

UNIT II Reaction Mechanisms

①

- 1) Explain, 1) Free radical mechanism in aliphatic compounds,
2) Condensation reactions.

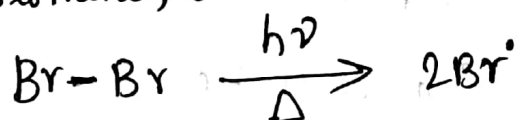
1) Free radical reaction

A free radical may be defined as an atom or group of atoms having a odd or unpaired electron.

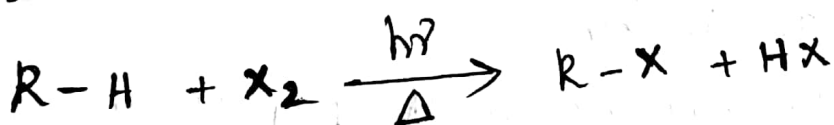
Free radicals are formed due to homolytic

Cleavage of covalent bond.

Example: Bromine, Chlorine.

Halogenation of alkanes:

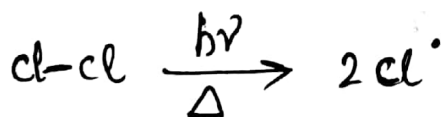
The alkanes react with halogens at high temperature in the presence of light to form haloalkane.



The order of reactivity of halogen is $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

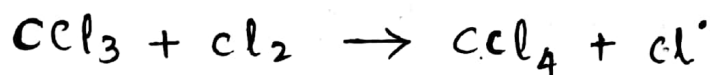
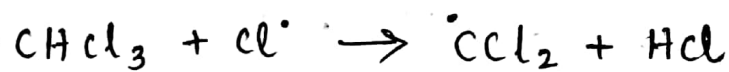
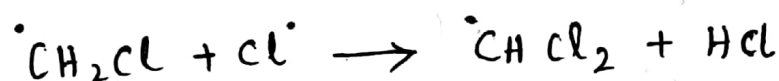
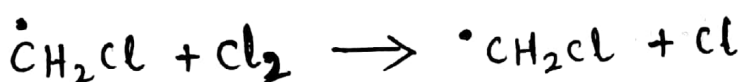
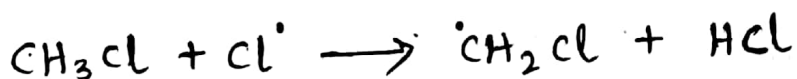
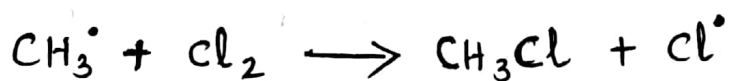
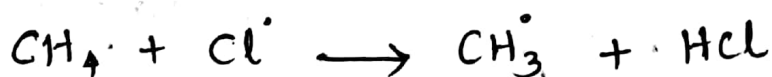
i) chain initiation:

Homolytic cleavage occurs in Cl_2 molecule to produce chlorine free radicals in presence of heat or light.



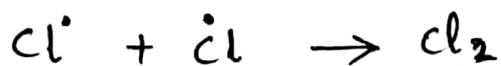
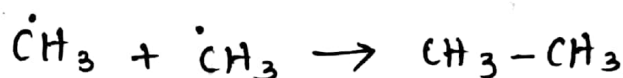
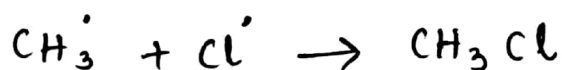
ii) Chain propagation :

It involves producing reactive free radicals by chain propagation until the free radicals are terminated.



iii) Chain Termination

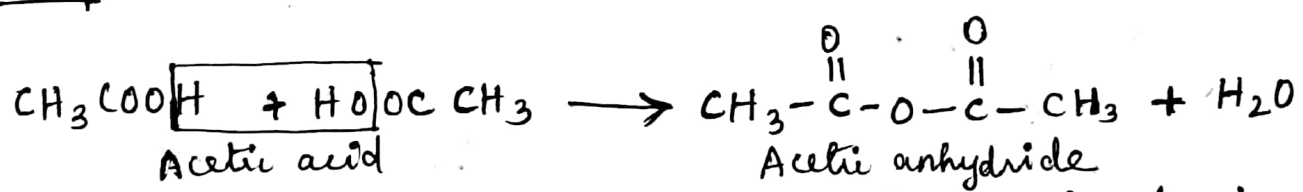
The radicals in the propagation step may be consumed by other radicals resulting in the termination of chain reaction.



2) Condensation reactions

⇒ A condensation reaction is a chemical reaction between two compounds. A condensation reaction is also known as a dehydration reaction. This type of reaction forms an addition product and water in the presence of a catalyst under acidic or basic conditions. The opposite of a condensation reaction is a hydrolysis reaction.

Example:



⇒ Condensation reactions are also involved in the production of many polymers. In organism, biosynthesis reactions form peptide bonds between amino acids and are involved in fatty acid formation.

⇒ The named condensation reactions include aldol condensation, Claisen condensation, Dieckmann Condensation, and Knoevenagel condensation reactions.

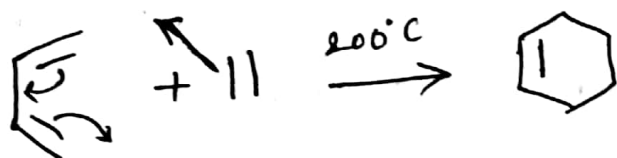
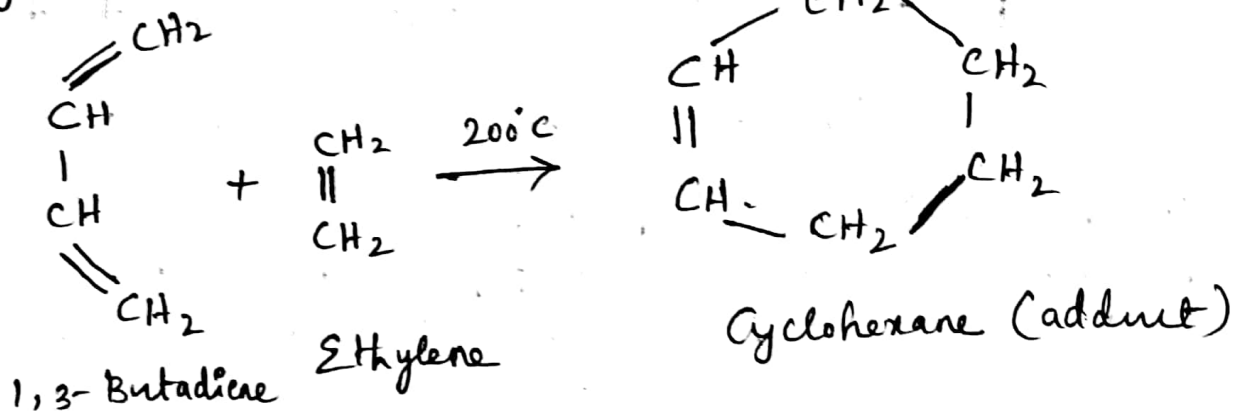
⇒ α-Hydrogen are required for this type of reaction to take place.

⇒ In general Aldol condensation and Claisen Condensations are the most important condensation reactions.

- ② Explain, 1) Cyclo addition reactions with suitable examples.
2) Nucleophilic substitution reactions.

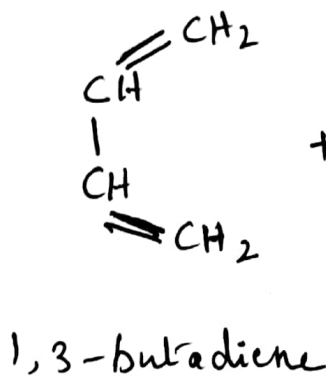
Cyclo addition reactions:

The reactions of conjugated dienes with alkenes to form a 6-membered cyclic adduct. is known as Diels-Alder reaction. It is a $[4+2]$ cyclo addition involving reaction of diene ($4\pi e^-$ s) with $2\pi e^-$ s containing alkene to form a cyclic product.

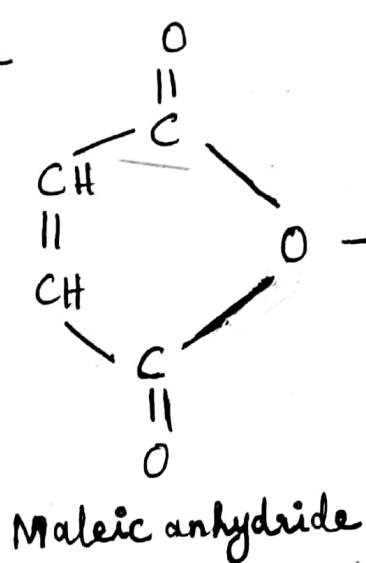


Electron attracting groups attached to alkene such as $-\text{CN}$, $-\text{CHO}$, $-\text{COR}$, $-\text{COOH}$, and $-\text{COOR}$ facilitate the reaction.

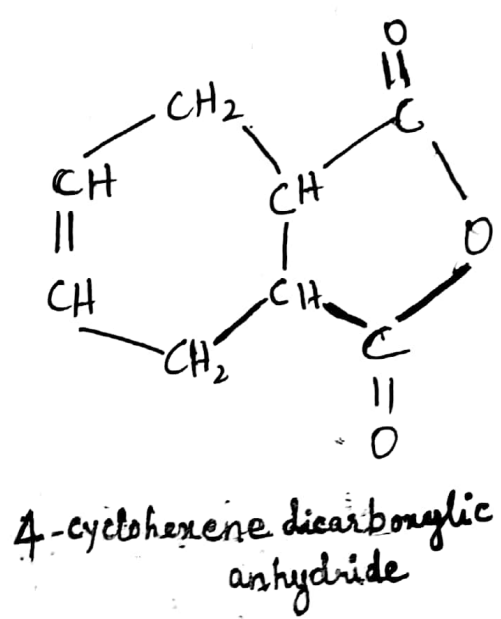
Example: Butadiene



+



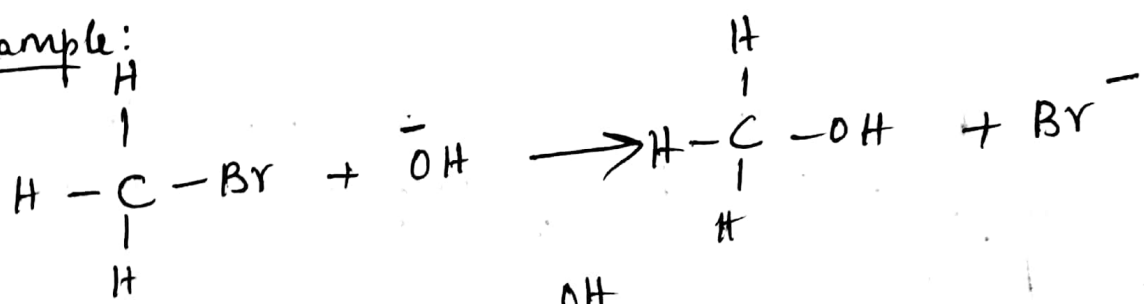
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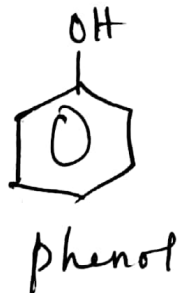
Nucleophilic substitution:

A type of chemical reaction in which one or more group of a compound is replaced by the attack of another group or atom (nucleophile) is called nucleophilic substitution reaction.

Example:



$\xrightarrow[360^\circ\text{C}]{\text{NaOH}}$



Chlorobenzene.

Reaction Mechanism

There are two types of mechanism

They are,

① S_N1 reaction

② S_N2 reaction

Where,

S \Rightarrow Represents Chemical substitution

N \Rightarrow Represents nucleophilic,

1, 2 \Rightarrow Represents the kinetic order of a reaction.

S_N1 Reaction:

\Rightarrow The S_N1 reaction is a nucleophilic substitution reaction where the rate determining step is unimolecular. S_N1 stands for substitution nucleophilic unimolecular and also dissociative substitution.

\Rightarrow S_N1 reaction mechanism has three steps.
For example taking the hydrolysis of tertiary butyl bromide.

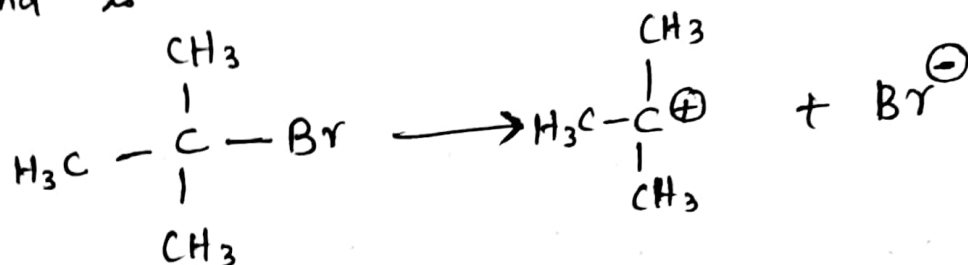
Step 1

\Rightarrow The carbon-bromine bond is a polar covalent bond. The cleavage of this bond allows the removal of the leaving group (Bromide ion).

\Rightarrow When the bromide ion leaves the tertiary butyl bromide, a carbocation intermediate

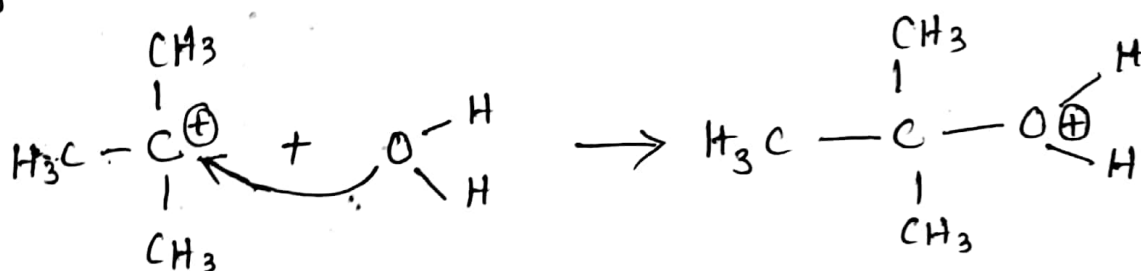
is formed.

⇒ The breaking of the carbon-bromine bond is endothermic.



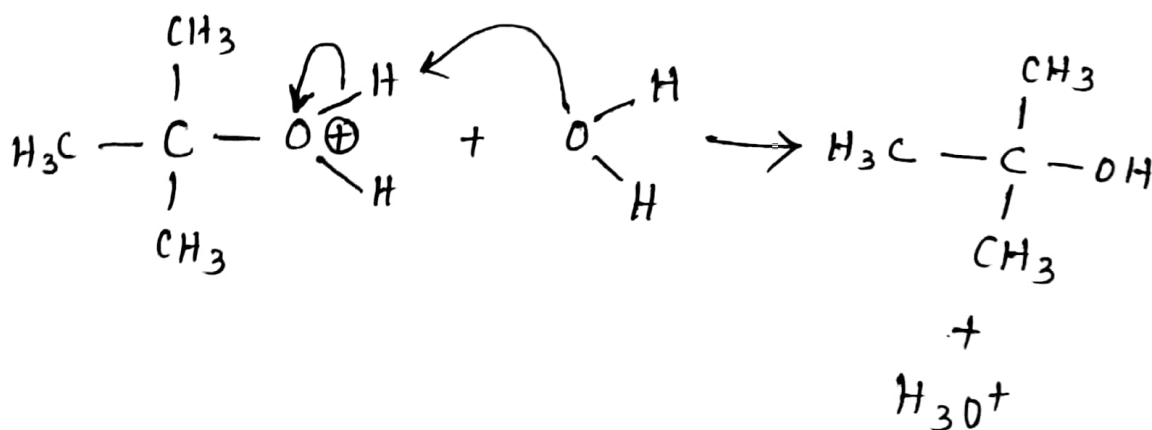
Step 2

The carbocation is attacked by the nucleophile form oxonium ion intermediate.



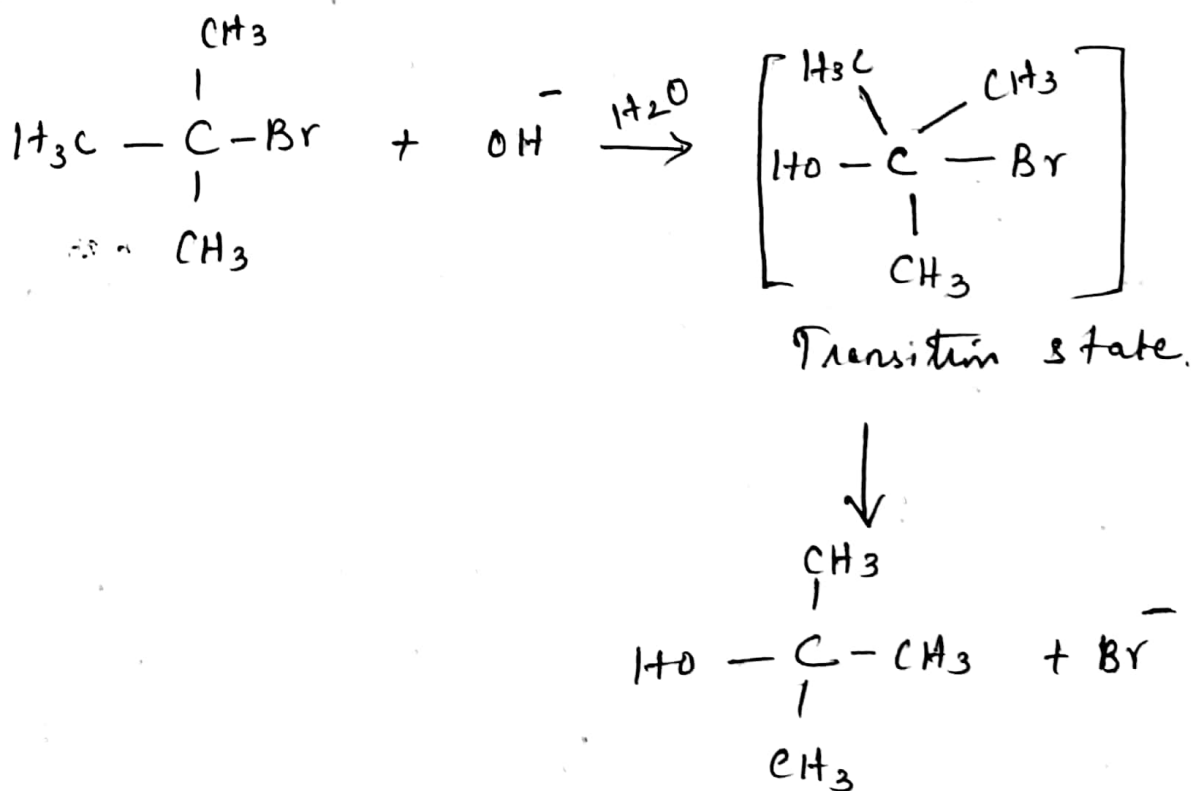
Step 3 : deprotonation

The water solvent now acts as a base and deprotonates the oxonium ion to yield the required alcohol along with a hydronium ion as the product.



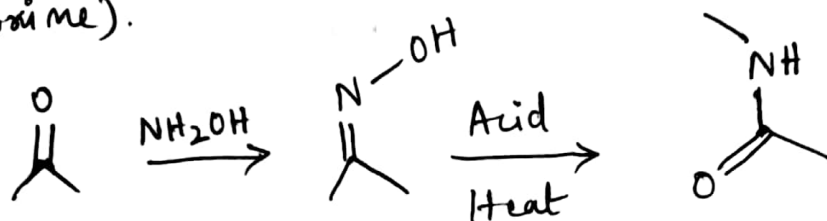
SN₂ Reaction:

Two reacting species are involved in the rate determining step of the reaction. The term SN₂ stands for substitution nucleophilic bimolecular. This type of reaction is also referred to as bimolecular nucleophilic substitution, associative substitution, and interchange mechanism.



③ Explain the mechanism of Beckmann rearrangement reaction with example.

⇒ The Beckmann rearrangement is a chemical reaction of the oximes that can bring about either nitriles or amides. These oximes that obtained from the ketones develop into amides. Oximes got from aldehydes shape into nitriles (Aldoxime).



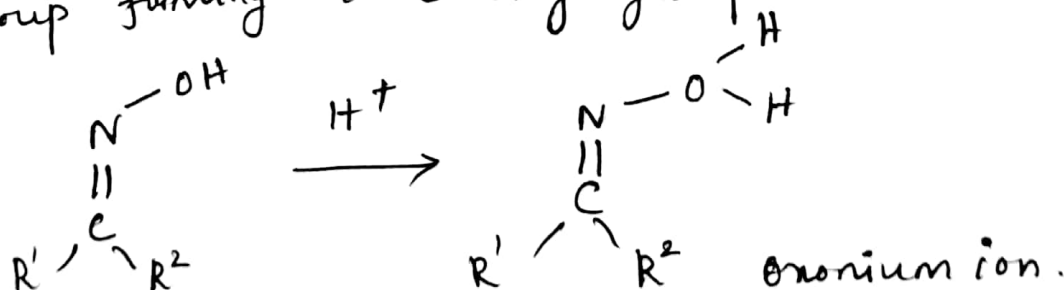
⇒ Acids are generally used as a catalyst for the conversion of keto oximes to N-substituted amides in Beckmann rearrangement.

Mechanism:

It is an intramolecular rearrangement (1,2 shift) reaction.

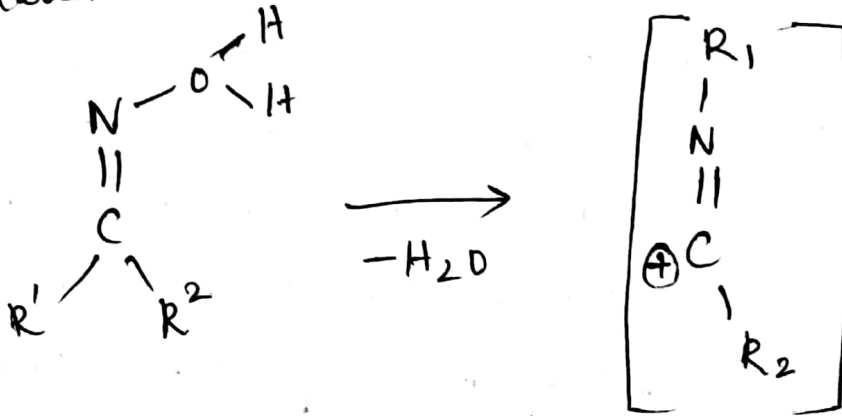
Step 1:

The reaction begins by protonation of alcohol group forming a leaving group.



Step 2

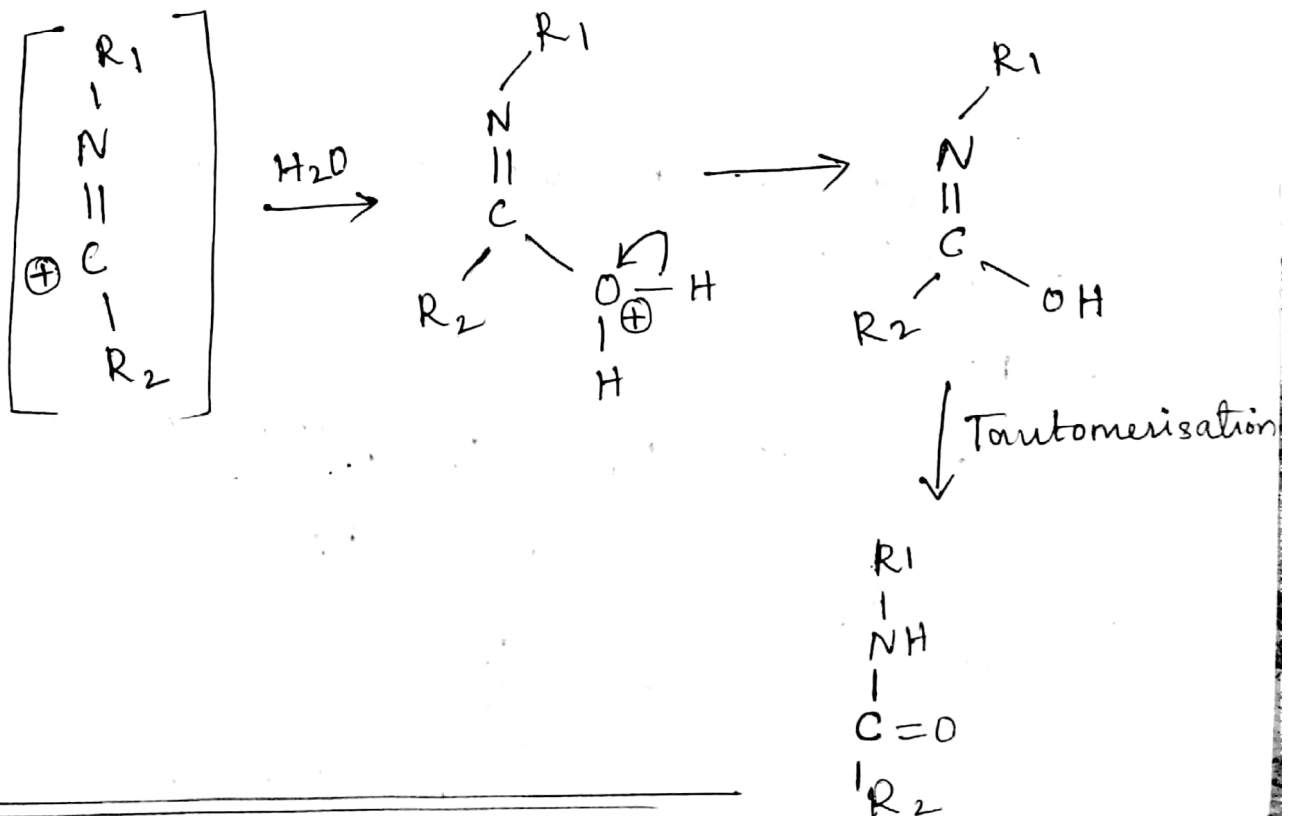
The R_1 group trans to leaving group migration to the nitrogen (1,2-Shift)



Carbocation

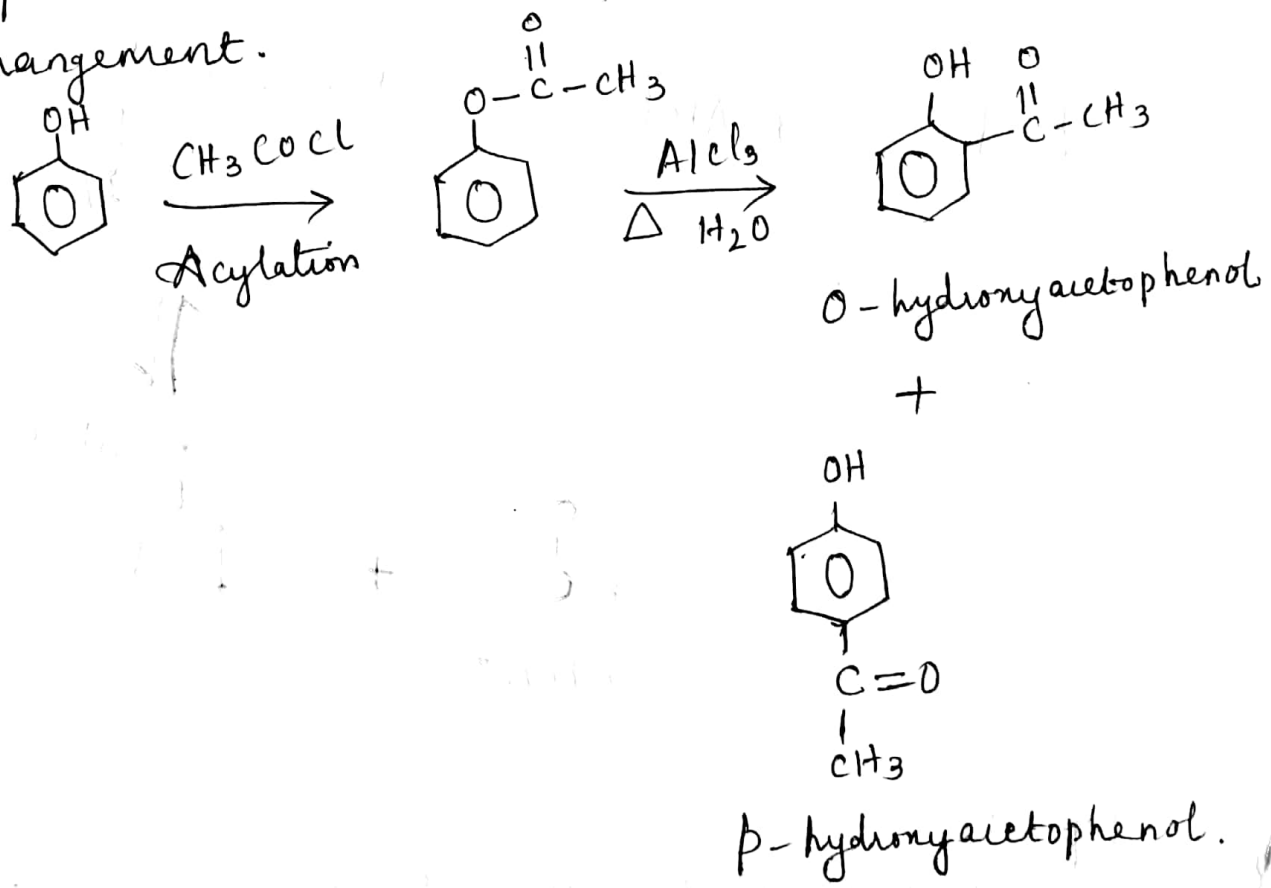
Step 3

The water molecule then attacks the carbocation and after deprotonation and tautomerisation results in the final amide product.



④ Fries rearrangement reaction mechanism
with example:

phenols on treatment with an acid chloride or acid anhydride form phenolic esters. These phenolic esters on treating with catalytic $AlCl_3$, followed by hydrolysis result in a rearrangement to form ortho and para acyl group. The reaction is known as Fries rearrangement.



The reaction forms same products in the presence of light using ethanol as solvent (without catalyst) is known as photofries rearrangement reaction.

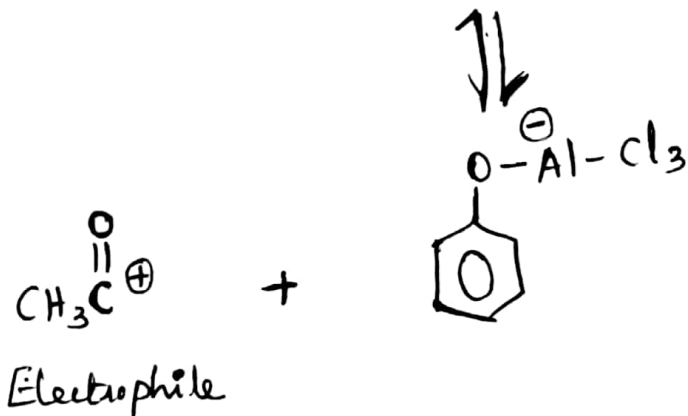
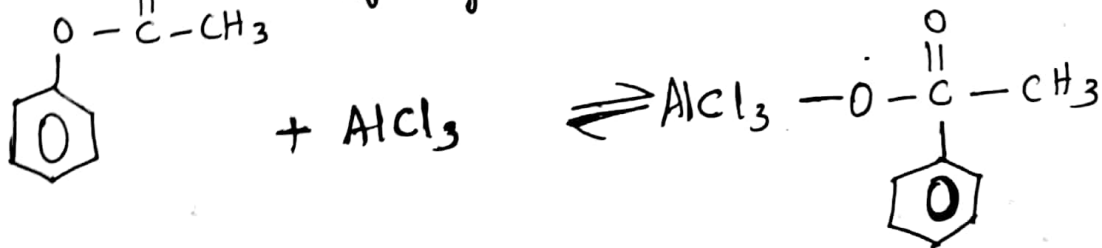
Reaction mechanism

The Fries rearrangement is an electrophilic substitution reaction that may proceed through an inter or intra molecular rearrangement.

Intramolecular rearrangement.

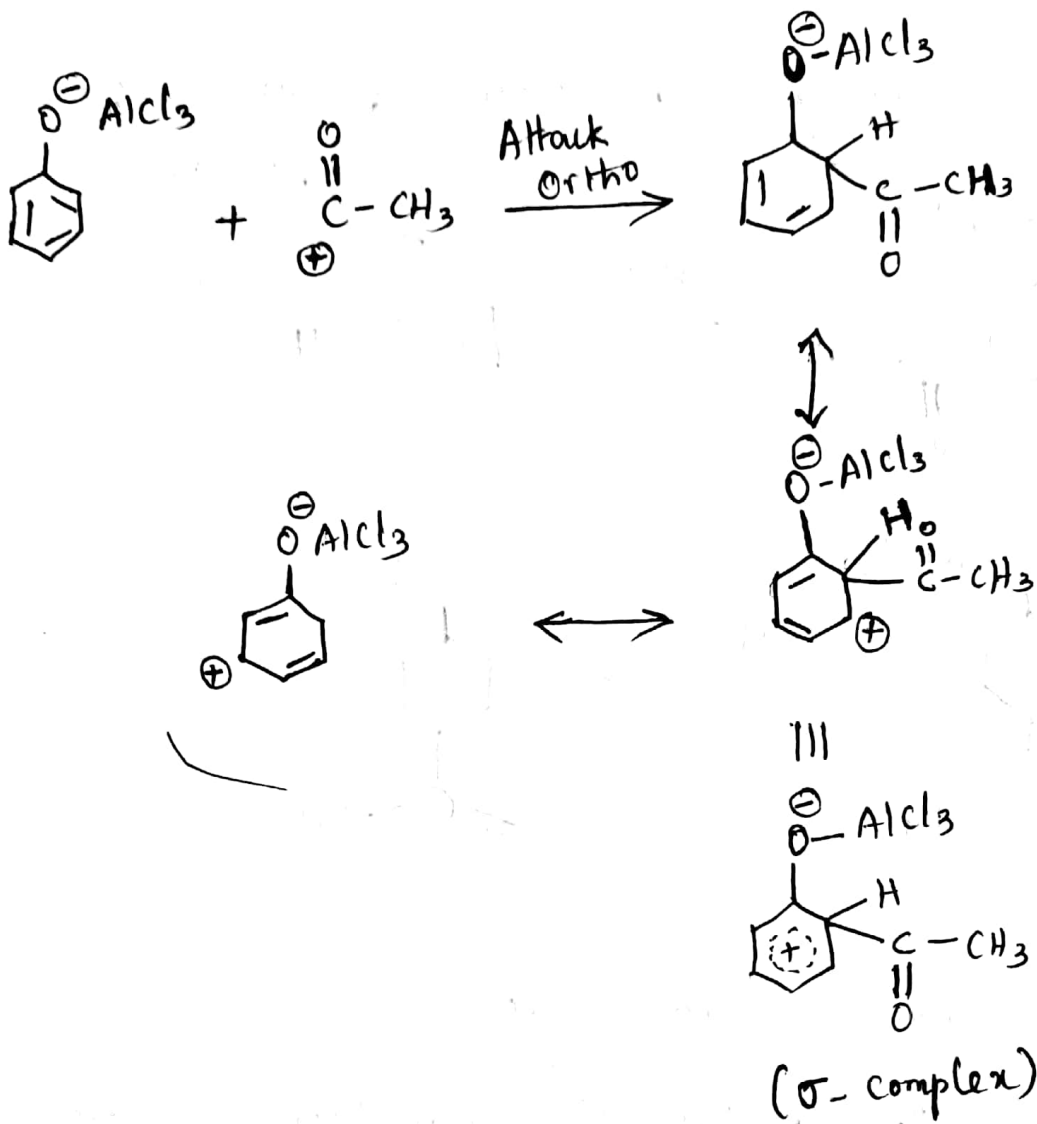
Step 1:

Complex formation with Lewis acid (AlCl_3). Formation of acyl cation (Electrophile)

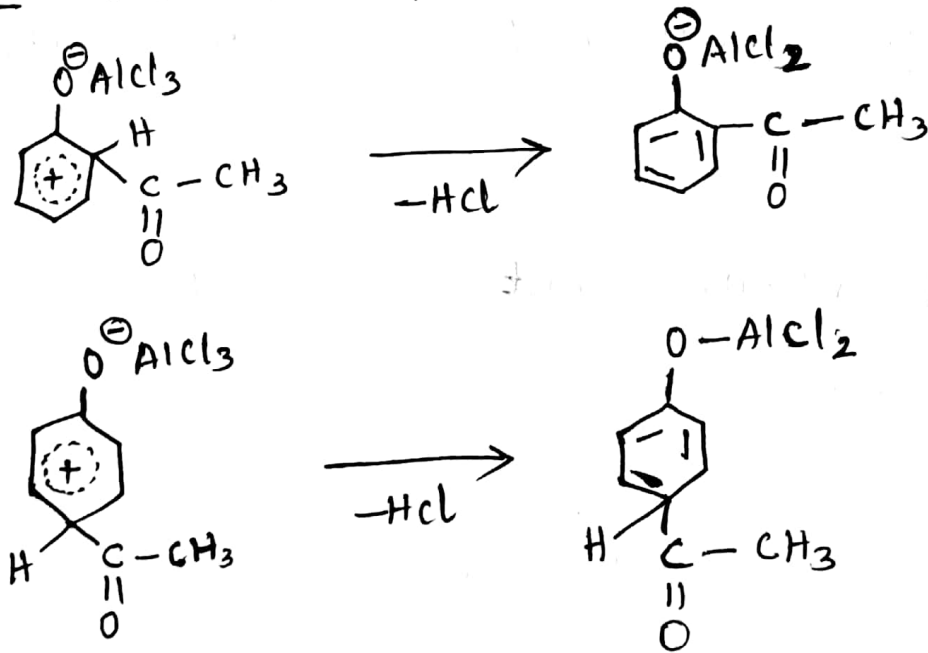


Step 2:

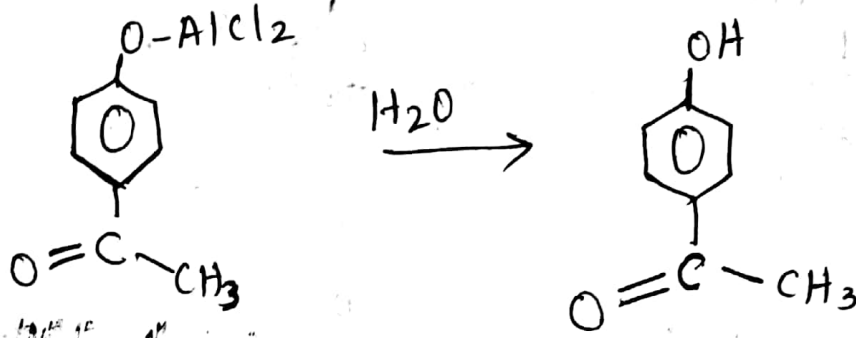
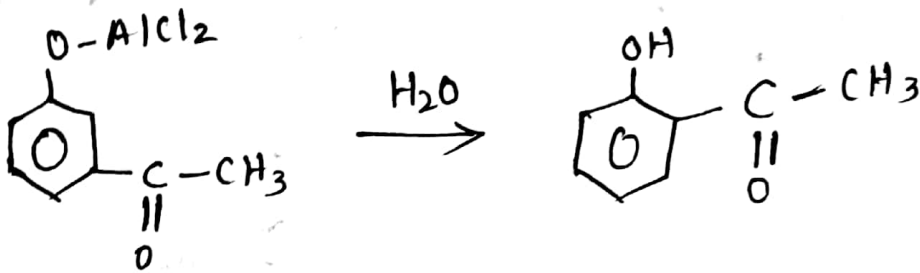
Attack of electrophile at ortho and para position of the ring and resonance stabilisation as arenium ion.



Step 3: Removal of proton from σ -Complex.



Step 4 : Hydrolysis [Formation of ortho & para acyl phenol]



Intramolecular Rearrangement :

It explains the formation of ortho isomer.

Step 1 :

Complex formation (phenolic ester) with Lewis acid.

Step 2 :

Intramolecular shift of a ~~substituted~~ acyl at ortho position.

Step 3 :

Hydrolysis (formation of ortho acyl phenol).

- 5) Explain nucleophilic substitution reactions? S_N1 and S_N2 mechanism. {Refer Q.No. [9, II]}
-
- 6) Write the mechanism of free radical substitution reaction. {Refer Q.No. 8 I}
-
- 7) Explain, i) Mechanism of electrophilic substitution reactions, ii) Mechanism of electrophilic addition reactions.

i) Electrophilic substitution reaction:

Substitution reaction is a type of chemical reactions in which an atom, ion or group of atoms or ions in a molecule is replaced by another atom or group.

An example of the reaction is the Chlorine atom in the chloromethane molecule is displaced by the hydroxide ion forming methanol.



If the chlorine atom is displaced by other groups such as cyanide ions ($-CN$), the ethoxide ion ($C_2H_5O^-$), and hydrosulfide ion (HS^-), - the CH_3Cl (chloromethane) is transformed respectively to acetonitrile (CH_3CN), methylethyl ether ($CH_3OC_2H_5$), and methanethiol (CH_3SH). Thus an organic compounds

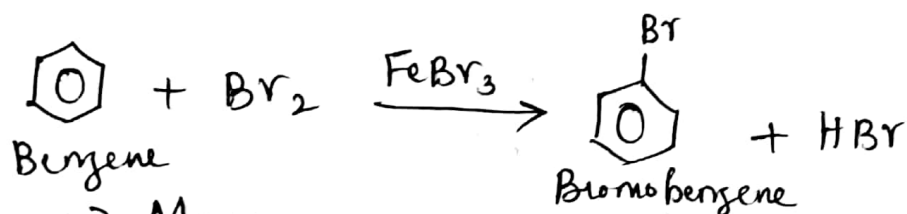
by substitution reactions with suitable reagents.

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

⇒ Some of the most important electrophilic aromatic substitutions are aromatic nitration, aromatic halogenation, aromatic sulfonation and alkylating Friedel-Crafts reaction.

⇒ Although aromatic compounds have multiple double bonds, these compounds do not undergo addition reactions. Their lack of reactivity toward addition reaction is due to the great stability of the ring systems that result from complete π - e^- delocalization (Resonance).

For example, benzene reacts with bromine to form bromobenzene.



⇒ Many functional group can be added to aromatic compounds via electrophilic aromatic substitution reactions.

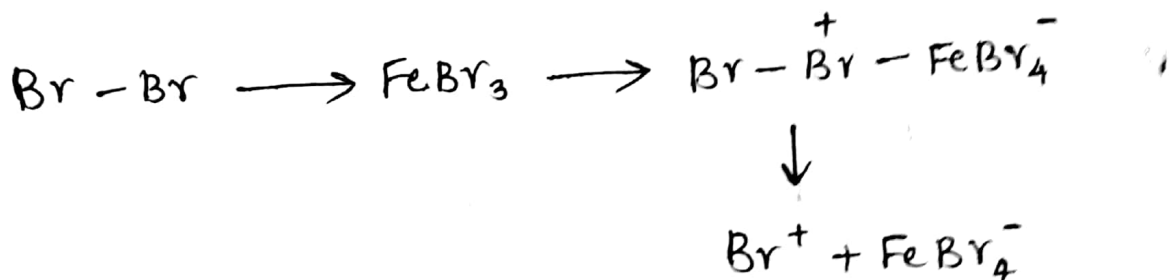
Reaction mechanism

This mechanism consists of five steps.

Step 1

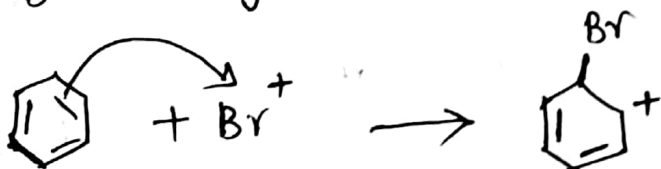
An electrophile - an e^- seeking reagent is generated.

For bromination of benzene reaction, the electrophile Br^+ ion is generated by the reaction of the bromine molecule with ferric bromide.



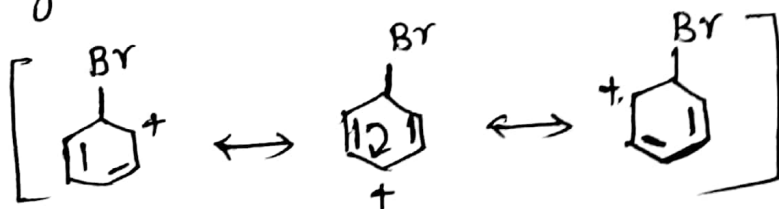
Step 2

The electrophile attacks the π - e^- system of benzene ring to form a non-aromatic carbocation.



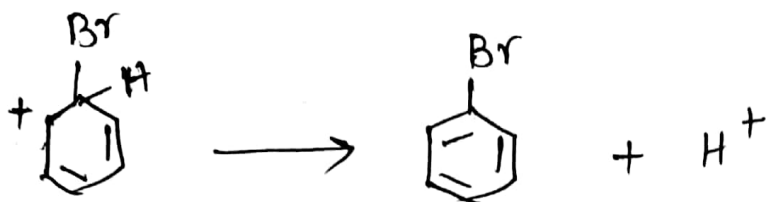
Step 3

The +ve charge on the carbocation is delocalized throughout the molecule.



Step 4

The aromaticity is restored by the loss of a proton.



Step 5:

Finally, the proton reacts with FeBr_4^- to regenerate the FeBr_3 catalyst and form the product HBr .



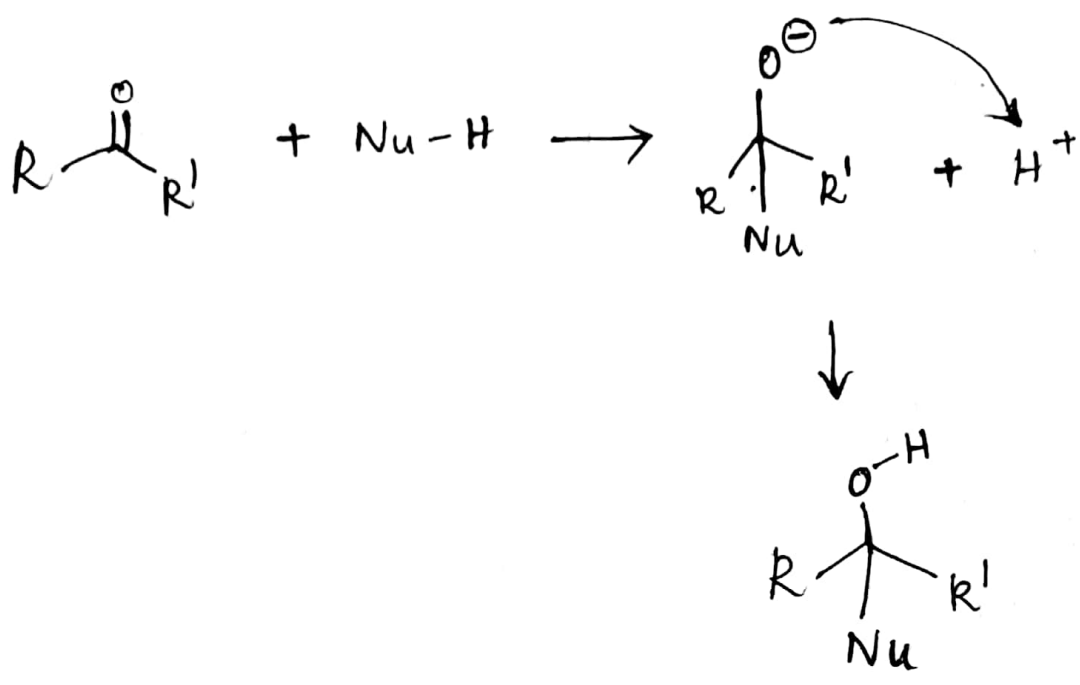
ii) Electrophilic addition reaction mechanism

⇒ A nucleophilic addition reaction is a chemical addition reaction in which a nucleophile forms a σ -bond with an e^- deficient species. These reactions are considered as very important in organic chemistry. Generally, nucleophilic addition reaction of carbonyl compounds have three steps.

1) The electrophilic carbonyl carbon forms a σ -bond with the electrophile.

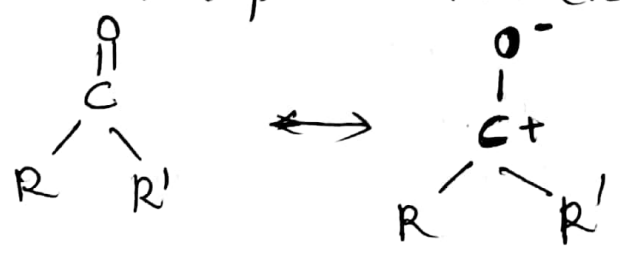
2) The carbon-oxygen π -bond is now broken forming an alkoxide intermediate.

3) The subsequent protonation of the alkoxide yields alcohol derivative.



⇒ The carbonyl group has a coplanar structure and its carbon is sp^2 hybridised. However, the attack of the nucleophile on the $C=O$ group results in the breakage of π -bond. The carbonyl carbon is now sp^3 hybridised and forms σ -bond with the nucleophile. The resulting alkoxide intermediate has a tetrahedral geometry.

⇒ In carbonyl compounds, the carbon-oxygen bond is polar owing to the relatively higher electronegativity of the oxygen atom, the e^- density is higher near the oxygen atom. This leads to the generation of a partial negative charge on the oxygen atom and a partial +ve charge on carbon atom.

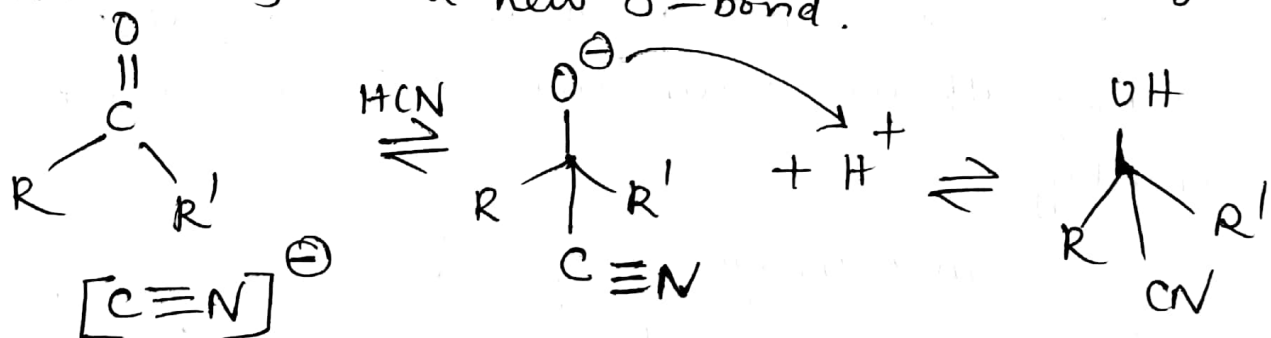


⇒ Aldehydes are relatively more reactive towards nucleophilic addition reactions when compared to ketones. This is because of the secondary carbocations formed by ketones are stabilised by the adjacent R-groups.

Examples ①

Reactions with hydrogen cyanide.

⇒ The nucleophilic addition reaction between hydrogen cyanide (HCN) and carbonyl compounds (aldehydes, ketones) results in the formation of cyanohydrins. Base catalysts are often used to increase the rate of the reaction. The cyanide anion (CN⁻) acts as a powerful nucleophile and attacks the carbonyl carbon to form a new σ-bond.

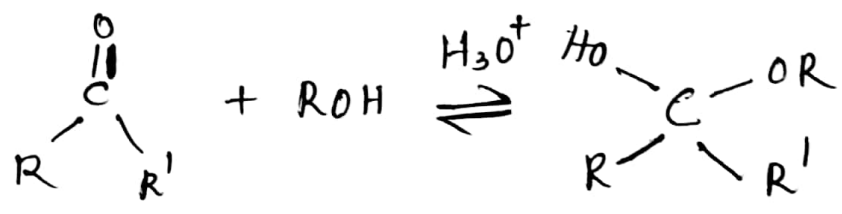


Examples ②

Nucleophilic additions with monohydric alcohols

⇒ Aldehydes and ketones undergo nucleophilic addition reactions with monohydric alcohols to yield hemiacetals. Since alcohols are weak nucleophiles, the reaction requires an acid catalyst.

for the activation of the carbonyl group towards nucleophilic attack.



⇒ other examples are nucleophilic addition with grignard reagents and primary amines.
