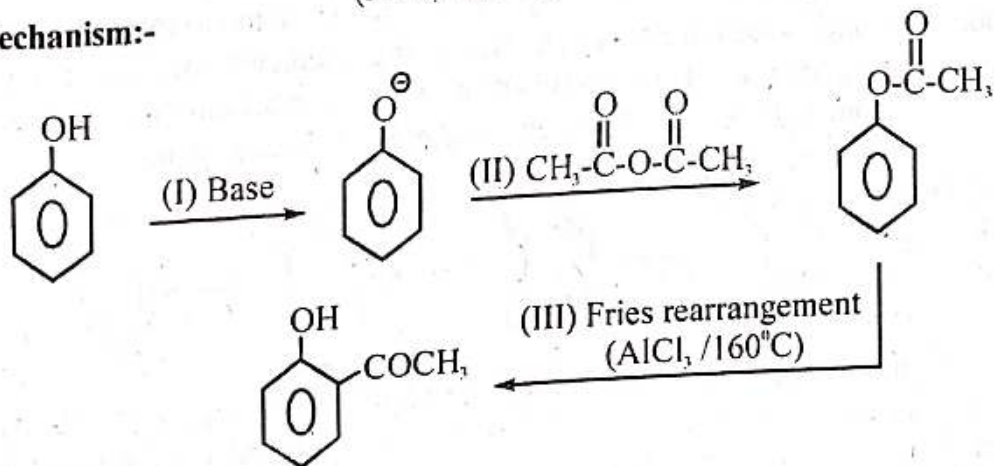
Mechanism:-



Mechanism:-



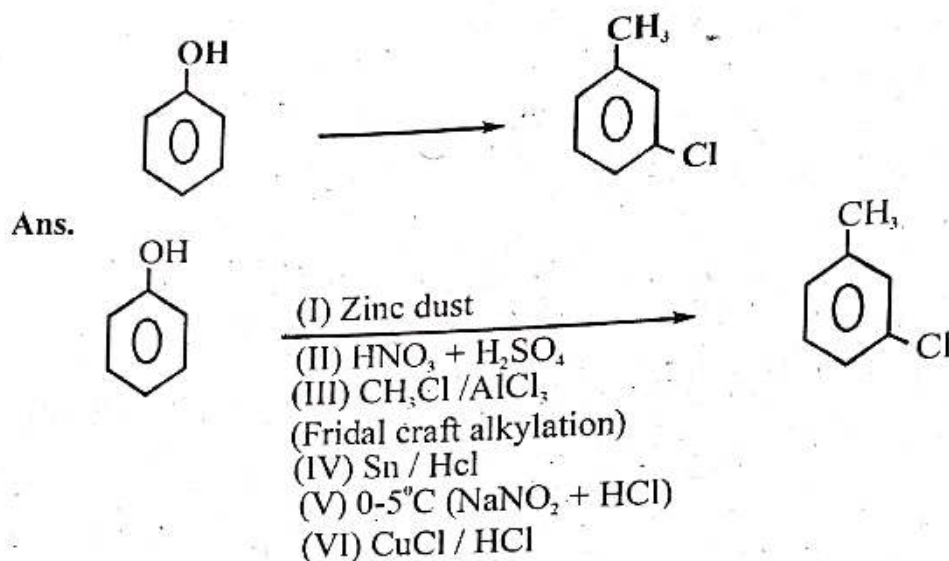
Mechanism:-



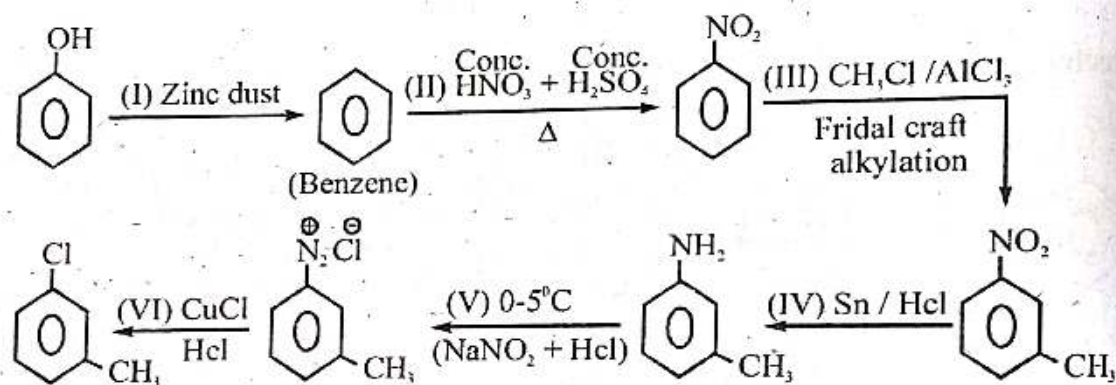
Q.6. How will you bring about the following conversation:

(2013)

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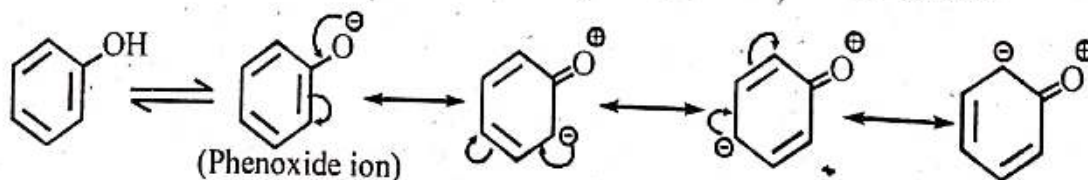
Mechanism:-



Metachloro toluene

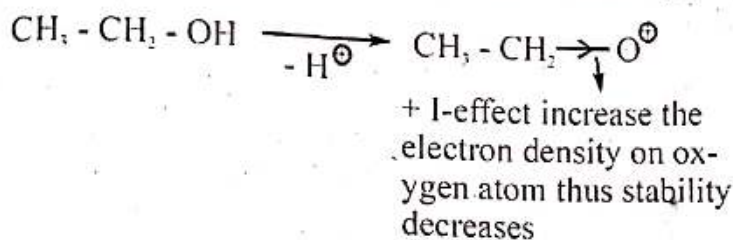
Q.7. Explain phenol is acidic but ethanol is neutral. (2013)

Ans. In phenol there is a -OH group directly attached to the benzene ring. The acidity of phenols is due to its ability to loss hydrogen ion to form phenoxide ion. This phenoxide ion are well stablize by the resonance effect and shows four resonating structure. The delocalization takes place because the lone pair on oxygen atom and π -cloud of benzene ring present in same plane.

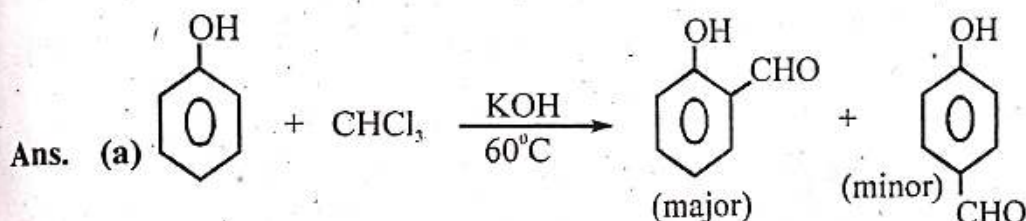
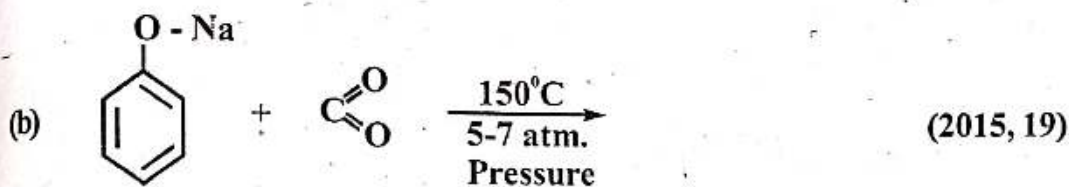
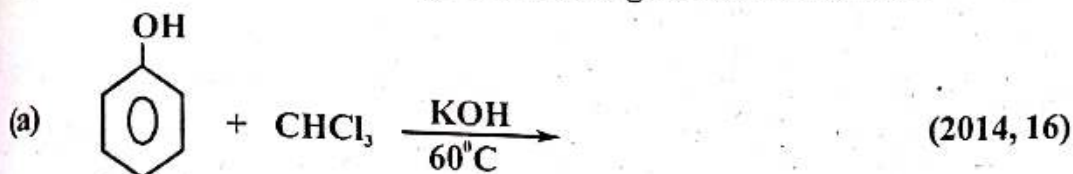


In the case of ethanol, after removal of hydrogen ion there are no any factor work to stablized the anion. Thus ethanol is neutral to stablised the anion. Thus ethanol is neutral.

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Q.8. Complete the following reaction and give their mechanism.

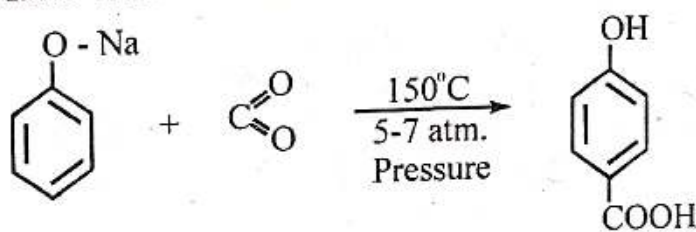


Note - Reimer - Tiemann Reaction.

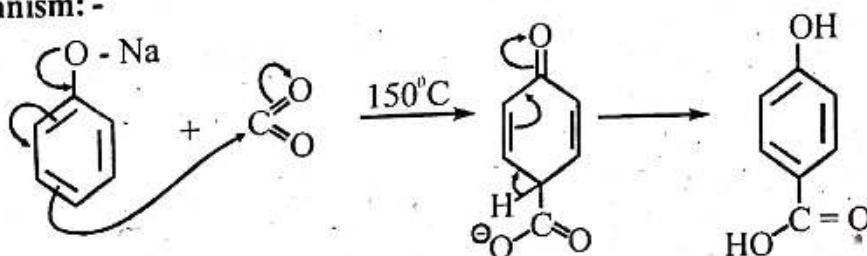
Mechanism -

Go through the theory part.

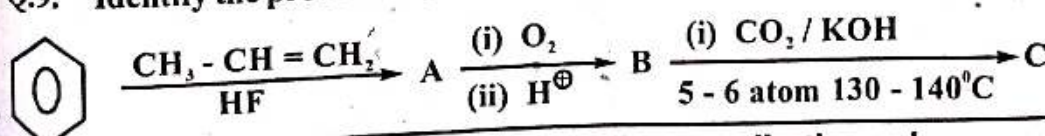
(b) Hint - Kolbe-Schmitt reaction.



Mechanism: -

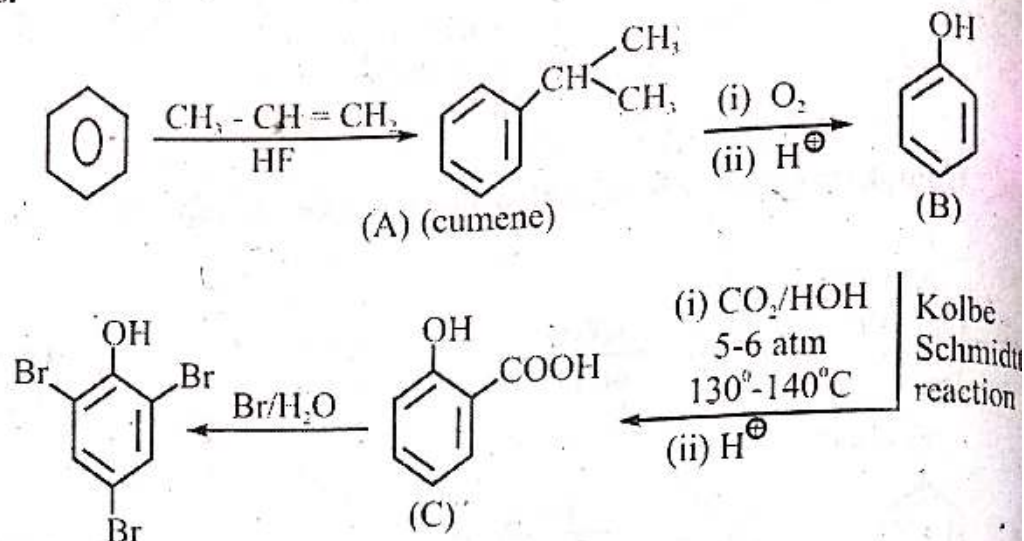


Q.9. Identify the products A, B, C and D in the sequence of the reaction.

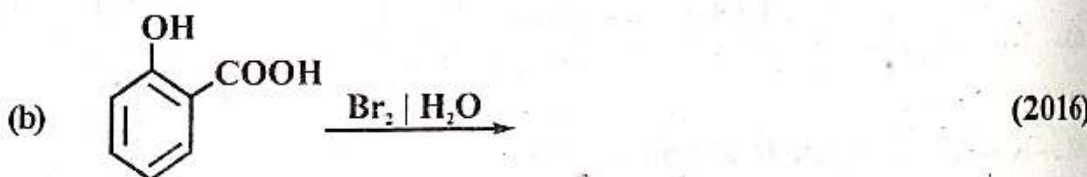
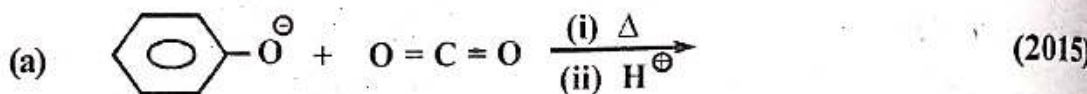


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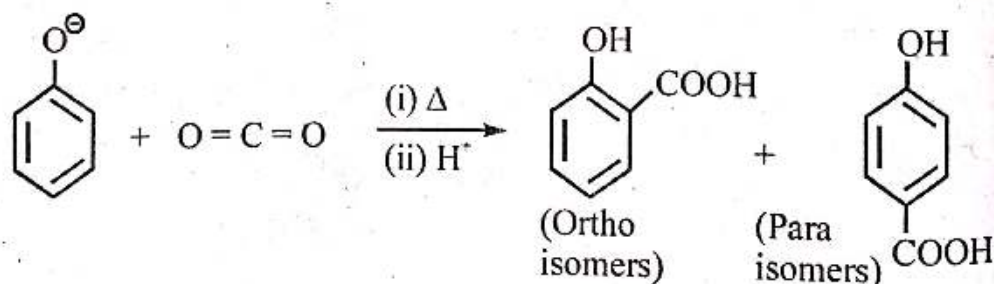
Ans.



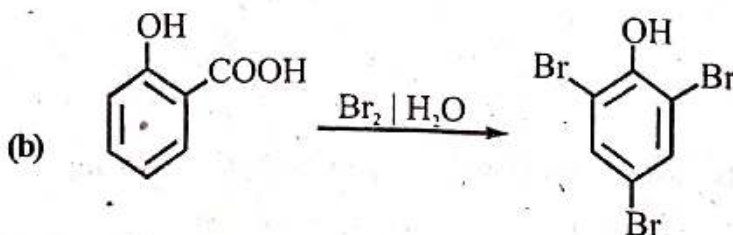
Q.10. Complete the following reaction



Sol. (a) Hint - Kolbe - Schmitt reaction.

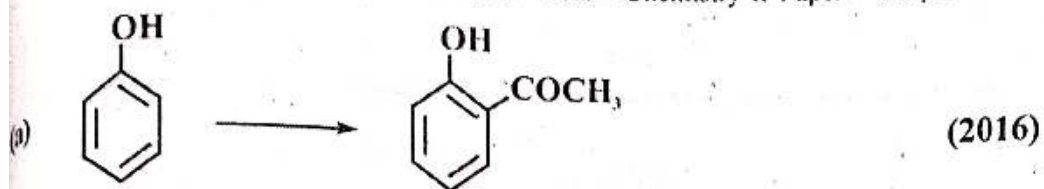


At higher temperature para isomers dominant over ortho product and vice versa.

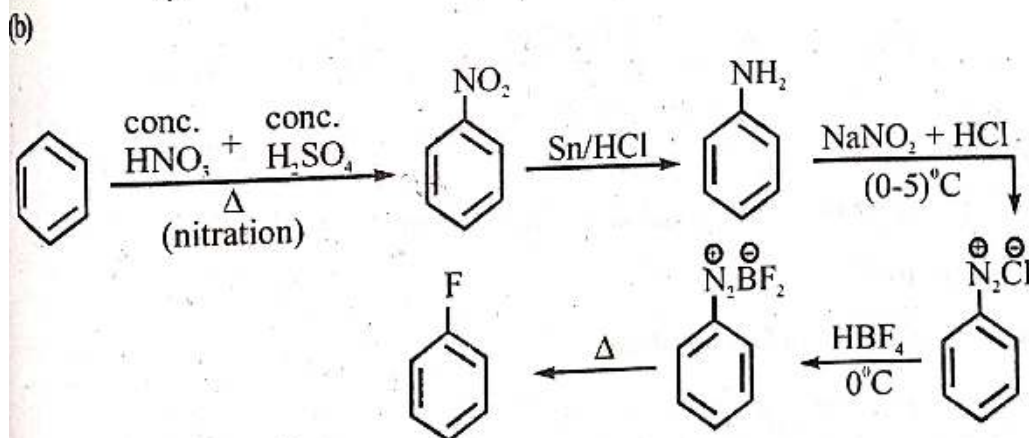
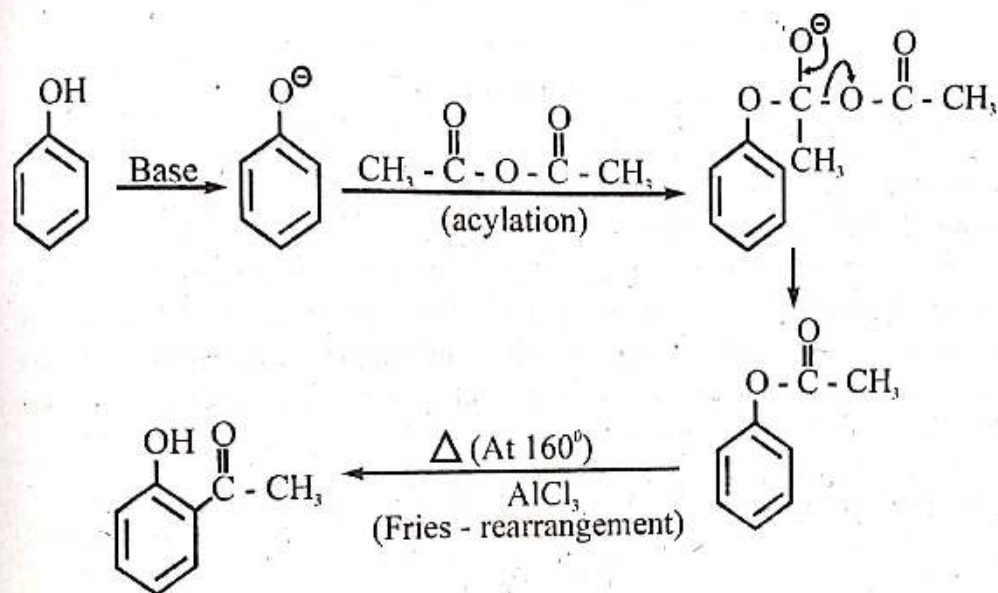


Q.11. How will you bring the following transformation -

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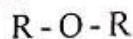
Ans. (a)



Chapter 4

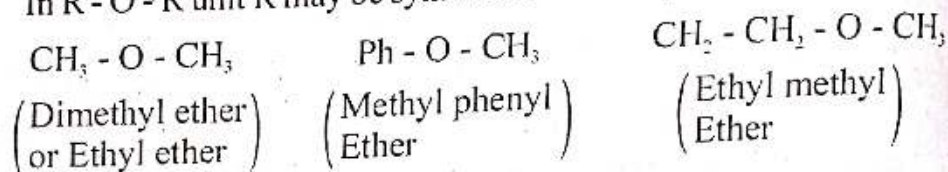
Ethers And Epoxides

Ethers: -



Ethers are those compounds which contains R - O - R unit.

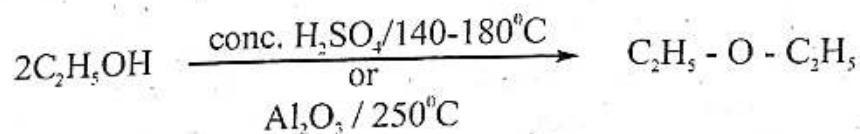
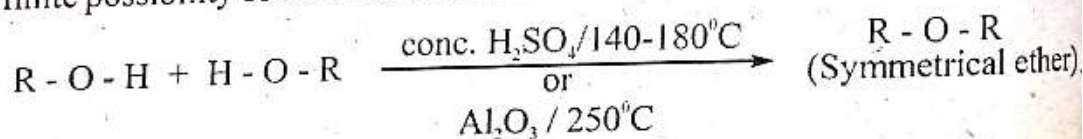
- In R - O - R unit, group R may be aliphatic or aromatic.
- In R - O - R unit R may be symmetrical or unsymmetrical.



Methods of Preparation: -

(i) From Alcohol (Dehydration) -

Symmetrical ether are prepared by heating on excess of alcohol with conc. H_2SO_4 . In this reaction primary alcohols undergoes dehydration to give ether. But secondary and tertiary alcohols undergoes dehydration to give mixture of ether and alkene because in secondary and tertiary alcohol there are finite possibility of elimination reaction.

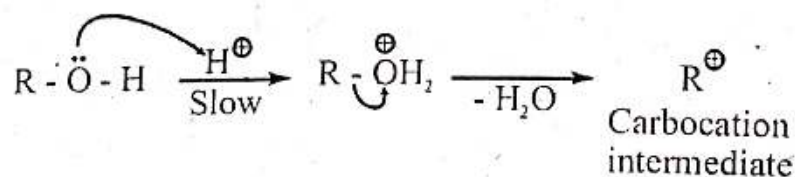


Mechanism: -

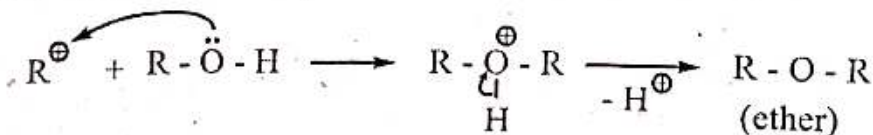
The reaction proceeds through either S_N1 or S_N2 mechanism.

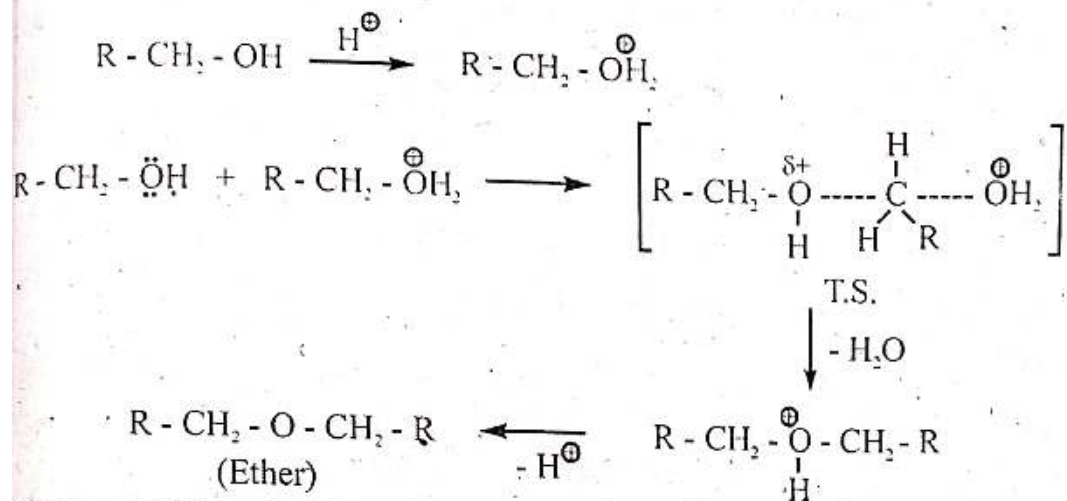
S_N1 Mechanism -

Step (i) - Formation of Carbocation -

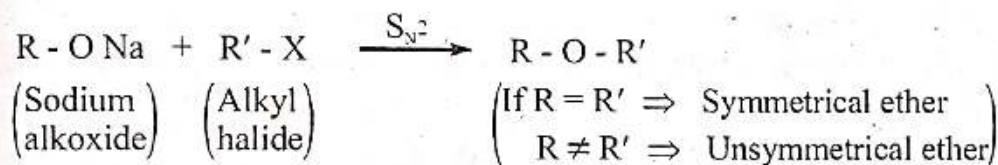
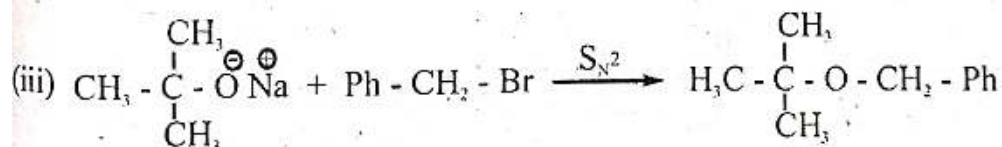
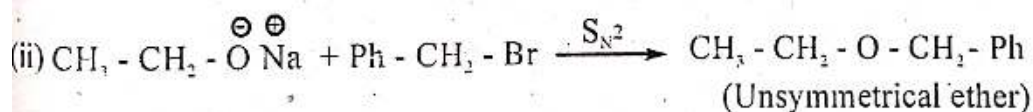
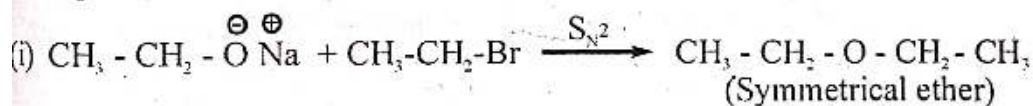


Step (ii) - Attack of nucleophile -



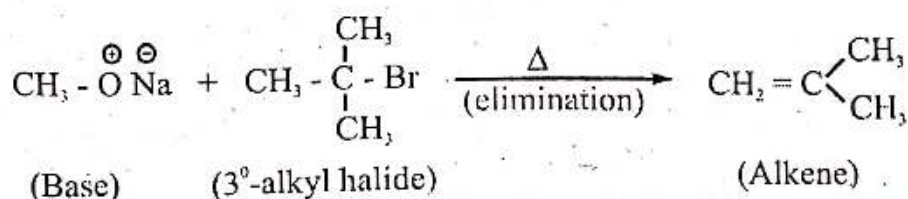
S_N² - Mechanism -**(II) From Williamson Ether Synthesis: -****(2019)**

In this reaction ether are prepared by reaction of sodium alkoxides with alkyl halide. This is the most important method for the preparation of symmetrical and asymmetrical ether or alkene.

**Example -**

- In this reaction sodium alkoxide may be alkoxide of primary or secondary alcohols.

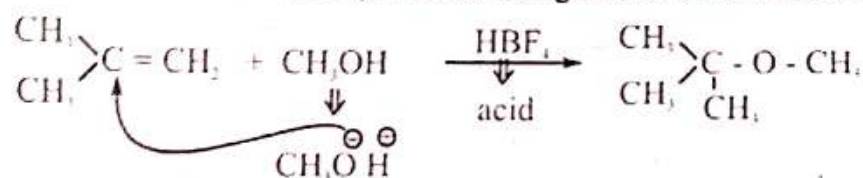
- In this reaction methyl halide are primary alkyl halide generally used. Secondary and tertiary alkyl halide give elimination reaction in the presence of sodium alkoxide base.



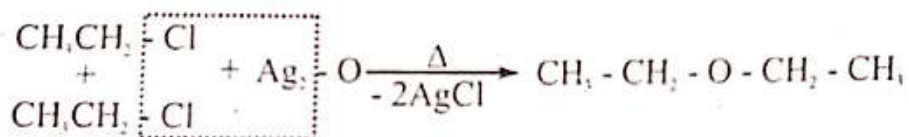
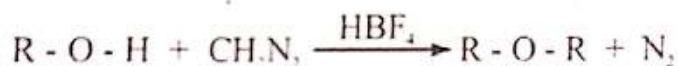
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(iii) From Alkenes: -

The reaction of alkene and alcohol in the presence of acid gives ether as a product. The reaction takes place according to the Markownikov's rule.

**(iv) By heating alkyl halide with dry silver oxide (Ag_2O): -**

Hint -

**(v) By action of diazomethane on alcohols: -**

Chemical reaction: -

(1) Reaction with acids: -

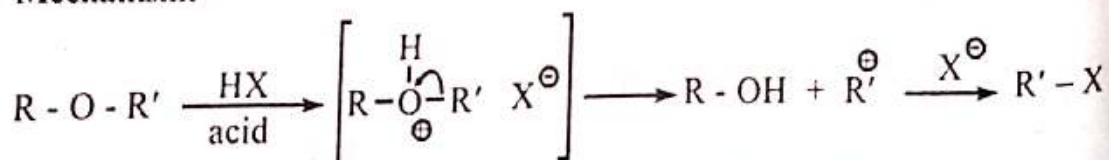
When ether reacts with Lewis acid then the formation of co-ordination complex takes place.



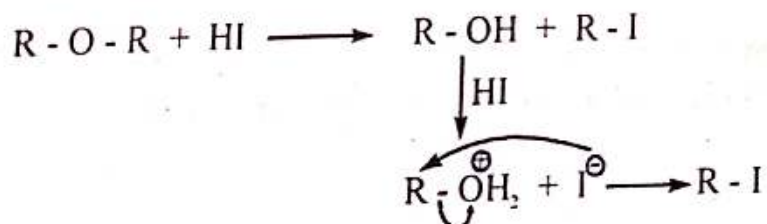
When ether reacts with acid halide like HI or HBr, the formation of alcohol and alkyl halide takes place.



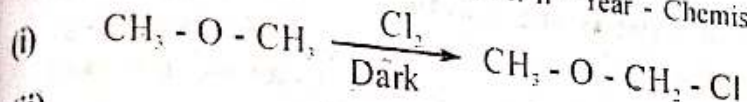
Mechanism: -



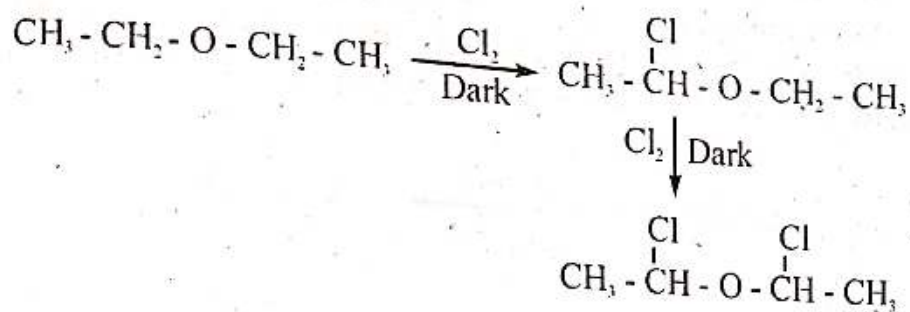
When HI is present in excess then only alkyl halide forms.

**(2) Halogenation reaction: -**

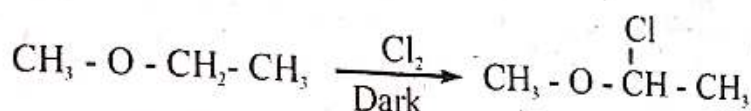
When ether is treated with " Cl_2 " or " Br_2 " in dark substitution product on α -carbon is formed.



(ii)

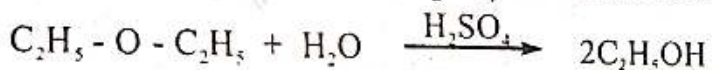


(iii)

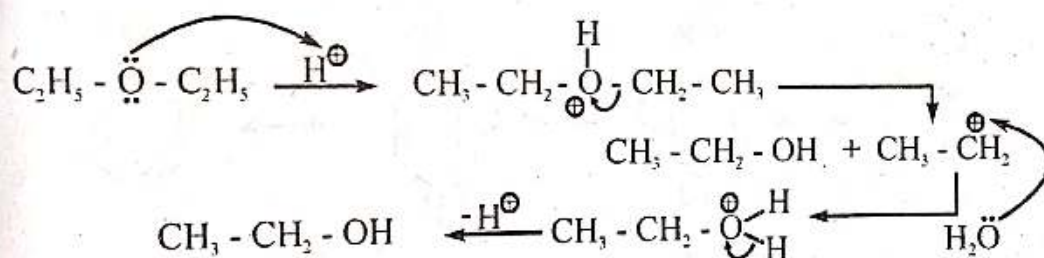


(3) Reaction with H_2SO_4 (Hydrolysis): -

When ether treated with dil H_2SO_4 , the formation of alcohol takes place.

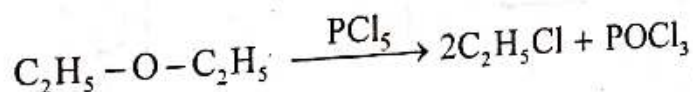
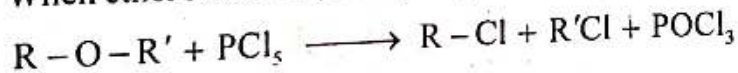


Mechanism: -

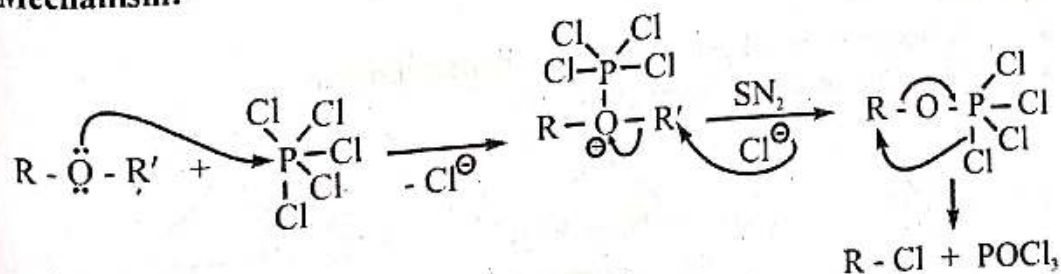


(4) Reaction with PCl_5 : -

When ether react with PCl_5 , they form alkyl halide.



Mechanism: -

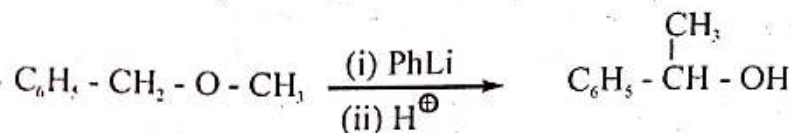


Q.1. Discuss the mechanism of Wittig reaction.

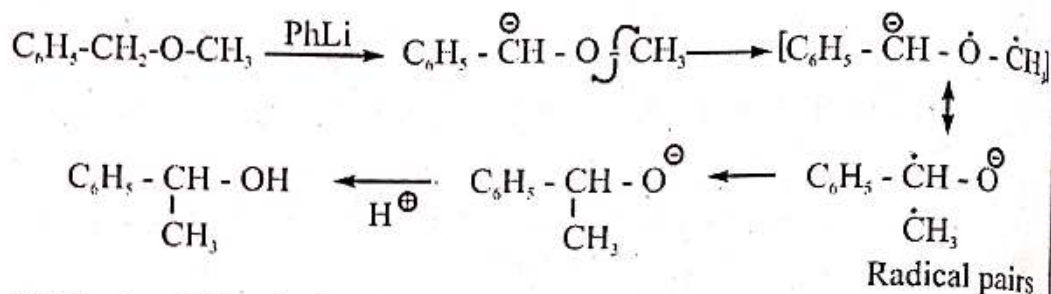
(5) Wittig Rearrangement:-

The base catalysed rearrangement of an ether to an alcohol via 1, 2 shift is known as Wittig rearrangement.

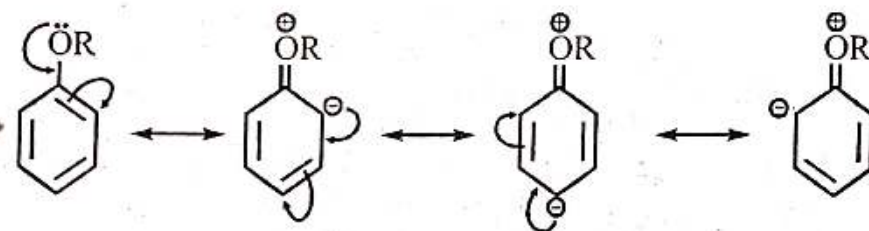
This rearrangement is given by Benzyl and Allyl ether whose carbanion is stabilized by resonance. Rearrangement takes place in the presence of strong base such as RLi and NaNH₂. Rearrangement takes place by radical pair mechanism.



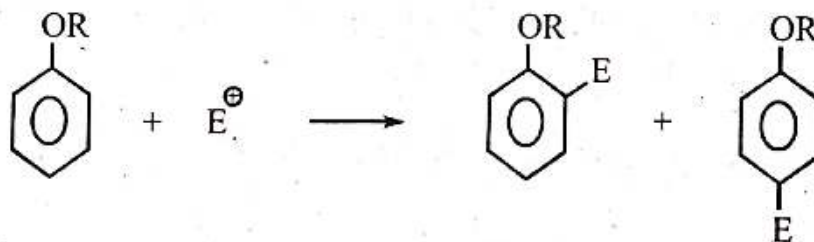
Mechanism:-



(6) Electrophilic substitution in aromatic ether:-

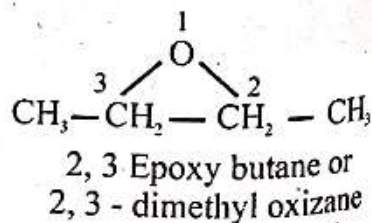
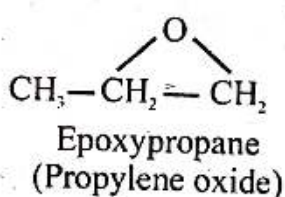
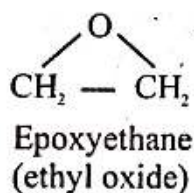


The aromatic ether behaves as an ortho-para directing group. Thus incoming electrophile attack on ortho and para position.



Epoxides:-

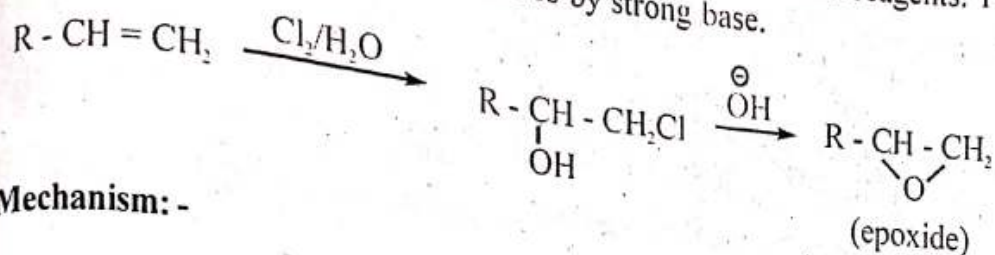
- Three membered cyclic ethers are called epoxide.
- Epoxide are also known as oxiranes.



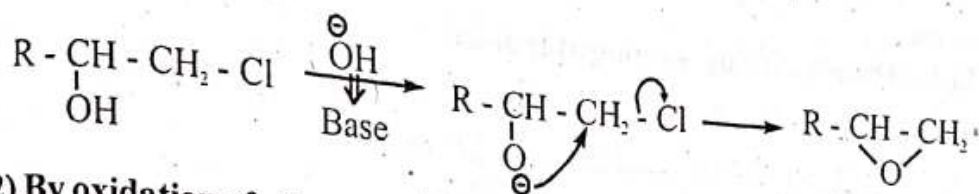
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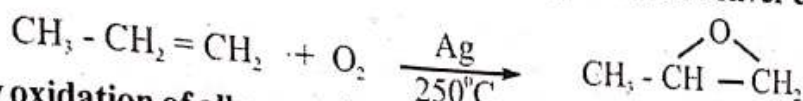
(1) From halohydrins - Alkenes form halohydrin with suitable reagents. The halohydrins are converted into epoxides by strong base.



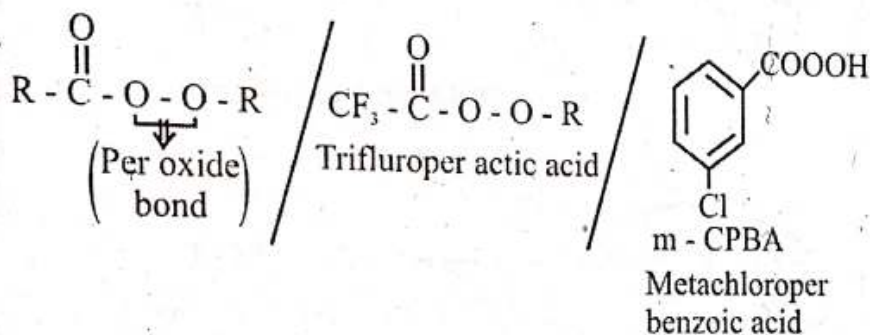
Mechanism: -



(2) By oxidation of alkene with oxygen in the presence of silver catalyst: -



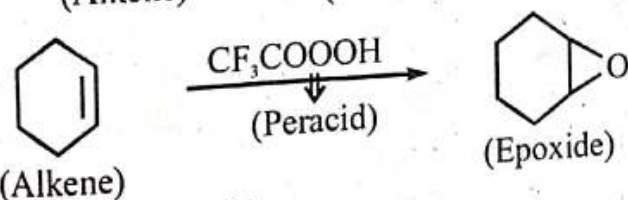
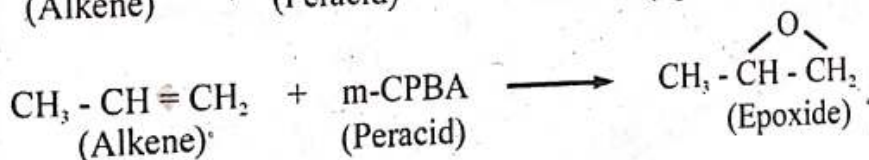
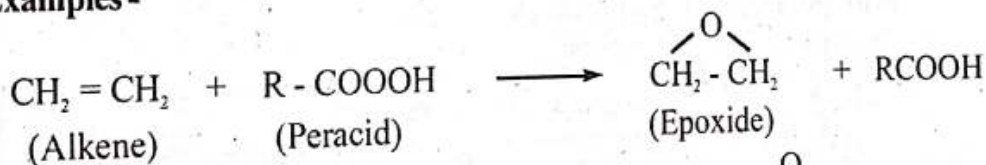
(3) By oxidation of alkenes with per acids: -



Per acids

Alkene + Peracids $\longrightarrow$ Epoxide

Examples -

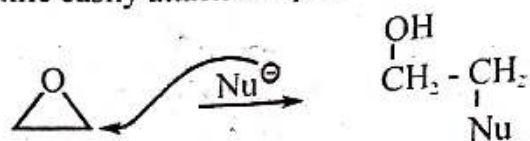


Reactions of epoxides -

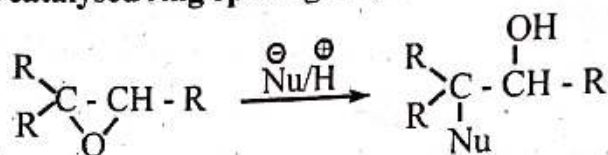
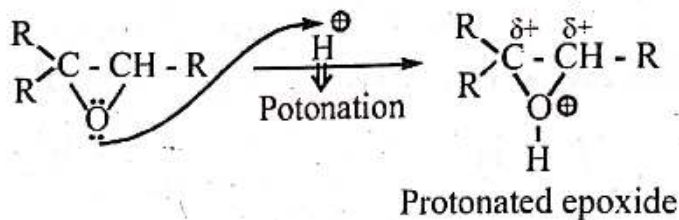
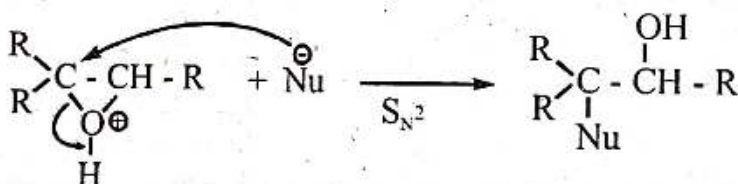
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Or Nucleophilic Substitution Reaction of Oxiranes: -

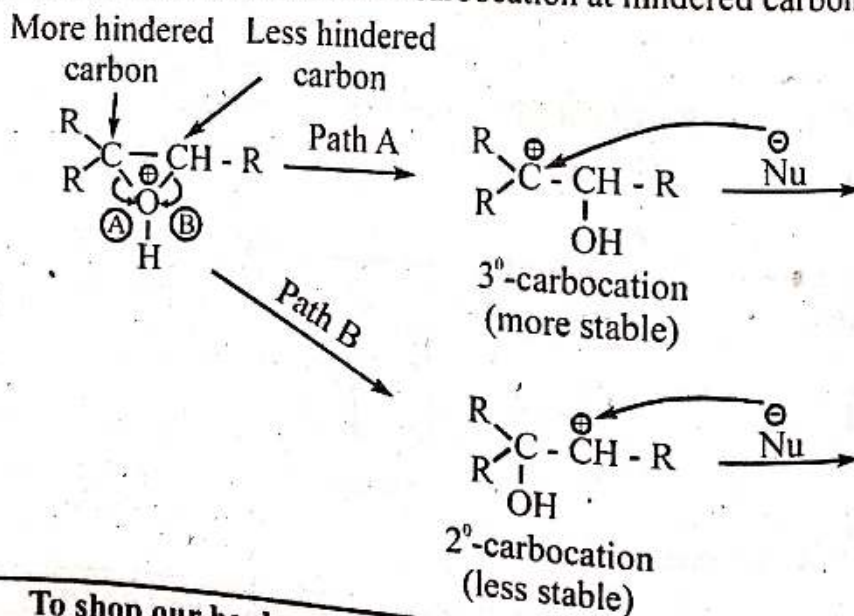
The most common reaction of epoxide is nucleophilic ring opening. Nucleophile easily attack on epoxide and open the three membered ring.



The nucleophilic ring opening of epoxide ring are catalysed by the acid or base.

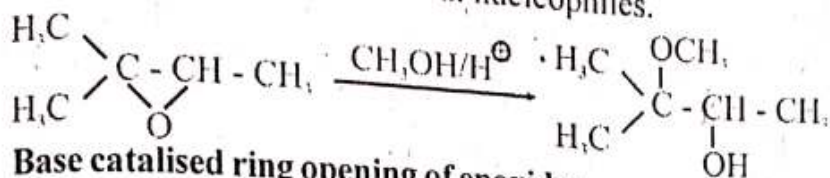
(A) Acid catalysed ring opening of epoxide: -**Step (i): -****Step (ii): -****Note: -**

- In the presence of acid, nucleophile attack on more hindered carbon because of formation of more stable carbocation at hindered carbon.

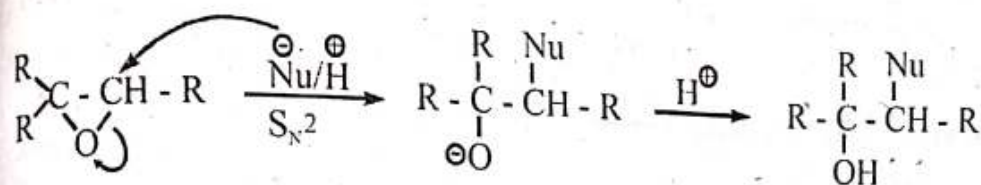


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2. -OH and -Nu are always trans to each other.
3. Reaction is favoured by neutral nucleophiles.

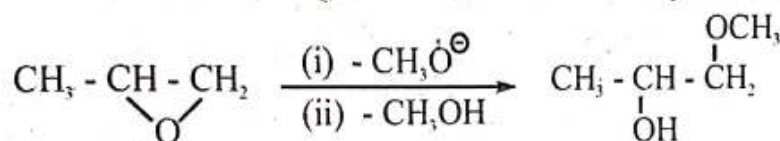


(B) Base catalysed ring opening of epoxide: -

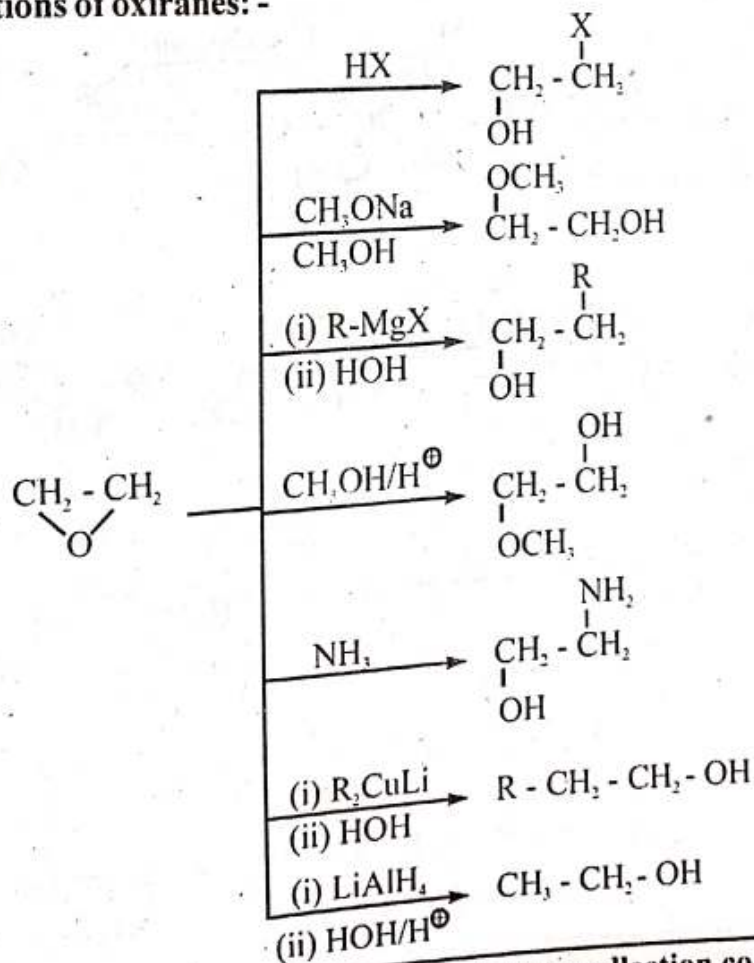


Note: -

1. In presence of base catalysed, nucleophile attacks on less hindered carbon of the ring.
2. Reaction is favoured by charged nucleophile.
3. Nucleophile of the reaction behaves as base catalyst.

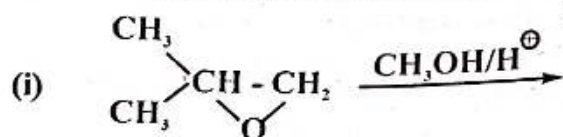


Some reactions of oxiranes: -

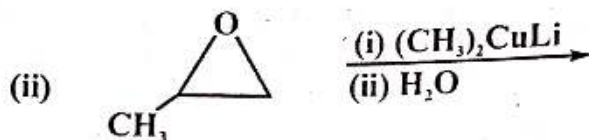


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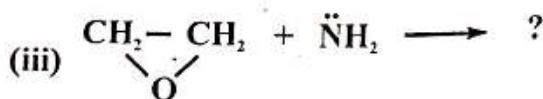
Q.2. Complete the following reaction -



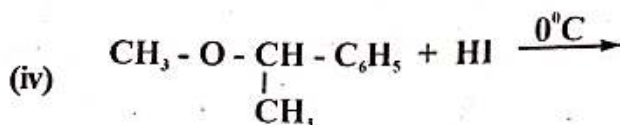
(2011, 19)



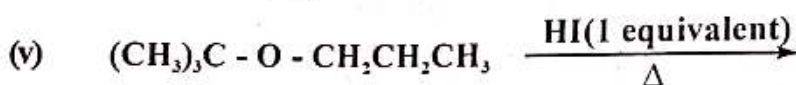
(2017)



(2019)



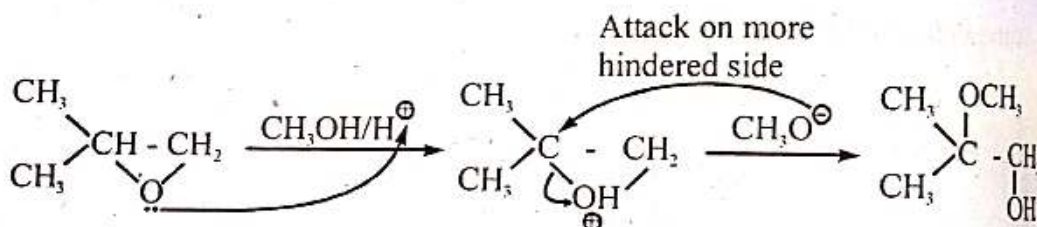
(2013)



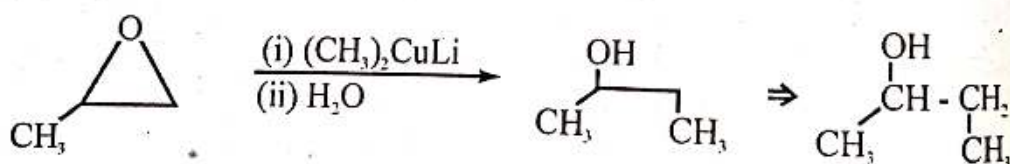
(2015)

Ans.

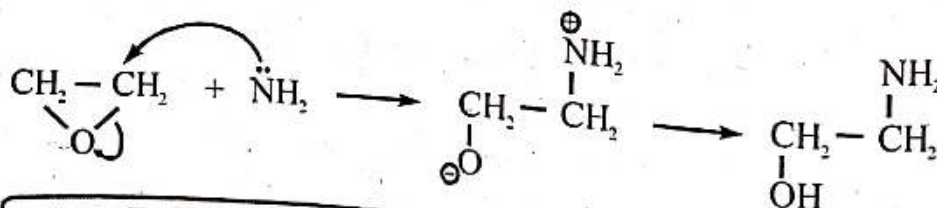
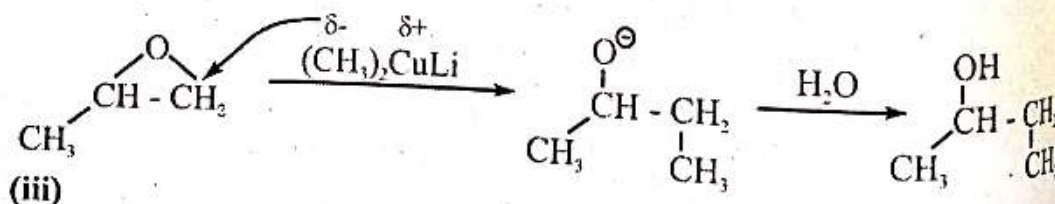
(i)



(ii)

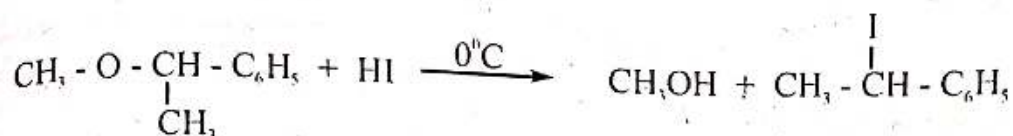


Mechanism -

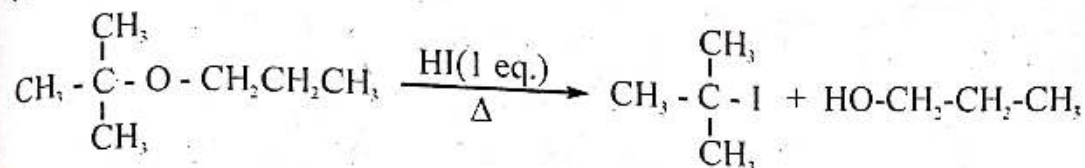


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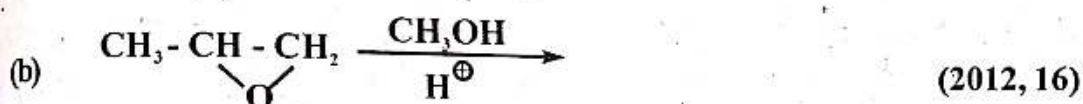
(iv)



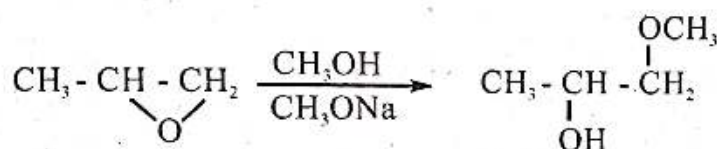
(v)



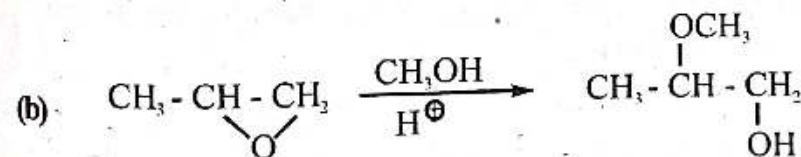
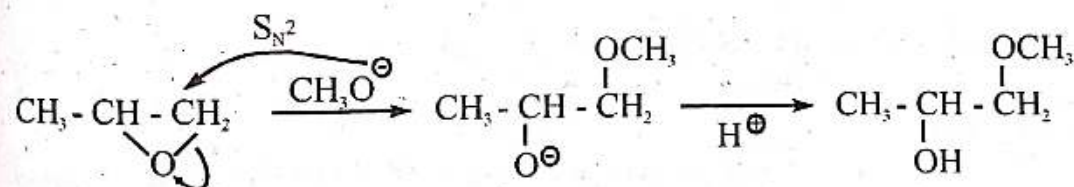
Q.3. Complete the following reaction and give their mechanism -



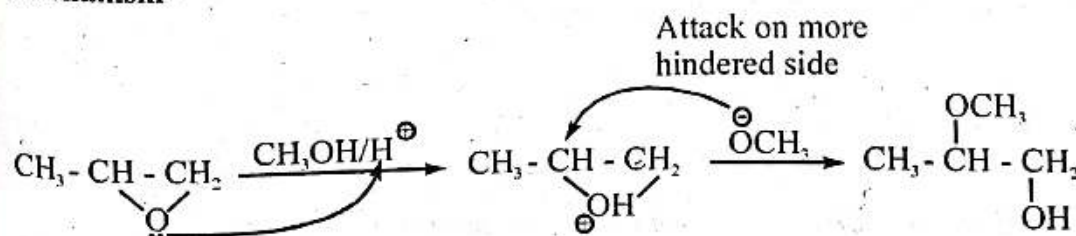
Ans. (a)



Mechanism -



Mechanism -



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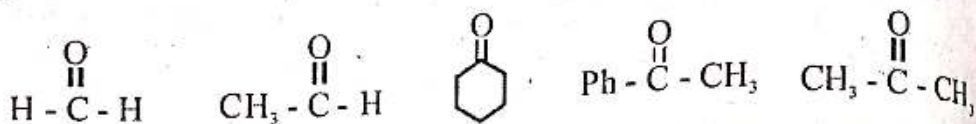
Chapter 5

Carbonyl compound:-

Carbonyl compounds are those compounds which contains carbonyl

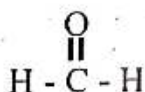
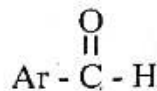
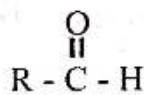
($>\text{C}=\text{O}$) functional group.

Ex:-

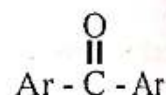
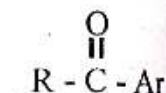
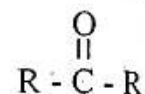


Carbonyl compounds

Aldehyde



Ketone



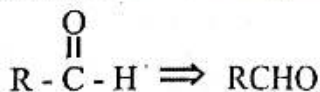
Carbonyl compounds divided into two categories-

1. Aldehyde
2. Ketone

1. Aldehyde:-

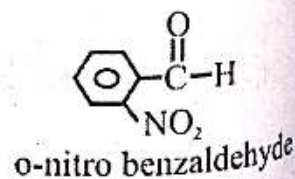
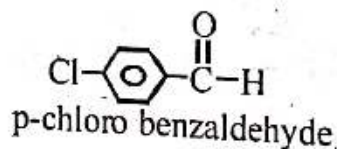
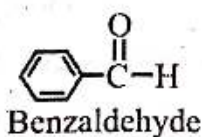
Aldehydes are those carbonyl compounds in which carbonyl carbon either attach with two hydrogen atom or attach with at least to one H-atom.

The general formula of aldehyde is-



where "R" is either alkyl group or aryl group. If "R" is alkyl group then the aldehydes are called aliphatic aldehydes.

Ex:-

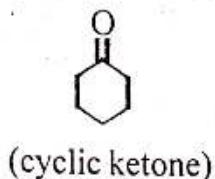
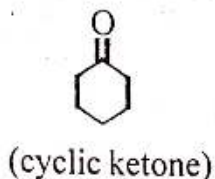
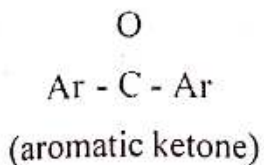
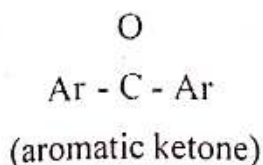
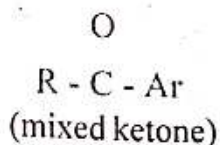


2. Ketone:-

Ketones are those carbonyl compounds in which carbonyl carbon

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$$\begin{array}{c} \text{O} \\ \parallel \\ \text{R} - \text{C} - \text{R} \\ \text{(aliphatic ketone)} \end{array}$$

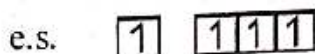
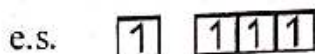
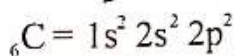
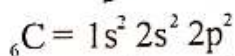
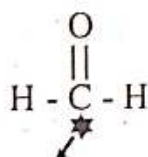
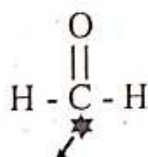
$$\begin{array}{c} \text{O} \\ | \\ \text{R} - \text{C} - \text{Ar} \\ \text{(mixed ketone)} \end{array}$$


Structure of carbonyl compounds:-

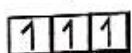
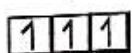
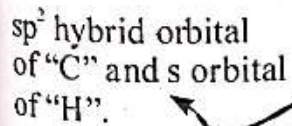
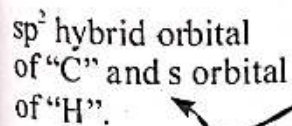
The hybridization state of carbonyl carbon is sp^2 and the geometry or shape of carbonyl carbon is trigonal-planar with bond angle 120° .

Carbonyl carbon contain three sp^2 -hybrid orbitals and one unhybridised p-atomic orbital. Out of three sp^2 -hybrid orbital two sp^2 -hybrid orbital form σ -bond with "s" orbital of H-atom by end to end overlapping and one sp^2 -hybrid orbital forms σ -bonds with p-atomic orbital of O-atom. Unhybridised p-atomic orbital of carbonyl carbon forms π -bonds by lateral overlapping with p-atomic orbital of "O"-atom. Thus carbonyl carbon forms three σ -bond and one π -bond.

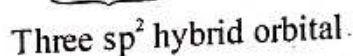
Ex:-

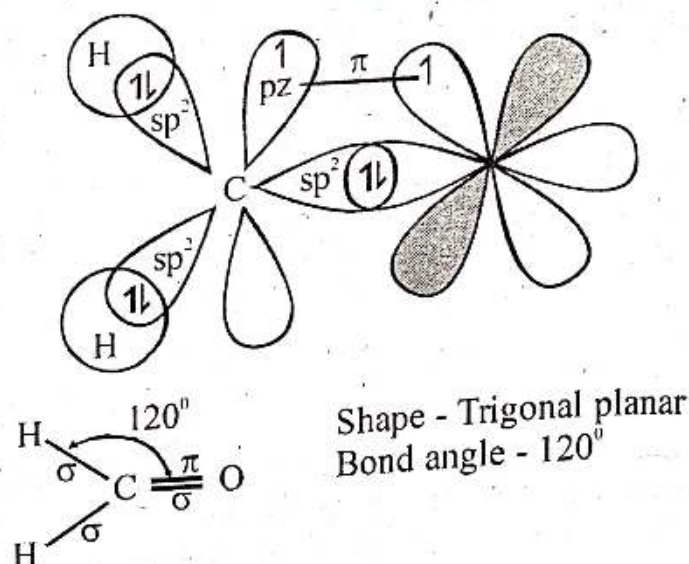


sp^2 hybridization



Unhybridized "p_z" atomic orbital.





Q.1. Write short note on reactivity of Carbonyl compounds for nucleophilic addition. (2012, 16)

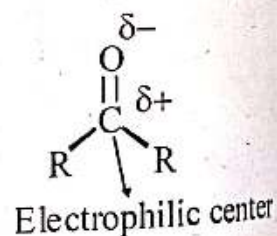
Other Related Questions -

Q. Write short note on reactivity of carbonyl compounds. (2015)

Ans. Reactivity of carbonyl compounds:-

Carbonyl carbon contain partial positive charge and oxygen contain partial negative charge due to partial displacement of $\sigma - e^-$ towards "O" atom (-I effect).

Due to presence of partial positive charge on carbonyl carbon it behaves as a electron deficient center or electrophilic centre. So carbonyl compounds are reactive towards nucleophile and gives nucleophilic addition reaction.



Carbonyl compounds shows two resonating structure which is given below -

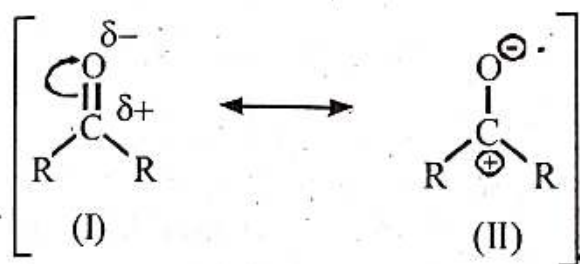
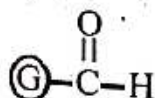


Figure - Resonance structure of carbonyl compounds

If the electrophilicity of carbonyl carbon increases then nucleophilic addition reaction rate increases or reactivity of carbonyl carbon increases.

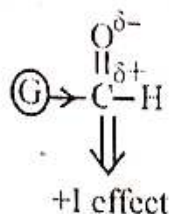
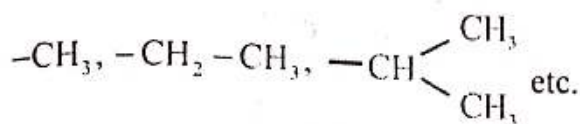


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Case (I):-

When G is +I - group:-

Ex:-

Increase δ^+ density on carbonyl carbon

Magnitude of partial positive charge on carbonyl carbon decrease



Electrophilicity of carbonyl carbon decreases



Reactivity of carbonyl group decreases

Thus,

$$\text{Reactivity of carbonyl compound} \propto \frac{1}{+\text{I effect}}$$

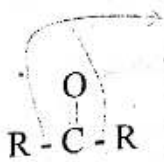
Q.2. Why aldehyde are more reactive than ketone?

Ans. Aldehyde are more reactive than ketone due to two factors-

(I) Electronic factor:-



(More electrophilic)



(Less electrophilic)

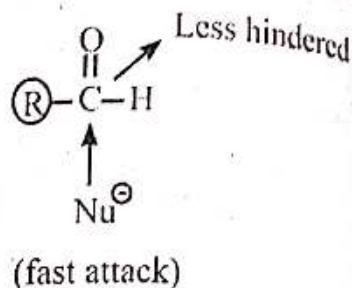
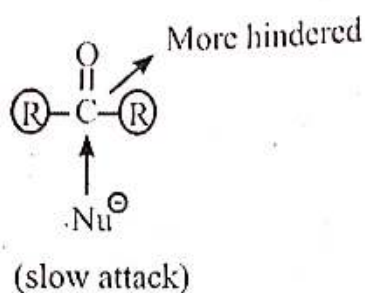
$$\left. \begin{array}{l} +\text{I effect decrease} \\ \text{electrophilicity of} \\ \text{carbonyl carbon by} \\ \text{increase electron} \\ \text{density} \end{array} \right\}$$

Aldehydic carbonyl carbon are more electrophilic than ketonic carbonyl carbon because aldehydic carbonyl carbon attached with only one alkyl group (+I group) whereas ketonic carbonyl carbon attach with two alkyl groups (+I group).

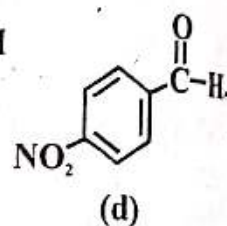
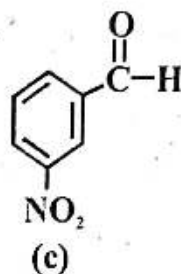
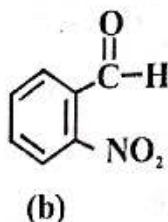
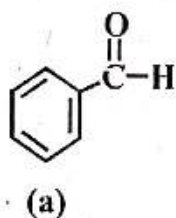
(II) Steric factor:-

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Nucleophile easily attack on aldehydic carbonyl carbon than ketonic carbonyl carbon because steric hindrance around ketonic carbonyl carbon is more than steric hindrance around aldehydic carbonyl carbon.



Q.3. Arrange the following in decreasing order of reactivity of carbonyl compound.



Ans. Reason:-

Compound (a) - Compound (a) does not substituted

Compound (b) (1). -M effect increase reactivity by decreasing $\pi - e^-$ density on carbonyl 'C'.

Compound (2). Strong -I effect also increases reactivity by decreasing $\sigma - e^-$ density on carbonyl "C".

Compound (c) (1). -M effect of NO_2 group does not affects the reactivity of carbonyl carbon.

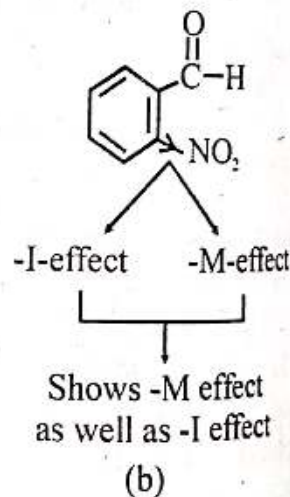
Compound (2). Moderate -I effect decrease $\sigma - e^-$ density on carbonyl "C".

Hence increase reactivity.

Compound (d) (1). -M effect increase reactivity by the decreasing $\pi - e^-$ density on carbonyl 'C'.

(2). Weak -I effect also increase reactivity by decreasing $\sigma - e^-$ density on carbonyl carbon.

Reactivity order - (b) > (d) > (c) > (a)
ortho para meta simple

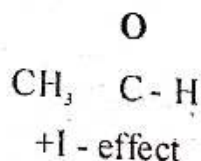


Q.4. Why aliphatic carbonyl compounds are more reactive than aromatic carbonyl compound for nucleophilic addition? (2011)

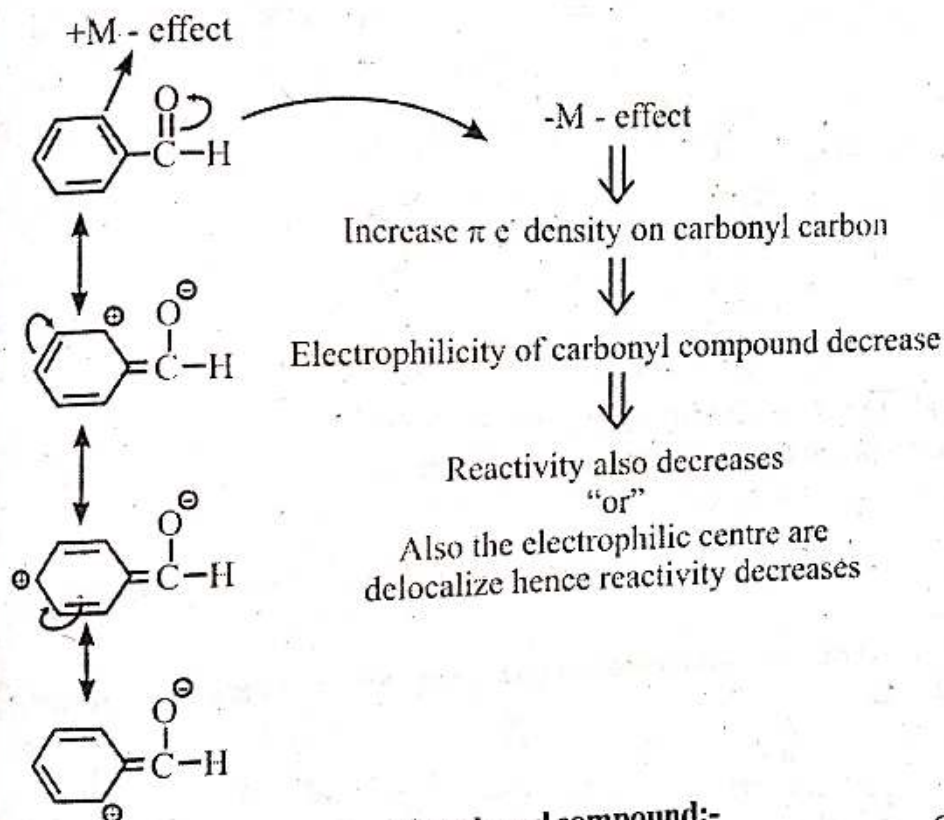
Ans. Aromatic carbonyl compounds are less reactive than aliphatic carbonyl compounds because due to +M - effect to benzen ring, the $\pi - e^-$ density on carbonyl carbon becomes increases so the electrophilicity of aromatic carbonyl

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Carbon become decreases and reactivity also decreases.



↓
↓
Decrease electrophilicity
of carbonyl carbon.
(In comparison with -I group)

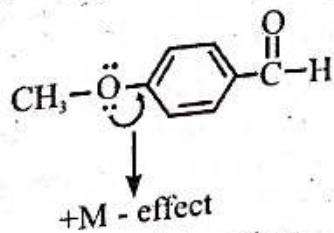


Reactivity of substituted aromatic carbonyl compound:-

Case I:-

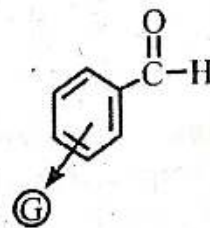
When "G" is +M group (at least one lone pair):-

Ex:- $-\ddot{\text{Cl}}:$, $-\ddot{\text{O}}\text{H}$, $-\ddot{\text{O}}\text{R}$, $-\ddot{\text{N}}\text{H}_2$, $-\ddot{\text{N}}\text{HR}$, $-\text{CH}_3$ etc.



↑ Increase π e^- density on carbonyl carbon
↑ Electrophilicity of carbonyl carbon decrease
↑ Reactivity also decrease.

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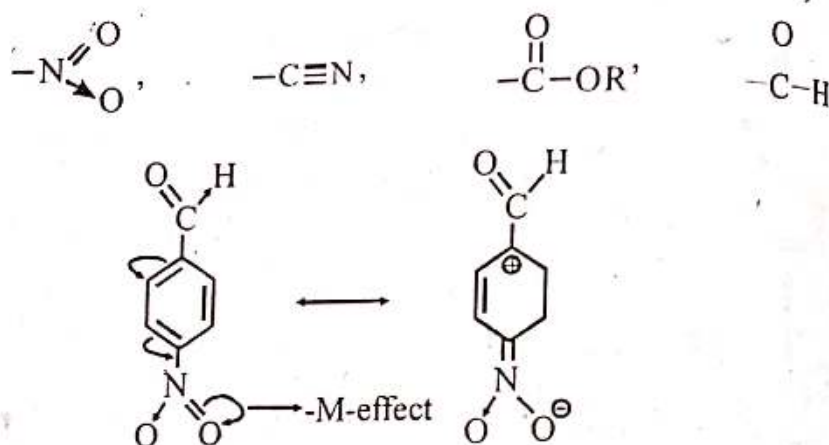
Reactivity of aromatic carbonyl compound $\propto$ $\frac{I}{+M\text{-effect}}$

+M - group on benzene ring of aromatic carbonyl compound decreases the reactivity of carbonyl group by increasing π - e⁻ density around the benzene ring.

Case II:-

when "G" is -M group (EWG group):-

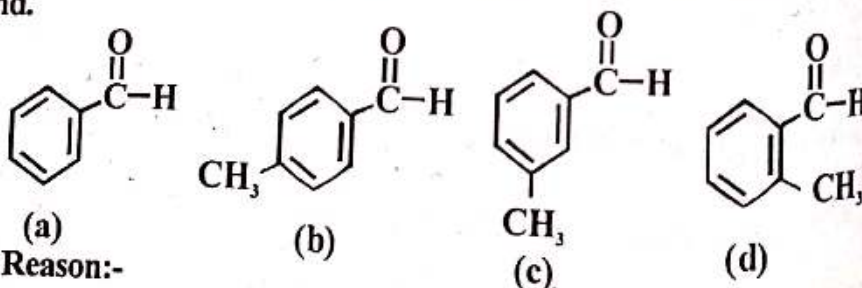
Ex:-



- ⇒ withdraw π - e⁻ density from carbonyl carbon
- ⇒ electrophilicity of carbonyl carbon increases
- ⇒ reactivity also increases

Reactivity of aromatic carbonyl compound $\propto$ -M group

Q.5. Arrange the following in increasing order of reactivity of carbonyl compound.



Ans. Reason:-

Compound (b) (1). Hyperconjugation of -CH₃ group decrease reactivity.
(2). Small +I - effect also decrease reactivity.

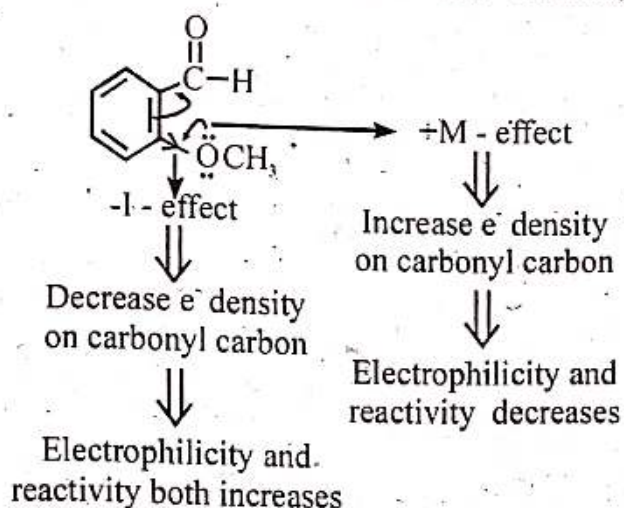
Compound (c) (1). Hyperconjugation does not effect the reactivity.
(2). Moderate +I effect decrease reactivity.

Compound (d) (1). Hyperconjugation of -CH₃ group decreases reactivity.
(2). Strong +I effect also decrease reactivity.

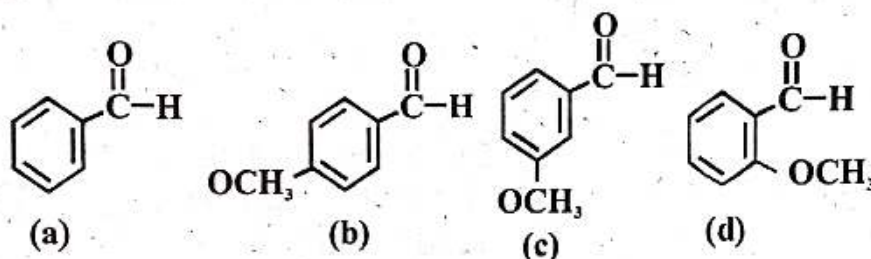
Reactivity order:- (d) < (b) < (c) < (a)

Note-

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Q.6. Arrange the following in decreasing order of reactivity of carbonyl compound.



Ans. Reason:- Compound (a) does not substituted.

Compound (b) (1). +M - effect decrease reactivity.

2). Small -I - effect increase reactivity.

Compound (c) (1). +M - effect of OCH_3 group does not affect reactivity of carbonyl group.

2) Moderate -I - effect increase reactivity.

Compound (d) (1). +M - effect decrease reactivity.

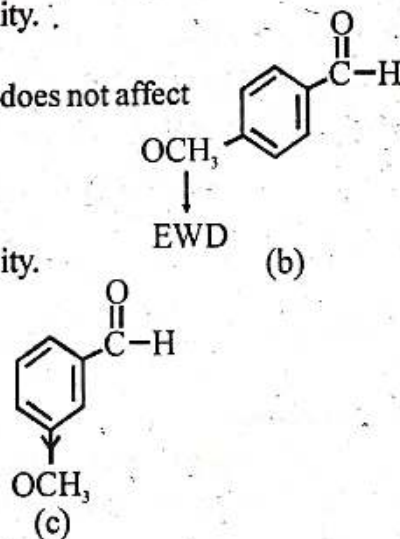
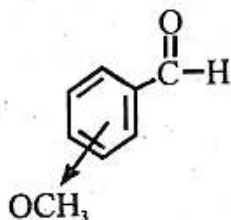
2). Strong -I - effect increase reactivity.

Reactivity order:- (c) > (a) > (d) > (b)

Note:-

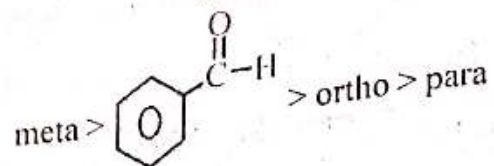
General formula:-

Case (I) - When EDG are attached on ring.



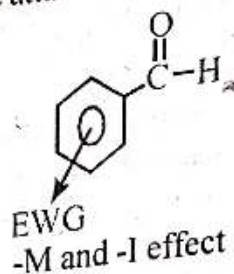
Reactivity Order -

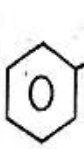
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(Simple)

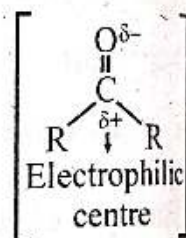
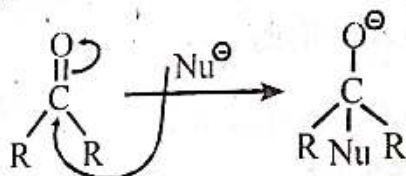
Case (II) - When EWG are attached on ring.



Reactivity Order - ortho-derivative > para-derivative > meta > 
(Simple)

Reactions of carbonyl compound:-

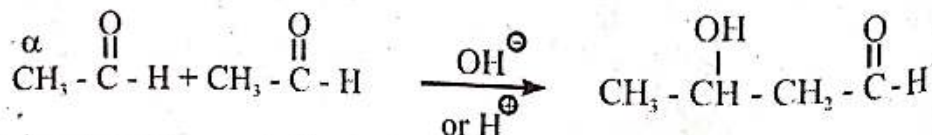
Carbonyl compound mainly give nucleophilic addition reaction due to displacement of $\sigma - e^-$, a partial negative charge generated on carbonyl oxygen and a partial positive charge generated on carbonyl carbon. Thus carbonyl carbon behaves as a electron deficient centre or electrophilic centre. Nucleophile easily attack on carbonyl carbon to give nucleophilic addition reaction.

**Nucleophilic addition:-**

Some important nucleophilic addition reaction of carbonyl compound are given below:-

Aldol reaction:-

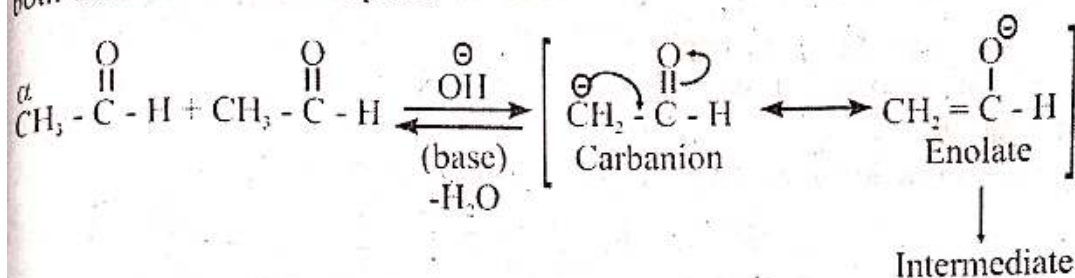
The base or acid catalysed dimerisation of carbonyl compound having ' α ' Hydrogen, are called aldol reaction.

**Mechanism of base catalysed Aldol reaction -**

Step (1):- Due to electron withdrawing nature (EWN) of carbonyl group, the $\alpha - \text{H}$ becomes acidic. So when carbonyl compound react with base the $\alpha - \text{H}$ easily remove and forms carbonion intermediate. This carbonion intermediate

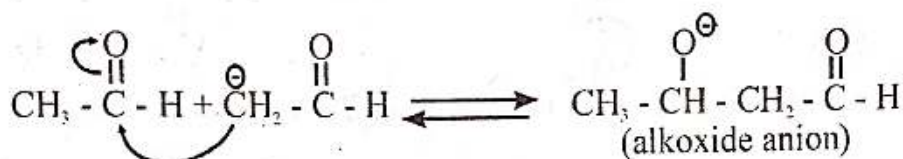
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radially converted into more stable enolate ion. Carbanion and enolate ion both behaves as a nucleophile.

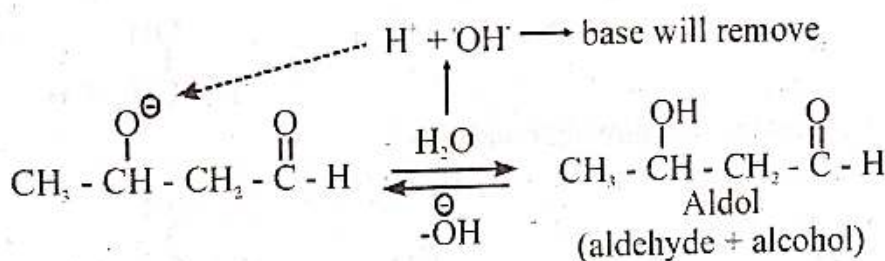


Step II:-

The carbanion intermediate or enolate ion intermediate gives nucleophilic addition reaction on another carbonyl compound.



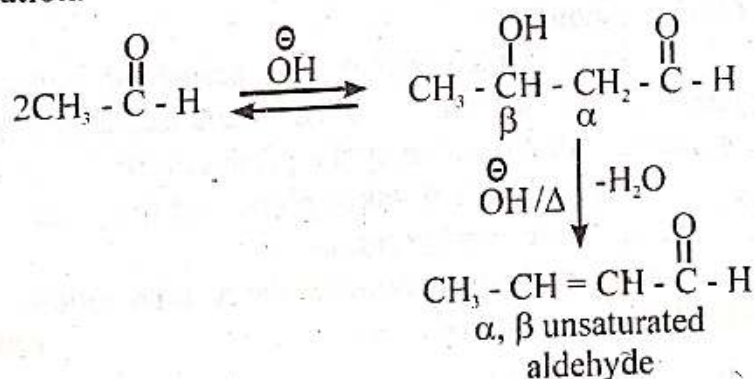
Step III:-



Aldol reaction is a reversible reaction.

Aldol condensation:-

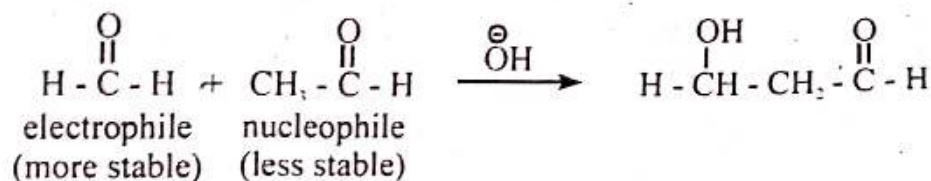
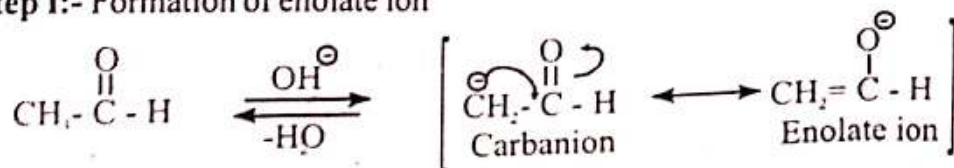
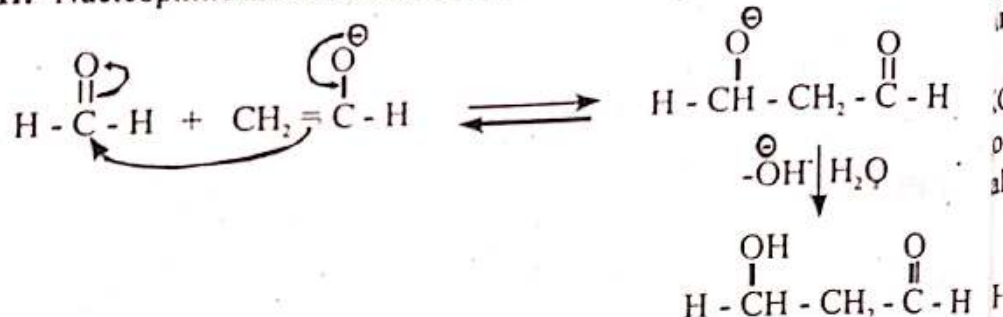
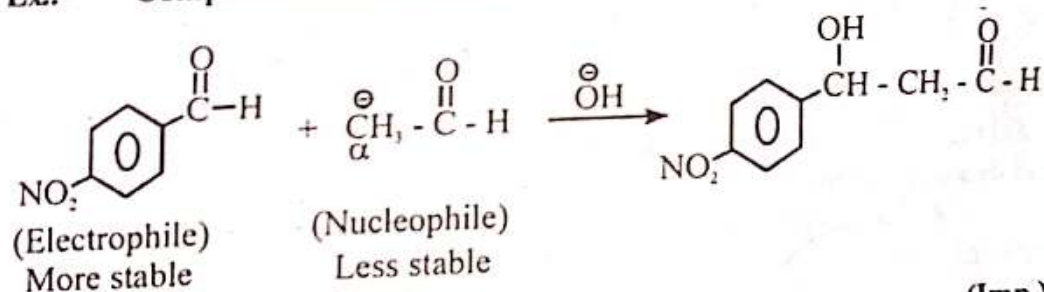
Aldol reaction followed by condensation reaction, are called Aldol condensation.



On heating, 'H' releases from α and 'OH' releases from β .

Cross - Aldol Reaction (Clason Smith reaction):-

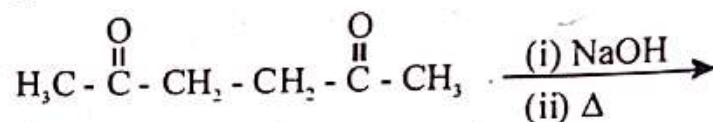
The aldol reaction between two different carbonyl compound are called cross - aldol reaction. For better reaction only one carbonyl compound contains α - Hydrogen.

**Mechanism:-****Step I:- Formation of enolate ion****Step II:- Nucleophilic attack of enolate ion****Ex:- Complete the following reaction -****Intramolecular Aldol reaction:-**

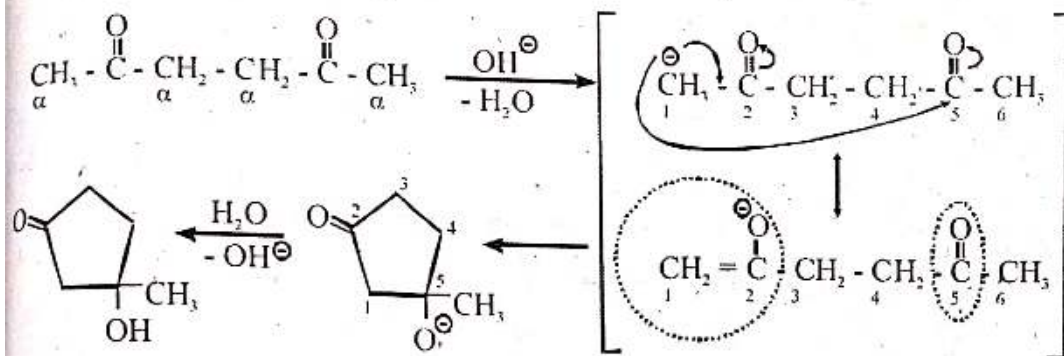
(Imp.) The aldol reaction in which nucleophilic partner and electrophilic partner both are present in same molecule are called intramolecular aldol reaction.

In intramolecular aldol reaction cyclic product form. In general the formation of highly substituted enolate takes place and ring size is 5 or 6 members (six member ring > five member ring).

Let us see some examples of Intramolecular Aldol reaction -

Ex - Complete the following reaction -

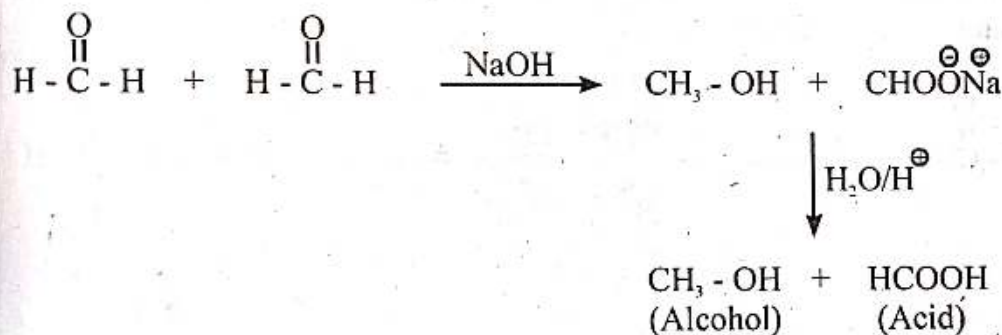
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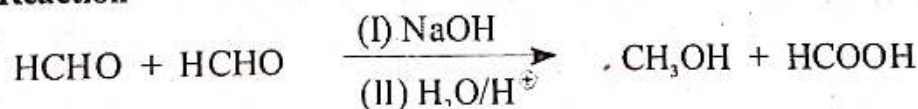
Q.7. Discuss the mechanism of Cannizzaro reaction. (2013, 18)

Ans. Cannizzaro reaction:-

The reaction of aldehyde having no α -hydrogen with NaOH or KOH, are called Cannizzaro reaction. In this reaction one aldehyde molecule undergoes oxidation and another aldehyde molecule undergoes reduction. So it is also called redox reaction. Cannizzaro reaction are given by only aldehydes not Ketones.

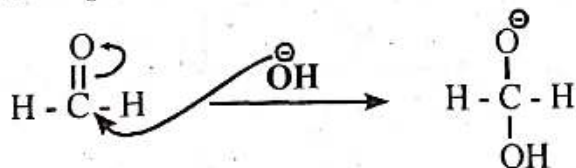


Overall Reaction -

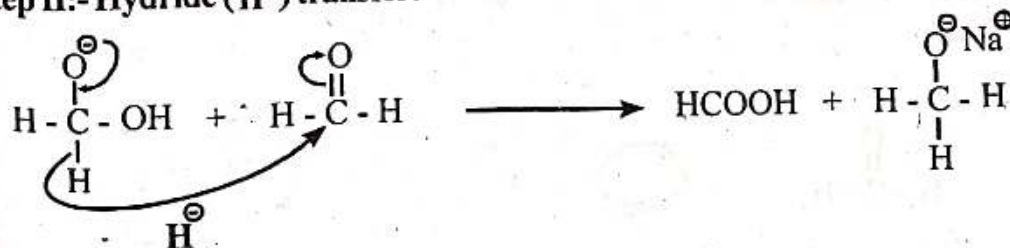


Mechanism:-

Step I:- Nucleophilic addition of $\text{OH}^\ominus$ on carbonyl carbon of aldehyde:-



Step II:- Hydride ($\text{H}^\ominus$) transfer:-

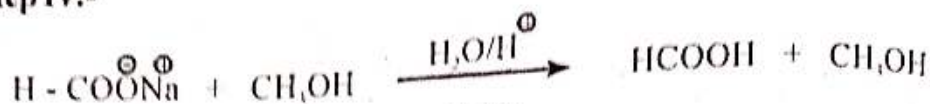


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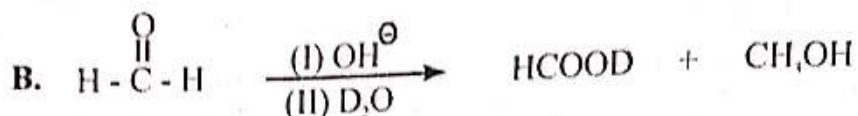
Step III:- Proton (H^+) transfer:-



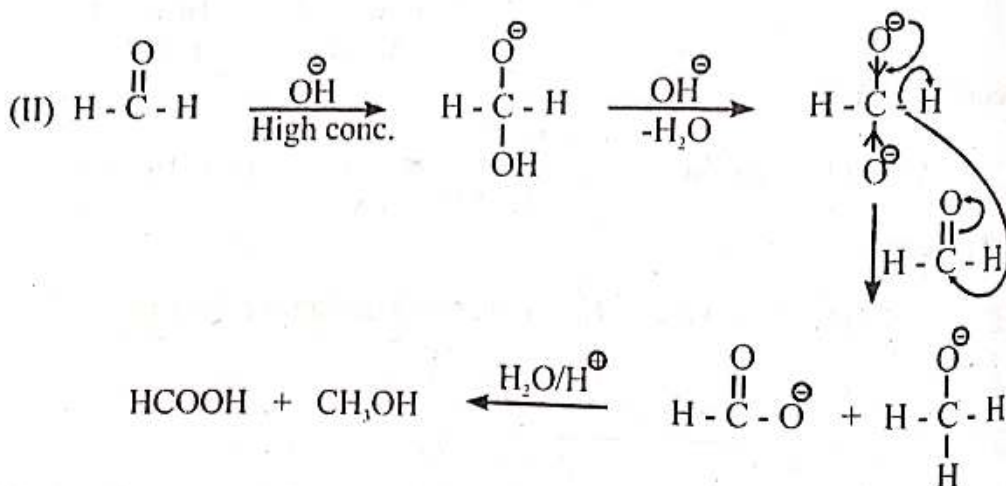
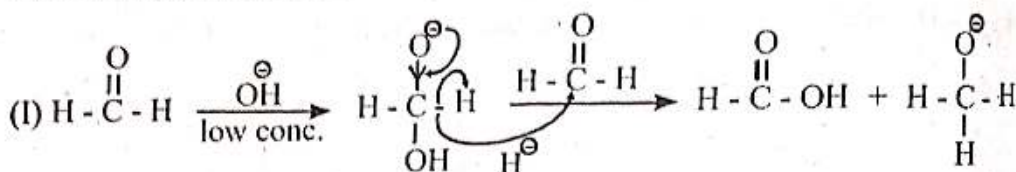
Step IV:-



Note:- Complete the following reactions -



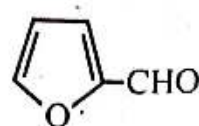
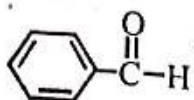
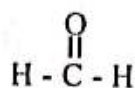
During Cannizzaro reaction the proton (H^+) given by water molecule attach with carboxylic acid and the proton attached on alcohol molecule comes from aldehyde molecules.



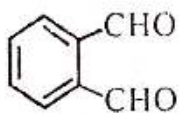
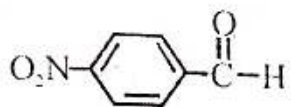
(II) reaction proceed faster than (I) reaction.

Cannizzaro reaction gives only those aldehyde which does not contain α -Hydrogen.

Ex:-

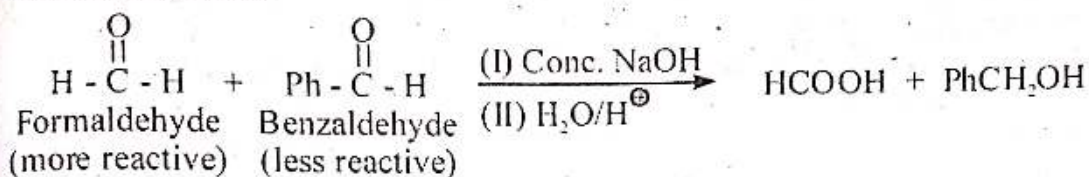
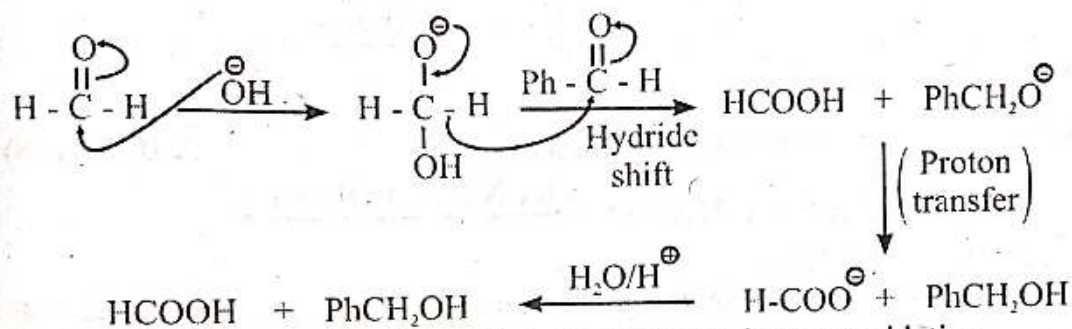


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**Cross Cannizzaro reaction:-**

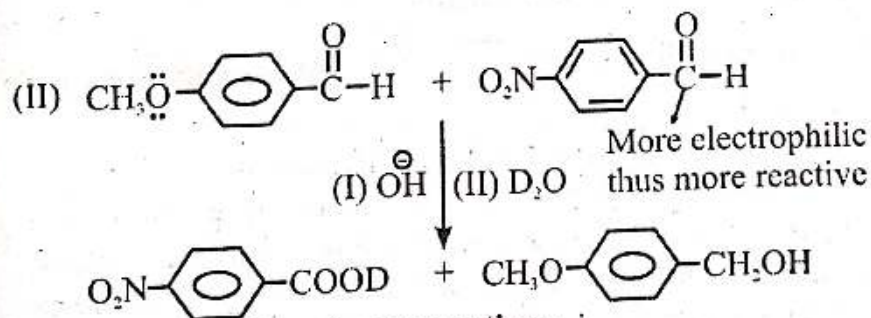
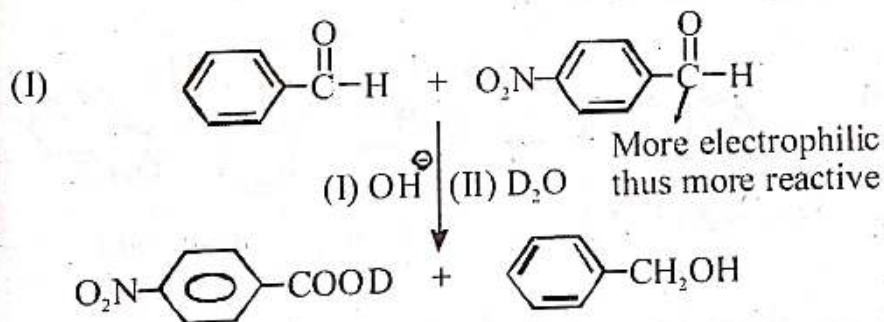
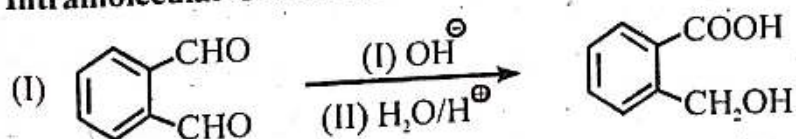
(2011, 13, 17)

Cannizzaro reaction between two different aldehyde are called cross cannizzaro reaction.

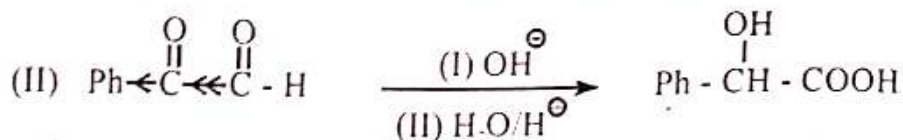
**Mechanism:-**

In cross cannizzaro reaction formaldehyde always undergoes oxidation.

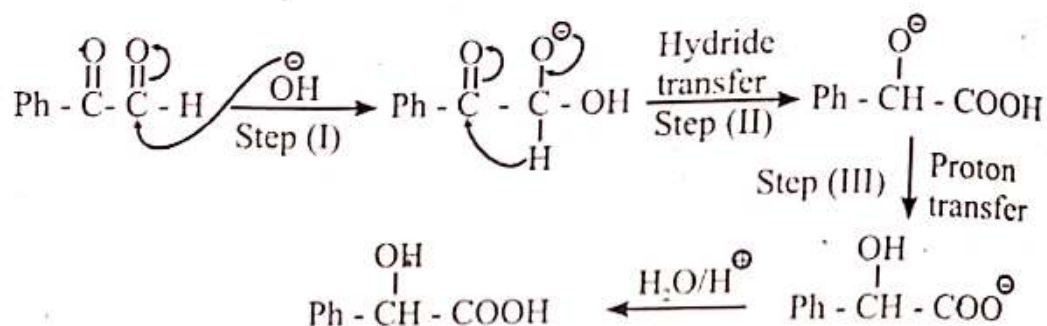
Ex.:- Complete the following reactions -

**Intramolecular Cannizzaro reaction:-**

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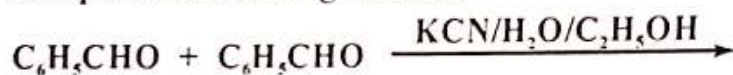


Mechanism:-



Q.8. Complete the following reaction -

(2013, 17, 18)



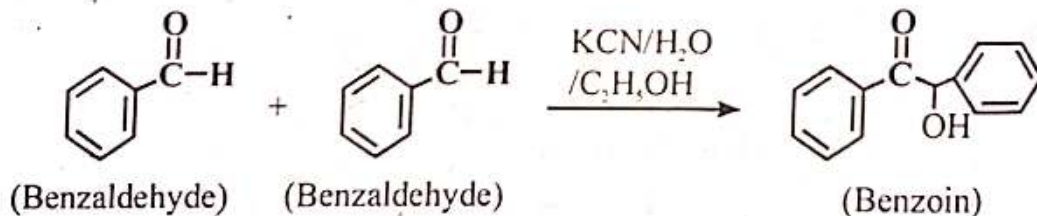
Other Related Questions -

Q. Discuss the mechanism of Benzoin condensation.

(2014)

Ans. Benzoin condensation:-

The reaction of benzaldehyde molecules in the presence of KCN are known as benzoin condensation.



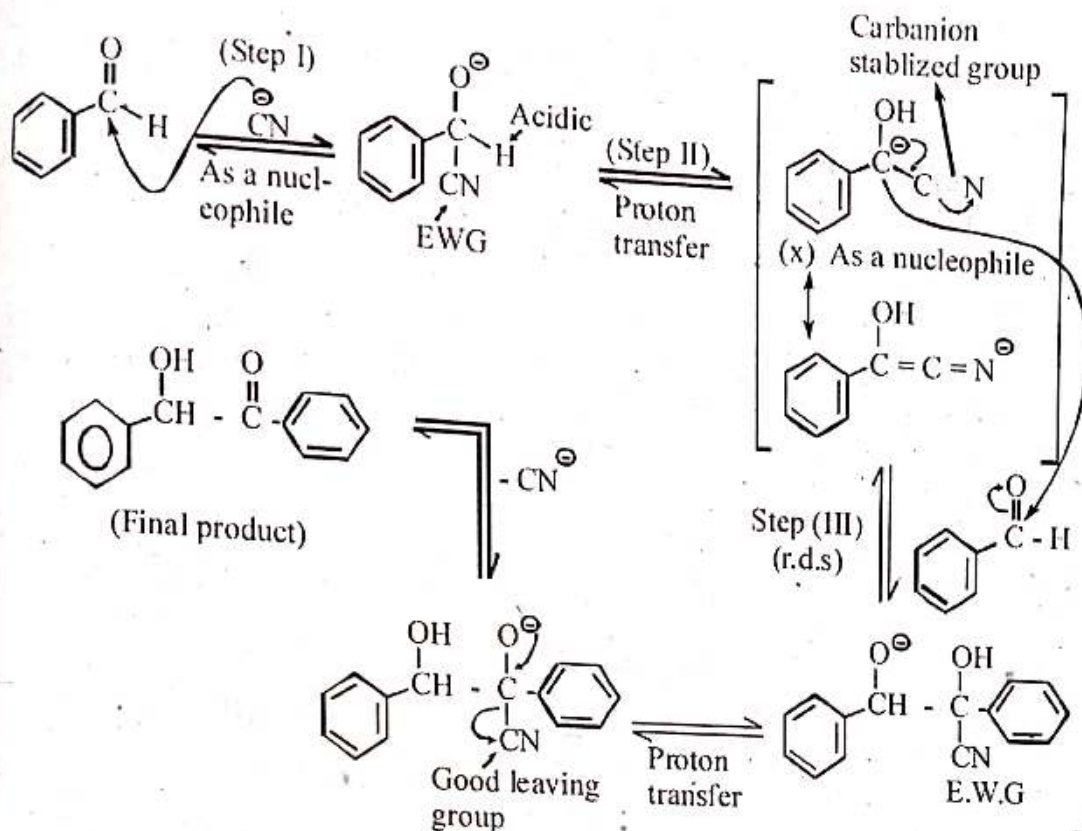
Mechanism:-

(1) Benzoin condensation is a reversible reaction.

(2) This reaction is specific for cyanide ion ($\text{CN}^{\ominus}$). Other anion does not catalyse benzoin condensation.

(3) Cyanide ion catalyses each state (each step) of the reaction.

(4) Presence of e^- withdrawing and electron donating group on benzene ring of benzaldehyde decrease the rate of benzoin condensation. EDG decrease the rate of step (I) by decreasing reactivity of carbonyl carbon. EWG decrease the rate of step (III) by decreasing nucleophilicity of carbanion "X".

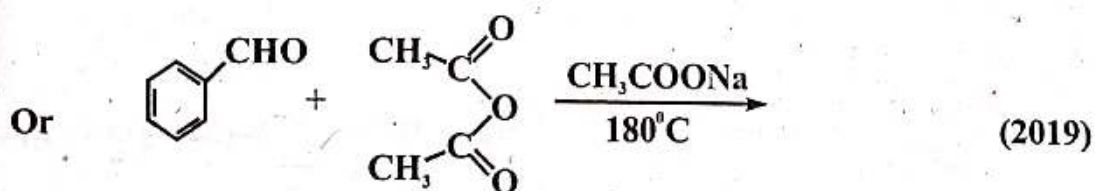
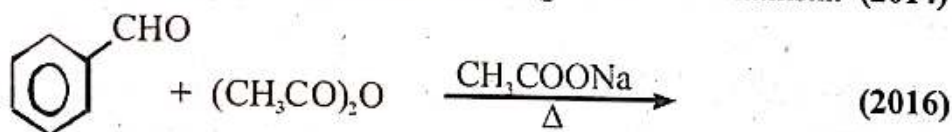


Q.9. Discuss the mechanism of Perkin reaction.

(2012, 18)

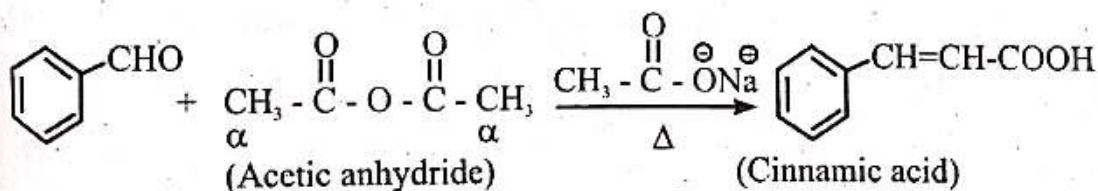
Other Related Questions -

Q. Complete the following reaction and give their mechanism. (2014)



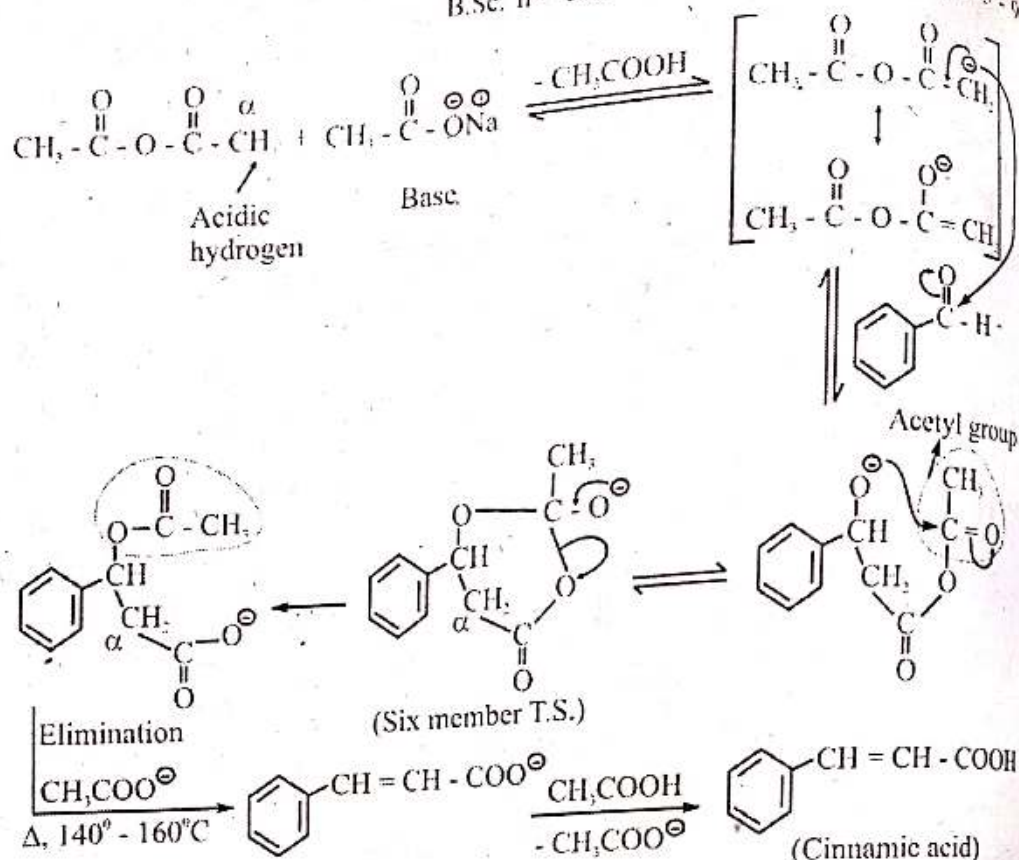
Perkin Reaction:-

The reaction of benzaldehyde with acidic anhydride in the presence of sodium acetate is known as Perkin reaction. In this reaction Cinnamic acid form.



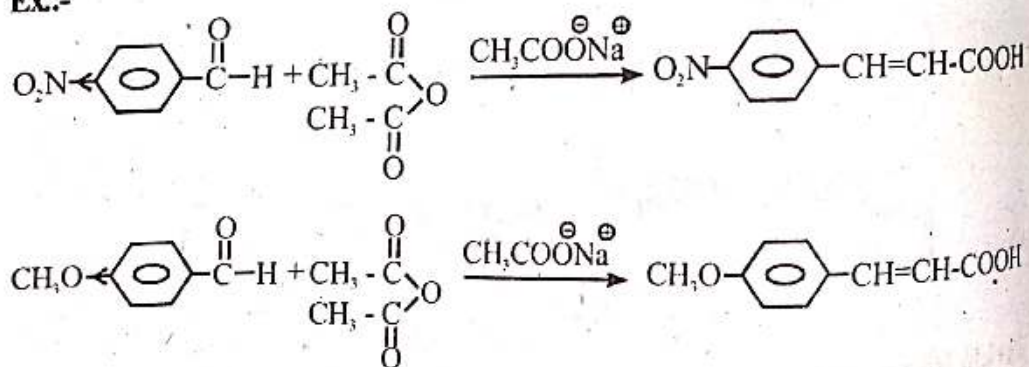
Mechanism:-

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- (1) The main driving force of Perkin reaction is transfer of acetyl group via six membered cyclic transition state.
- (2) Only those anhydride give Perkin reaction which contain atleast two α -Hydrogen.

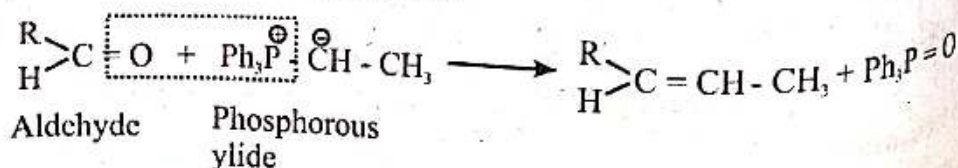
Ex:-



Q.10. Discuss the mechanism of Wittig reaction. (2012, 14)

Ans. Wittig Reaction:-

The reaction between Phosphorous ylide and carbonyl compound is known as wittig reaction.



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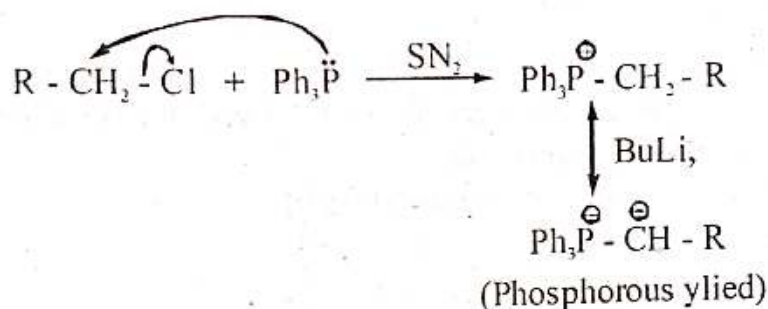
phosphorous ylide: -

The dipolar species in which positive charge present of phosphorous (P) atom and negative charge present on adjacent carbon atom, are called phosphorous ylide.

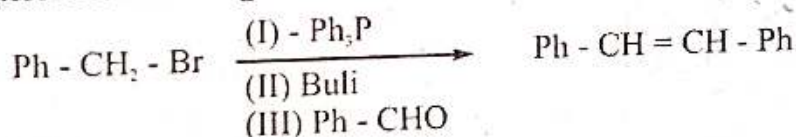


Preparation of ylide: -

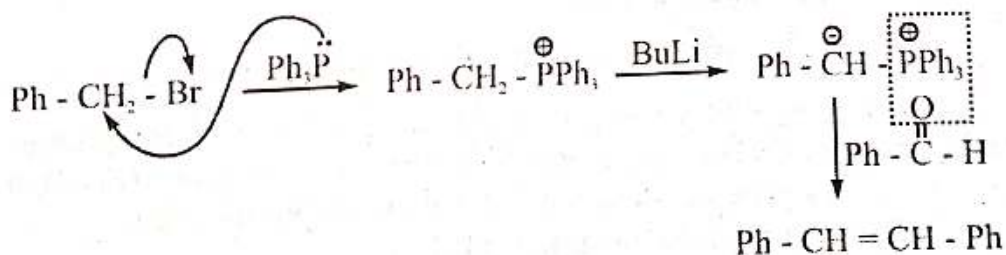
It is prepared by the reaction of alkyl halide with triphenyl phosphine followed by the reaction with strong base like butyl lithium.



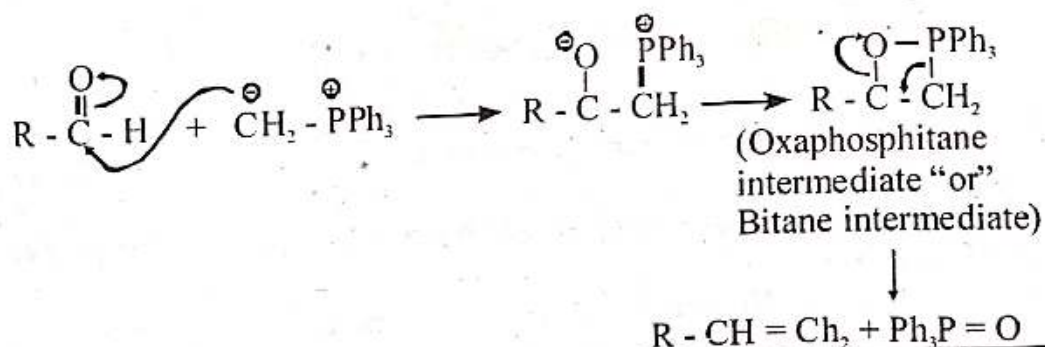
(i) Complete the following reaction -



Mechanism -



Mechanism of Wittig reaction: -



(1) Wittig reaction proceed through four member cyclic T.S. (Oxaphosphitane intermediate) or Bitane intermediate.

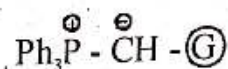
(2) The main driving force of this reaction is formation of strong "(P=O)" bond.

Stereochemistry of Witting Reaction: -

Stablized phosphorous ylide give "E" alkene wheras non stablized phosphorous ylide gives "Z" - alkene.

Let us try to understand that what is stablized phosphorous ylide and non stablized phosphorous ylide?

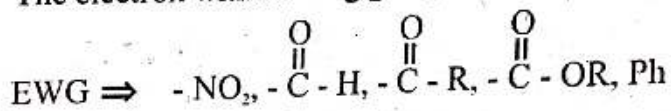
Stablized Phosphorous ylide: -



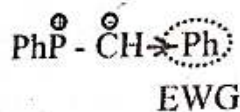
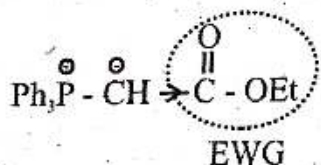
Where $\text{G} \Rightarrow \text{EWG}$

If the negatively charged carbon atom adjacent to phosphorous is attached through the electron with drawing group (EWG) then the phosphorous ylide is called stablized phosphorous ylide.

The electron withdrawing group may be -

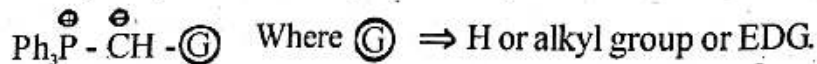


Example -



The stablized phosphorous ylide gives E-alkene in wittig reaction.

Non Stablized phosphorous ylide: -

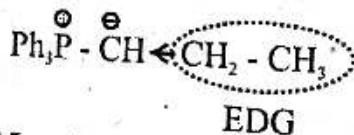
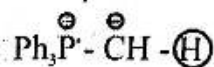


If the negatively charged carbon atom adjacent to phosphorous is attached through "H" or alkyl group or electron donating group (EDG), then the phosphorous ylide is called non stablized phosphorous ylide.

The electron donating group may be

EDG $\Rightarrow$ Alkyl group or "H"

Example -



Q.11. Write short note on Mannich reaction.

Other Related Questions -

Q. Discuss the mechanism of Mannich reaction.

Mannich Reaction: -

The reaction between formaldehyde, 2^o-amine and acidic hydrogen

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Mechanism: -

$$\begin{array}{c}
 \text{H} - \text{C}(=\text{O}) - \text{H} \xrightleftharpoons{\text{H}^+} \text{H} - \text{C}(=\text{OH}^+) - \text{H} \xrightarrow{\text{H} - \text{N}(\text{R})_2} \text{H} - \text{C}(\text{OH})(\text{H}) - \text{N}^+(\text{R})_2 \xrightarrow{-\text{H}^+} \text{H}_2\text{C}=\text{N}^+(\text{R})_2 \\
 \text{Iminium salt} \\
 \text{(Behave as electrophile)}
 \end{array}$$

$$\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_3 \xrightleftharpoons{\text{Tautomeric}} \text{CH}_3 - \overset{\text{O}^+ - \text{H}}{\parallel} \text{C} = \text{CH}_2 \xrightarrow{\text{CH}_2 = \text{N}^+ \begin{smallmatrix} \text{R} \\ \text{R} \end{smallmatrix}} \text{CH}_3 - \overset{\text{OH}^+}{\parallel} \text{C} - \text{CH}_2 - \text{CH}_2 - \text{N}^+ \begin{smallmatrix} \text{R} \\ \text{R} \end{smallmatrix} \xrightarrow{\text{H}^+} \text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_2 - \text{CH}_2 - \text{N}^+ \begin{smallmatrix} \text{R} \\ \text{H} \end{smallmatrix} \text{R}$$

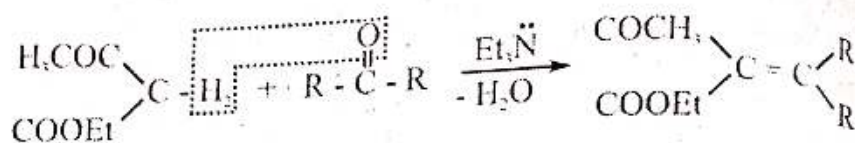
$$\text{CH}_3 - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_2 - \text{CH}_2 - \text{NH} \begin{matrix} \text{R} \\ \diagup \\ \text{R} \end{matrix} \xrightarrow{\text{OH}^\ominus} \text{CH}_3 - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_2 - \text{CH}_2 - \text{N} \begin{matrix} \text{R} \\ \diagup \\ \text{R} \end{matrix}$$

(Mannich base)

(2013)

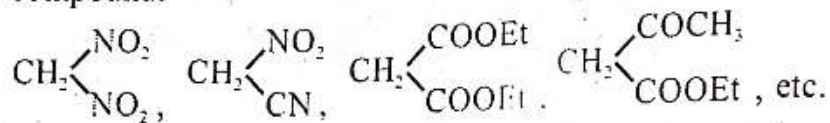
Ans. **Knoevenagel Condensation:-**
The reaction between active methylene and carbonyl compound in the presence of amine base are called Knoevenagel condensation.

Scanned with CamScanner

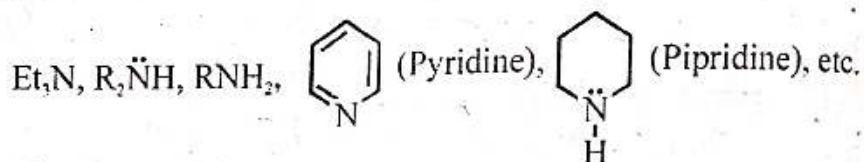


Active Methylene Group: -

When methylene group ($-\text{CH}_2-$) attached with two electron withdrawing group the resulting compounds are called active methylene compound.

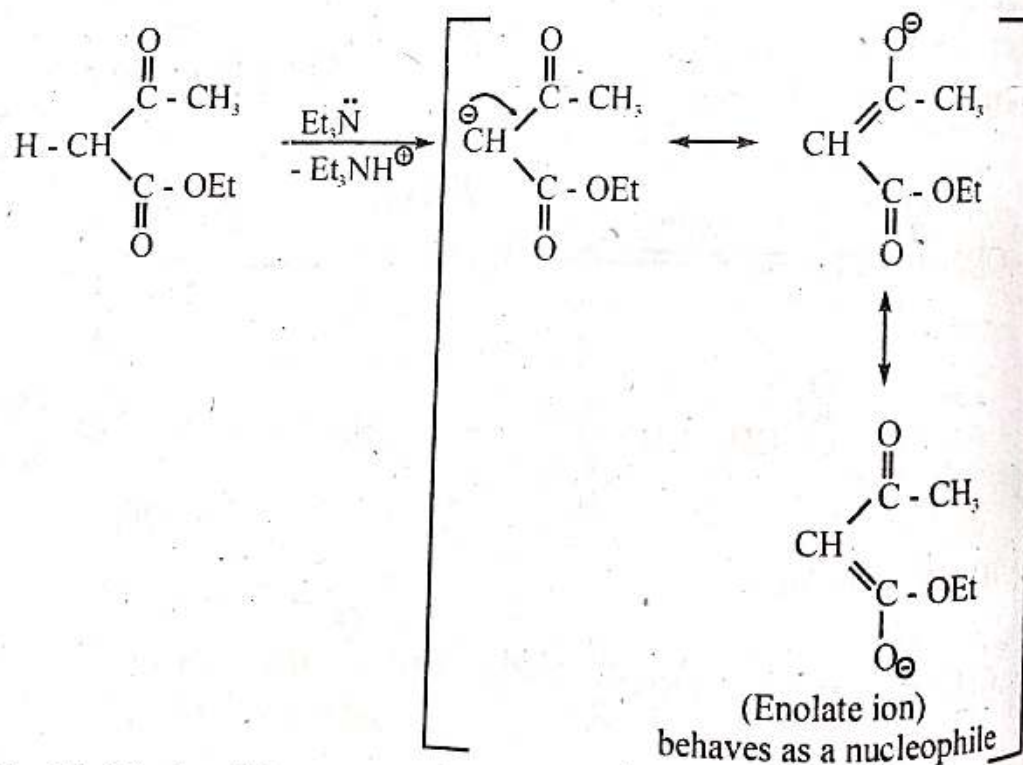


Amine Base: -

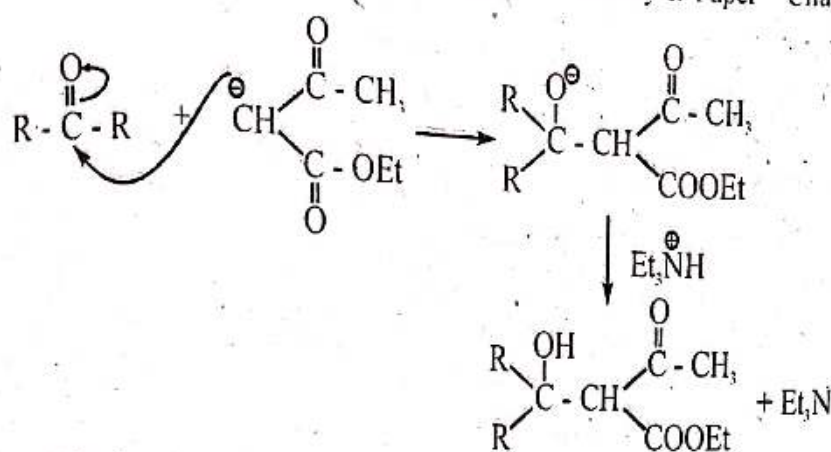


Mechanism -

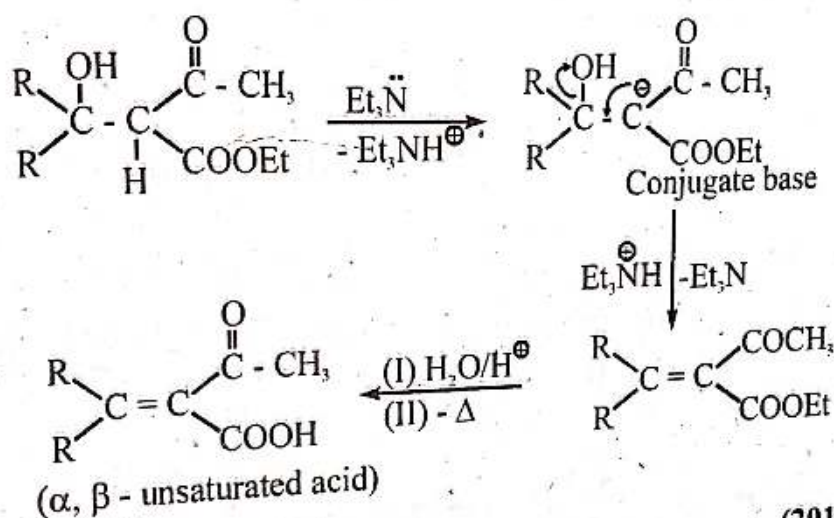
Step I - Formation of enolate ion from active methylene group:



Step II - Nucleophilic addition of enolate ion or carbonyl compound:

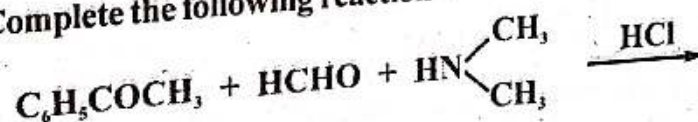


Step (III) - Elimination of water by E₁cb mechanism.

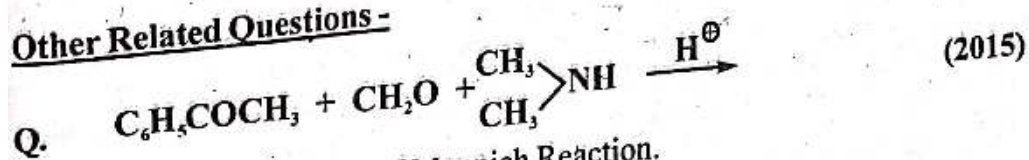


(2013, 17)

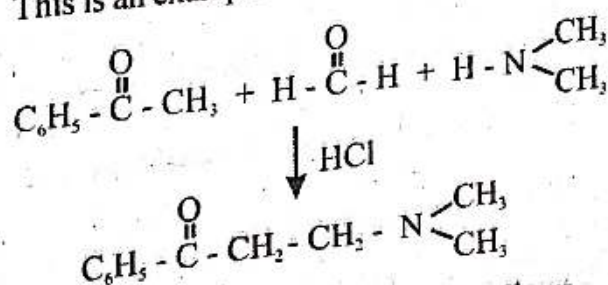
Q.13. Complete the following reaction -



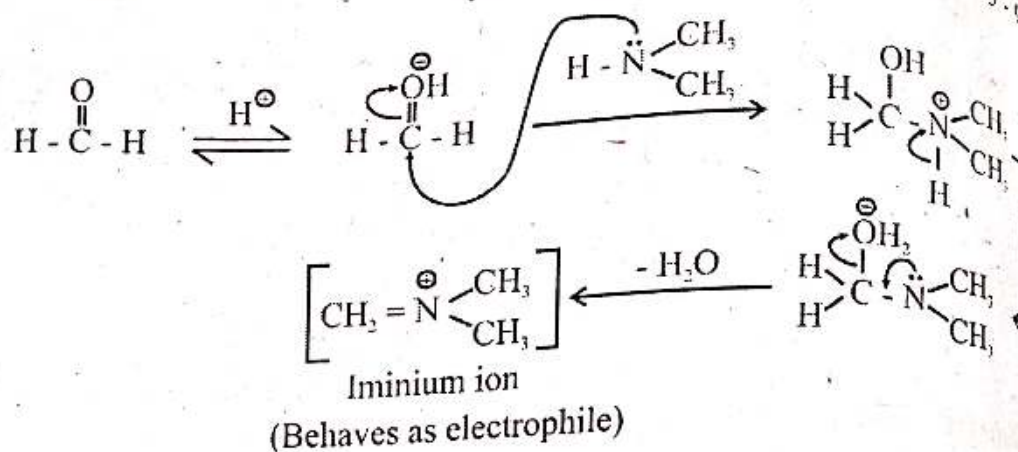
Other Related Questions -



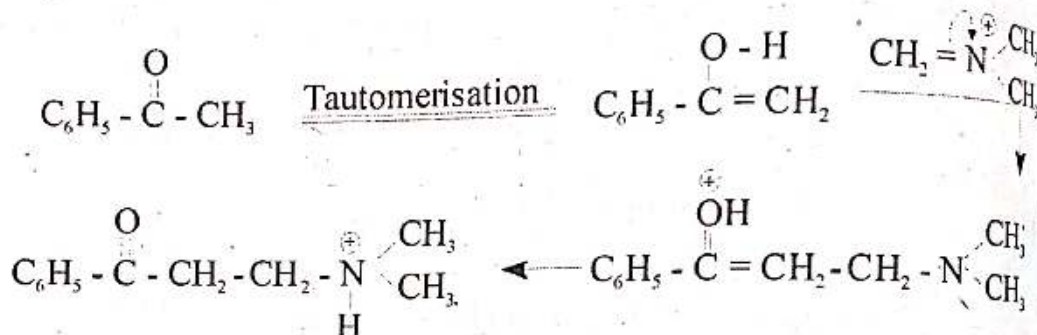
Ans. This is an example of Mannich Reaction.



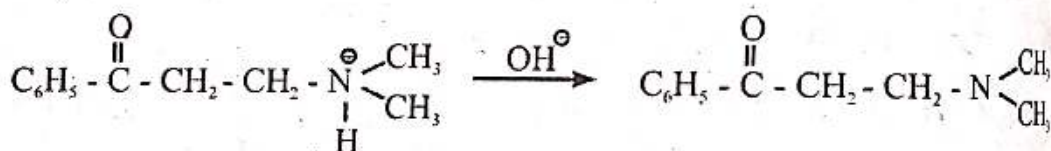
The mechanism of above reaction are as follows -
Step (I) Formation of iminium ion -



Step II -



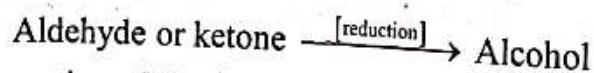
Step III - Basification -



Q.14. Write short note on reduction of aldehyde and ketones. (2011, 14)

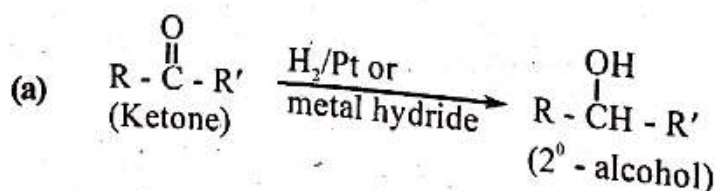
Ans. Reduction of aldehyde and ketone: -

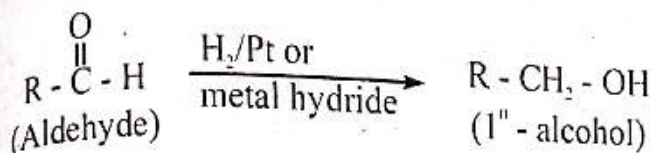
Aldehyde and ketone can be reduced by taking suitable reducing agent. The reduction of aldehyde and ketone results in the formation of alcohol or a hydrocarbon or an amine.



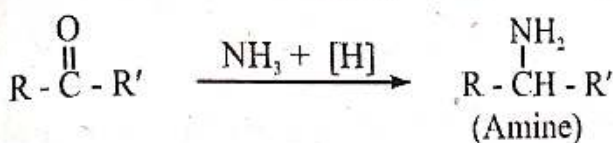
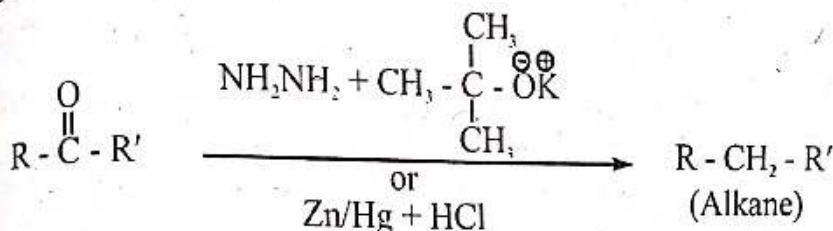
The formation of alcohol after reduction depends on both factors i.e. structure of carbonyl compound and reducing agent.

There are following reagent which are suitable for the reduction of aldehyde and ketone.



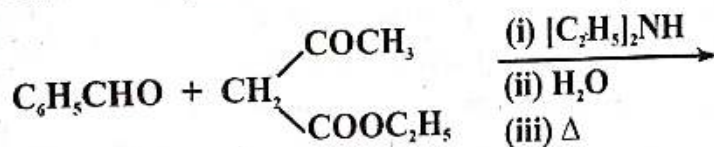


The reduction of ketone gives 2^o - alcohol while the reduction of aldehyde gives 1^o - alcohol.

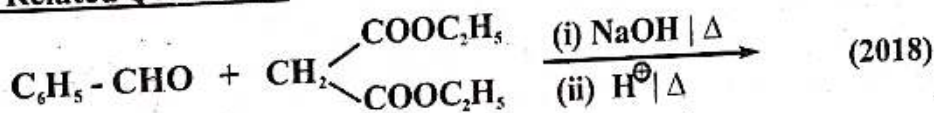


5. Give the mechanism of following reaction -

(2011)

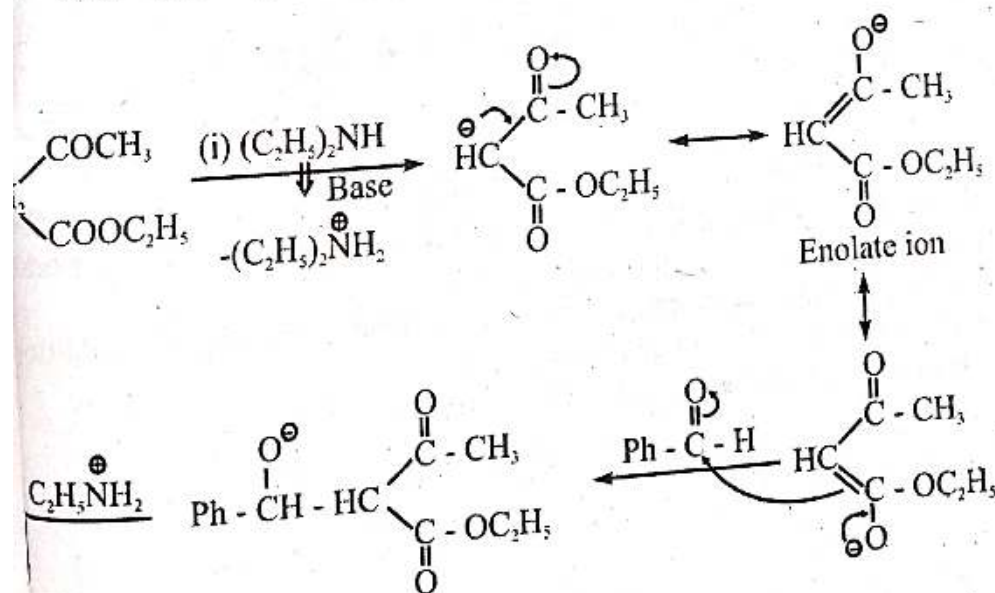


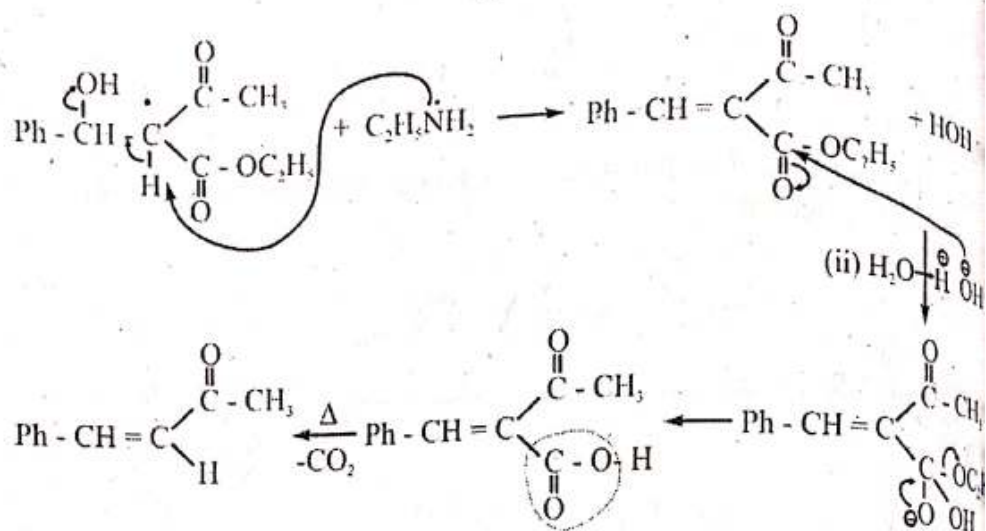
Other Related Questions -



[Hint - Here NaOH act as base]

Hint - Knoevenagel condensation





Q.16. Write a note on Acid and base catalysed nucleophilic addition of carbonyl compounds. (2011)

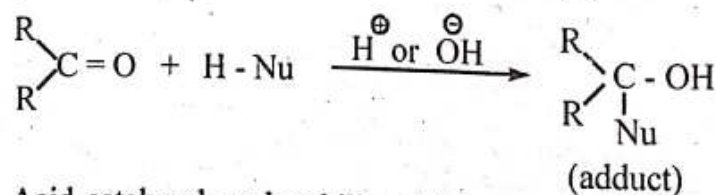
Ans. Aldehydes and ketones undergo many reactions. The reactivity of carbonyl compounds arises because the carbonyl carbon contains a partial positive charge due to the partial displacement of σ -electrons towards the oxygen atom.



Electrophilic centre

Due to the presence of a partial positive charge on the carbonyl carbon, it behaves as an electron-deficient centre or an electrophilic centre. So, carbonyl compounds are reactive towards nucleophiles and give nucleophilic addition reactions.

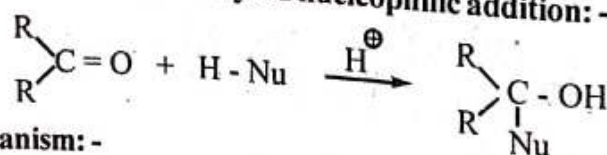
The nucleophilic addition reaction in carbonyl compounds can take place by acid and base both.



Acid-catalysed nucleophilic addition works by making the carbonyl group more electrophilic, and base-catalysed nucleophilic addition works by making the nucleophile more nucleophilic.

The mechanism of acid and base-catalysed nucleophilic addition of carbonyl compounds is as follows -

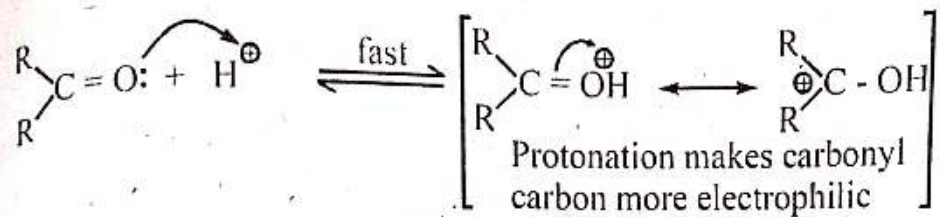
Mechanism of acid-catalysed nucleophilic addition: -



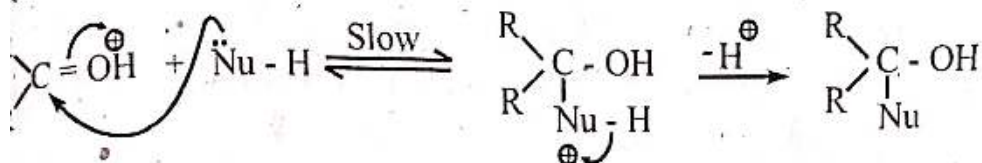
Mechanism: -

Step(i) -

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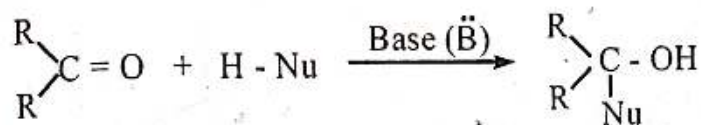


(ii) -

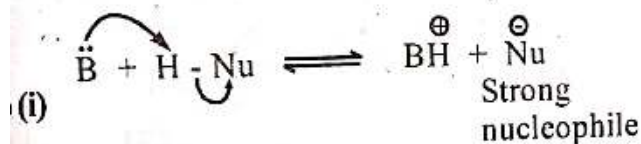


Weak nucleophile such as water and alcohols often add to carbonyl under acidic condition because the electrophilicity of carbonyl carbon increases by the reaction of acid.

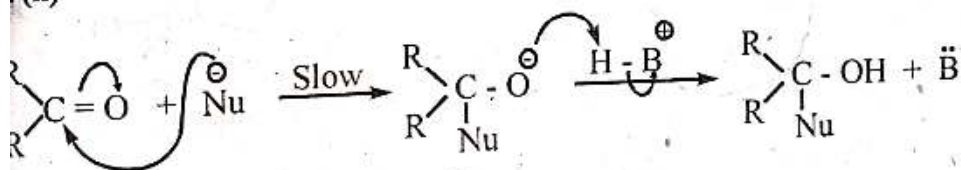
Mechanism of Base catalysed nucleophilic addition: -



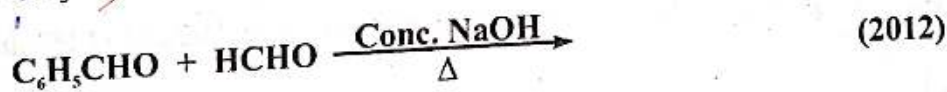
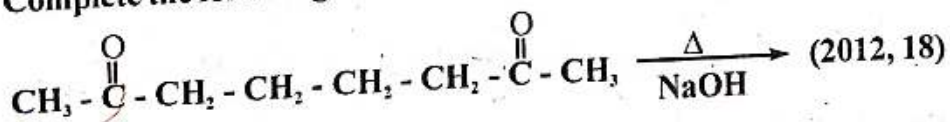
Mechanism: -



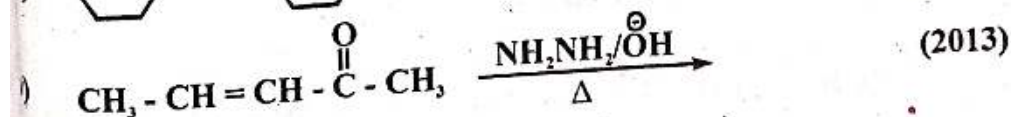
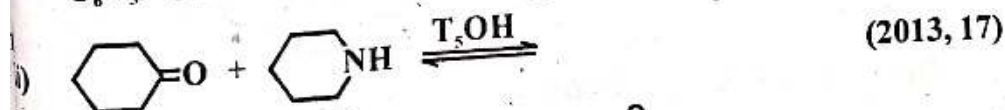
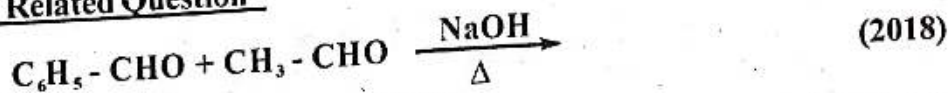
(ii)



7. Complete the following reaction -

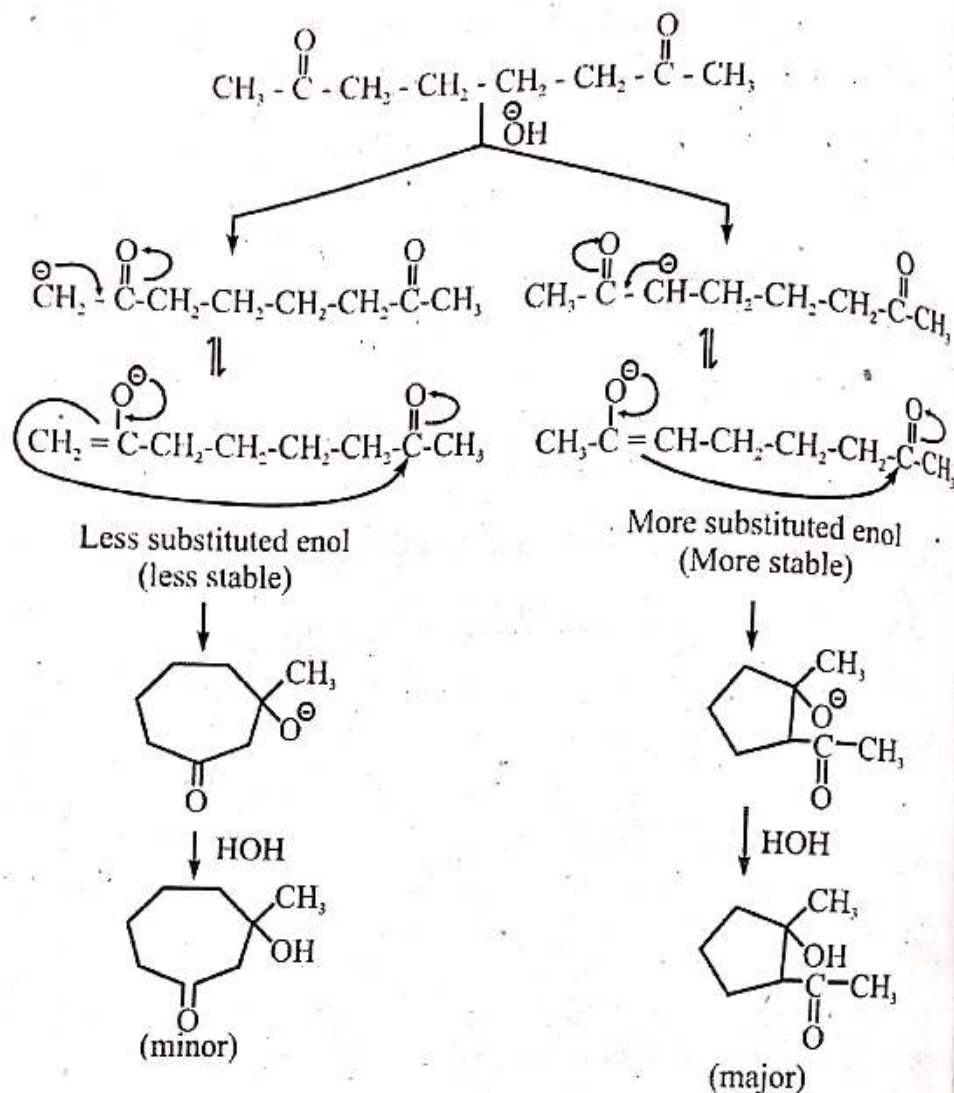


Other Related Question -

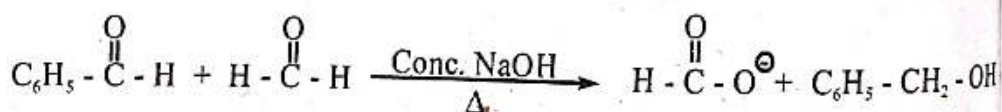


Ans. (i)

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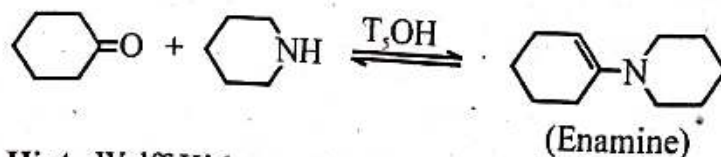


(ii)

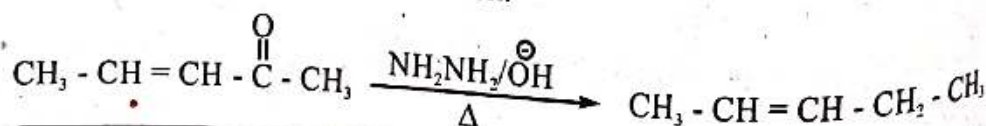


[Hint - Cross Cannizzaro reaction with first step only. Here $\text{H}_2\text{O}/\text{H}^\oplus$ are not used]

(iii)

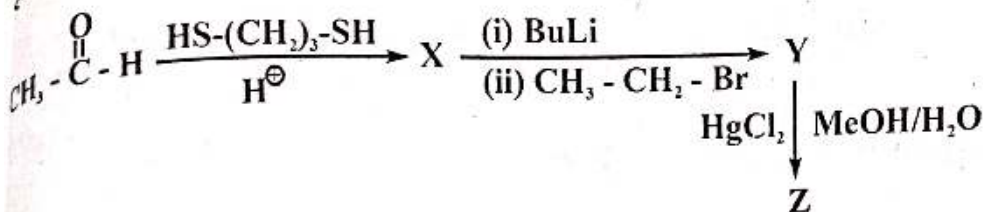


(iv) Hint - Wolff-Kishner reduction.



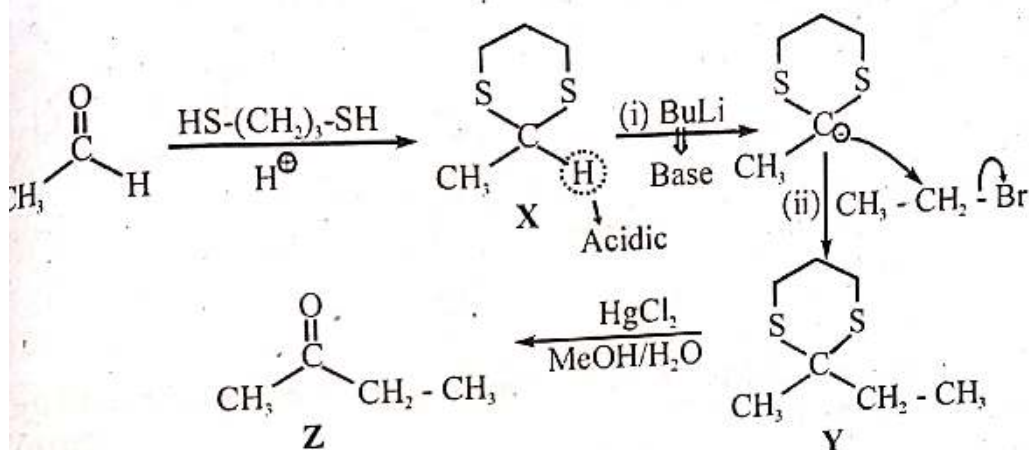
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Q.18. Identify the products x, y and z in the following sequence of reaction

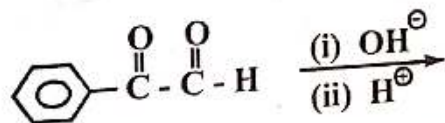


(2014)

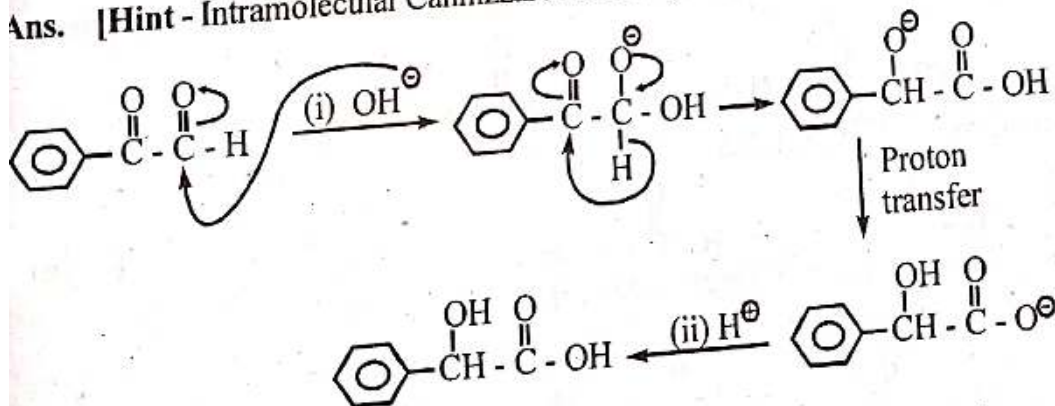
Ans.



Q.19. Complete the following reaction and give the mechanism of the reaction. (2014)

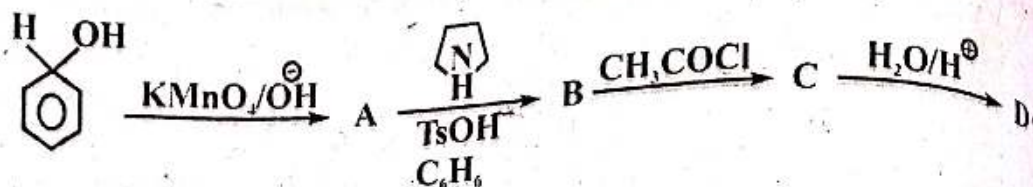


Ans. [Hint - Intramolecular Cannizzaro reaction]

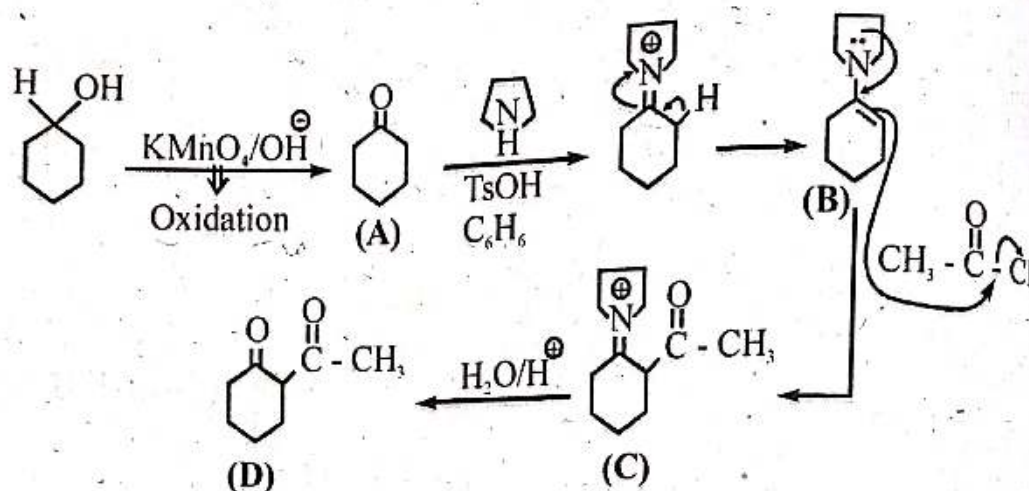


Q.20. Identify the products A, B, C and D in the following sequence of reaction. (2014)

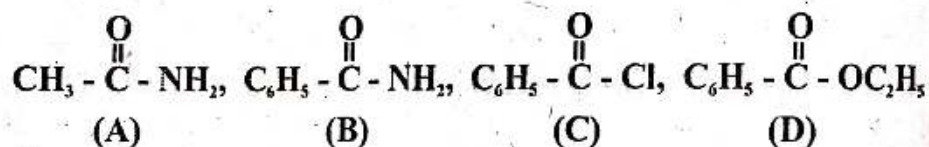
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Ans. [Hint - Stark-Enamine reaction]

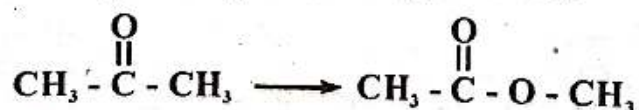


Q.21. Arrange reactivity of given compounds in their decreasing reactivity for hydrolysis reaction. (2016)



Ans. Reactivity order -
(C) > (D) > (B) > (A)

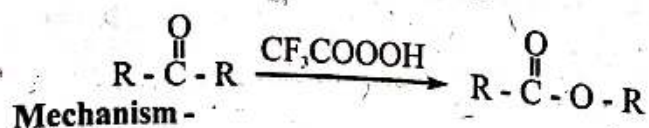
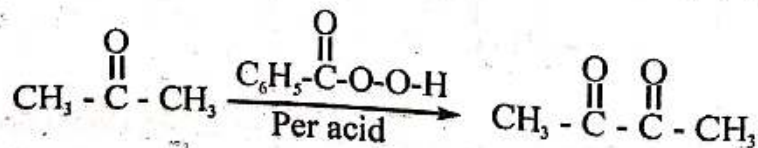
Q.22. How will you bring the following conversion - (2014)



Other Related Questions -

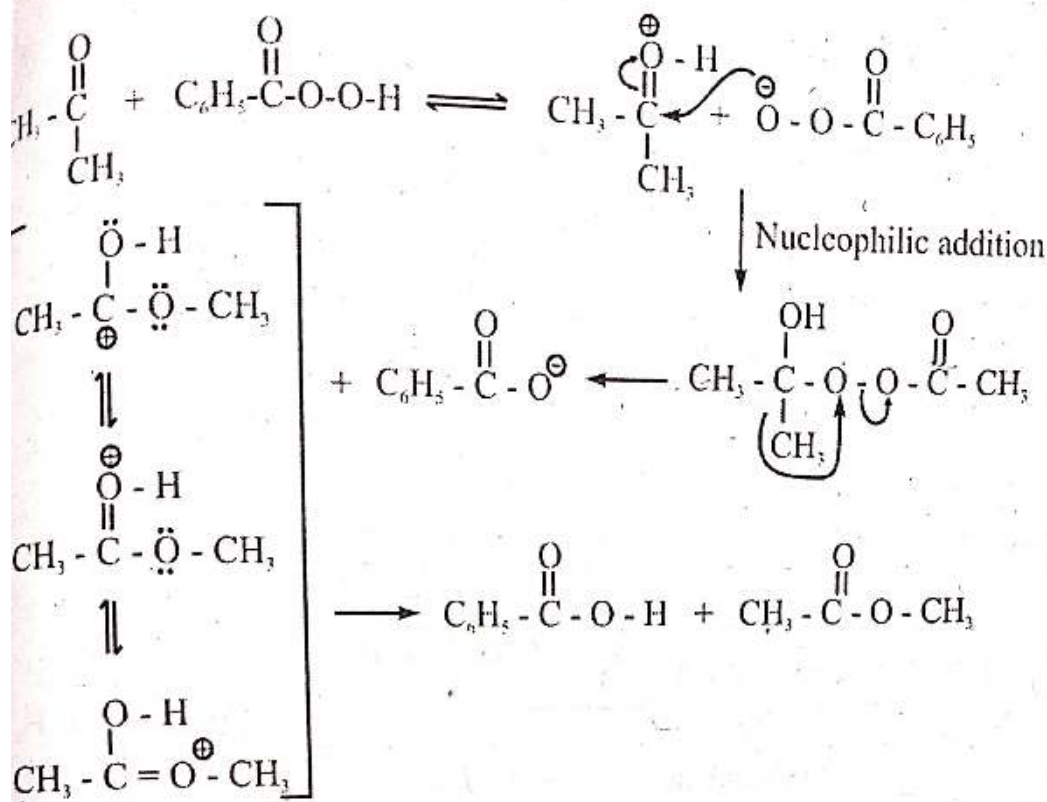


Ans. [Hint - Berger - Villiger oxidation]

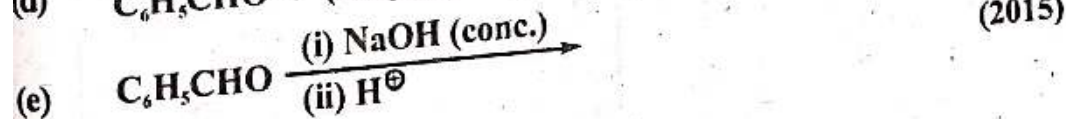
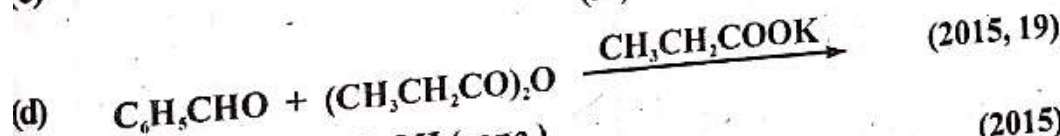
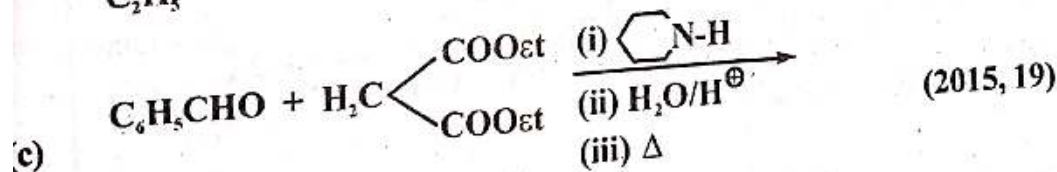
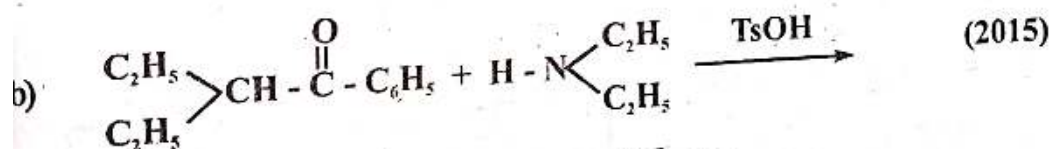
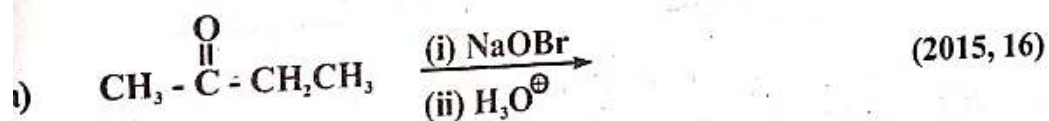


Mechanism -

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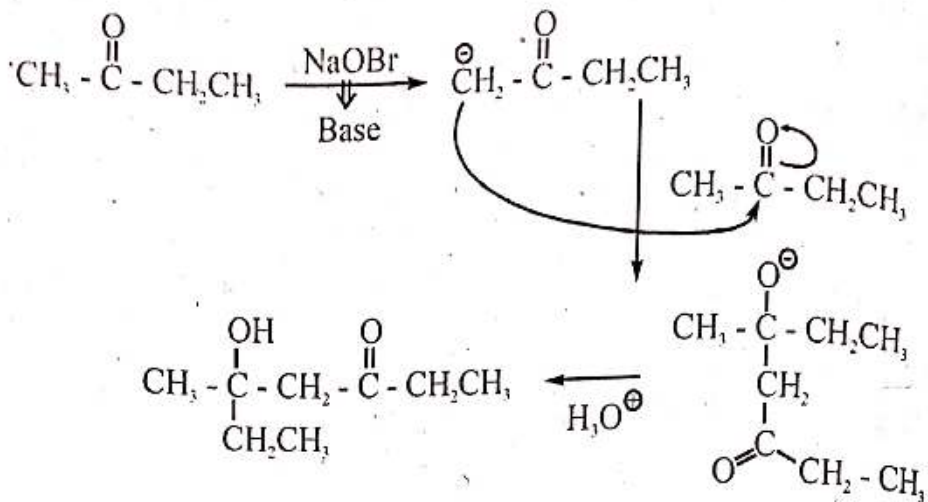


23. Complete the following reaction and give their mechanism -

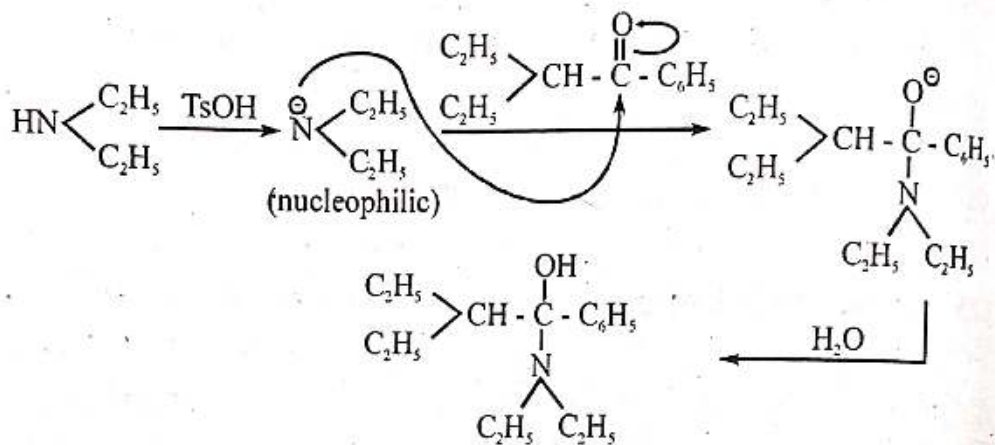


Ans. (a)

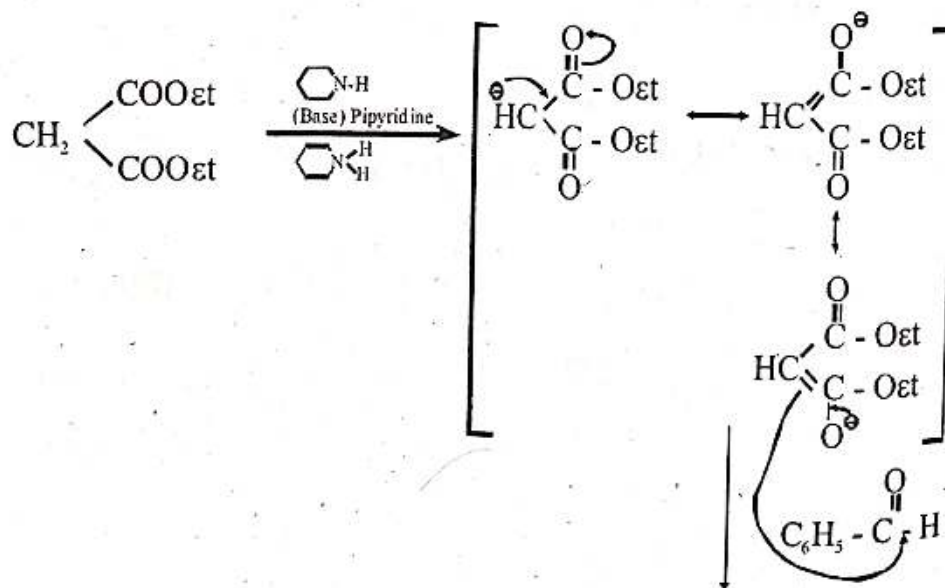
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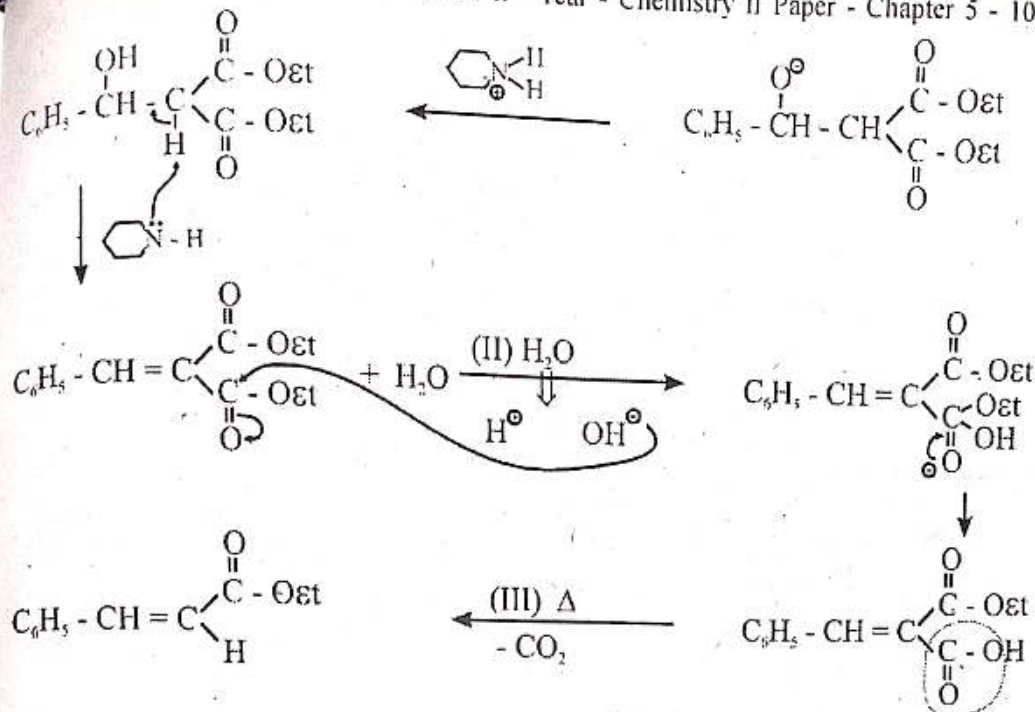
(b)



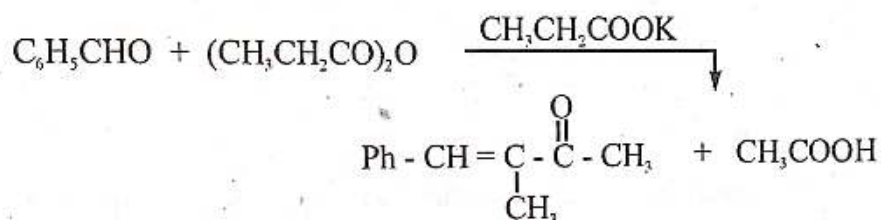
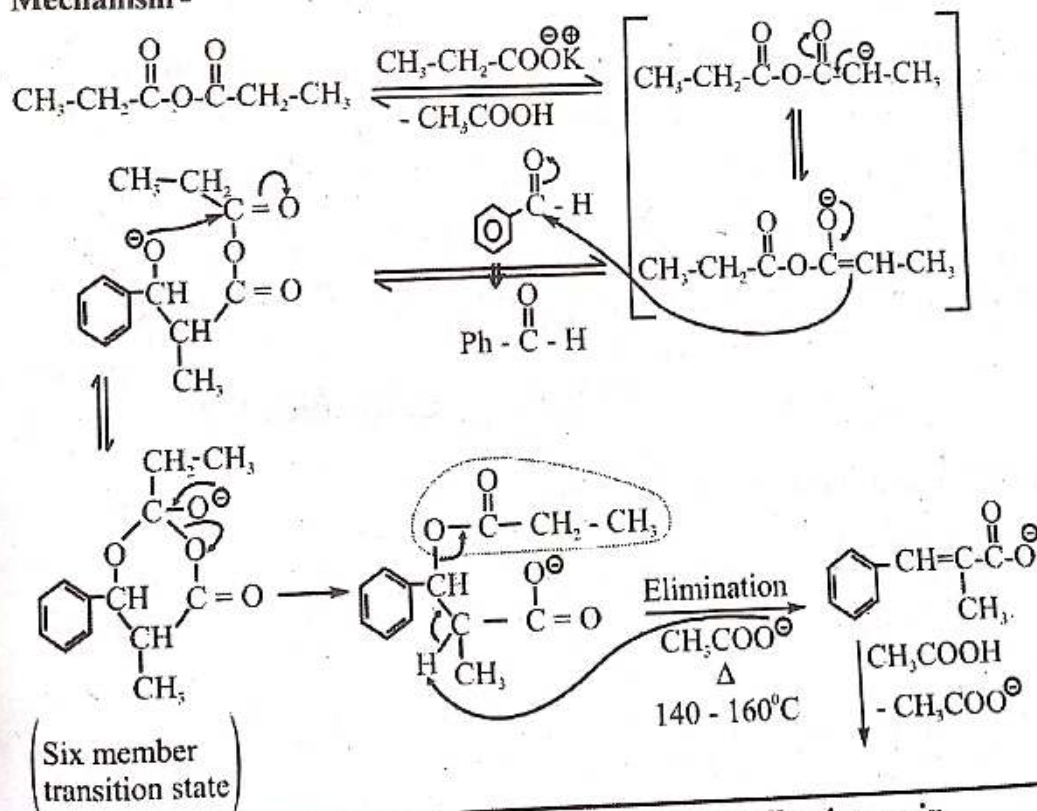
(c) **Hint : Knoevenagel Condensation -**

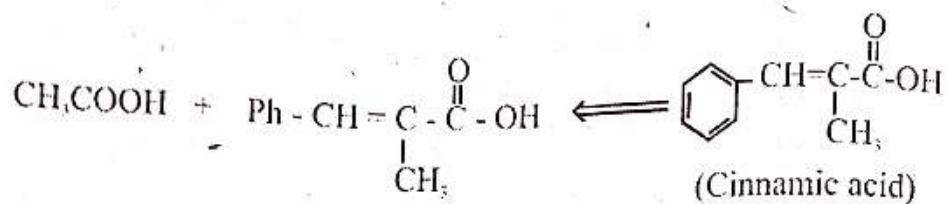


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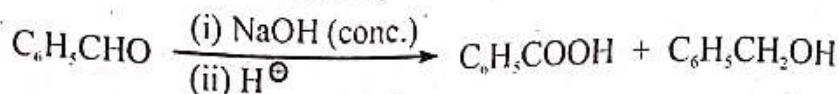


(d) [Hint - Perkin Reaction]

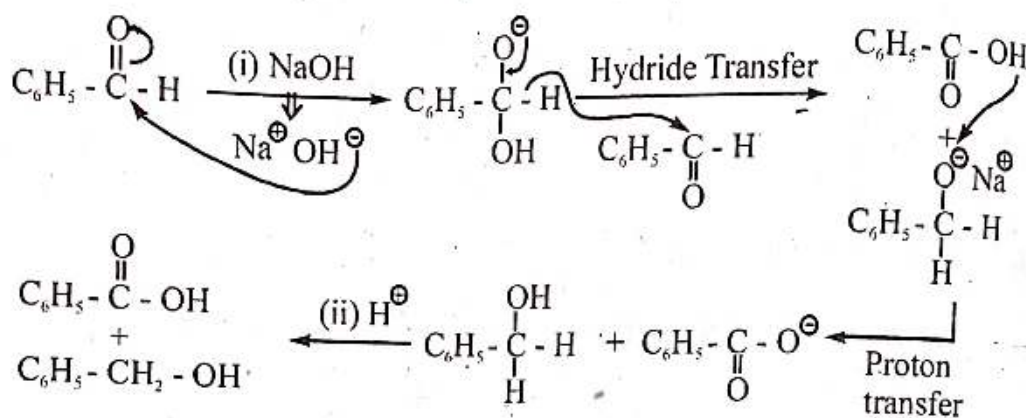
**Mechanism -**To shop our books visit at www.winsomecollection.co.in



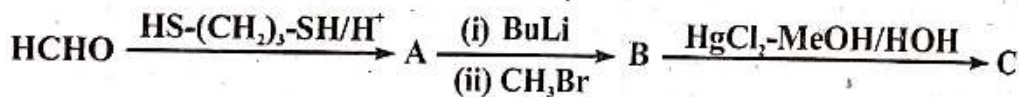
(e) [Hint - Cannizzaro Reaction]



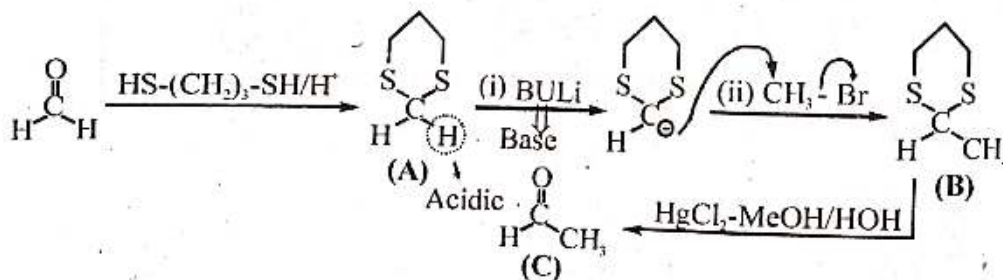
Mechanism -



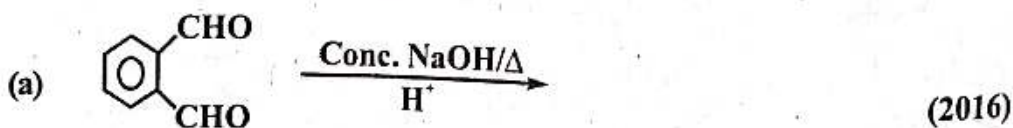
Q.24. Identify products A, B and C in the following reaction sequences - (2015)



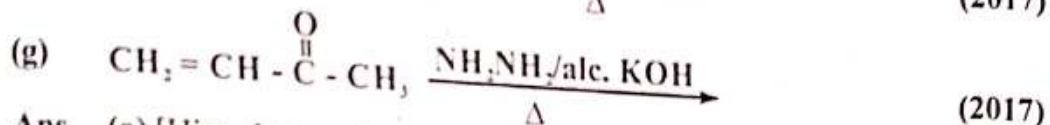
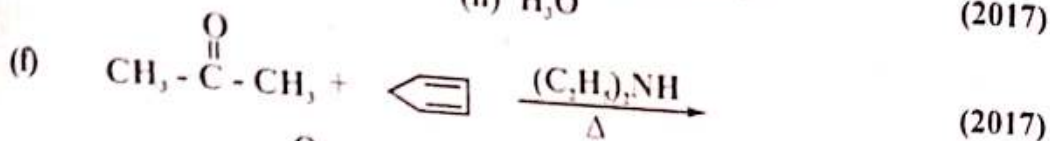
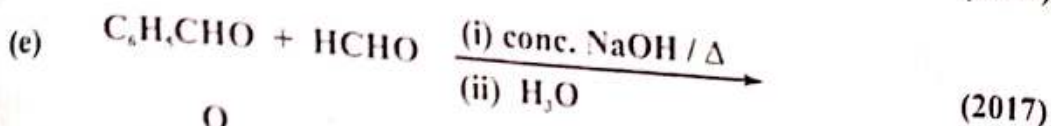
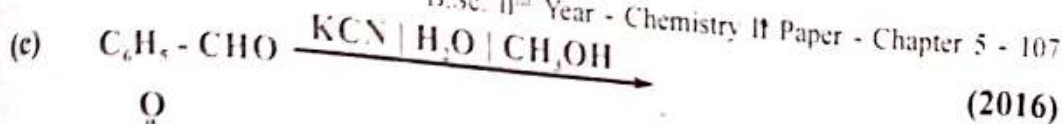
Ans.



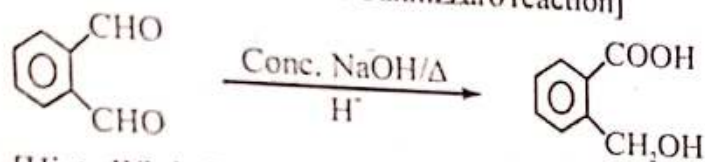
Q.25. Complete the following reaction -



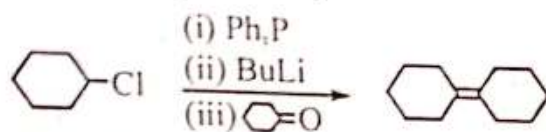
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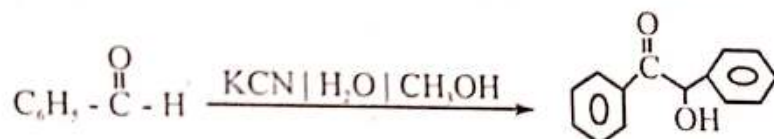
Ans. (a) [Hint - Intramolecular Cannizzaro reaction]



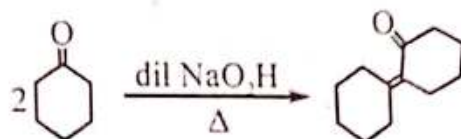
(b) [Hint - Wittig Reaction]



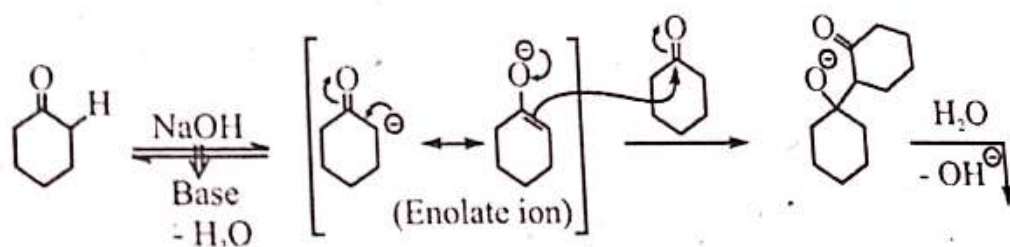
(c) [Hint - See theory part of topic - Benzoin condensation]

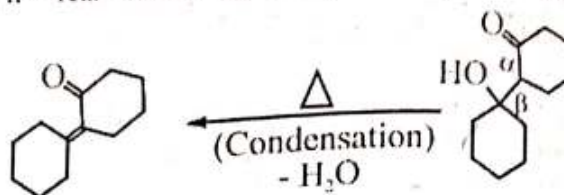


(d) [Hint - Aldol reaction]

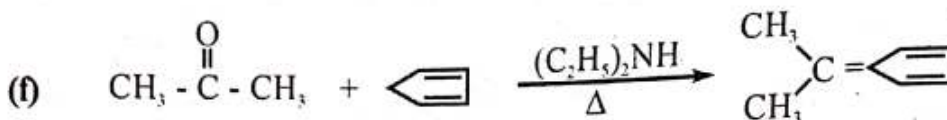
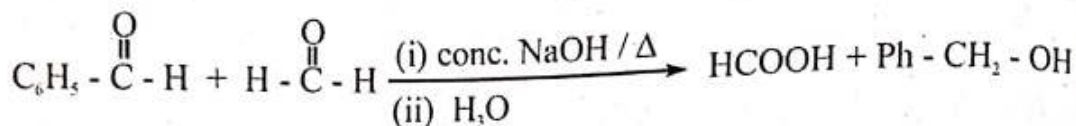


Mechanism -



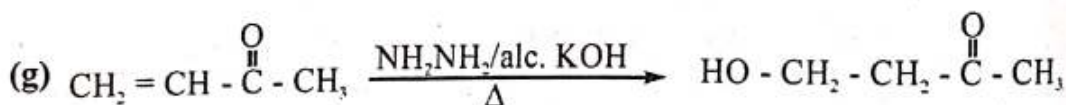
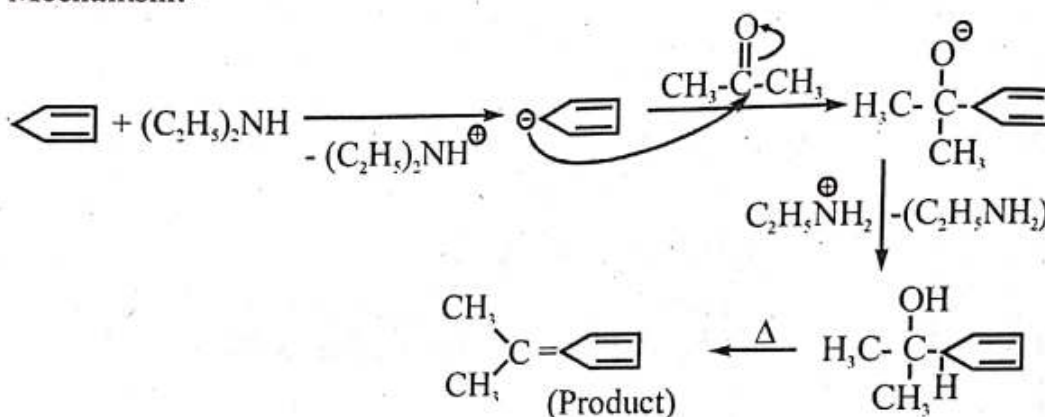


(e) [Hint - Cross Cannizzaro reaction]



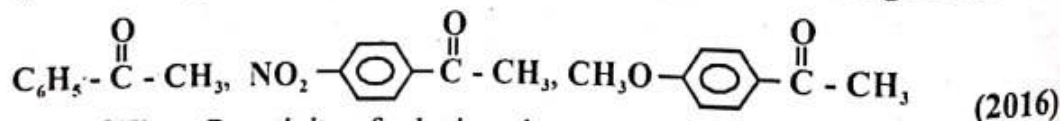
[Hint - Knoevenagel condensation]

Mechanism: -

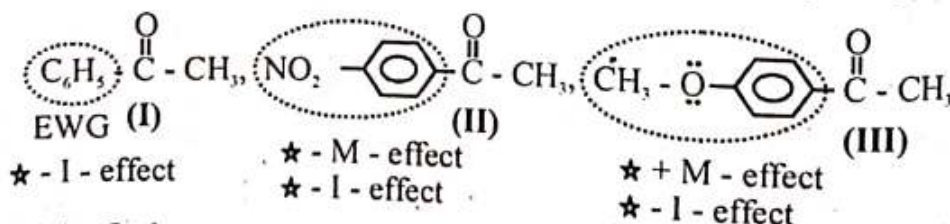


(β-hydroxy ketone)

Q.26. Arrange stability of given compounds in their decreasing order.



Ans. [Hint - Reactivity of substituted aromatic carbonyl compound]



Reactivity Order: -

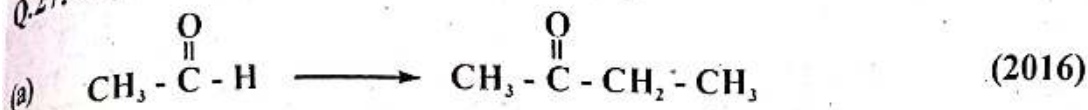
II > I > III

Stability Order: -

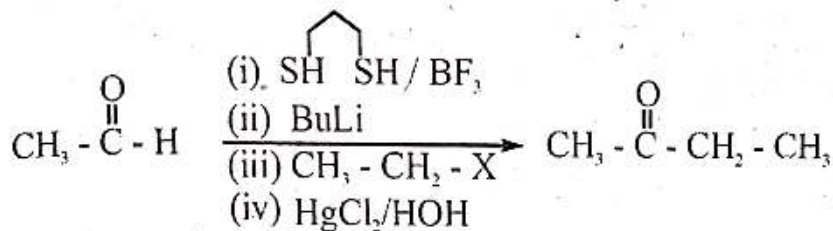
To show our best performance...

III > I > II

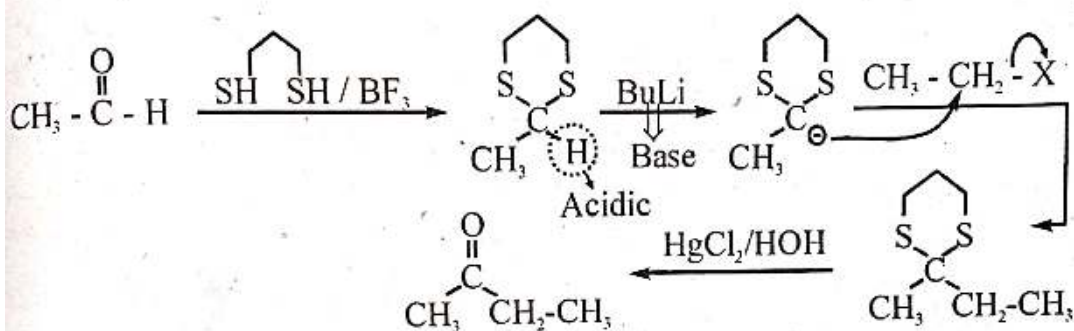
Q.27. How will you bring about the following transformation?



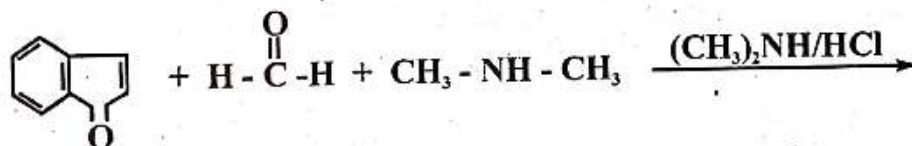
Ans. (a)



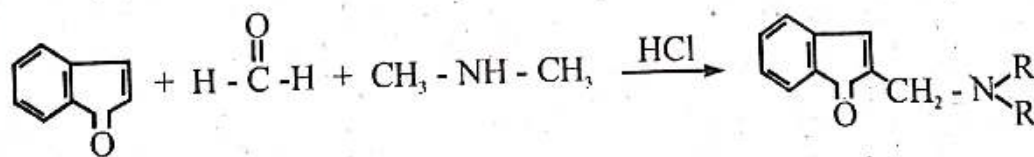
Mechanism -



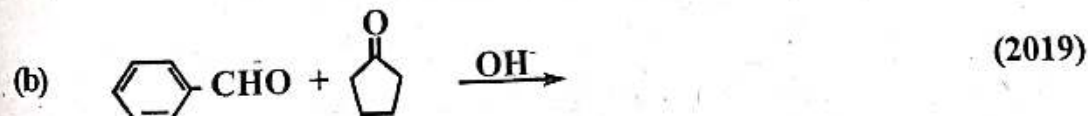
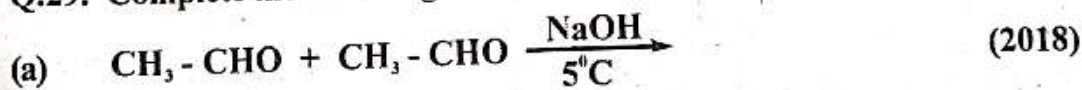
Q.28. Complete the following reaction and give the major product. (2018)



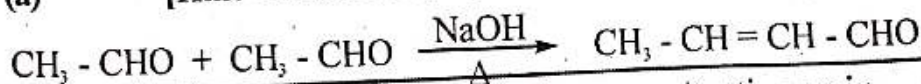
Ans. [Hantzsch - Mannich reaction]



Q.29. Complete the following reaction and give their mechanism.

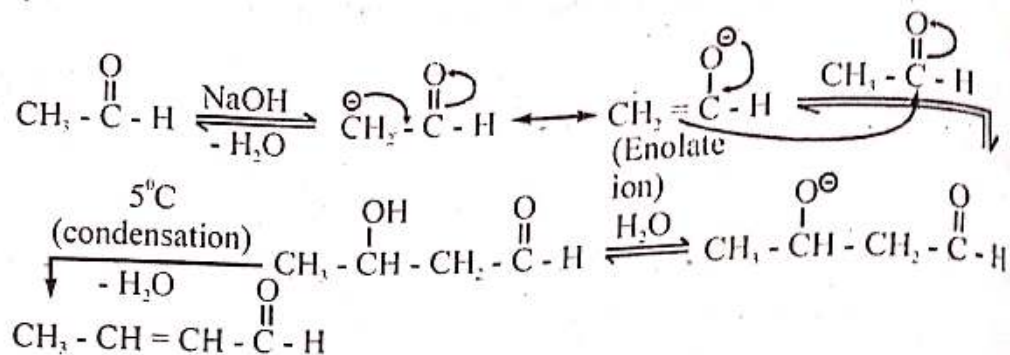


Ans. (a) [Hint - Aldol reaction]

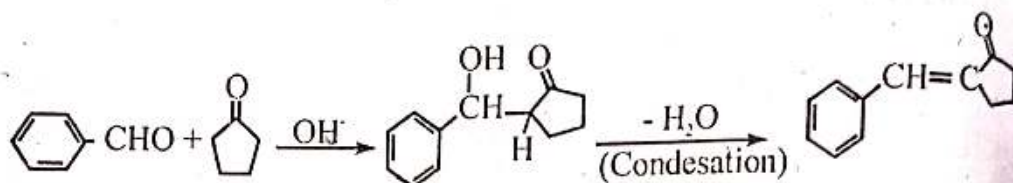


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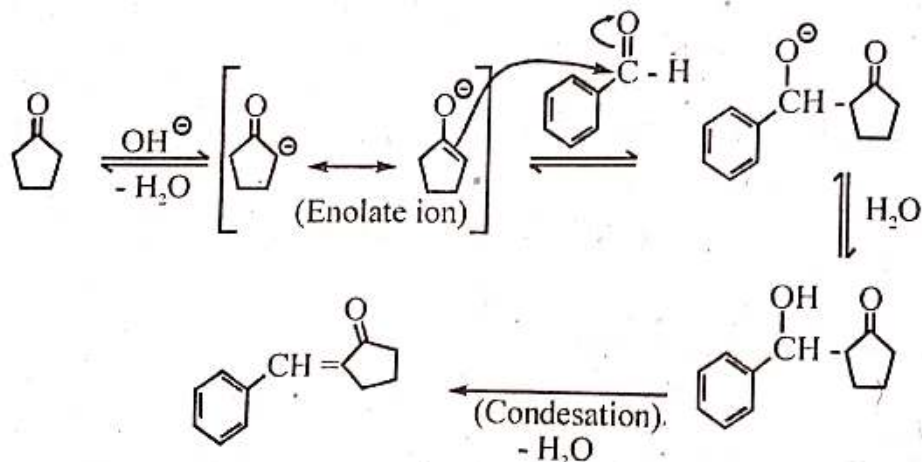
Mechanism: -



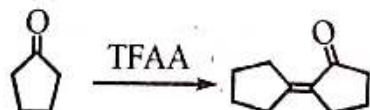
(b) [Hint - Aldol Reaction]



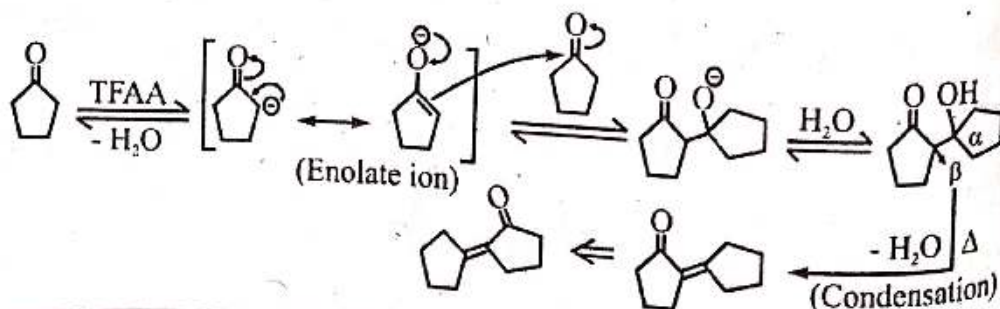
Mechanism: -



(d) [Hint - Aldol reaction]



Mechanism - In this reaction TFAA behaves as base



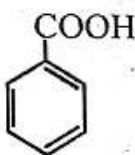
Chapter 6

Carboxylic acids

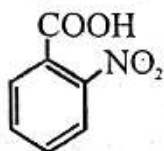
Introduction:-

Carboxylic acids are structurally characterized by the presence of a carboxylic group $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH} \end{array}$, which is some times also represented as $-\text{COOH}$ or $-\text{CO}_2\text{H}$. This carboxylic group may be attached with an aliphatic, aromatic, saturated, or alicyclic moiety. The carbon atom in carboxylic group are present in highest oxidation state which makes it stable towards further oxidation. The highest oxidation state of carbon atom in carboxylic group makes it very stable towards the further oxidation. For this reason, they are stable and occur abundantly in nature as oils, fats and amino acids, etc. The name carboxyl is derived from CARBonyl ($\text{C}=\text{O}$) and hydroXYL ($-\text{OH}$) because in the carboxylic group these two groups are directly bonded to each other.

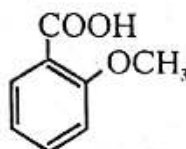
If the carboxylic acid attached with aromatic ring then it is called aromatic carboxylic acid.



(Benzoic acid)



(O-Nitro Benzoic acid)



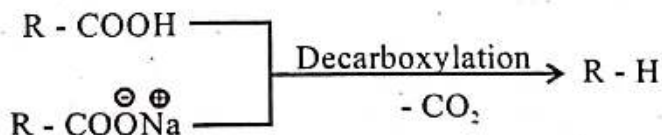
(O-Methoxy Benzoic acid)

Q.1. Give the mechanism of decarboxylation of carboxylic acid with soda lime ($\text{NaOH} \mid \text{CaO}$) in the presence of an acidic condition?

Ans. Before discussing the reaction we must know about decarboxylation and soda lime.

Decarboxylation:- A carboxylic acid has the formula $\text{R}-\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array}-\text{OH}$, where "R" can be hydrogen or a hydrocarbon group such as alkyl group.

In decarboxylation, the $-\text{COOH}$ or sodium salt $-\text{COO}^- \text{Na}^+$ group is removed and replaced with a hydrogen atom.

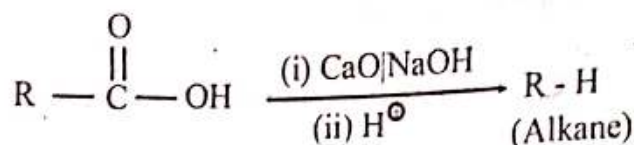


Soda-lime :-

Soda lime is manufactured by adding sodium hydroxide (NaOH) solution to solid calcium oxide (CaO). It is essentially a mixture of sodium hydroxide, calcium oxide and calcium hydroxide. It comes as white granules.

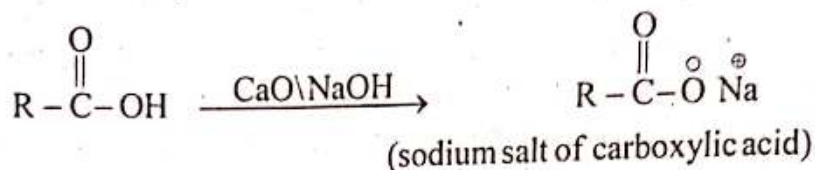
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Reaction:- When the carboxylic acid is treated with the soda lime in the presence of an acidic condition, then the formation of alkanes as a product take place. This reaction is also known as the "Duma reaction". This reaction proceeds through the carbanion intermediate.

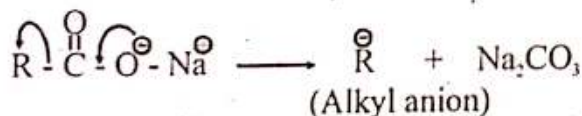


This reaction proceeds through following steps -

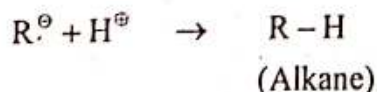
Step (i) - In the first step, the carboxylic acid reacts with soda-lime to form sodium salt of carboxylic acid or carboxylate anion.



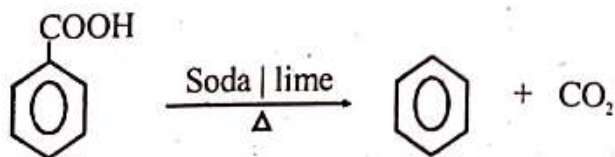
Step (ii) - In the second step, the sodium salt of carboxylic acid removes its alkyl group as an alkyl anion.



Step (iii) - In the third step, the alkyl anion reacts with acid to give alkanes as a product.



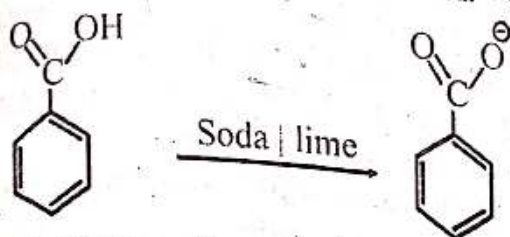
Decarboxylation in aromatic carboxylic acid :-



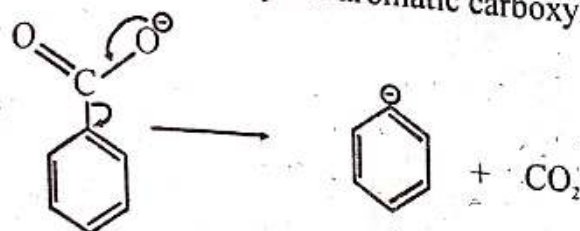
Like aliphatic carboxylic acid, the aromatic carboxylic acid proceeds through the **carbanion intermediate** (carboxylate anion). This carboxylate anion then reacts with a proton-containing compound to give a new carbon-hydrogen bond.

The mechanism of reaction is as follows -

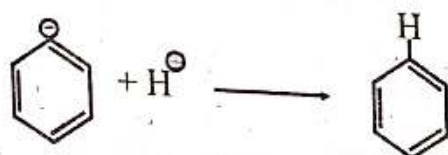
Step (i) - In the first step, the aromatic carboxylic acid reacts with soda lime i.e. base to form sodium salt of aromatic carboxylic acid or aromatic carboxylate anion.



Step (ii) - In the second step the aromatic carboxylate anion react as follows.



Step (iii) - The above species react with proton containing compound to give a new carbon hydrogen bond.



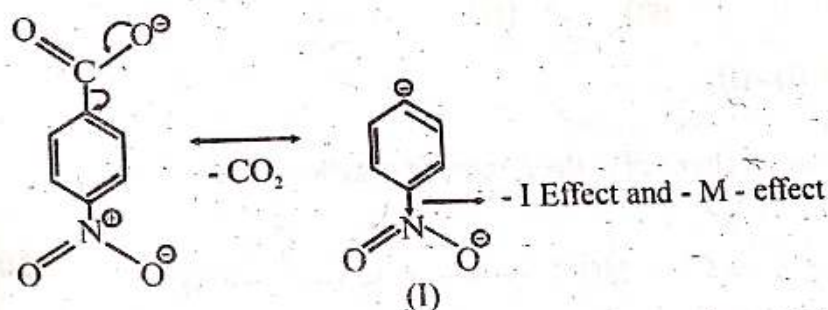
Rate of decarboxylation in aromatic substituted carboxylic acid: - [2011]

Since the decarboxylation of aromatic carboxylic acid proceed through benzyl carboxylate anion. Thus the substitution on benzene ring have greater means on rate of reaction. The substituting group affect the rate of decarboxylation.

Since the decarboxylation proceed through the carbanion intermediate, therefore those substituted group which stabilize the carbanion will give faster decarboxylation. Generally the substitution on ortho and para position more effect the rate of decarboxylation in aromatic substituted carboxylic acid.

1) When electron withdrawing group (EWG) are substituted para position-

The electron withdrawing group increases the stability of benzyl carboxylate anion intermediate (carbanion intermediate) by the - I - effect and sometime by - M - effect.



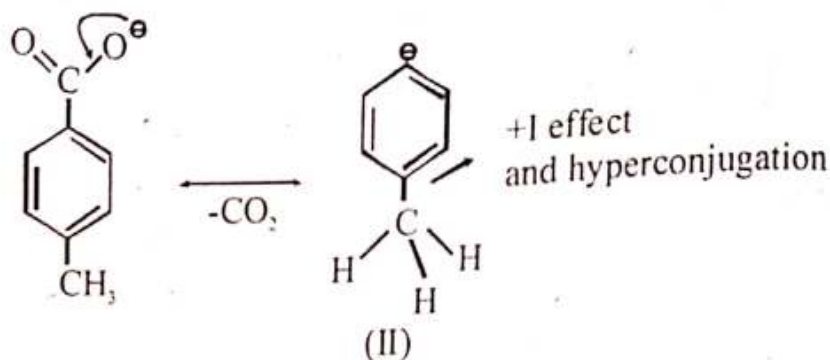
In the compound (I) The substituted group is - NO2. Which is good

EWG. Thus due to the electron withdrawing nature of $-\text{NO}_2$ decrease the magnitude of electron density of carbanion thus it stabilize the carbanion.

Similarly $-\text{NO}_2$ group also behaves as $-M$ group which also stabilize stability of carbanion by the delocalization of negative charge.

(2) When electron donating group (EDG) are substituted at para position:-

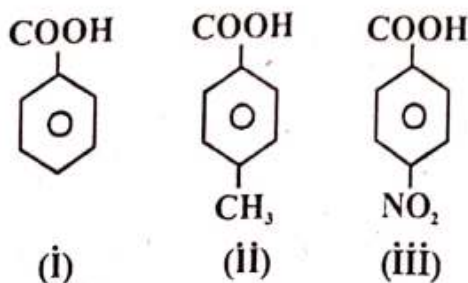
Electron donating group decreases the stability of benzyl carboxylate anion intermediate (carbanion intermediate) by the $+I$ - effect and hyper conjugation.



In compound (II), the substituted group is $-\text{CH}_3$, which behaves as electron donating group. In this case both $+I$ - effect and hyper conjugation decreases the stability of carbanion intermediate by increasing the electron density of carbanion.

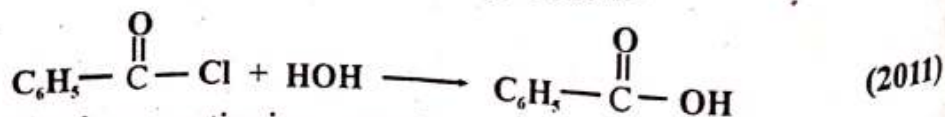
Thus from the above discussion it is clear that the EWG present at ortho and para position give faster decarboxylation. While the electron donating group (EDG) at ortho and para position give slower decarboxylation.

Q.2. Which one of the following Carboxylic acids will be most reactive for decarboxylation? (2011)



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

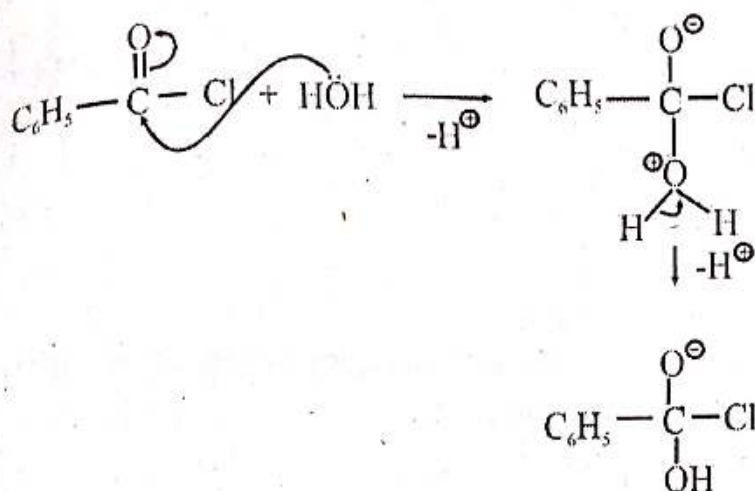
Q.3. Give the mechanism of the following reaction -



Ans. The above reaction is an example of nucleophilic addition - elimination reaction. The mechanism of the reaction proceed through two steps -

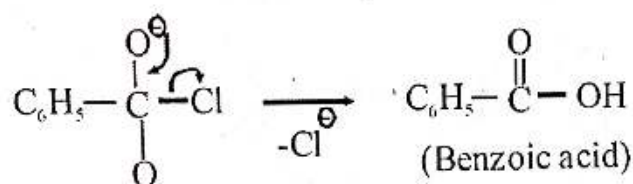
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Step (i) Addition - In the first step the nucleophile attack on carbonyl carbon. This step is called addition step -



Step (ii) Elimination -

In the second step the elimination of chloride ion (i.e. Cl^-) takes place. Thus this step is called elimination step.



Q.4. Write note on action of heat on dibasic acids.

(2011)

Other Related Questions -

Q. Write note on Action of heat on dicarboxylic acid.

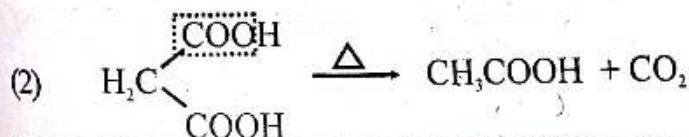
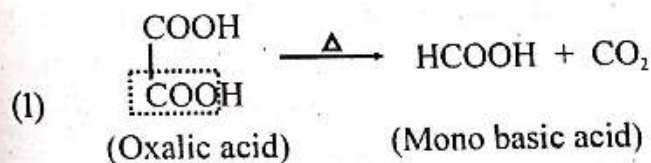
Ans. When the carboxylic acids are heated, the different products are obtained. The nature of products depends on the carbon chain length separating two -COOH groups.

(1) Acids with one or no carbon between two -COOH groups (1,2 or 1,3 - carboxylic acids) -

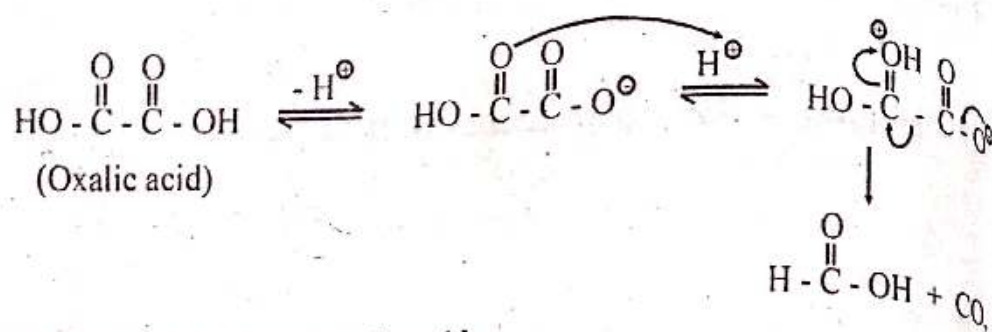
This type of dicarboxylic acids lose carbon dioxide (ie $-\text{CO}_2$)



for example



Mechanism -

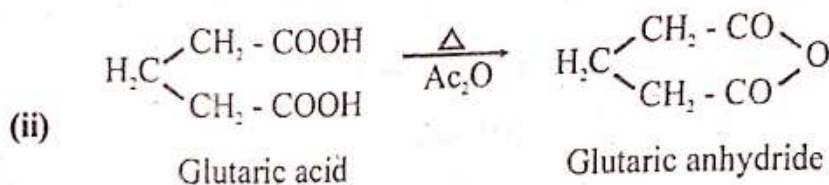
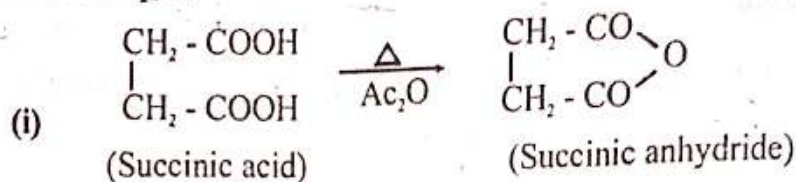


(2) 1,4 and 1,5 - dicarboxylic acid -

This type of dicarboxylic acid lose water molecules (ie - H_2O) and the formation of anhydride takes place.



For example :-

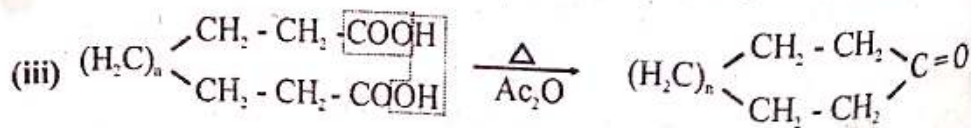
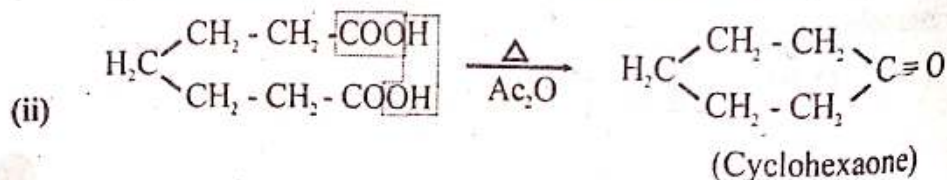
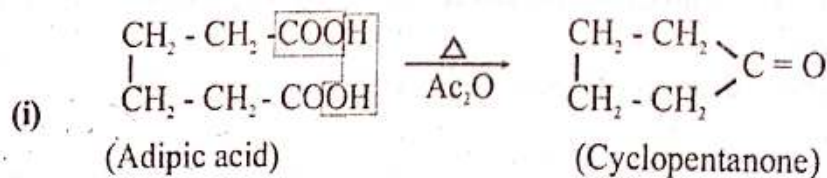


(3) 1,6 and higher than 1,6 dicarboxylic acid: -

This type of carboxylic acid lose both CO_2 and H_2O and the formation of cyclic ketone takes place



For example :-



Where $n \geq 6$

To show our !

Q.5. Complete the reaction and give their mechanism -

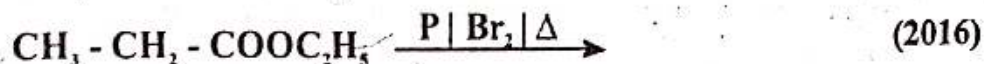


Other Related Questions -

Q. How will you bring following transformation give the mechanism. (2015)

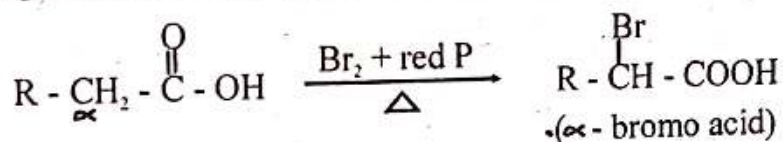


Q. Complete the following reaction

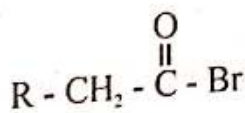
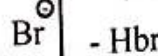
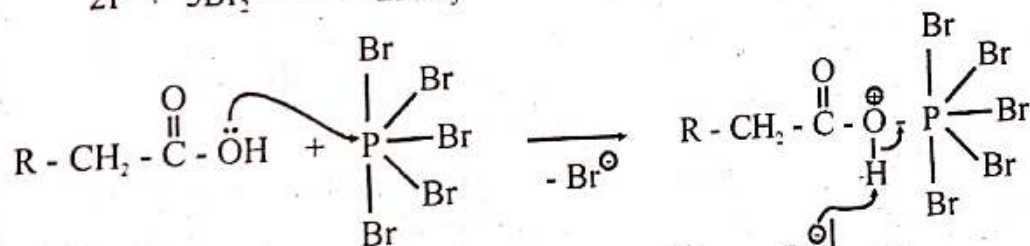


Ans. Hell - Volhard - Zelinsky reaction (HVZ reaction) or α -halogenation: -

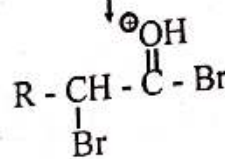
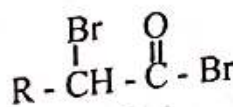
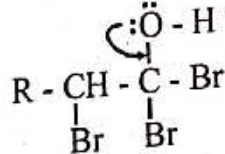
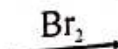
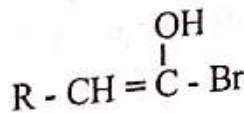
When a carboxylic acid having α -hydrogen is treated with halogen (Br_2/Cl_2) in the presence of red phosphorus, the α - hydrogen atoms are replaced by halogen. This reaction is known as Hell-Volhard - Zelinsky Reaction.



Mechanism of the above reaction is as follows -

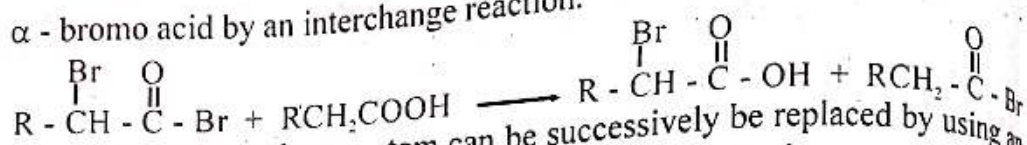


Tautomerisation $\rightleftharpoons$

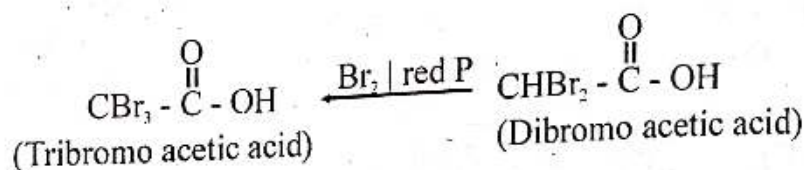
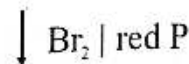
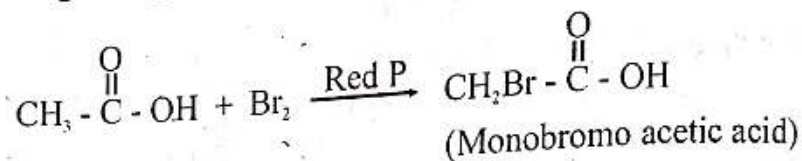


(I)

This α -bromoacyl bromide (ie - compound (i)) react with acid to give α -bromo acid by an interchange reaction.

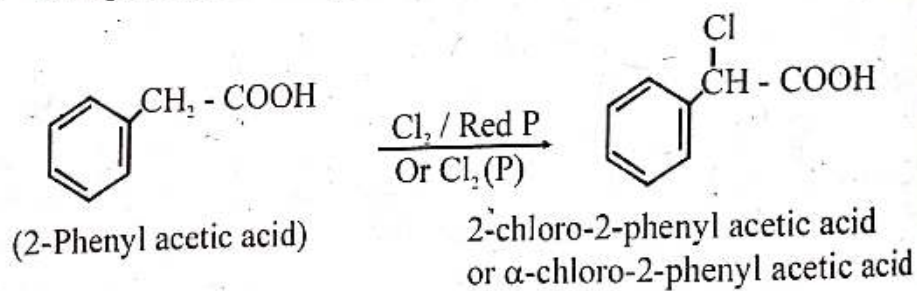


All the α -hydrogen atom can be successively be replaced by using an excess of halogen. The reaction can however, be stopped at mono, di- or tri substituted stage using appropriate amount of halogen. for example -



Q.6. Complete the following reaction

(2019)

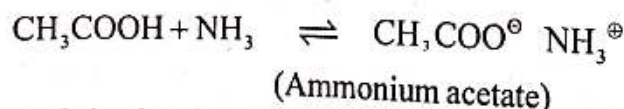


Ans. (The mechanism proceed through similar manner as shown above in HVZ - reaction).

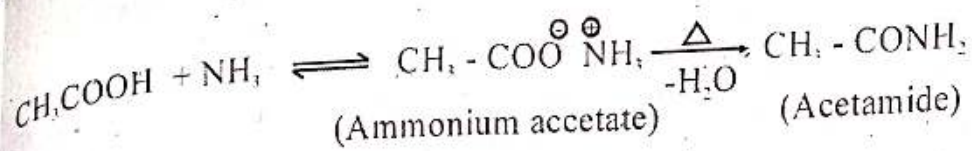
Q.7. What is the product of the reaction of a carboxylic acid and ammonia?

(2016)

Ans. The reaction between carboxylic acid and ammonia is basically an acid base neutralization reaction, Where RCOOH will furnish H^+ and NH_3 having a lone pair on N will act as lewis base and accept the H^+ leading to the formation of ammonium salt.



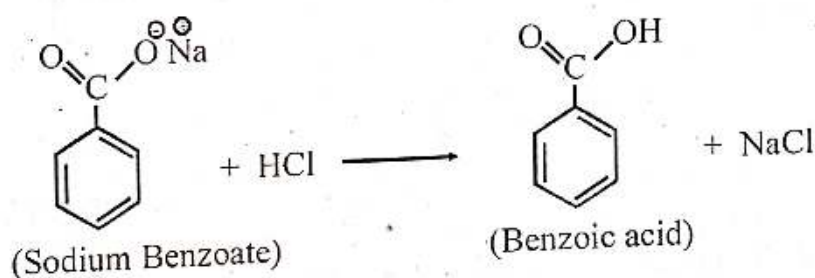
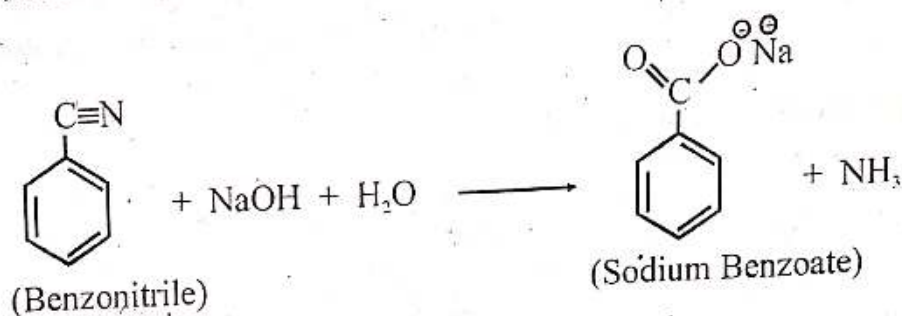
On further heating, the ammonium salt undergoes dehydration, resulting into an amide and releasing a molecule of water.



Q.8. How to convert benzoic acid from benzonitrile? (2017)

Ans. Benzonitrile is converted to benzoic acid by basic hydrolysis. When benzonitrile is heated with aqueous sodium hydroxide (NaOH) solution, it liberates ammonia gas and converts to sodium benzoate which on acidification gives benzoic acid.

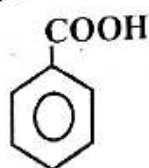
The mechanism of above conversion are as follows -



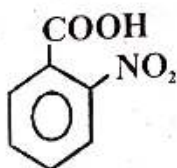
Q.9. Discuss the acidity of mononitro benzoic acids. (2017)

Other Related Questions -

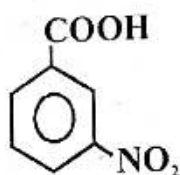
Q. Arrange the following compound in decreasing order of their acidic strength -



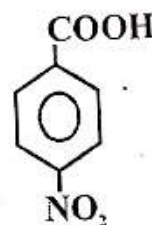
(Benzoic acid)
(I)



(Ortho nitrobenzoic acid)
(II)



(Meta nitrobenzoic acid)
(III)



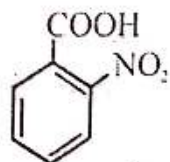
(Para nitrobenzoic acid)
(IV)

Ans. Decreasing order of acidic strength-
(II) > (IV) > (III) > (I)

The explanation are as follows.

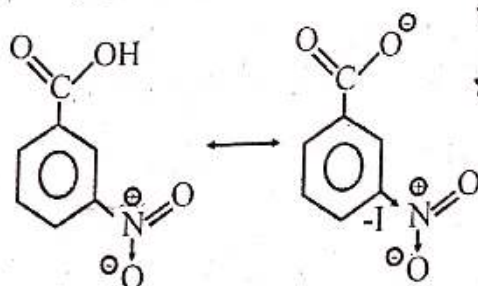
Compound (II) :-

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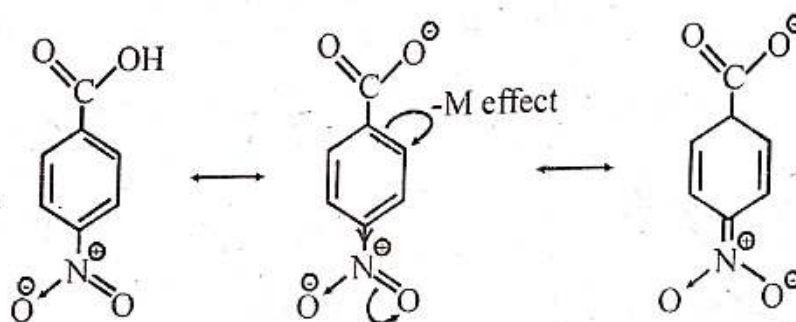
Ortho substituted benzoic acid are more acidic than the para and meta substituted benzoic acid due to ortho effect.

Compound (III) :-



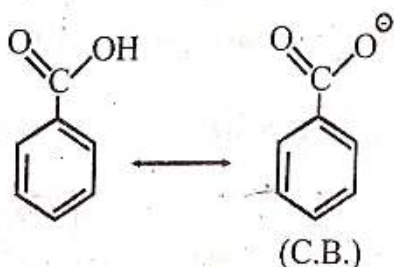
- ★ No mesomeric effect at meta position.
- ★ Moderate -I- effect increase the acidity by increasing the electrophilicity of carbonyl carbon of carboxylic group.

Compound (IV) :-



- ★ -M effect increase the acidity by increasing stability of the carboxylate anion by increasing the electrophilicity of carbonyl carbon.
- ★ Weak -I- effect increase the acidity by increase the electrophilicity of carbonyl carbon of carboxylic group.

Compound (I) -

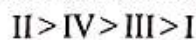


Nither -I nor -M stabilize the carboxylate anion.

Thus from above discussion it is clear that the compound (II) is most acidic due to ortho effect.

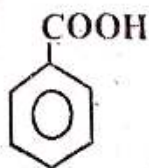
And compound (IV) is more acidic than the (III) due to -M- effect and compound (III) is more acidic than the (I) due to -I- effect.

Thus the decreasing order of acidic strength.

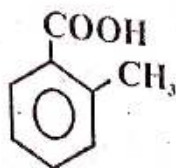


Q.10. Discuss the decreasing order of acidic strength

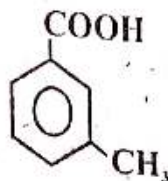
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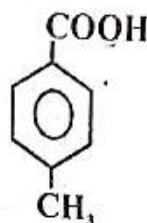
(I)



(II)



(III)

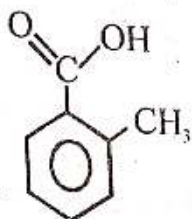


(IV)

Ans. Decreasing order of acidic strength-
(II) > (I) > (III) > (IV)

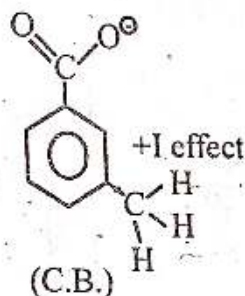
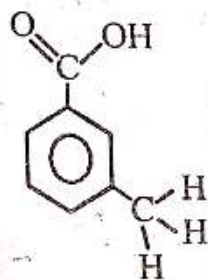
The explanation are as follows -

Compound (II) :-



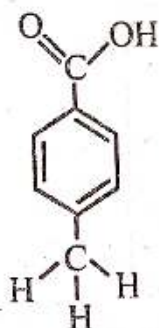
Ortho substituted benzoic acid are more acidic than meta and para benzoic acid due to ortho effect.

Compound (III) :-

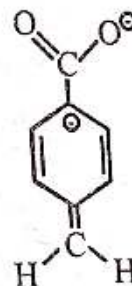


- * No hyperconjugation effect at meta position
- * Moderate + I effect decrease the acidity by decreasing the electrophilicity of carbonyl carbon of carboxylate anion.

Compound (IV) :-



Hyper-conjugation

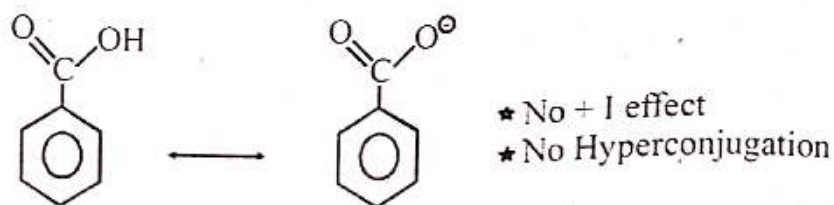


* Weak + I - effect decrease the acidity by decreasing the electrophilicity of Carbonyl carbon of carboxylic group.

* Hyperconjugation effect also decrease the acidity by decreasing electrophilicity of carbonyl carbon of carboxylic group.

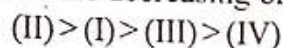
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Compound - (I) :-



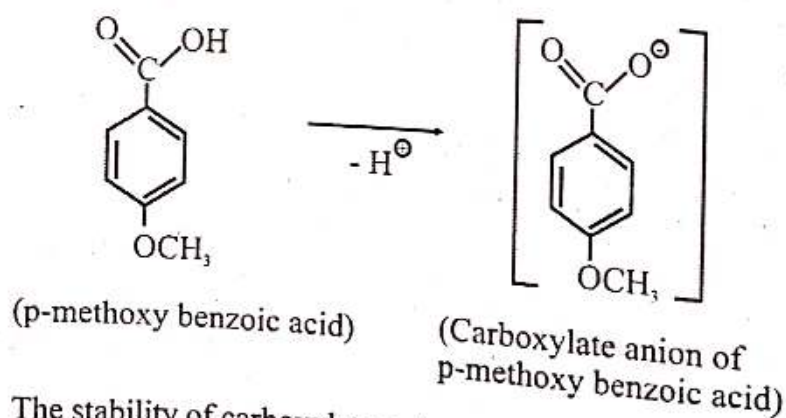
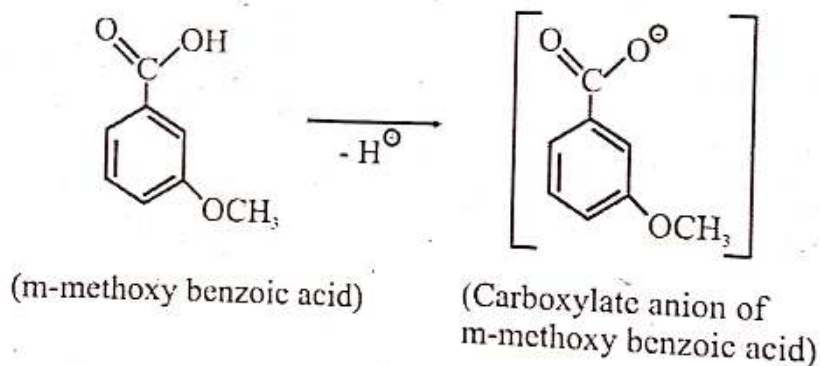
Thus from the above discussion it is clear that the compound (II) is most acidic due to the ortho effect. And compound (I) is more acidic than compound (III) and (IV) because the compound (III) and (IV) decrease the stability of carboxylate anion and compound (III) is more acidic than (IV) because compound (IV) decreases the stability of carboxylate anion by two factors i.e. - hyperconjugation and + I - effect.

Thus the decreasing order of acidity -



Q.11. m-methoxy benzoic acid is stronger acid than p-methoxy benzoic acid why? (2016)

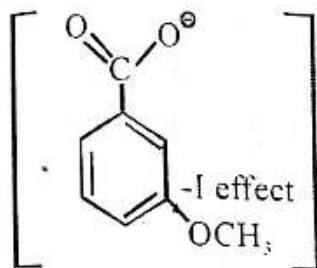
Ans. The acidity of benzyl carboxylic acids are depend upon the stability of corresponding benzyl carboxylate anion.



The stability of carboxylate anion depends on the substituted group on benzyl carboxylic acid which stabilize the negative charge of corresponding

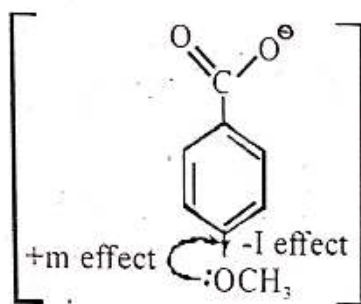
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benzyl carboxylate anion (by increasing the electrophilicity of carbonyl carbon of acid) will be more acidic. While those substituted group on benzyl carboxylate anion (by decreasing the electrophilicity of carbonyl carbon of acid) will be less acidic.



- ★ Moderate -I effect increase the stability of benzyl carboxylate anion by increasing electrophilicity of carbonyl carbon.

- ★ No mesomeric effect at meta position.



- ★ Weak -I effect slightly increase the stability of benzyl carboxylate anion by increasing electrophilicity of carbonyl carbon.

- ★ +M effect or resonance decreases the stability of benzyl carboxylate anion by decreasing electrophilicity of carbonyl carbon.

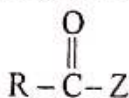
In m-methoxy benzoic acid the corresponding m-methoxy benzyl carboxylate anion are well stabilize by the -I-effect of methoxy group ($-OCH_3$) which causes increase the electrophilicity of carbonyl carbon of the m-methoxy benzyl carboxylate anion. In this case no mesomeric effect affect the stability. While in the p-methoxy benzoic acid, the corresponding p-methoxy benzyl carboxylate anion are well stabilize by the weak -I - effect of methoxy group ($-OCH_3$) which causes to increase the electrophilicity of carbonyl carbon of p-methoxy benzyl carboxylate anion. But + M effect destabilize the corresponding p-methoxy benzyl carboxylate anion by decreasing electrophilicity of carbonyl carbon of m-methoxy benzyl carboxylate anion.

Chapter 7

Carboxylic acid derivatives

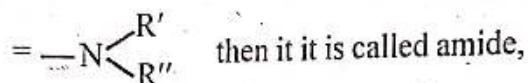
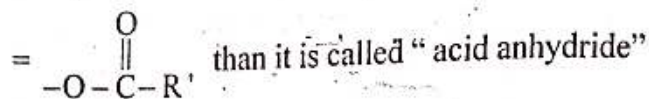
Introduction :-

Carboxylic acid derivatives can be expressed as the formula-



Where R = Aryl, alkyl or a hydrogen

and If z = Cl, then it is called "acid chloride"



Q.1. Discuss the mechanism of nucleophilic acyl substitution. (2012)

Ans. Mechanism of Nucleophilic acyl Substitution -

Like aldehydes and ketones, the carbonyl carbon of the acyl derivatives is electrophilic in nature thus any nucleophile can attack on that carbon. The main reactions of these classes of compounds are nucleophilic substitution reactions. These compounds bear a potential Lewis base leaving group which can be replaced by another stronger nucleophile as shown below-

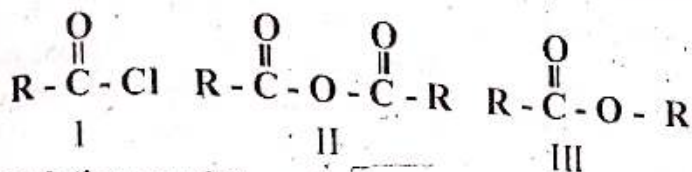


In all the cases the L has at least one lone pair of electrons which is conjugated to π - bond of carbonyl group. The following conditions should be fulfilled for the reaction.

- (1) Leaving ability of L is more than $\text{y}^{\ominus}$ otherwise reverse reaction would take place.
- (2) Nucleophilicity of $\text{y}^{\ominus}$ should be strong enough to attack the electron deficient carbonyl carbon of the acyl group, and
- (3) Carbonyl carbon of the acyl group should be good electrophile to react with $\text{y}^{\ominus}$.

Q.2. Arrange the following compounds in their decreasing order of reactivity of acyl substitution:

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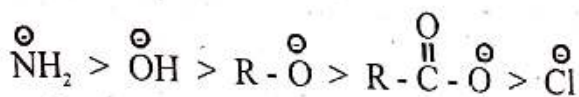
Ans. **Relative reactivity and stability of acid derivatives:-**

Relative reactivity and stability of acid derivatives depend on the following factors -

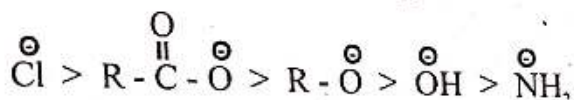
1) **Leaving power of L (Leaving group):-**

The Leaving ability of L depends on its basicity. The weaker the basicity of group the better is its leaving ability.

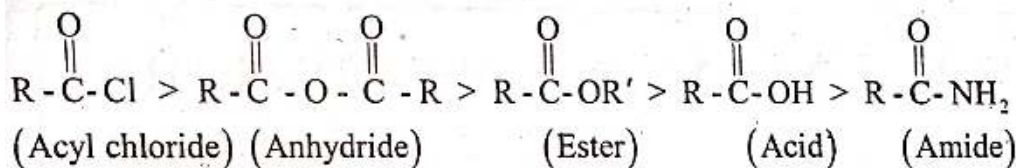
The relative basicity of the leaving groups in decreasing order is as follows -



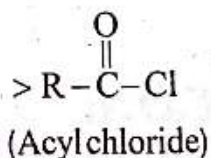
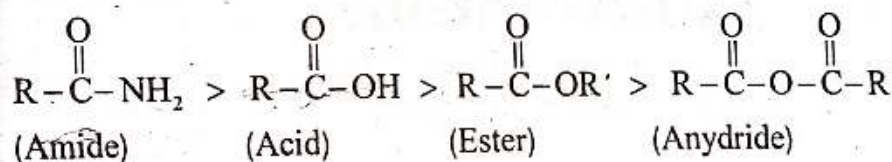
Thus leaving character in decreasing order is follows -



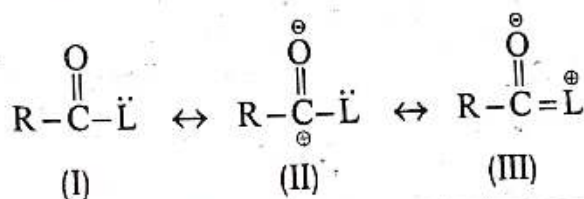
Thus the relative reactivity of acids and acid derivatives in decreasing order is as follows -



Thus the order of relative stability -



(2) The relative reactivities and stabilities of the compounds $\text{R} - \overset{\text{O}}{\parallel} \text{C} - \text{L}$ can be understood in term of the following resonance form.



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Those factors which stabilises acid derivatives reduce the reactivity of acid derivatives. Stability of acid derivatives can be best explained by the structure (II). Thus more is the stability of the structure (II) less is the reactivity of acyl derivatives.

Thus those leaving group "L" have more delocalised lone pair ability will stabilise the structure (II). We know that strong base can easily delocalise its non bonding (lone pair) electron into the antibonding of carbonyl group. Due to this the electrophilicity of carbonyl carbon decreases and nucleophilic addition reacting can not take place easily. Thus strong base makes the acyl derivative more stable and therefore less reactive.

(3) Reactivity of these compounds also depends on the electron deficiency of the carbonyl carbon. More the electron deficiency of carbonyl carbon, more will be reactivity of the compound for nucleophilic addition reaction.

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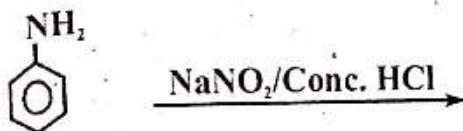
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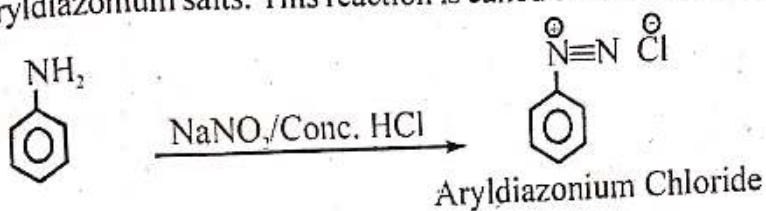
Chapter 8

Q.1. Complete the given reaction.

(2011)



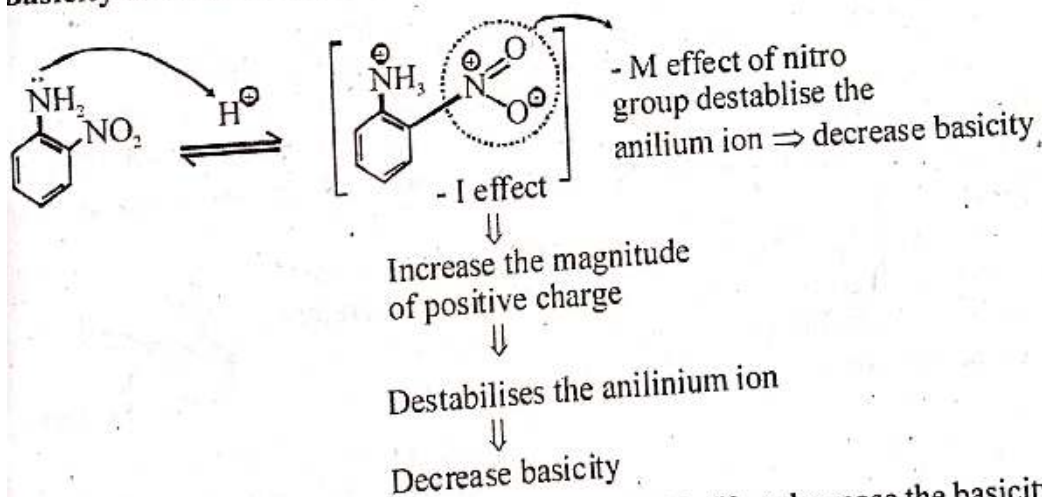
Sol. Aromatic primary amine react with nitrous acid ($\text{NaNO}_2/\text{Conc. HCl}$) to form aryldiazonium salts. This reaction is called **diazotization reaction**.



Q.2. Explain why O-nitroaniline are less basic than O-methoxy aniline? (2011)

Ans. The basicity of o-nitroaniline and o-methoxy aniline depends upon the stability of corresponding anilinium ion. More the stability of anilinium ion, more will be the basicity.

Basicity of O-nitroaniline: -



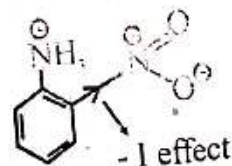
In case of orthonitroaniline both -I effect and -M effect decrease the basicity. Thus basicity of orthonitroaniline can be explained by both inductive effect and mesomeric effect.

Inductive effect -

-I effect of nitro group increase the magnitude of positive charge of anilinium ion therefore destabilise the anilinium ion hence basicity decrease.

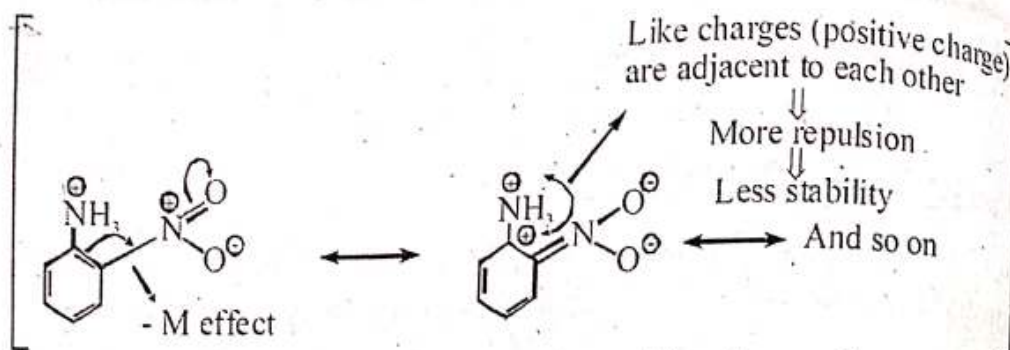
Mesomeric effect -

-M effect of nitro group creates the positive



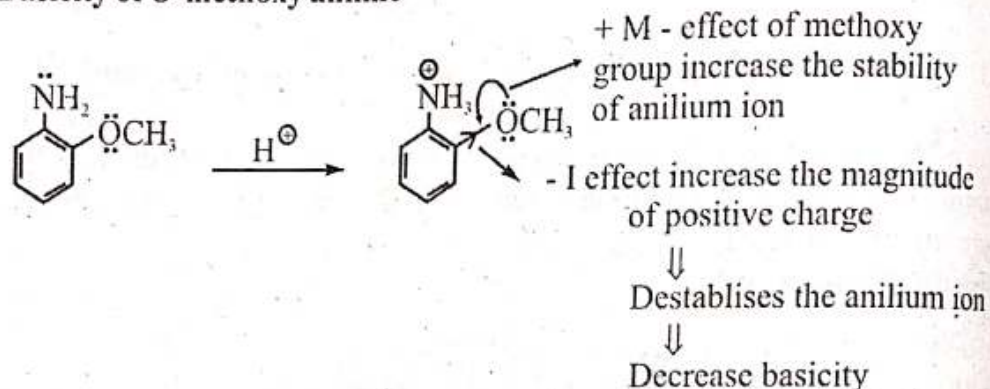
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charge adjacent to each other, therefore the repulsion increases and thus stability of anilium ion decreases hence the basicity also decreases.



- M effect of nitro group creates the positive charge adjacent to each other, therefore the repulsion increases and thus stability of anilium ion decreases therefore the basicity also decreases.

Basicity of O-methoxy aniline -

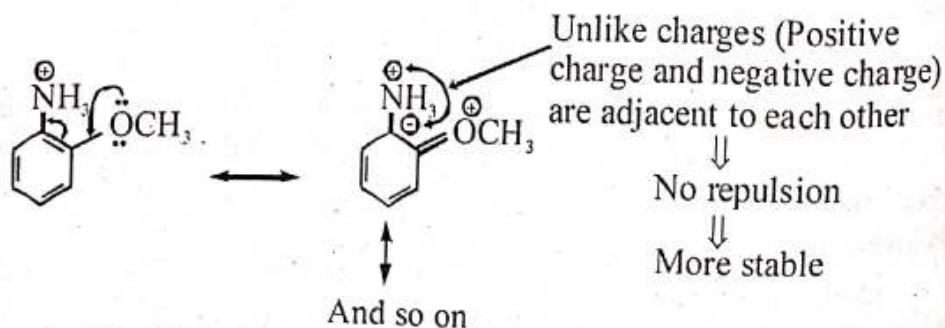
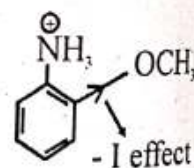


In case of o-methoxy aniline - I effect decrease the basicity but +M effect increase the basicity. Thus basicity of orthomethoxy aniline (O-methoxy aniline) also can be explain by both inductive effect and mesomeric effect.

Inductive effect -

- I effect of methoxy group (- OCH₃ group) increase the magnitude of positive charge of anilium ion, therefore destabilise the anilium ion hence basicity decrease.

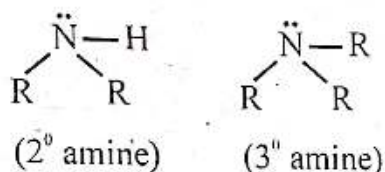
Mesomeric effect -



+ M effect of methoxy group creates the negative charge adjacent to each other, therefore no repulsion and thus stability of anilium ion increases therefore the basicity increases.

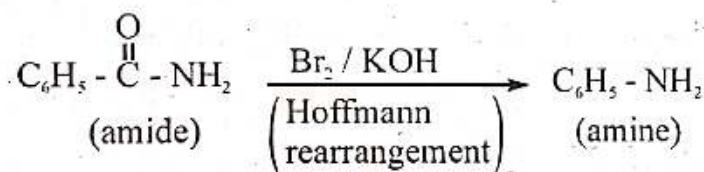
Q3. Why secondary amine (2° amine) are more basic than tertiary amine (3° amine) ?

Ans. The tertiary amines are less basic than the secondary amines. The reason is that a tertiary amine, has three alkyl groups which can donate electrons to the nitrogen atom but they also cause crowding (also called steric hindrance) around nitrogen. This hinders generation of protonation at nitrogen atom and hence, reduces the basicity. (2016)

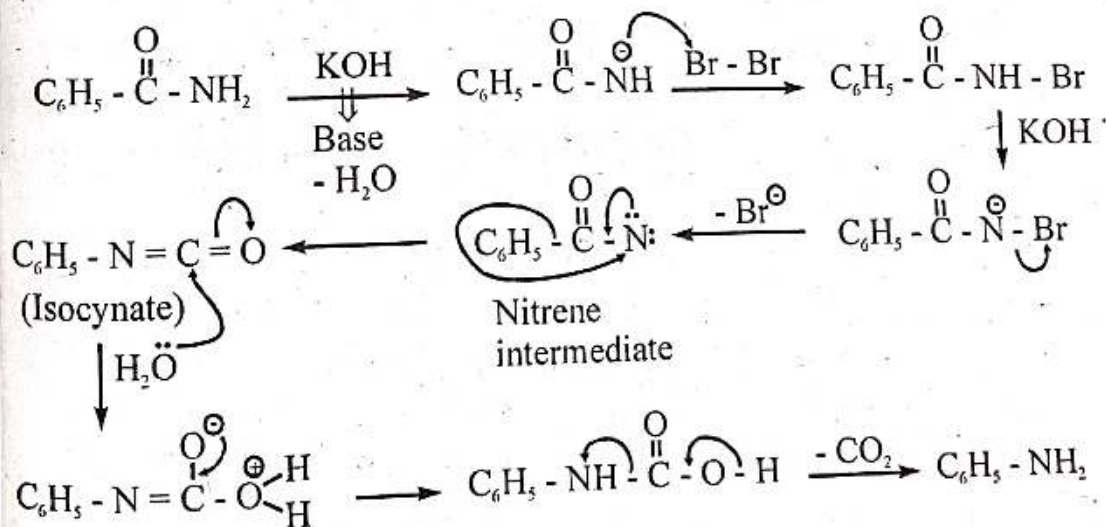


Q.4. Complete the given reaction and give their mechanism (2016, 17)

Ans.



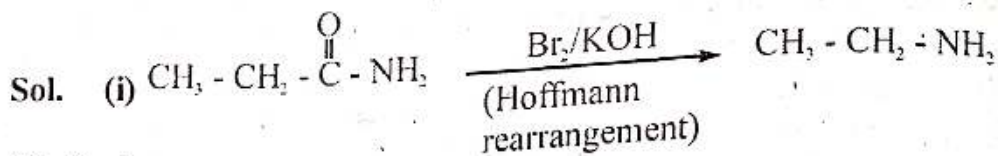
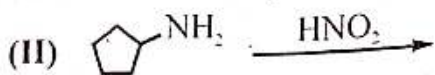
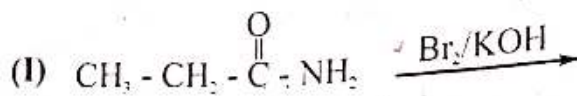
Mechanism -



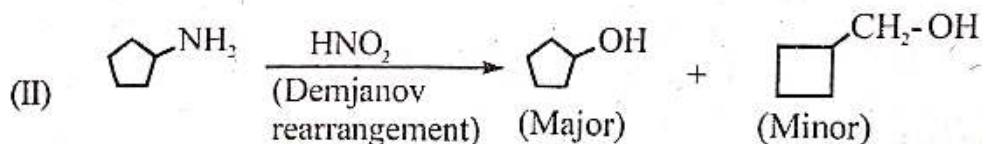
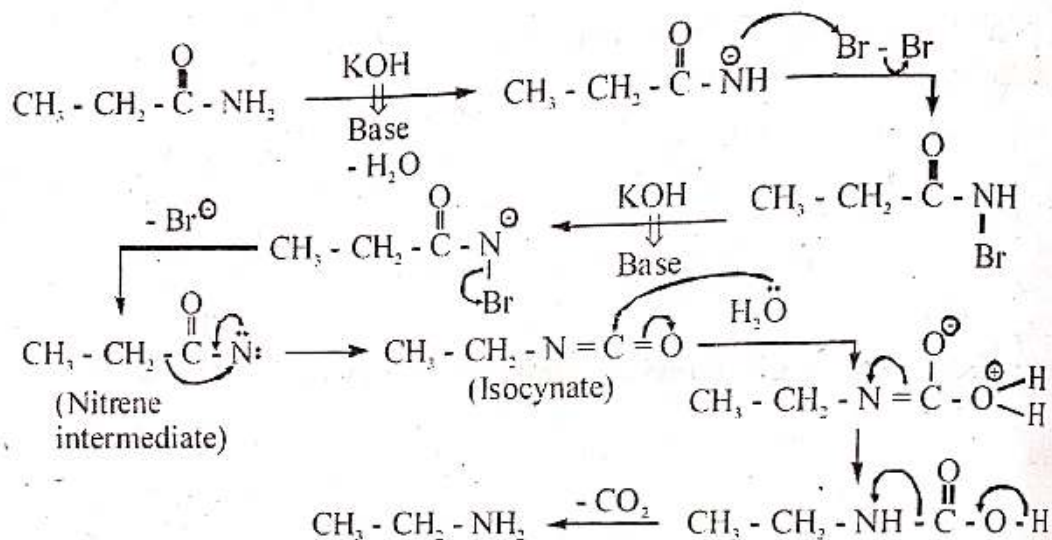
Q.5. Give the mechanism of the given reactions.

(2012)

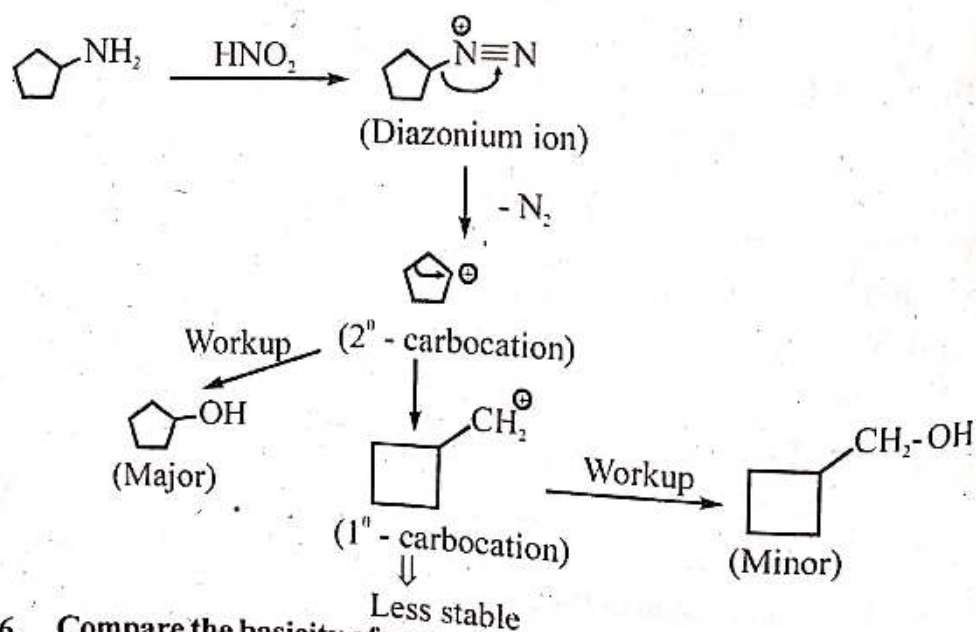
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Mechanism -



Mechanism -



Q.6. Compare the basicity of mononitroaniline?

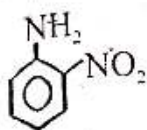
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(2015, 16)

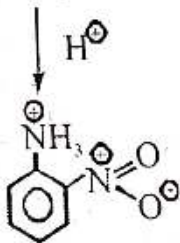
Other Related Questions -

Q. Compare the basicity of o-nitroaniline, m-nitroaniline and p-nitroaniline? (2013)

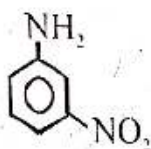
Ans. The basicity of nitroaniline depends upon the stability of corresponding anilinium ion. More the stability of anilinium ion, more will be the basicity.



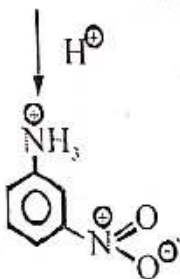
(o-nitroaniline)



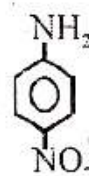
(o-nitro anilinium ion)



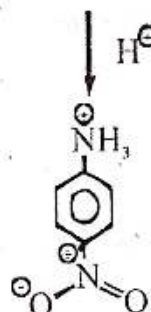
(m-nitroaniline)



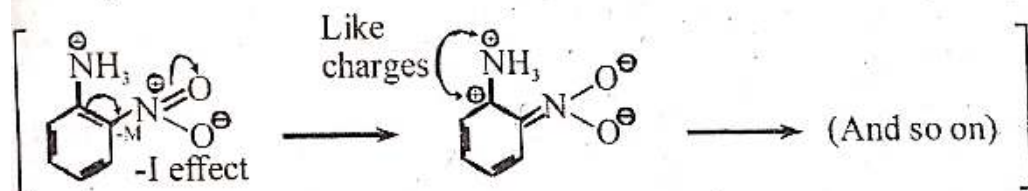
(m-nitro anilinium ion)



(p - nitroaniline)



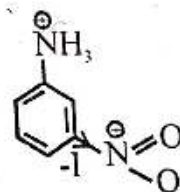
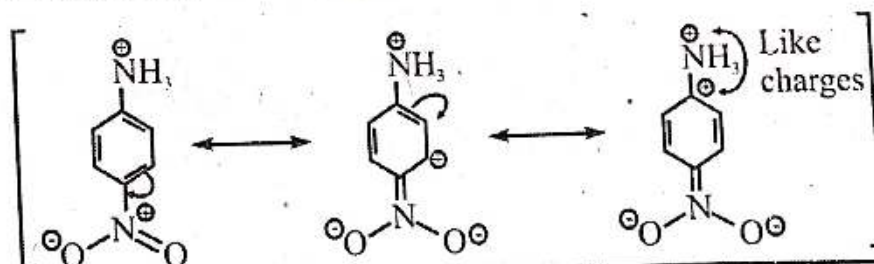
(p-nitro anilinium ion)

Basicity of o-nitroaniline: -

- Strong - I effect of nitro group decreasing the stability of anilinium ion.
- - M effect of nitro group decreases the basicity by decreasing the stability of anilinium ion, because a positive charge is created adjacent to the carbon of the $-NH_3^+$ group which causes to increase the repulsion (like charges repel to each other).

Basicity of m-nitro aniline: -

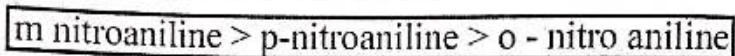
- Moderate - I effect of nitro group decreases basicity by decreasing the stability of anilinium ion.
- No - M effect of nitro group at the meta position. Thus it does not affect the basicity.

**Basicity of p-nitro aniline -**

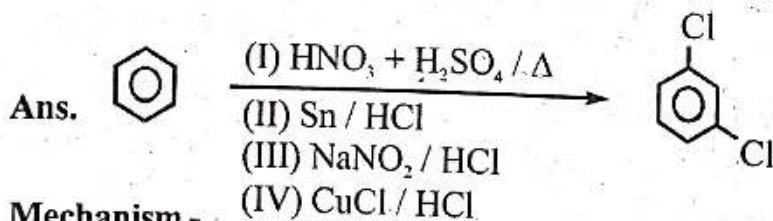
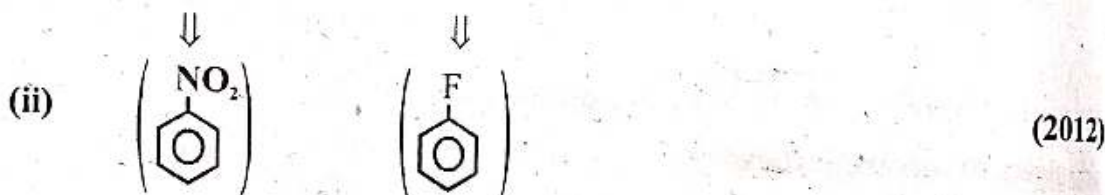
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- Weak, - I effect of nitro group decrease the basicity by decreasing the stability of anilinium ion.
- - M effect of nitro group decrease the basicity by decreasing the stability of anilinium ion because a positive charge created adjacent carbon of $-\text{NH}_2^+$ group which causes to increase the repulsion (Like charges repel to each other).

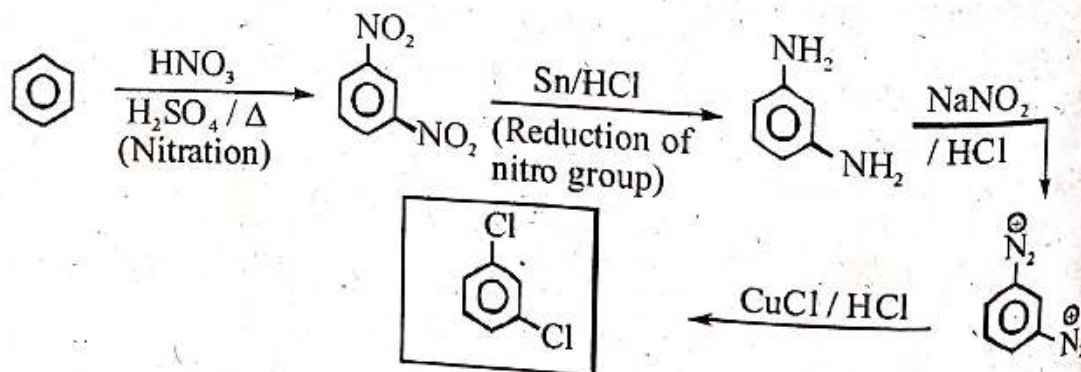
Thus basicity order will be as follows -

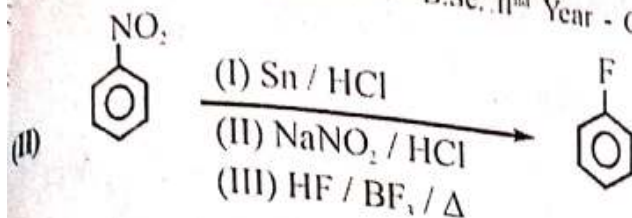


Q.7. How the following conversion can be achieved?

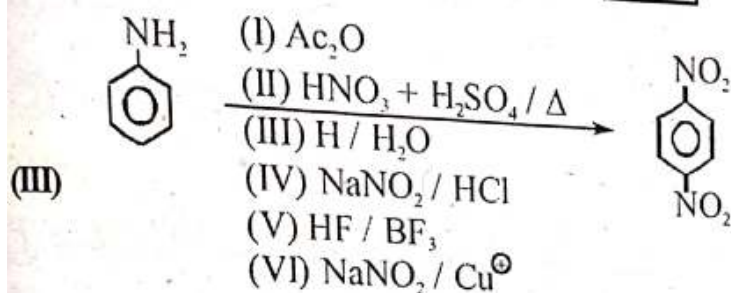
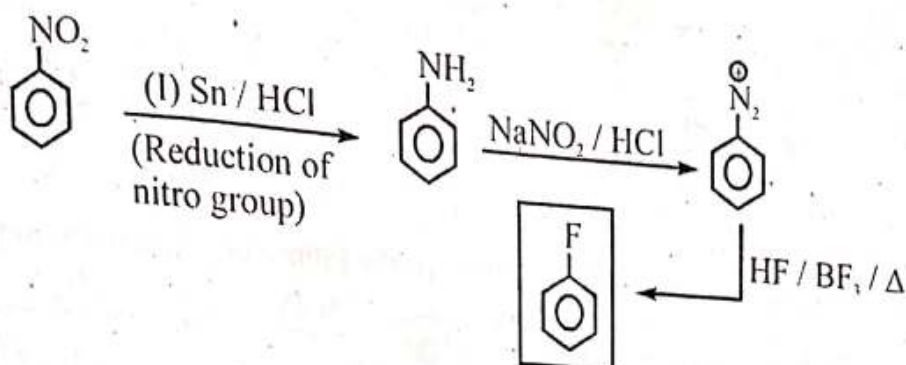


Mechanism -

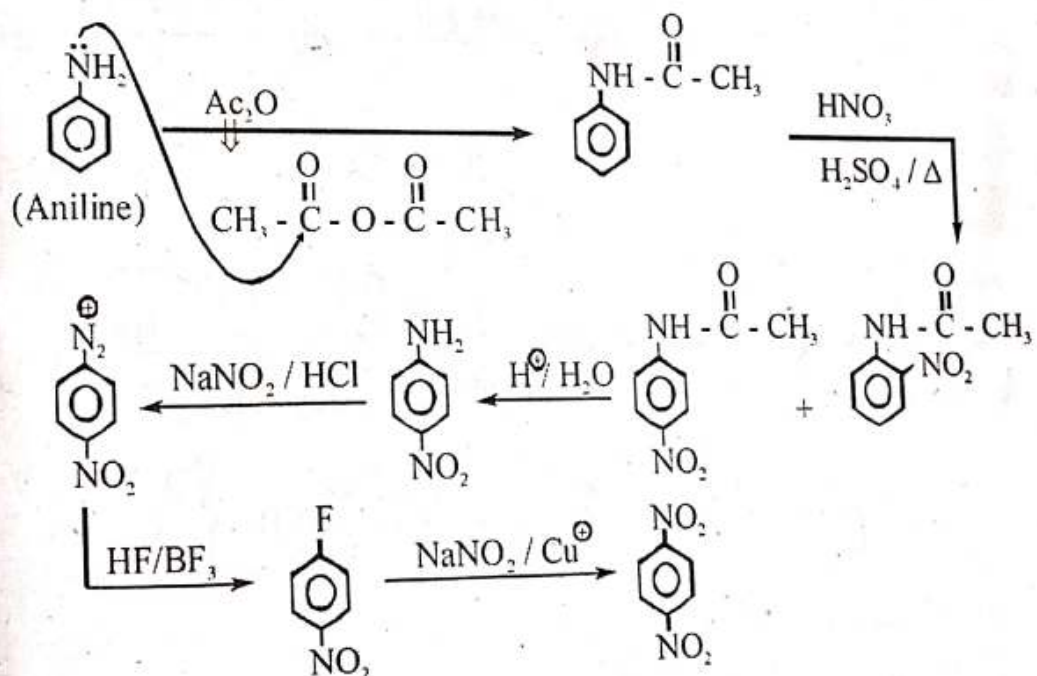




Mechanism -

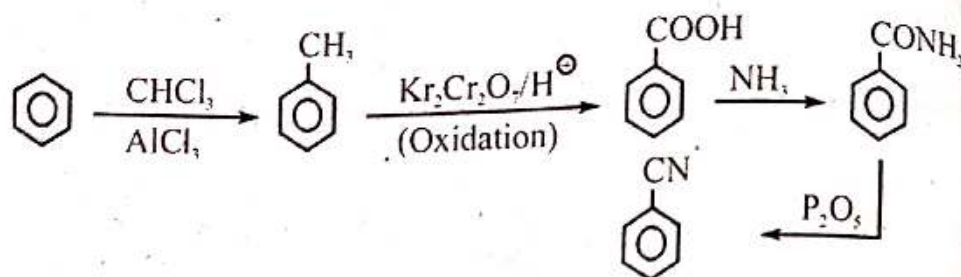
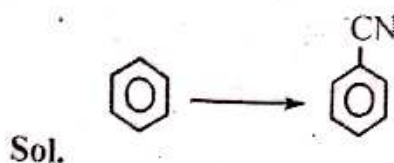


Mechanism -

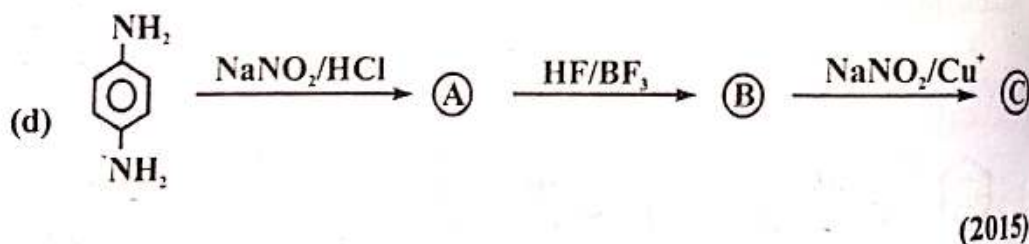
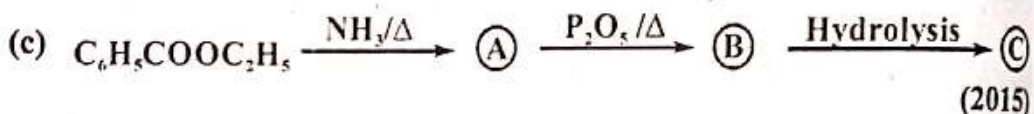
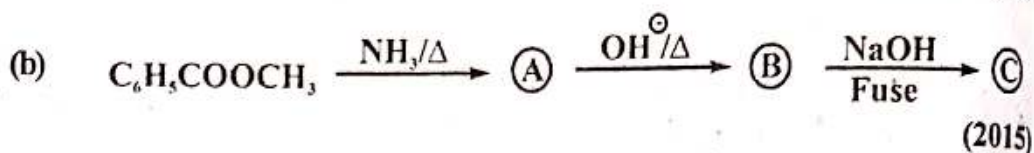
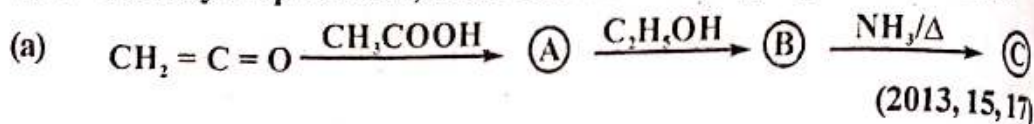


Q.8. How will you bring about the given conversion.

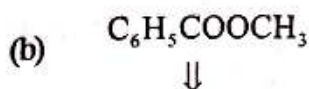
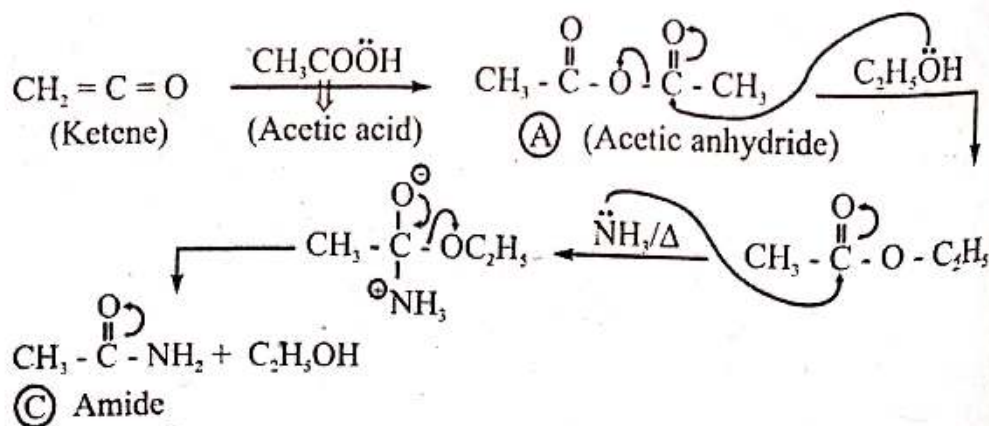
(2013, 14)

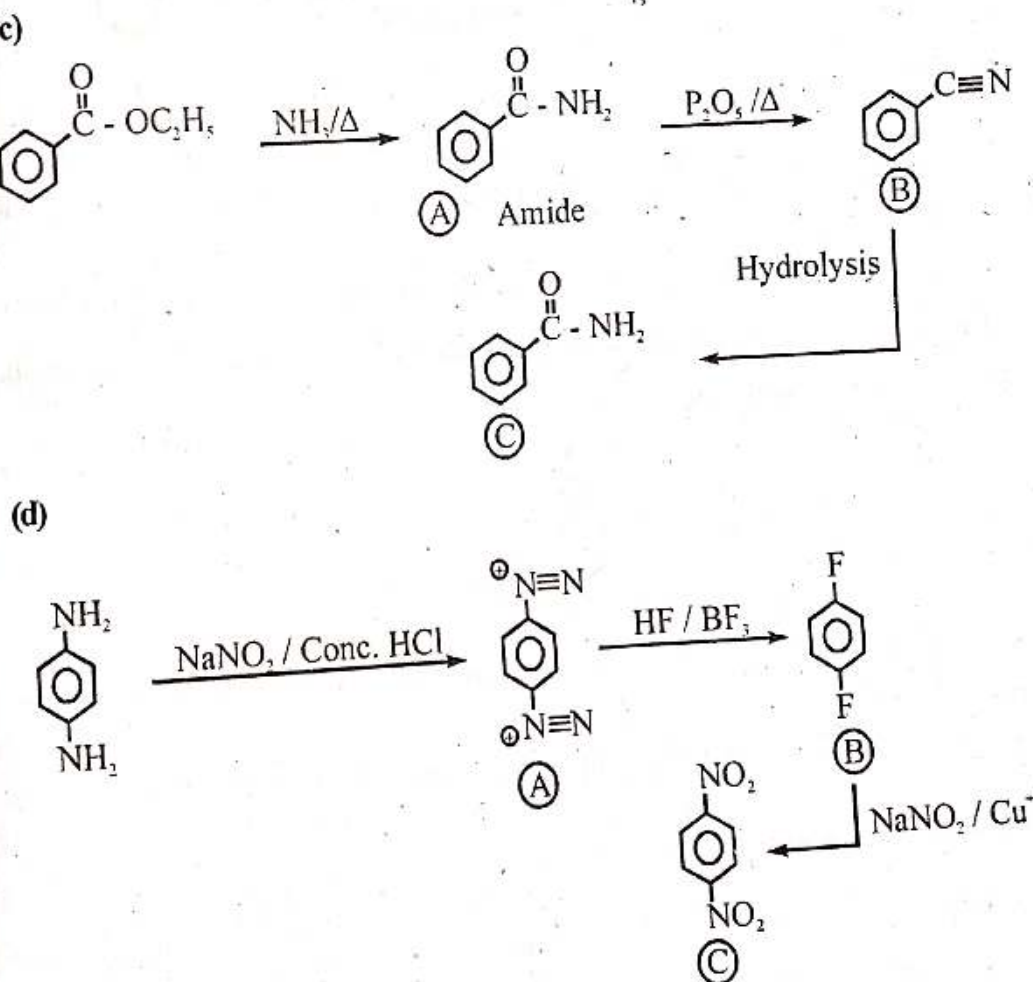
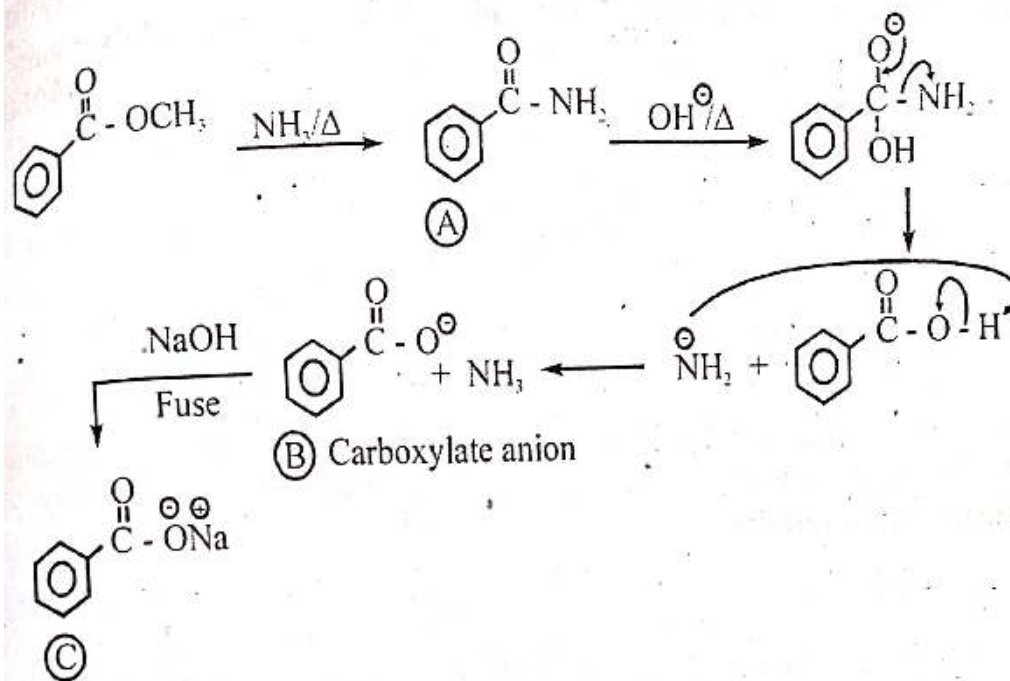


Q.9. Identify the product A, B and C in the following sequence reaction.



Ans.

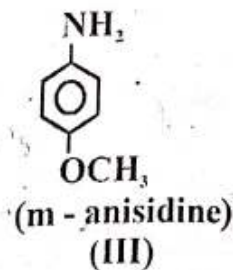
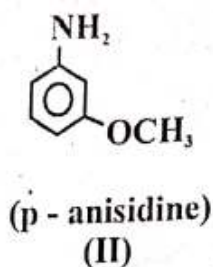
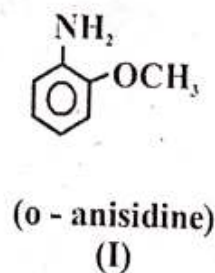




Q.10. Compare the basicity of Anisidines.
 Other Related Questions -

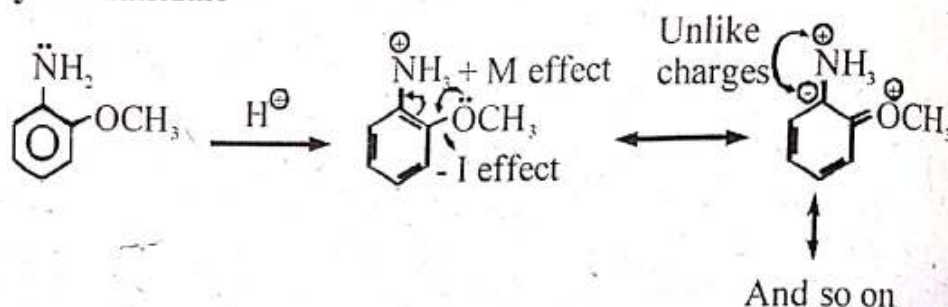
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Q.11. Arrange the following compounds in decreasing order of their basicity. (2014)



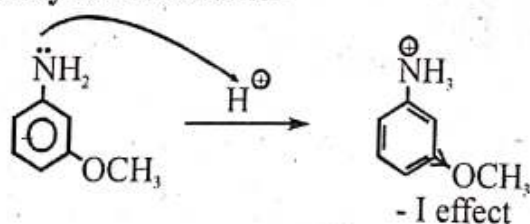
Ans. The basicity of Anisidines depends on the stability of corresponding Anilinium ion. More the stability of anilinium ion, more will be the basicity.

Basicity of o-anisidine -



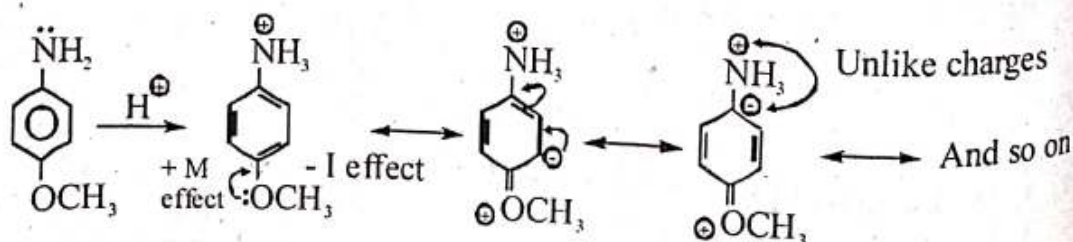
- Strong -I effect of $-\ddot{\text{O}}\text{CH}_3$ group decrease the basicity by decreasing the stability of anilium ion.
- + M effect of $-\text{OCH}_3$ group increase the basicity by increasing the stability of anilium ion because a negative charge created adjacent carbon of $-\text{NH}_3^+$ group.

Basicity of m-anisidine -



- Moderate - I effect of $-\ddot{\text{O}}\text{CH}_3$ group decrease the basicity by decreasing the stability of anilium ion.
- No + M effect of $-\text{OCH}_3$ group at meta position thus it does not affect the basicity.

Basicity of p-anisidine -



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- Weak - I effect of $-\ddot{\text{O}}\text{CH}_3$ group decrease the basicity by decreasing the stability of anilium ion.
- + M effect of $-\ddot{\text{O}}\text{CH}_3$ group increase the basicity by increasing the stability of anilium ion because a negative charge create adjacent to carbon of $-\overset{\oplus}{\text{N}}\text{H}_2$ group.

Thus the basicity order will be as follows -

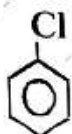


or p - anisidine > o - anisidine > m - anisidine.

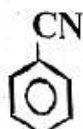
Q.12. How will you prepare following compounds from aniline? (2014)



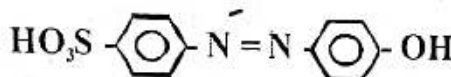
(I)



(II)

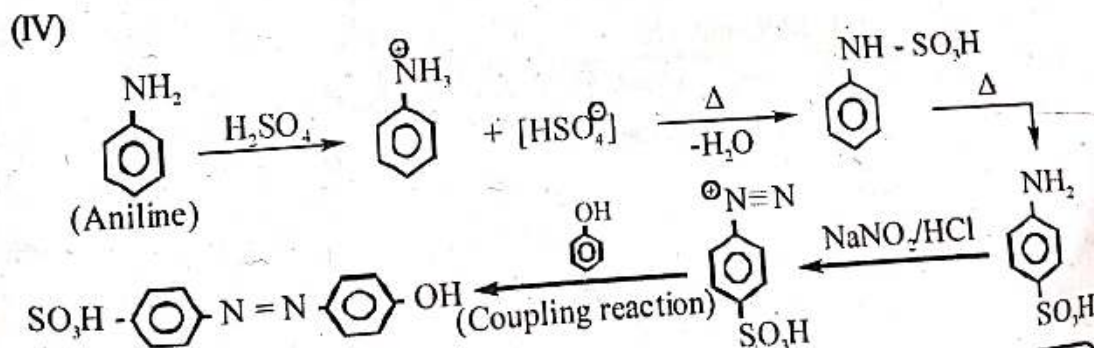
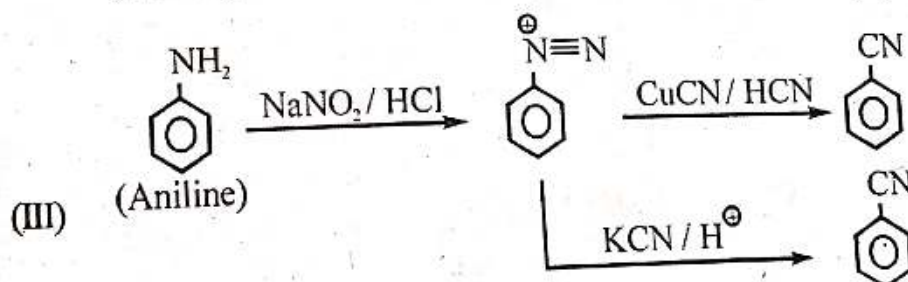
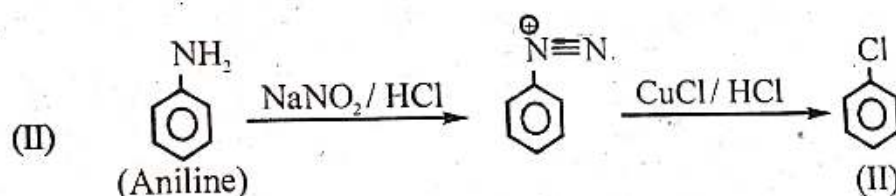
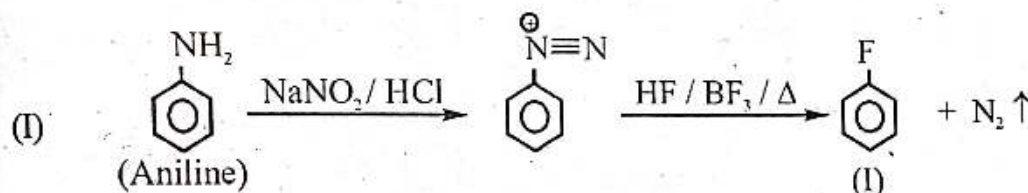


(III)



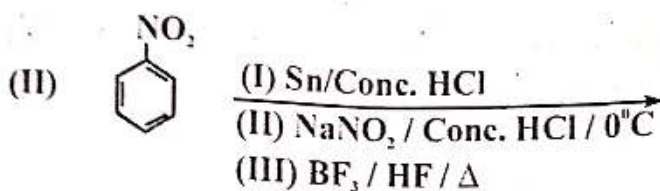
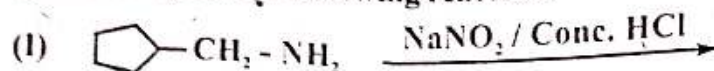
(IV)

Ans.

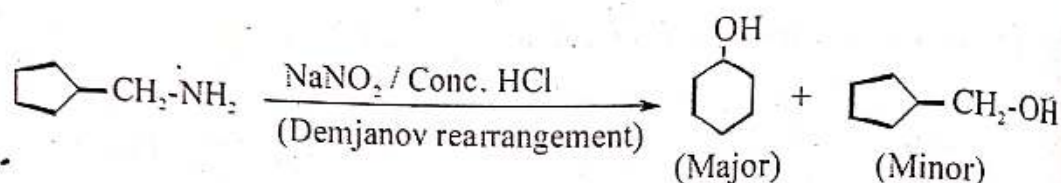


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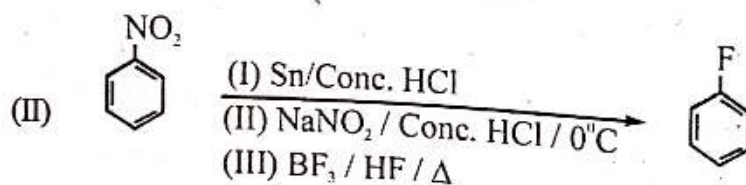
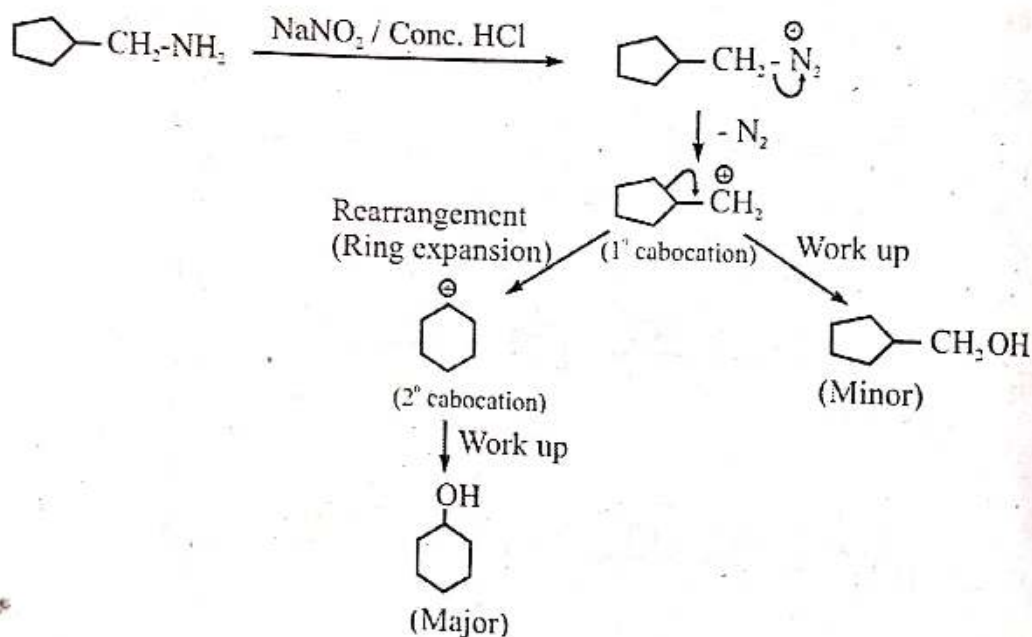
Q.13. Complete the following reactions



Ans.

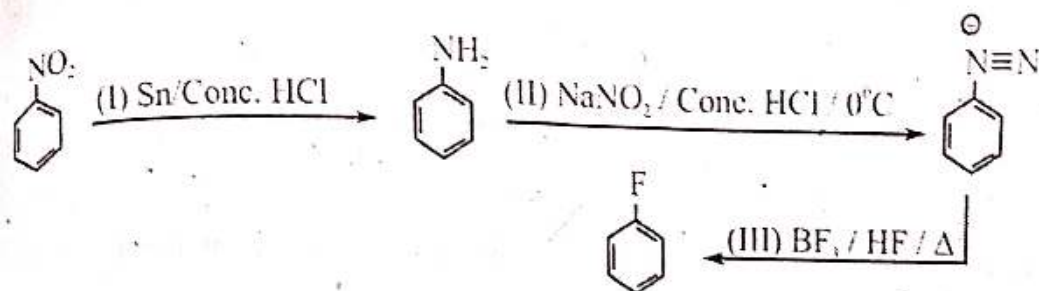


Mechanism -

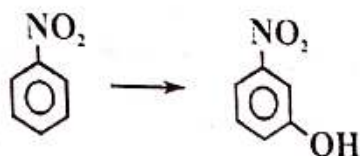


Mechanism -

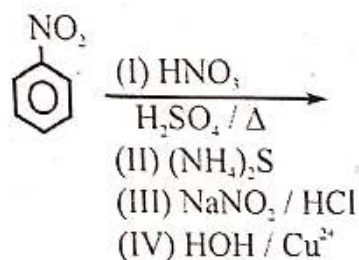
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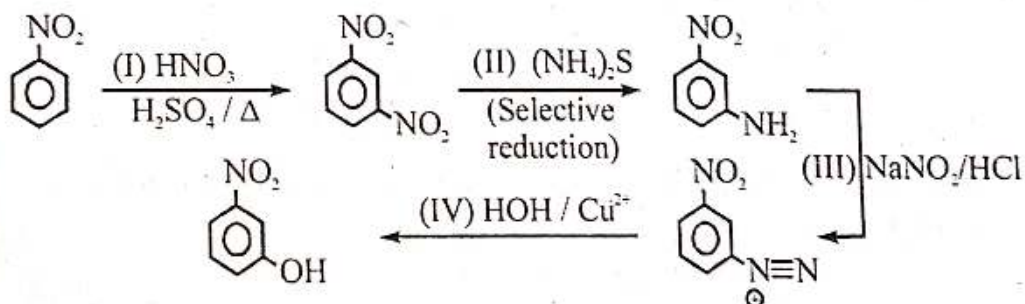
Q.14. How will you bring about the following transformation. (2016, 17)



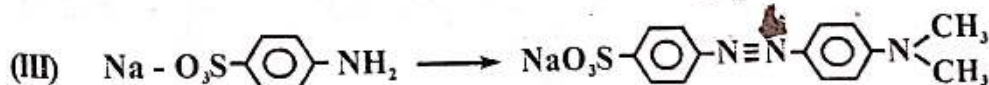
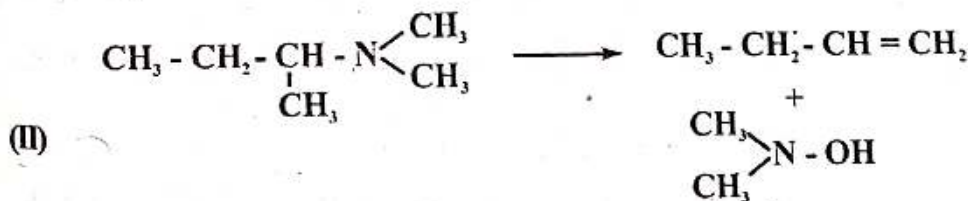
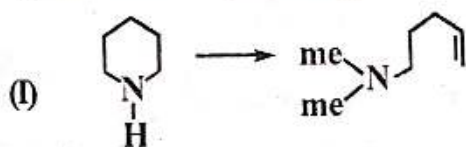
Ans.



Mechanism -

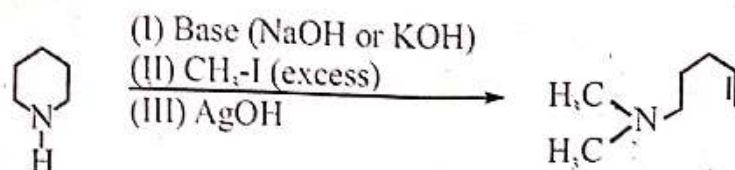


Q.15. How will you bring out following transformation. (2018)



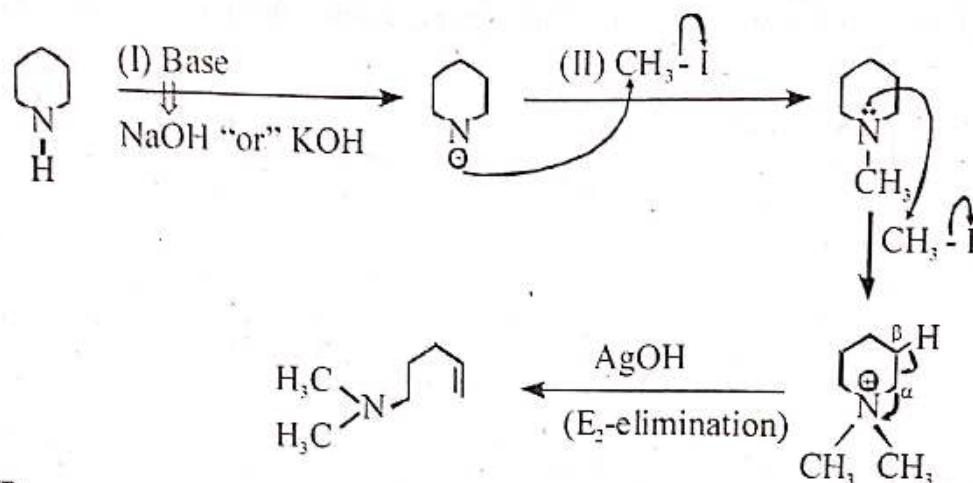
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Sol. (I)

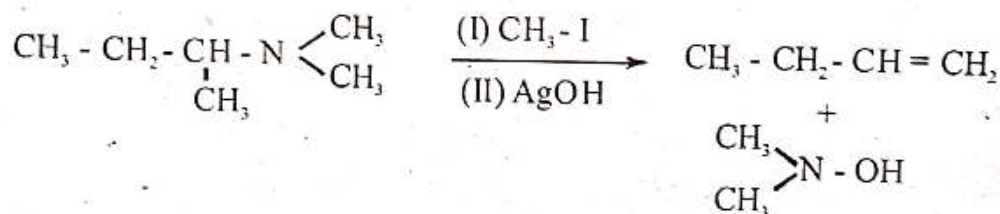


Hint - The above reaction is called "Haffmann exhaustive methylation".

Mechanism -

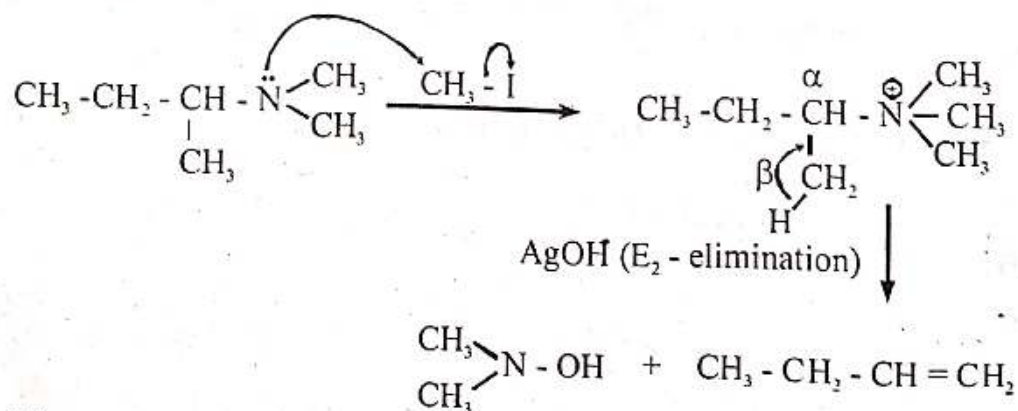


(II)

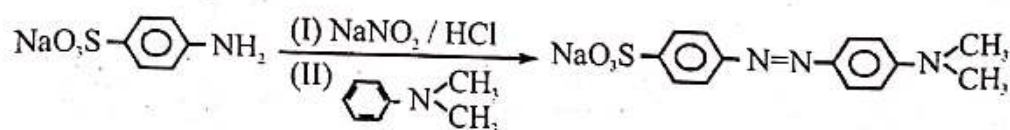


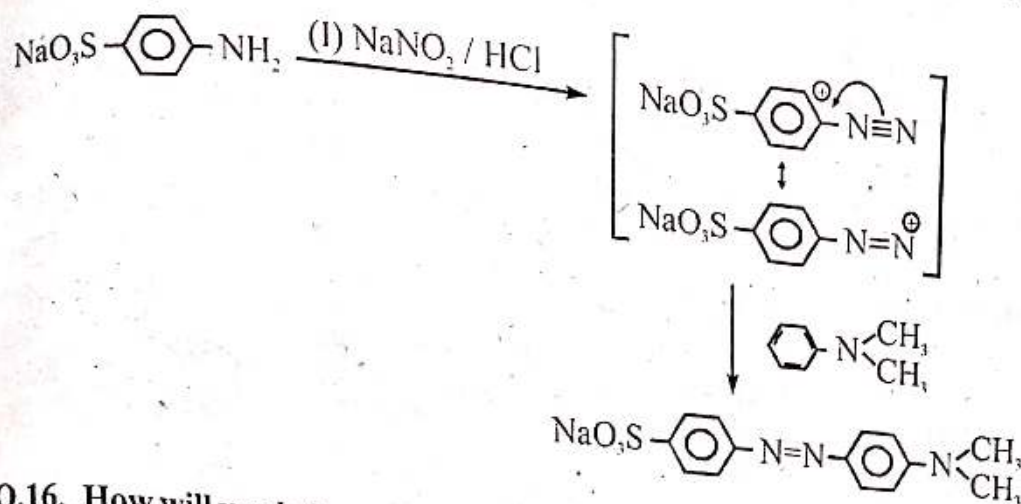
Hint - The above reaction is called "Haffmann exhaustive methylation".

Mechanism -



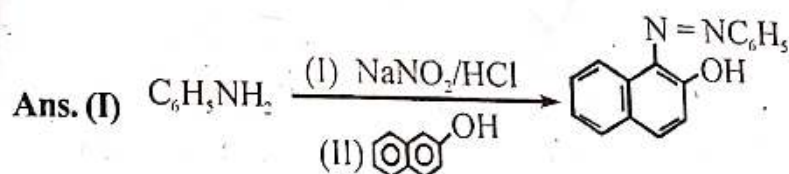
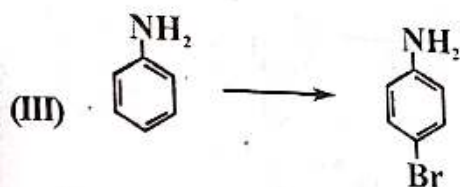
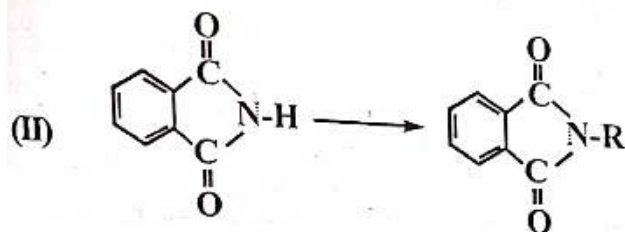
(II)

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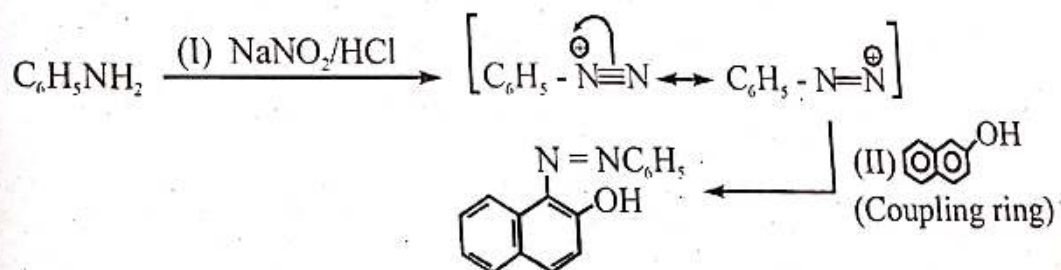


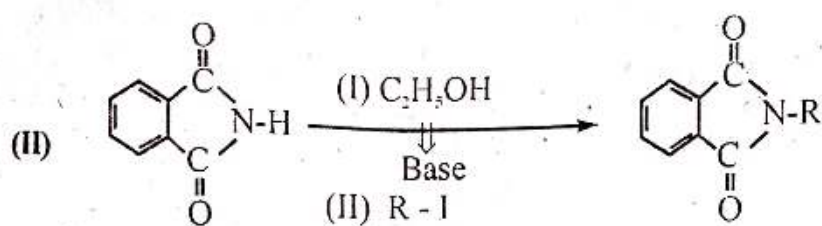
Q.16. How will you bring out following transformation.

(2019)

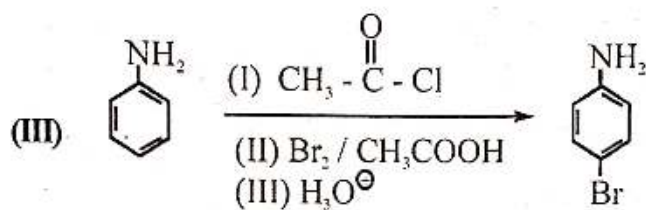
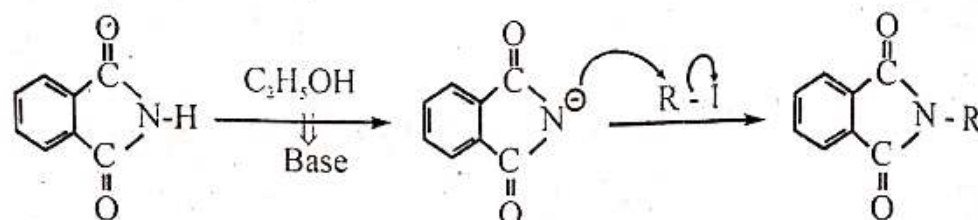


Mechanism -





Mechanism -



Mechanism -

