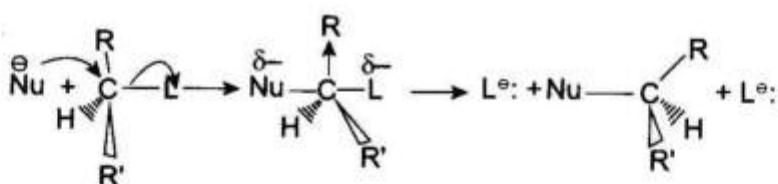


Reactant System	Transition State Produced	Stabilization of Transition State w.r.t Reactant in Polar Protic Solvent.	Effect on Reaction State
3. $R - L^{\oplus} + Nu^{\ominus}$	$\overset{\delta+}{Nu} \cdots \overset{\delta+}{R} \cdots \overset{\delta+}{L}$	Less	Decreases
4. $R - L^{\oplus} + Nu^{\ominus}$	$Nu^{\delta-} \cdots R \cdots L^{\delta+}$	Much less	Large decrease

On the basis of the above facts, we can conclude that for  $S_N2$  reaction polar protic solvent is more suitable except, where substrate molecule is positively charged for  $S_N2$  reaction, polar protic solvent is not suitable. It is best to proceed in a polar aprotic solvent except where both substrate and nucleophile are neutral.

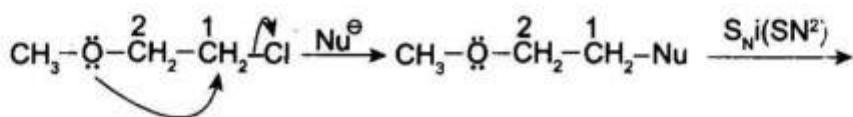
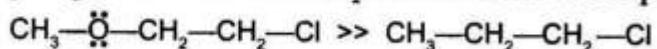
#### Mechanism involved in nucleophilic substitution reaction :

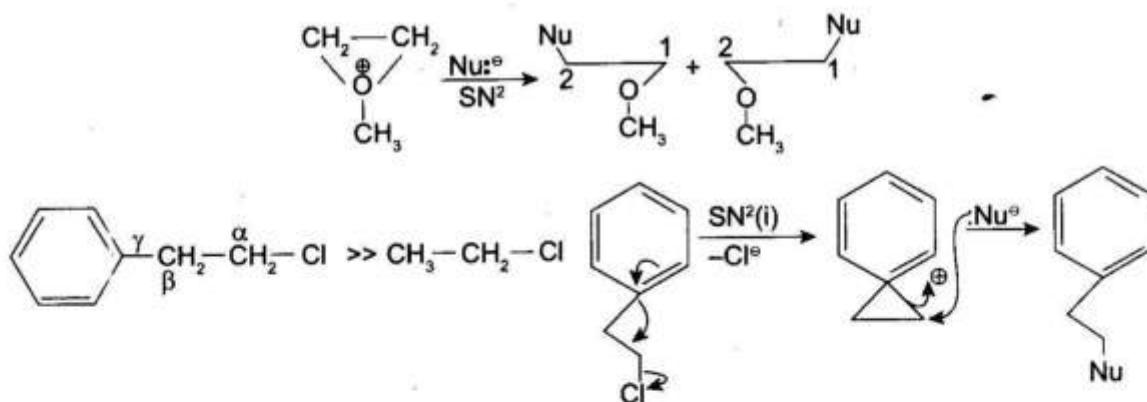
**$S_N2$  reaction:** When a substrate molecule having a good nulceofuge is treated with a nucleophile, Where attack of nucleophile occurs from opposite side to that of leaving group, then there occurs the formation of a pentavalent transition which gets converted into inverted product if leaving group is directly attached with chiral centre in substrate.



#### 24.5 CHARACTERISTICS OF $S_N2$ REACTION

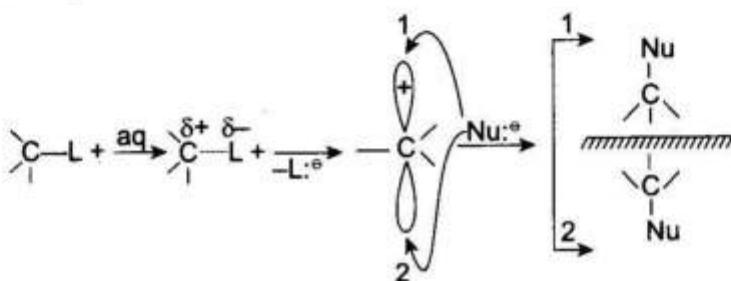
- Since reaction completes in a single step, therefore rate of reaction depends upon the concentration of substrate and nucleophile due to which reactions follows second-order kinetics  $r = K [R - L] [\text{base}]$
- Presence of good nucleofuse increases the reactivity of substrate towards  $S_N2$  reaction.
- If nucleophile is strong and its concentration is high, then  $S_N2$  reaction is favourable.
- $S_N2$  reaction best proceeds in a polar aprotic solvent like acetone, DMSO, DMF, etc.
- If leaving group is directly attached with a chiral carbon, then during the reaction Walden inversion takes place.
- Primary substrate where  $\beta$ -carbon is primary or secondary and secondary substrate where  $\beta$ -carbon is primary always follows  $S_N2$  path but secondary substrate where  $\beta$ -carbon is secondary follows  $S_N1$  or  $S_N2$  path depending upon other reaction condition.
- Substrate molecule having hetero atom containing lone pair of electron at  $\beta$ -carbon or containing unsaturated  $\gamma$ -carbon are highly reactive towards  $S_N2$  reaction because of Anchimeric participation/ neighbouring group participation. In anchimeric participation, product is produced through retention in configuration because in such cases, two  $S_N2$  attack occur successively one due to presence of internal nucleophile and other due to presence of external nucleophile.





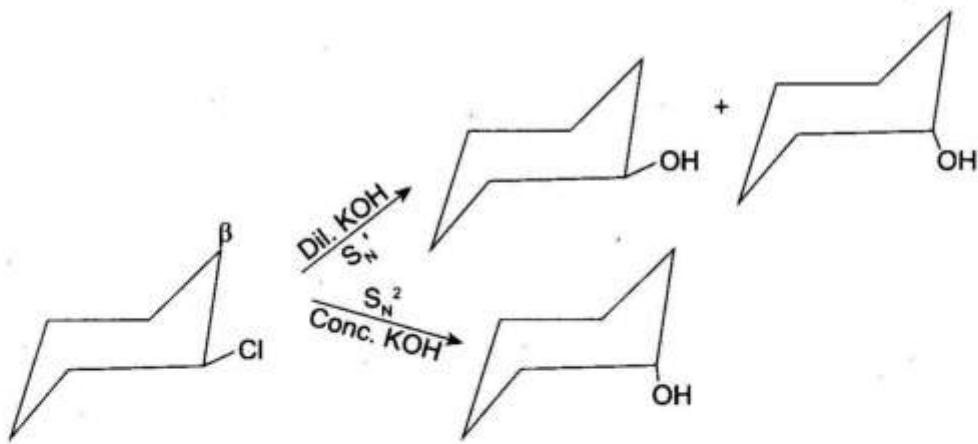
### Uni molecular Nucleophilic substitution: $\text{S}_{\text{N}}1$ Reaction

When a substrate molecule having a good nucleofuge is treated with a nucleophile in polar protic solvent, then the formation of two products occur equally, one through retention in configuration while other through inversion in configuration. If product produced possess a chiral centre, therefore during the reaction racemization takes place



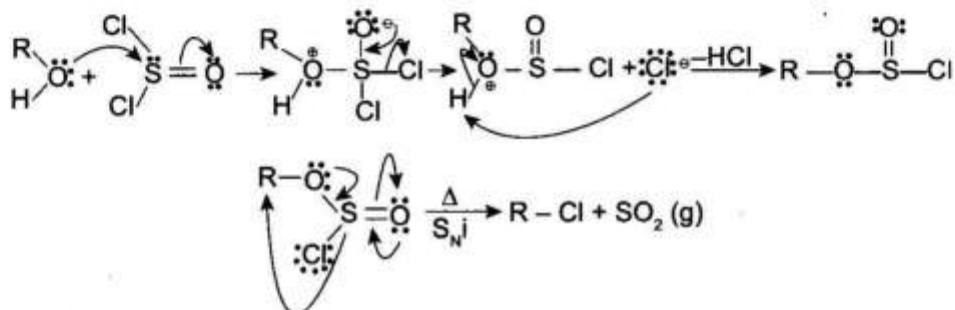
#### 24.5.1 Characteristics of $\text{S}_{\text{N}}1$ Reaction

1. Since slowest step of the reaction involves the substrate only therefore reaction follows first-order kinetics  
 $R = k [R - L]$
2. Presence of good nucleofuge increases the reactivity of substrate towards  $\text{S}_{\text{N}}1$  reaction.
3. If nucleophile is weak or its concentration is low, then  $\text{S}_{\text{N}}1$  reaction is favourable.
4. Reaction best proceeds in polar protic solvent because it favours the formation of transition state as well as stabilizes the carbocation intermediate produced.
5. Primary and secondary substrates whose  $\beta$ -carbon is tertiary or quaternary always follow  $\text{S}_{\text{N}}1$  mechanism.
6. Tertiary substrate always follows  $\text{S}_{\text{N}}1$  mechanism.
7. Since reaction proceeds through the formation of carbocation intermediate therefore rearrangement is possible during the reaction.
8. Vinyl and aryl substrates are inert towards both  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$  mechanisms.
9. If nucleofuge is present on bridgehead carbon of bridged bicyclic compound, then such substrates are inert towards both  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$ .
10. In majority of  $\text{SN}^1$  reaction 80–95 per cent racemic mixture and 5–20 per cent inverted product is obtained.
11. If we consider a mixture of polar protic and polar aprotic solvents then as the amount of polar aprotic solvent in the mixture increases yield of inverted product also increases and thus yield of racemic mixture decreases.



### 24.5.2 Internal Nucleophilic Substitution (S<sub>N</sub>i)

In some nucleophilic substitution reactions, there occurs the formation of retention product though there is no possibility of anchimeric participation. Such reactions are example of internal nucleophilic substitution. In S<sub>N</sub>i a part of leaving group attacks the carbon of substrate by detaching itself from the leaving group.

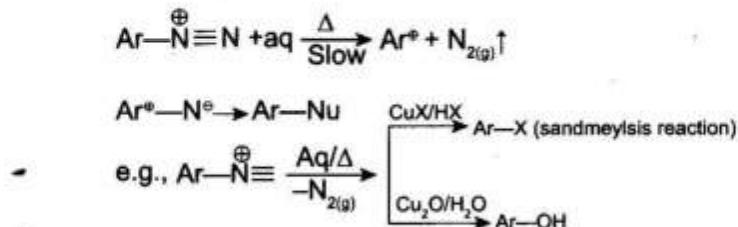


In Darzen's method, SOCl<sub>2</sub> can be replaced by COCl<sub>2</sub>. However, in case of COCl<sub>2</sub> yield of product produced is poor S<sub>N</sub>1, S<sub>N</sub>2' and S<sub>N</sub>i'

If substrate used is allylic and reaction conditions are corresponding to S<sub>N</sub>1, S<sub>N</sub>2 and S<sub>N</sub>i respectively, then formation of product occurs through allylic shift. During the formation of this product, S<sub>N</sub>1', S<sub>N</sub>2', S<sub>N</sub>i' mechanisms are observed.

### Unimolecular aromatic nucleophilic substitution (ArS<sub>N</sub>')

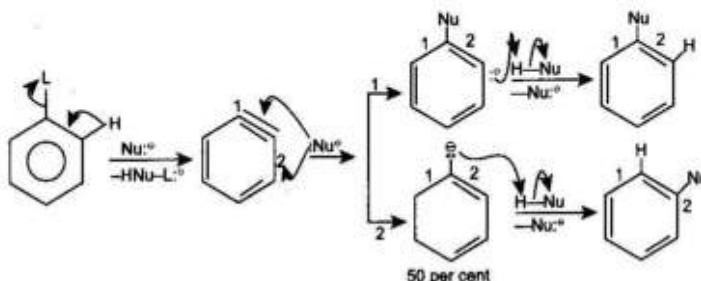
1. In this mechanism substrate molecule removes nucleofuse to produce aryl carbonation in presence of polar protic solvent which further reacts with a nucleophile to produce substitution product.



### Bimolecular aromatic nucleophilic substitution (ArS<sub>N</sub>2)

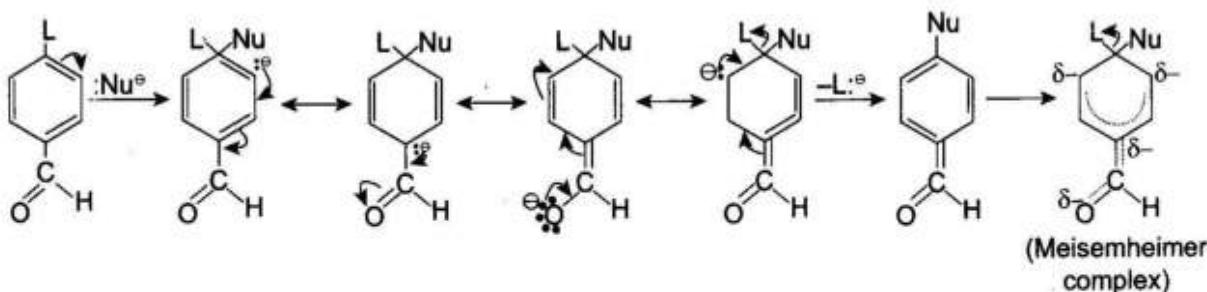
Following two mechanism are observed in this case:

- 1. Benzyne intermediate formation mechanism:** This mechanism is observed in those cases where
  - Substrate molecule has atleast one ortho hydrogen w.r.t. nucleofuse
  - There is no EWG at ortho or para position w.r.t. nucleofuge
  - Reaction requires vigorous conditions, i.e., (high T, high P, strongly basic medium etc.)



## 2. Meisenheimer complex formation mechanism

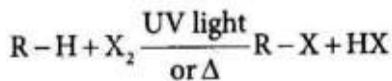
This mechanism is observed in those cases where atleast one strong EWG is present at ortho or para position w.r.t. nucleofuge. As the number of strong EWG group at ortho or para position increases, the reactivity of substrate also increases.



## 3. Free radical substitution:

Alkane mainly participate in this type of reaction.

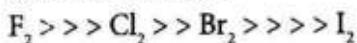
**Halogenations:** When alkane is treated with halogen in presence of UV light or on heating at 250–400°C, alkyl halide is obtained. During the reaction, fluorine participates violently by involving the cleavage of C–H as well as C–C bond. F is so reactive towards this reaction that even fluorination takes place in dark. However, iodine is almost inert towards this reaction. Direct iodination is possible only when if oxidizing agents like nitric acid, mercuric oxide,  $\text{HIO}_3$ , etc. are used.



The most complicated characteristic of free radical substitution is multiple substitution. This is due to the fact that all H present inside the alkane are potentially capable to participate in free radical substitution.

Extent of multiple substitution depends upon

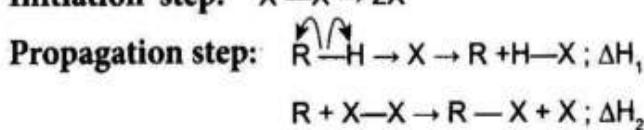
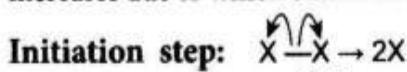
- Reactivity of halogen involved:** As the reactivity of halogen increases, extent of multiple substitution also increases.



Therefore, chances of multiple substitution is maximum in F and minimum in case of I. Only alkyl chloride and alkyl bromide can be effectively produced by direct halogenation of alkane.

- Thermodynamics of propagation step:**

As the amount of heat evolved in propagation step increases (2), the reactivity of halogen also increases due to which extent of multiple substitution increases.



	$F_2$	$Cl_2$	$Br_2$	$I_2$
$\Delta H_1$	< 0	< 0	> 0	> 0
$\Delta H_2$	< 0	> 0	< 0	< 0
$\Delta H_{\text{net}}$	< 0	< 0	< 0	> 0

3. **Relative amount of reactant used:** By maintaining appropriate stoichiometry of the reaction, i.e., by taking alkane in excess and halogen in limiting amount, extent of multiple substitution can be controlled. But this cannot be removed completely.

- Determination of relative yield of product produced during free radical substitution.

Yield of a product produced depends upon nature of halogen involved and type of H being substituted.

- The nature of halogen involved affects the reactivity of hydrogen.

For chlorination, relative reactivity of hydrogen is  $3^\circ - H : 2^\circ - H : 1^\circ - H : 5 : 3.8 : 1$

**For bromination, relative reactivity of hydrogen is  $3^\circ - H : 2^\circ - H : 1^\circ - H : 1600 : 81 : 1$**

From the above data

It can be seen that towards the replacement of a particular H, bromine is more selective than

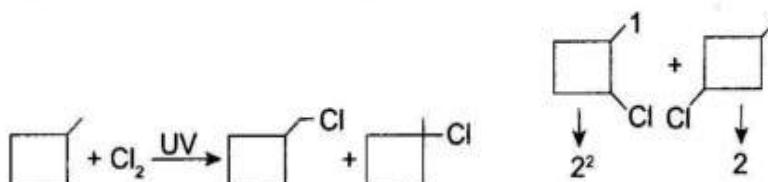
that of chlorine. Selectivity of a product  $\propto \frac{1}{\text{Reactivity of halogen involved}}$

- Reactivity of H being substituted depends upon the stability of free radical produced per cent

$$\text{yield of a product produced towards halogenation} = \frac{\text{Total reactivity of H being substituted}}{\text{Total reactivity of all hydrogen}} \times 100$$

Total reactivity of a particular hydrogen = (number of that type of H)  $\times$  relative reactivity of that hydrogen

- Total number of product produced during halogenation of alkane depends upon the total number of different type of H present as well as upon the stereochemistry of the product produced.



Total product through fractional

## 24.6 REARRANGEMENT REACTION

If during an organic reaction, a part of substrate changes its position within the molecule, then the reaction is termed as rearrangement reaction. That part of substrate which changes its position is called migrating group. The atom by which migrating group is attached before rearrangement is called migration origin and after migration, the atom by which it attaches is called migration terminus.

If more than one migratory group are present, then that group migrates first which possess highest migratory aptitude.

Among aryles, presence of EDG increases its migratory aptitude, which presence of EWG decreases its migratory aptitude.

Also more the hinderance lesser is its migratory aptitude. Classification of rearrangement reaction

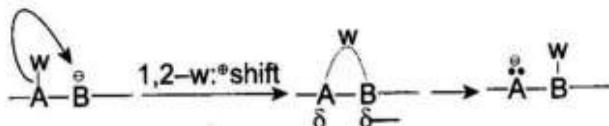
**1. Intermolecular rearrangement:** If during a rearrangement reaction migrating group is detached completely from the substrate molecule and then either it reattaches with the same molecule or attaches with some other molecule then reaction is termed as intermolecular rearrangement.

Such reactions are less common, e.g., tautomerism (except 1, 2-tautomerism); some aromatic rearrangement and Cannizzaro reaction.

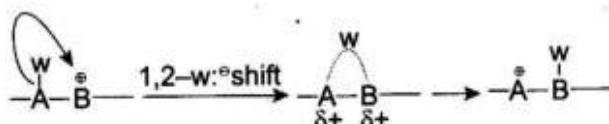
**2. Intramolecular rearrangement:** If during a rearrangement reaction migrating group is not completely detached from the substrate molecule, then reaction is termed as intra-molecular rearrangement. Such reactions are more common.

**Classification of intramolecular rearrangement reactions:** Depending upon the nature of migrating group, intermolecular rearrangement reaction are classified into three categories.

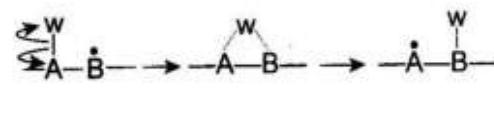
**1. Nucleophilic rearrangement:** If migration terminus of the substrate is electron deficient (due to +ve charge or incomplete octet or presence of d or f-orbitals), then nucleophilic rearrangement takes places and most rearrangement reactions belong to this category.



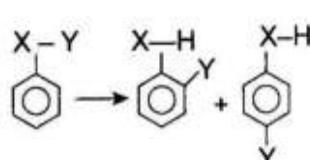
**2. Electrophilic rearrangement:** If migration terminus is electron rich, then this rearrangement takes place. It is rearrangement and is observed rarely.



**3. Free radical rearrangement:** If migration terminus contains unpaired electron, then free radical rearrangement takes place. This rearrangement is observed rarely.

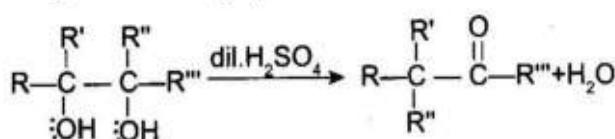


**4. Aromatic rearrangement:** In aromatic rearrangement, migration origin is either O or N, and migration of migrating group occurs from N or O side chain to ortho or para position of the ring. (y may be completely separated or partially separated from substrate and thus it is included in both inter and intra molecular rearrangement).

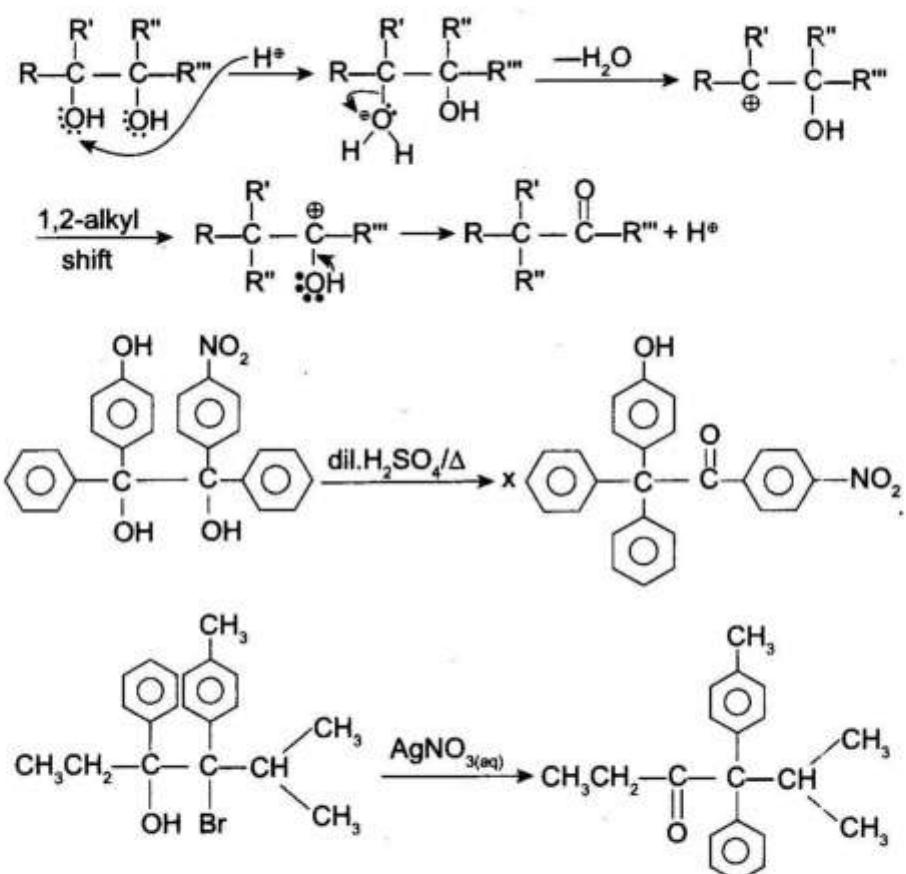


**5. Carbon to carbon rearrangement reaction:** If migration origin migration terminates and both are carbon atoms, then rearrangement reaction belongs to this category.

**6. Pinnacol Pinnacolone reaction:** When vic diol (also called pinna col) is treated with dilute  $H_2SO_4$ , it undergoes rearrangement to produce a ketone, also called pinnacolone. In this reaction, bromohydrin can also participate on treatment with aq.  $AgNO_3$  solution and hydroxylamine can participate on treatment with nitrous acid.

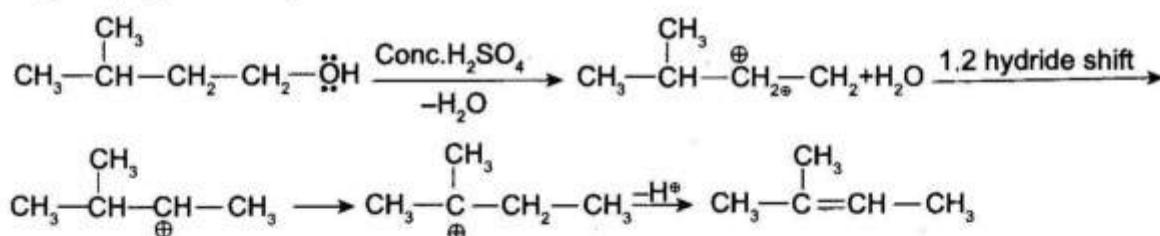


- During the reaction, protonation of that hydroxyl group occurs first corresponding to which directly formed carbocation is more stable.



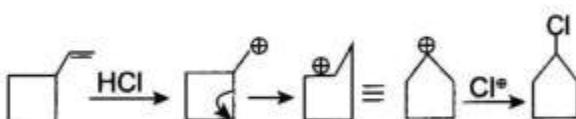
## 2. Wagner Meerwein rearrangement or Retro pinnacol rearrangement

This rearrangement is observed in those E<sub>1</sub> reactions where carbocation intermediate produced undergoes rearrangement to form more stable carbocation. In Wagner Meerwein rearrangement, migratory aptitude of hydride is maximum.



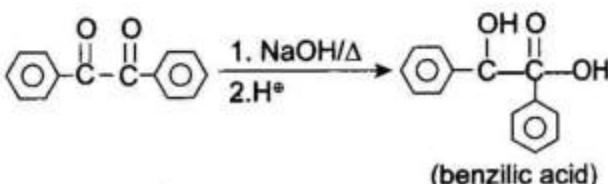
## 3. Demzanov rearrangement:

This rearrangement is observed in those reactions where carbocation, carbene or nitrene intermediate undergo ring expansion or ring contraction to produce final product.

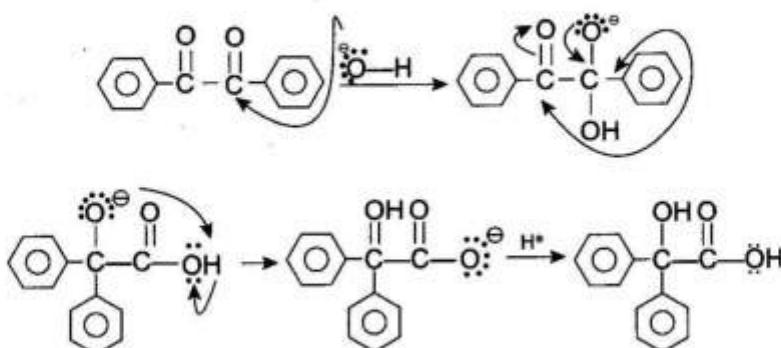


## 4. Allylic rearrangement:

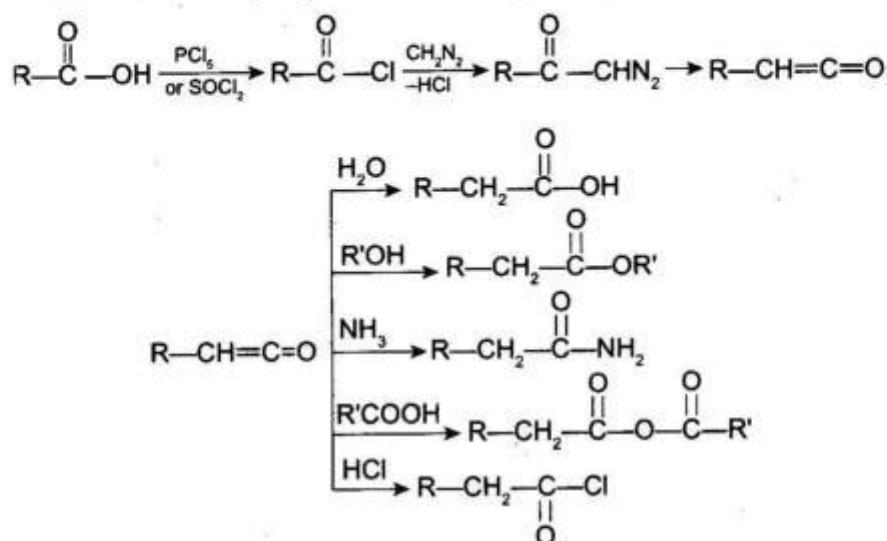
This rearrangement is observed in those reactions where formation of product occurs by allylic shift of substrate. It is observed in S<sub>N</sub>1', S<sub>N</sub>2' and in S<sub>N</sub>i' mechanism.



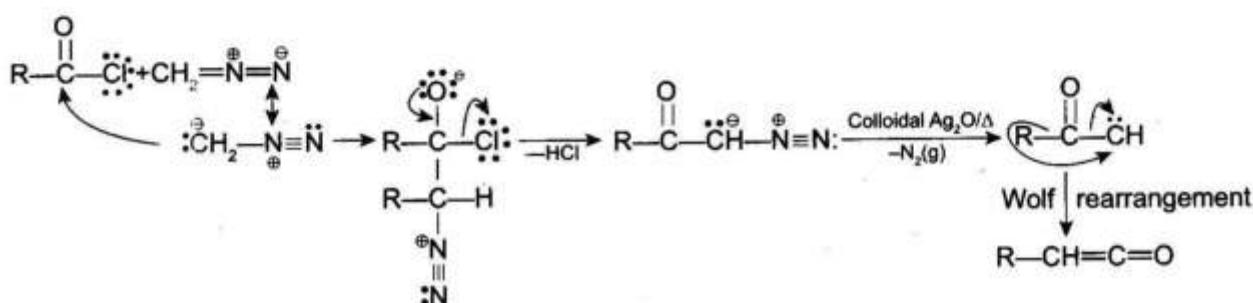
- 5. Benzilic rearrangement:** When aromatic  $\alpha$ -diketone also called benzil, is treated with alkali like NaOH and KOH, followed by acidification, benzilic acid is obtained.  
During the reaction attack of  $\text{OH}^-$  ion occurs on that carbonyl carbon which is more  $e^-$  deficient.



- 6. Arndt Eistert synthesis:** This is an effective method for homologation of carboxylic acid or its derivative. In this method, lower homologue gets converted into successive higher homologue. In this method, acid halide is first treated with diazomethane, from where diazoketone is obtained and then this diazoketone is heated with colloidal  $\text{Ag}_2\text{O}$  from where ketene is obtained through Wolff rearrangement which on hydrolysis or alcoholysis or acidolysis or ammonolysis gets converted into carboxylic acid, ester, acid anhydride, acid amide respectively with one additional carbon.

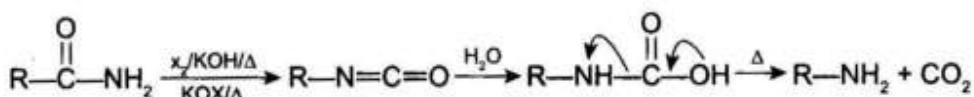


#### Mechanism:

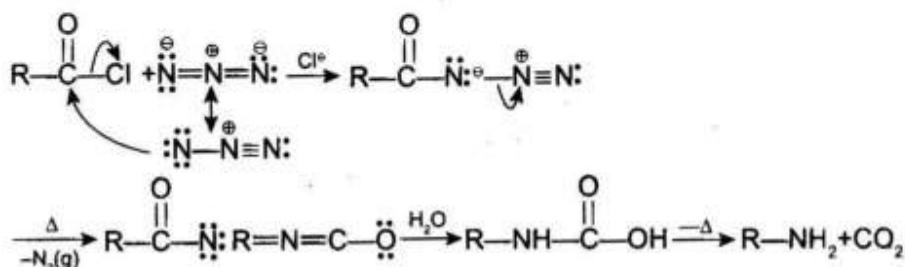


- 1. Carbon-to-nitrogen rearrangement:** If migration origin is carbon and nitrogen terminus is nitrogen, then rearrangement reaction belongs to this category.

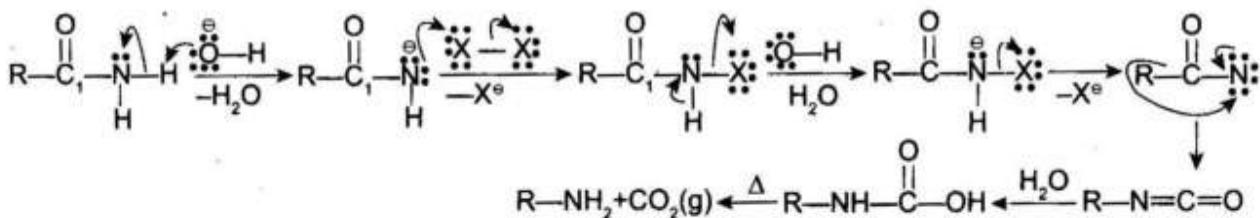
**Hoffmann's bromamide synthesis:** When un substituted amide is treated with halogen along with alkali or metal hypohalite, formation of alkyl isocyanate occurs which on hydrolysis produces primary amine with the evolution of  $\text{CO}_2$ .



**Mechanism:**

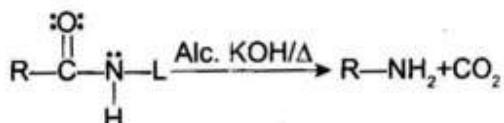


**Mechanism:**

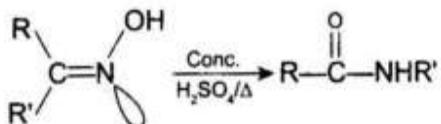


2. **Curtius rearrangement:** When acid halide is treated with metal azide, acyl azide is obtained, which on heating gets converted into isocyanate with a good yield. Then, isocyanate undergoes hydrolysis to produce primary amine with evolution of  $\text{N}_2$  gas.

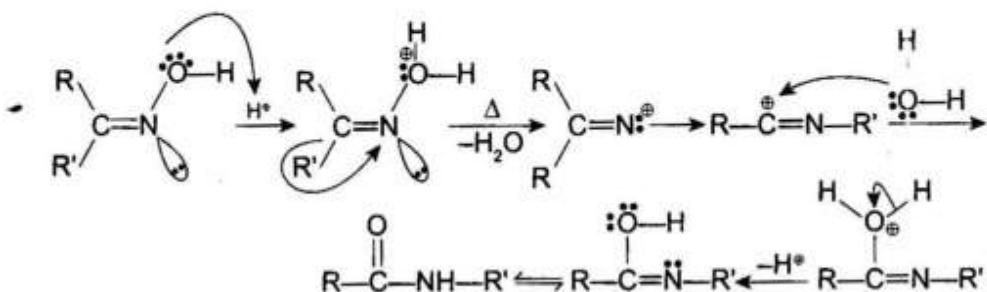
3. **Lossen rearrangement:** When substituted amide containing a good nucleophile and hydrogen attached with N atom, is treated with a strong base, it undergoes elimination to produce isocyanate which on hydrolysis gives primary amine and  $\text{CO}_2$ .



4. **Bakemann's rearrangement:** When ketoxime is heated with dehydrating agent like conc.  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ , dry  $\text{HCl}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{BF}_3$ , etc. it undergoes rearrangement to produce substituted amide during the reaction, alkyl group which is present anti to that of  $-\text{OH}$  group in ketoximes migrates and that alkyl group is attached to N atom in substituted amide. Therefore, this reaction is very effective for identification of configuration of ketoxime.



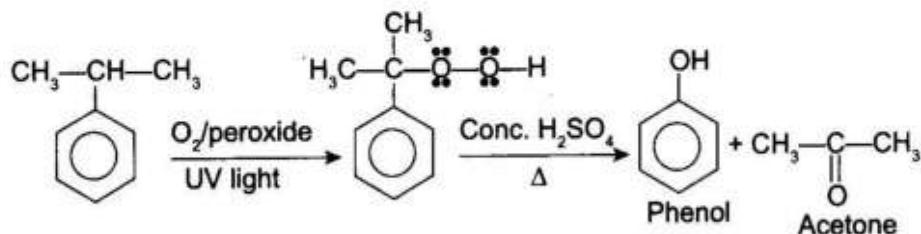
**Mechanism:**



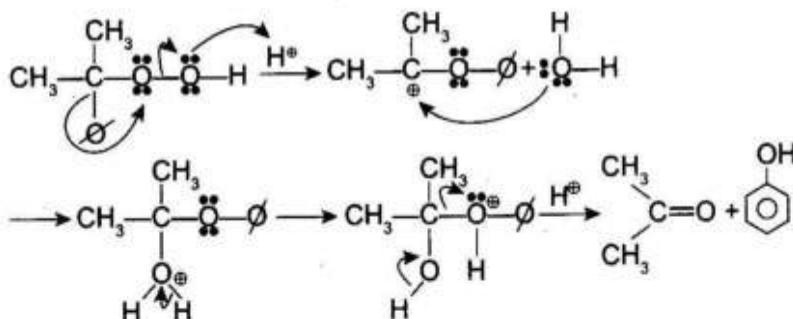
### 3. Carbon to oxygen rearrangement:

#### (i) Cumene hydro peroxide rearrangement:

When cumene hydroperoxide is treated with conc.  $H_2SO_4$ , it undergoes rearrangement to produce phenol and acetone, where cumene hydroperoxide is prepared by treating cumene, i.e., isopropyl benzene with oxygen air in the presence of UV rays.



#### Mechanism:



#### (ii) Baeyer-Villigar Oxidation:

When ketone is treated with peroxy acid or some other compound containing peroxide linkage alongwith some Lewis acid catalyst, ester is obtained.



#### Mechanism:

During the reaction, migration of that alkyl group occurs from C to O which possess highest migratory aptitude. During the reaction, ester produced may be involved in trans-esterification reaction with the acid present on product side. However, trans-esterification process is pH dependent. Due to trans-esterification, yield of required ester decreases. In order to maximize the yield of required ester, buffering agents like  $NaH_2PO_4$ ,  $Na_2HPO_4$ ,  $NaHCO_3$ , or some other incomplete salt is added to reaction mixture, which do not allow that pH to be established, which is required for trans-esterification. Then, trans-esterification does not take place.

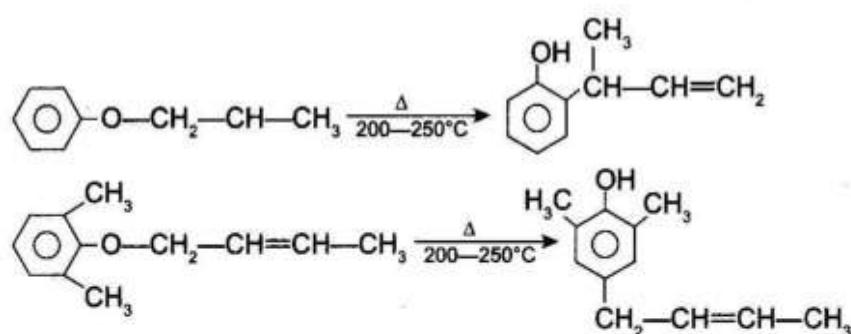
#### 4. Aromatic rearrangement:

This rearrangement is given by aryl substrate where migrating group is attached with N or O side chain.

### 24.7 CLAISEN REARRANGEMENT

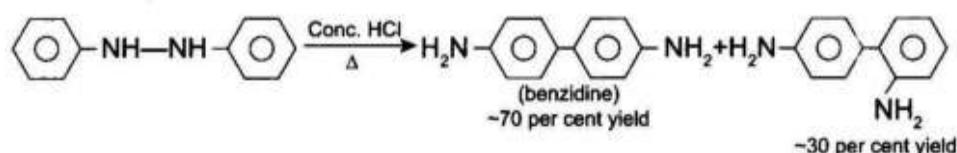
When allyl aryl ether is heated at  $200-250^\circ C$ , in absence of catalyst, ortho and para-allyl phenol is obtained, paramigration occurs only when both orthopositions are blocked.

During o-migration, allylic shift of product is obtained. However, during p-migration allylic shift is not observed because two allylic shifts occur in succession.



## 24.8 BENZIDINE REARRANGEMENT

When hydrazo benzene is treated with conc. HCl, it undergoes rearrangement to produce p, p-diamino biphenyl as major product alongwith o, p-diamino biphenyl and some other products in trace amounts.

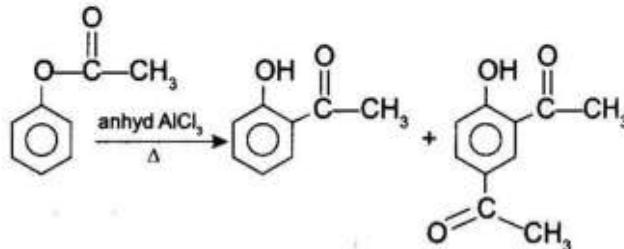


## 24.9 FRIES REARRANGEMENT

When phenolic ester is heated with anhy AlCl<sub>3</sub>, it rearranges to produce o-and p-acyl phenol.

Major product obtained during the reaction depends upon the following factors.

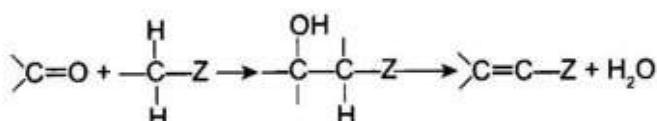
- (i) **Temperature:** At low temperature, H bond in o-product is significant, due to which its yield increases. At high temperature, p-product is major product.
- (ii) **Amount of catalyst used:** Since energy barrier of a reaction depends upon the concentration of a catalyst used therefore at high catalyst concentration, decrease in energy of transition state is greater due to which formation of ortho product predominates.  
But for para, product temperature is high due to which catalyst required is less, since activation energy can be easily provided at high temperature; therefore, yield of para product increases.
- (iii) **Nature of solvent used:**  
In presence of a polar aprotic solvent, due to lack of competitive H-bond strength of intramolecular H bond increases, which results in increase in yield of o-product. However, in presence of the polar protic solvent which is also capable to form H bond creates competitive H-bond and therefore yield of o-product decreases and yield of p-product increases.
- (iv) **Favòrskii rearrangement:**  
When  $\alpha$ -halogenated ketone is treated with aqueous alkali or with alcoholic metal alkoxide or with NaNH<sub>2</sub>/NH<sub>3</sub>( $\ell$ ) it gets converted into carboxylic acid, ester and acid amide respectively.  
If ketone used is cyclic, then ring contraction occurs; however, if it is acyclic, then chain shortening of principle chain occurs.



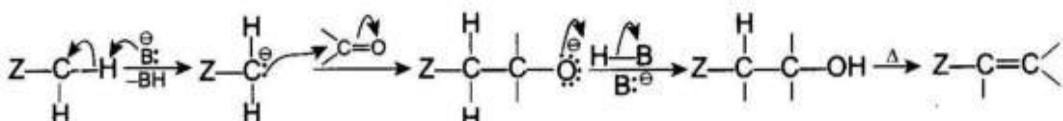
## 24.10 CONDENSATION REACTION

In condensation reaction, substrate molecule generally possess a carbonyl group and in some cases, ester and cyanide may also act as a substrate. Reagent involved during the reaction must have at least one  $\alpha$ -hydrogen which is sufficiently acidic to proceed in presence of base as a catalyst.

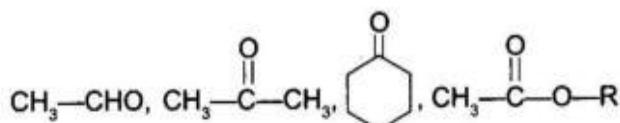
**General reaction:**



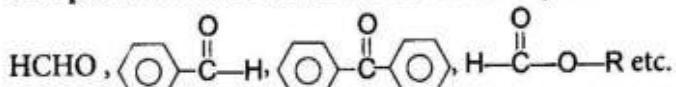
**Reaction mechanism:**



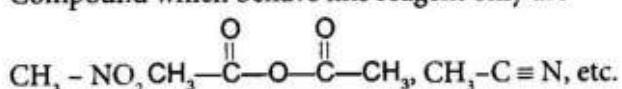
Compound which can act as substrate and reagent both in condensation reaction, are



Compounds which behave like substrate only are



Compound which behave like reagent only are

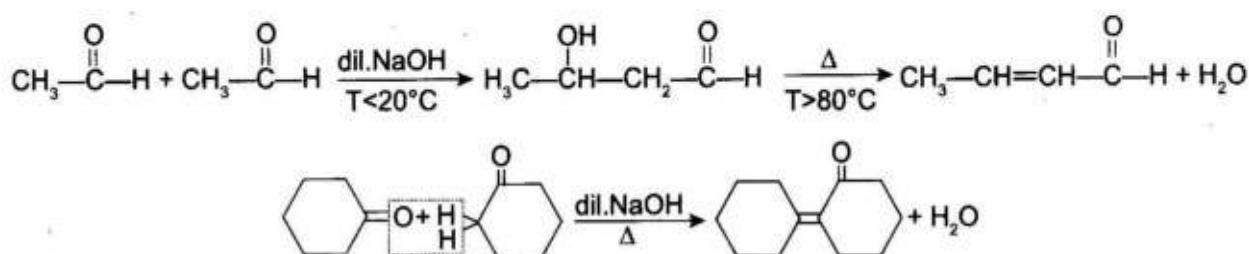


## 24.11 ALDOL CONDENSATION

When a carbonyl compound containing at least two  $\alpha$ -hydrogen is heated with dil. alkali, at low temperature, i.e.,  $< 20^\circ\text{C}$ , formation of addition product aldol occurs which undergoes dehydration at high temperature,  $> 80^\circ\text{C}$  to produce,  $\alpha, \beta$  unsaturated carbonyl compound.

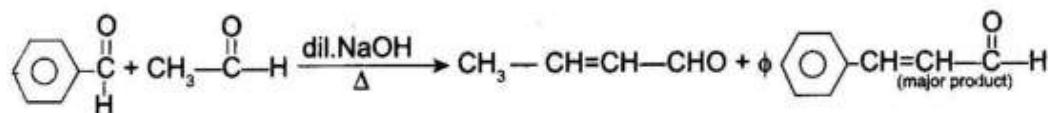
### 24.11.1 Classification of Aldol Condensation

**Self-alcohol condensation:** When reaction occurs between two molecules of same carbonyl compound, then reaction is termed as self-alcohol condensation

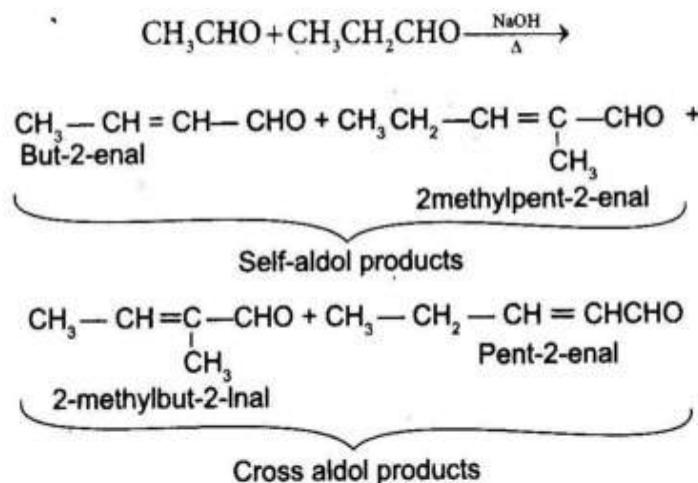


**Cross aldol condensation:** This reaction takes place between two different carbonyl compound where cross product is always a major product.

**Case I:** If only one of them possess  $\alpha$ -hydrogen:

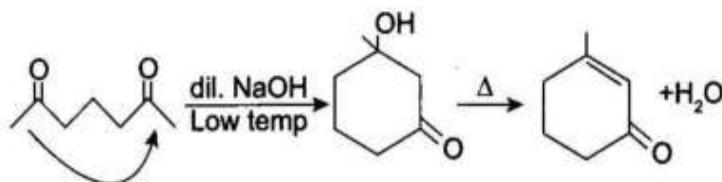


**Case II: When both contain  $\alpha$ -hydrogen:** Under such a condition, four products are produced out of which two are cross condensation products and two are self-condensation products.

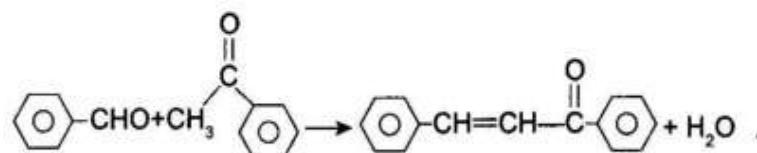


Intramolecular aldol condensation, i.e., cyclization via aldol condensation

This reaction is given by dialdehyde or diketone or by ketoaldehyde, when they are treated with dil. alkali, and during the reaction, formation of 5-or 6-membered ring is favourable.



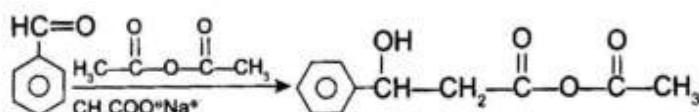
**Claisen Schmidt's condensation:** Cross aldol condensation between aromatic aldehydes and aliphatic or mixed ketone is called Claisen Schmidt's condensation.



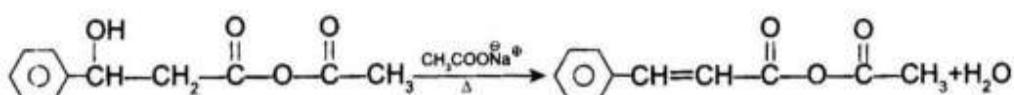
## 24.12 PERKIN'S CONDENSATION

When an aromatic aldehyde is heated with an aliphatic acid and anhydride with atleast  $\alpha$ -H atoms in presence of Na or K salt of corresponding acid, a condensation product  $\alpha, \beta$ -unsaturated acid is formed. Reaction proceeds in the following three steps.

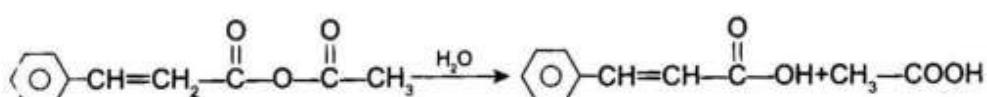
**Step 1:** In this step, nucleophilic addition occurs between aromatic aldehyde with acid anhydride.



**Step 2:** Dehydration of nucleophilic addition product occurs to produce  $\alpha, \beta$ -unsaturated acid anhydride.



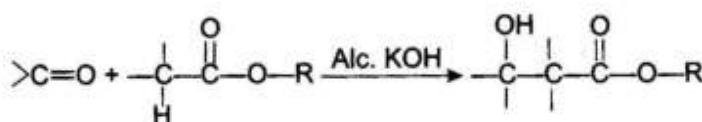
**Step 3:** In this step, hydrolysis of dehydrated product takes place, which results in the formation of  $\alpha, \beta$ -unsaturated acid.



### 24.13 STOBBE CONDENSATION

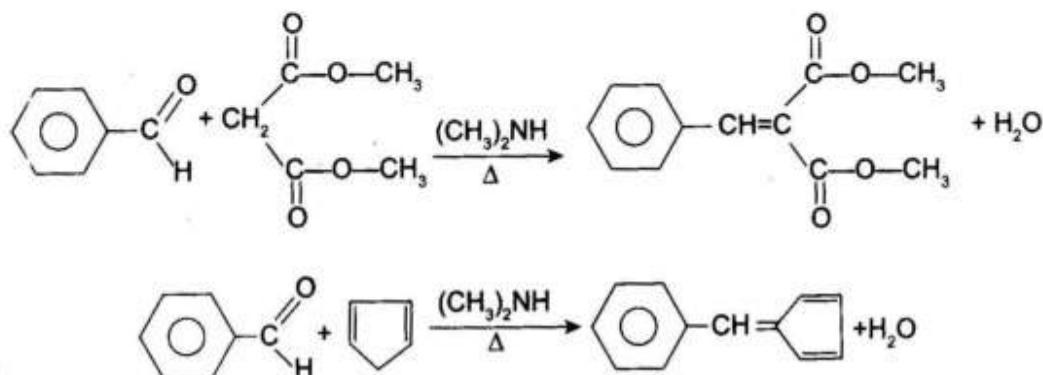
This reaction takes place between a carbonyl compound which may or may not have  $\alpha$ -hydrogen and ester having at least one  $\alpha$ -hydrogen. Reaction is catalysed by strong bases such as alc. KOH, metal alkoxide,  $\text{NaNH}_2$ , etc.

Product of the reaction is  $\beta$ -hydroxy ester which may or may not be dehydrated to produce  $\alpha, \beta$ -unsaturated ester.



### 24.14 KNOEVENAGEL REACTION

When aromatic aldehyde is treated with an active methylene compound in presence of weak base as a catalyst, condensation product is obtained.



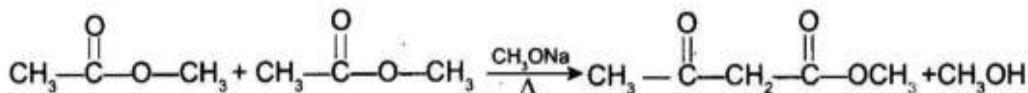
## 24.15 CLAISEN CONDENSATION

When an ester containing atleast one  $\alpha$ -hydrogen is treated either with the same molecule or with some other ester molecule in presence of strong base like metal alkoxide  $\text{NaNH}_2$ , etc.  $\beta$ -keto ester is obtained. Reaction is further classified into two categories.

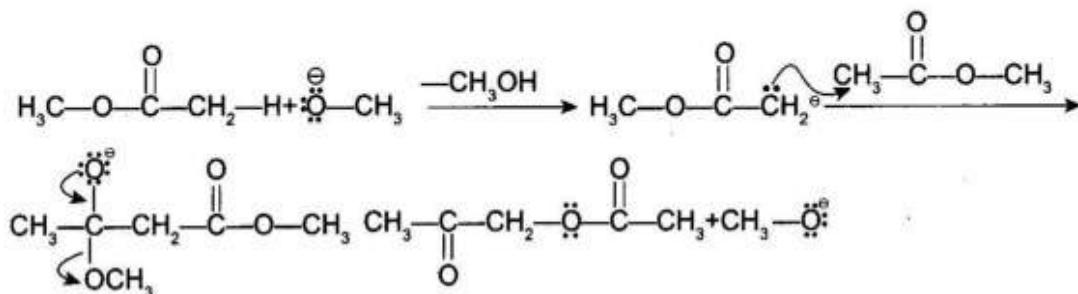
- (i) **Intermolecular claisen condensation**
- (ii) **Intramolecular claisen condensation**

- (i) **Intermolecular claisen condensation:** This reaction takes place between two molecules of ester whether they are same or different. It is further classified into two categories:

(a) Self-Claisen condensation: When reaction occurs between same ester molecules

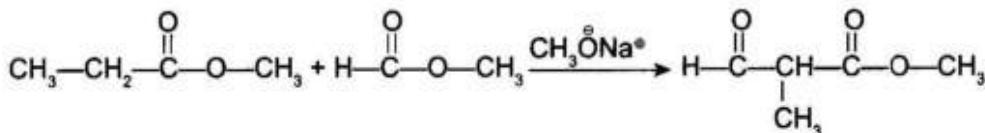


### Mechanism

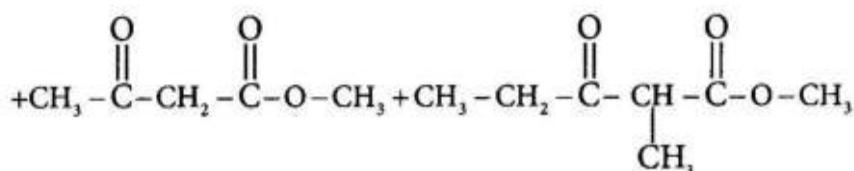
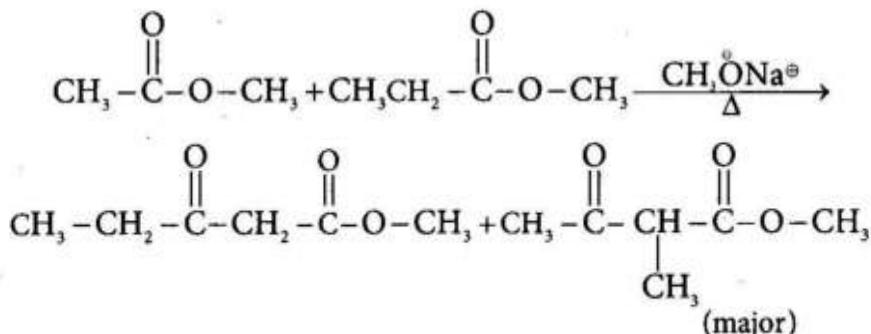


- (b) Cross Claisen condensation:

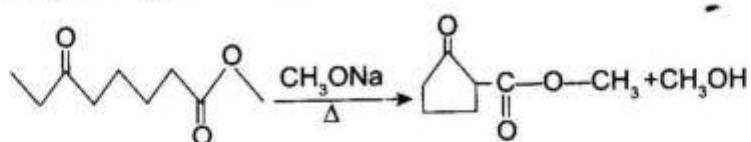
**Case I:** If only one of them possess  $\alpha$ -hydrogen



**Case II:** If both posses  $\alpha$ -hydrogen, then mixture of the product is obtained, where cross product is a major product



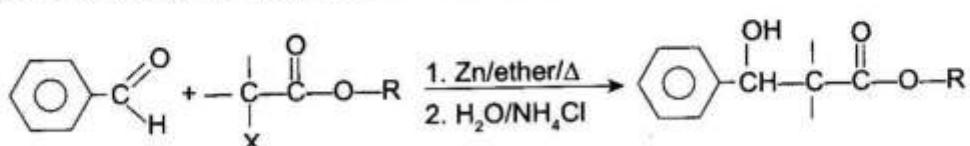
- (ii) **Intramolecular claisen condensation:** It is also called Dieckmann condensation or cyclization via claisen condensation. This reaction is given by diesters when they are treated with metal alkoxide or  $\text{NaNH}_2$ . During the reaction, 5 or 6 membered ring is produced.



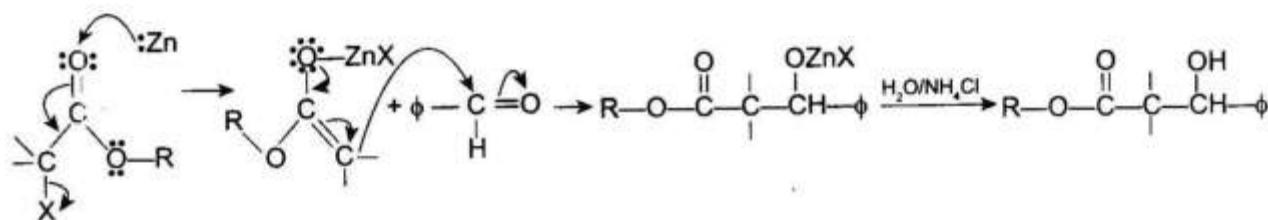
## 24.16 REFORMATSKY REACTION

This reaction takes place between aromatic aldehyde and  $\alpha$ -halogenated ester where they are treated with Zn and ether followed by hydrolysis in a slightly acidic medium to produce  $\beta$ -hydroxy ester which may or may not be dehydrated to produce  $\alpha,\beta$ -unsaturated ester.

During the reaction cyanide may also act as a substrate and in such cases,  $\beta$ -keto esters are obtained.

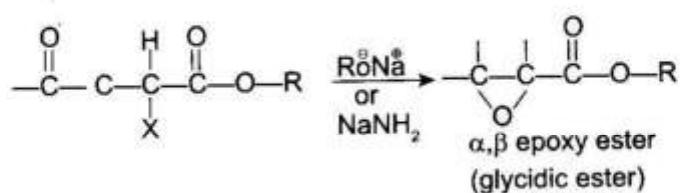


**Mechanism:**



## 24.17 DARZEN'S GLYCIDIC ESTER CONDENSATION

When a carbonyl compound containing  $\alpha$ -hydrogen or not is heated with  $\alpha$ -halogenated ester containing atleast one  $\alpha$ -hydrogen in presence of strong base  $\alpha,\beta$ -epoxy ester, also called glycidic ester, is produced.

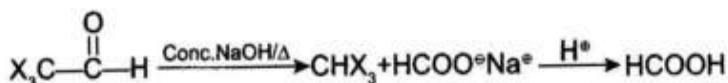


**Disproportionation reaction:** In a disproportionation reaction, same species undergo oxidation and reduction simultaneously.

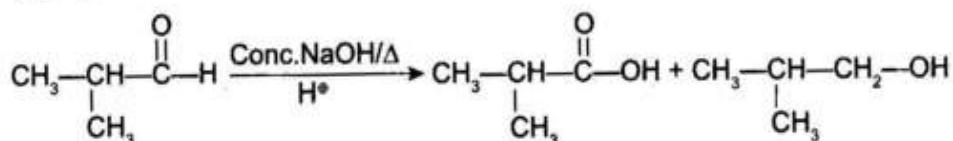
## 24.18 CANNIZZARO REACTION

When an aldehyde containing no  $\alpha$ -hydrogen is treated with conc. alkali followed by acidification produce carboxylic acid and alcohol. Exceptions of Cannizzaro reaction are

- (i) **Tri-halogenated acetaldehyde** has no  $\alpha$ -hydrogen; still, it cannot participate in Cannizzaro reaction under similar conditions to produce haloform.



- (ii) 2-methyl propanal has one  $\alpha$ -H and still it can participate in Cannizzaro reaction



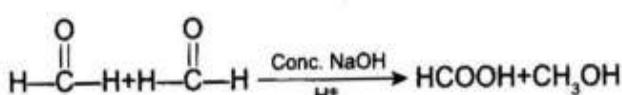
**Reaction further classified into two categories:**

- (a) Intermolecular Cannizzaro reaction  
 (b) Intra-molecular Cannizzaro reaction or internal cannizzaro reaction.

## 24.19 INTERMOLECULAR CANNIZZARO REACTION

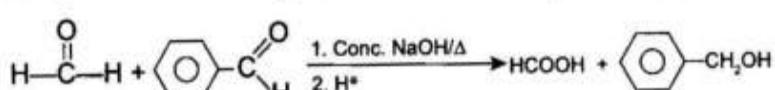
This reaction takes place between two molecules of aldehyde having no  $\alpha$ -hydrogen.

- (i) **Self-Cannizzaro reaction:** When same aldehyde molecule is used during reaction.

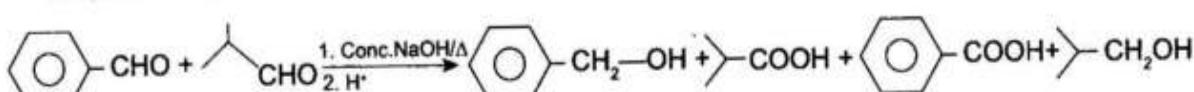


- (ii) **Cross Cannizzaro Reaction:** If two different molecules of aldehyde are used.

**Case I:** If one of them is formaldehyde, then HCHO always undergo oxidation.



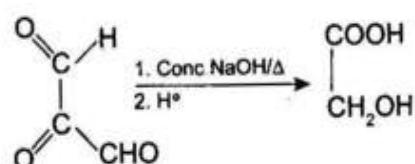
**Case II:** If none of them is HCHO, then mixture of the product is obtained.



## 24.20 INTRAMOLECULAR CANNIZZARO REACTION OR INTERNAL CANNIZZARO REACTION

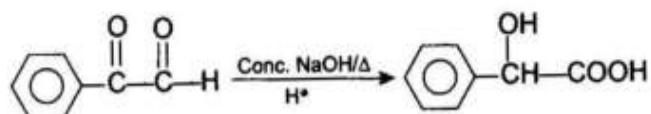
- (i) **Internal self Cannizarro reaction:**

This reaction is given by dialdehyde containing no  $\alpha$ -hydrogens.



- (ii) **Internal cross canizaaro reaction:**

This reaction is given by keto aldehyde containing no  $\alpha$ -hydrogen where aldehyde is always converted into carboxylic acid by oxidation, whereas keto group undergo reduction.



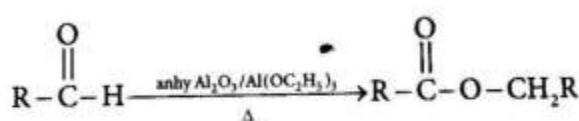
## 24.21 TISHCHENKO REACTION

When aldehyde containing  $\alpha$ -hydrogen or not is treated with anhydrous  $\text{Al}_2\text{O}_3$ , or with  $(\text{C}_2\text{H}_5\text{O})_3\text{Al}$ , or with some other Lewis acid catalyst, ester is obtained.

Reaction is also termed as extended Cannizzaro reaction on the basis of final products, produced.

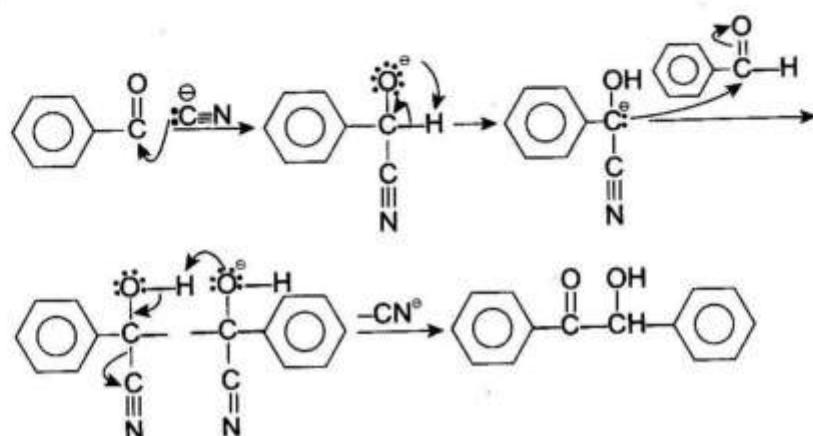
If aldehyde used is aromatic, then reaction best proceed in complexes like  $\text{Na}_2[\text{Fe}(\text{CO})_4]$ .

During the reaction, oxidation of that aldehyde occurs which combines with Lewis acid catalyst, whereas the other aldehyde undergo reduction.



## 24.22 BENZOIN CONDENSATION

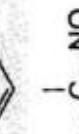
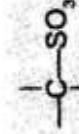
When an aromatic aldehyde is treated with alcohol in aqueous  $\text{KCN}$ , aromatic  $\alpha$ -hydroxy ketone also called benzoin is obtained which gives positive test with Tollen's, Benedict's, and Fehling's reagent though having no aldehydic group.



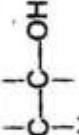
**An Institute  
which challenged  
ALL  
the IIT-JEE Coaching Institutes  
of India,  
Including those of  
Kota, Delhi, Mumbai,  
Kolkata, Hyderabad,  
Patna, Chennai etc., etc.....  
(National or Local Level)  
In a question  
of JEE-Advanced 2014  
and finally  
winning through  
decision of IIT  
on 1<sup>st</sup> June, 2014.**

### 24.23 ALKANE

S. No.	Reactants	Reagents	Products	Mechanism involved	Name of reaction
1.	$\begin{matrix} \text{O} \\   \\ \text{R}-\text{C}-\text{O}-\text{H} \end{matrix}$	$\text{NaOH}/\text{CaO}/\Delta$	$\text{R}-\text{H}$	Carbanion formation	Decarboxylation
2.	$\text{R}-\text{X}$	$\text{R}_2'\text{CuLi}$ (Gilmann's reagent)	$\text{R}-\text{R}'$	Nucleophilic substitution ( $\text{S}_{\text{N}}2$ )	Corey-house synthesis
3.	$2\text{R}-\text{X}$	Na/dry ether	$\text{R}-\text{R}$	Free radical and ionic mechanism	Wurtz reaction
4.	$\text{R}-\text{COOK}$	$\text{H}_2\text{O}$ /electrolysis	$\text{R}-\text{R}$	Free radical mechanism	Kolbe's electrolytic method
5.	$\begin{matrix} \text{O} \\    \\ \text{R}-\text{C}-\text{R} \end{matrix}$	$\text{Zn}-\text{Hg}/\text{HCl}$	$\text{R}-\text{CH}_2-\text{R}$	Reduction	Clemmensen reduction
6.	$\begin{matrix} \text{O} \\    \\ \text{R}-\text{C}-\text{R} \end{matrix}$	$\text{NH}_2\text{NH}_2/\text{KOH/glycol}/\Delta$	$\text{R}-\text{CH}_2-\text{R}$	Reduction	Wolf-Kishner reduction
7.	$\begin{matrix} \text{O} \\    \\ \text{R}-\text{C}-\text{R} \end{matrix}$	$\begin{matrix} \text{CH}_2\text{SH} \\   \\ \text{CH}_2\text{SH} \end{matrix}$ / Raney Ni/ $\Delta$	$\text{R}-\text{CH}_2-\text{R}$	Reduction	Mozingo method
8.	$2\text{R}-\text{X}$	$\text{Zn}/\text{C}_2\text{H}_5\text{OH}$ or ether	$\text{R}-\text{R}$	Nucleophilic substitution	Frankland's reaction
9.	$\text{R}-\text{X}$	$\text{Zn}/\text{CH}_3\text{COOH}$ or $\text{Zn}/\text{HCl}$ or $\text{Zn}-\text{Cu}/\text{C}_2\text{H}_5\text{OH}$	$\text{R}-\text{H}$	—	Reduction of alkyl halide
10.	$\text{R}-\text{X}$	$\text{LiAlH}_4$ or $\text{NaBH}_4$ or $\text{Ph}_3\text{SnH}$	$\text{R}-\text{H}$	Nucleophilic substitution	Reduction of alkyl halide
11.	$\begin{matrix} >\text{C}=\text{C}< \\ \text{or} \\ -\text{C}\equiv\text{C}- \end{matrix}$	$\text{H}_2/\text{Ni}$ or $\text{H}_2/\text{Pt}$ or Raney Ni	$\begin{matrix} \text{H} & \text{H} \\   &   \\ \text{C} & -\text{C} \\   &   \\ \text{H} & \text{H} \end{matrix}$ or $\begin{matrix} \text{H} & \text{H} \\   &   \\ \text{C} & -\text{C} \\   &   \\ \text{H} & \text{H} \end{matrix}$	Adsorption	Hydrogenation of alkene or alkyne

S. No.	Reactants	Reagents	Products	Mechanism involved	Name of reaction
12.	R - X or R - OH	H <sub>2</sub> /red P	R - CH <sub>3</sub>	Reduction	
13.	Be <sub>2</sub> C or Al <sub>4</sub> C <sub>3</sub>	H <sub>2</sub> O	CH <sub>4</sub>	Neutralization	Hydrolysis of carbide
14.	n-hexane	V <sub>2</sub> O <sub>5</sub> /Cr <sub>2</sub> O <sub>3</sub> - Al <sub>2</sub> O <sub>3</sub> , 500°C		Free radical mechanism	Aromatization
15.		Conc. HNO <sub>3</sub> /Conc. H <sub>2</sub> SO <sub>4</sub> , 500°C		Free radical substitution	Nitration of alkane
16.		Conc. H <sub>2</sub> SO <sub>4</sub> or fuming H <sub>2</sub> SO <sub>4</sub> , 500°C		Free radical substitution	Sulphonation of alkane

## 24.24 ALKENE

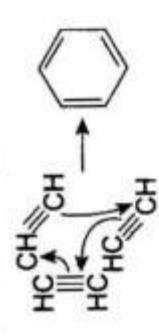
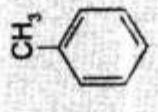
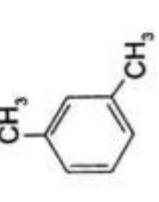
S. No.	Reactants	Reagents	Products	Mechanism involved	Name of reaction
1.		Conc. H <sub>2</sub> SO <sub>4</sub> /Δ or P <sub>2</sub> O <sub>5</sub> /Δ or AlCl <sub>3</sub> /Δ	>C=C<	Elimination (E <sub>1</sub> )	Dehydration of alcohol
2.		Alc. KOH/Δ or RONa/Δ or NaNH <sub>2</sub> /Δ	>C=C<	Elimination (E <sub>2</sub> )	Dehydrohalogenation
3.	>C=O	Ph <sub>3</sub> P = CH - R	>C=CH-R	Nucleophilic addition elimination	Wittig reaction
4.		Δ	>C=C< + (CH <sub>3</sub> ) <sub>3</sub> N + H <sub>2</sub> O	Elimination (E <sub>2</sub> )	Hofmann's degradation

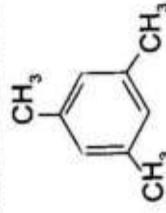
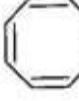
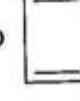
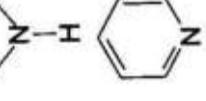
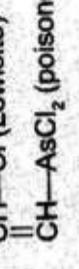
S. No.	Reactants	Reagents	Products	Mechanism involved	Name of reaction
5.	$-C \equiv C -$	1. $B_2H_6/THF$ 2. $CH_3COOH$	$H > C = C < H$	Syn-addition reaction	Hydroboration-reduction
6.	$-C \equiv C -$	$Na/NH_3$ or $Li/NH_3$	$H > C = C < H$	Anti-addition	Birch reduction
7.	$-C \equiv C - + H_2$	Pd/CaCO <sub>3</sub> /BaSO <sub>4</sub> or quinoline (Lindlar's catalyst) or Ni <sub>2</sub> B (P-2 catalyst)	$H > C = C < H$	Syn-addition reaction	Syn-hydrogenation
8.	$\begin{array}{c} O \\    \\ R-C-O-C(H)-C(H)-C(H)- \\   \quad   \quad   \\ H \quad O^e \quad N^e-R \\   \quad   \quad   \\ -C-C-N^e-R \end{array}$	$\Delta/400^\circ C$	$>C=C< + R-C(O)=O-H$	Pyrolytic elimination	Pyrolysis of ester
9.	$\begin{array}{c} H \\   \\ R-C(H)-C(H)-C(H)-C(H)- \\   \quad   \quad   \\ H \quad O^e \quad N^e-R \\   \quad   \quad   \\ -C-C-N^e-R \end{array}$	$\Delta/200^\circ C$	$>C=C< + R>N-\dot{O}H$	Pyrolytic elimination	Cope elimination
10.	$R-C(H)-C(H)-H$	Dil. $H_2SO_4$	$\begin{array}{c} OH \\   \\ -CH-CH_3 \end{array}$	Electrophilic addition (MR)	Direct hydration
11.	$R - CH = CH_2$	$B_2H_6/THF/CH_3COOH$	$R - CH_2 - CH_3$	Syn-addition reaction	Hydroboration-reduction
12.	$>C=C<$	Cold, dil. alkaline $KMnO_4$ (Bayer's reagent) or $OsO_4/NaHSO_4/H_2O$	$\begin{array}{c}   \quad   \\ -C-C- \\   \quad   \\ OH \quad OH \end{array}$	Syn-addition reaction	Syn-hydroxylation
13.	$>C=C<$	Peroxy acid/ $H_2O/OH^-$	$\begin{array}{c} OH \quad OH \\   \quad   \\ -C-C- \\   \quad   \\ OH \quad OH \end{array}$	Prileschaev reaction	Anti-hydroxylation

S. No.	Reactants	Reagents	Products	Mechanism involved	Name of reaction
14.	$\begin{matrix} R & > C = C < R \\ H & \quad   \quad   \\ & \quad C=C \end{matrix}$	$O_2/Zn/H_2O$	$\begin{matrix} R & > C = O + O = C < R \\ H & \quad   \quad   \\ & \quad C=C \end{matrix}$	—	Reductive ozonolysis
15.	$\begin{matrix} R & > C = C < R \\ H & \quad   \quad   \\ & \quad C=C \end{matrix}$	$DMSO_3/H_2O$	$\begin{matrix} O & \\ R & - C - OH + R - C - R \\ & \quad   \quad   \\ & \quad O \quad O \end{matrix}$	Oxidative ozonolysis	
16.	$\begin{matrix} R & > C = C < R \\ H & \quad   \quad   \\ & \quad C=C \end{matrix}$	Dil. alk $KMnO_4/\Delta$ or $K_2Cr_2O_7/H^+/\Delta$	$\begin{matrix} O & \\ R & - C - OH + R - C - R \\ & \quad   \quad   \\ & \quad O \quad O \end{matrix}$	Oxidation	Oxidative cleavage of alkene
17.	$\begin{matrix} & > C = C < C - H \\ & \quad   \quad   \quad   \\ & \quad C=C \end{matrix}$	NBS/CCl <sub>4</sub> /UV light	$\begin{matrix} > C = C < C - Br \\ \quad   \quad   \\ > C = C < C - OH \end{matrix}$	Free radical substitution	Allylic bromination
18.	$\begin{matrix} & > C = C < C - H \\ & \quad   \quad   \quad   \\ & \quad C=C \end{matrix}$	$SeO_2/CH_2Cl_2$	$\begin{matrix} > C = C < C - OH \\ \quad   \quad   \\ > C = C < C - OH \end{matrix}$	Free radical mechanism	Allylic oxidation
19.	$\begin{matrix} R & > C = C < H \\ H & \quad   \quad   \\ & \quad C=C \end{matrix}$	1. $PdCl_2H_2O$ 2. $CuCl_2$ , air/ $\Delta$	$\begin{matrix} O & \\ R & - C - CH_3 \\ & \quad   \quad   \\ & \quad O \quad R - C - CH_3 \end{matrix}$	—	Wacker's process

## 24.25 ALKYNE

S. No.	Reactants	Reagents	Products	Mechanism involved	Name of reaction
1.	$R - CH = C - Cl$	$NaNH_2/\Delta$	$R - C \equiv CH$	$E_2$	Dehydrohalogenation reaction
2.	$\begin{matrix} & C \\ &   \\ R - & C - Cl \\ &   \\ & H \end{matrix}$	$H_2O$	$H - C \equiv CH + Ca(OH)_2$	Neutralization reaction	Hydrolysis of carbide
3.	$2Mg^{2+} [C \equiv C]^{2-}$	$H_2O$	$CH_3 - C \equiv CH$	Neutralization reaction	Neutralization reaction
	$2 - C \equiv X$	Ag powder/ $\Delta$	$-C \equiv C -$	Elimination	Dehalogenation of gem trihalide

S. No.	Reactants	Reagents	Products	Mechanism involved	Name of reaction
4.	$\text{R}-\text{C}\equiv\text{C}-\text{H}$	1. $\text{HgSO}_4/\text{H}_2\text{SO}_4$ 2. $\text{NaBH}_4$	$\text{R}-\overset{\text{OH}}{\underset{\text{C}\equiv\text{CH}}{\text{C}}}=\text{CH}_2 \rightleftharpoons \text{R}-\overset{\text{O}}{\underset{\text{C}}{\text{C}}}-\text{CH}_3$	Nucleophilic addition (Markownikoff rule)	Oxymercuration- demercuration (anti-addition)
5.	$\text{R}-\text{C}\equiv\text{C}-\text{H}$	1. $\text{B}_2\text{H}_6/\text{THF}$ 2. $\text{H}_2\text{O}/\text{OH}^-$	$\text{R}-\overset{\text{OH}}{\underset{\text{CH}\equiv\text{CH}}{\text{C}}}=\text{CH} \rightleftharpoons \text{R}-\overset{\text{O}}{\underset{\text{CH}_2-\text{C}\equiv\text{H}}{\text{C}}}-\text{H}$	Syn-addition (anti- Markownikoff's rule)	Hydroboration - oxidation
6.	$\text{R}-\text{C}\equiv\text{C}-\text{R}'$	$\text{O}_2/\text{Zn/H}_2\text{O}$ or $\text{DMSO}_3/\text{H}_2\text{O}$	$\text{R}-\overset{\text{O}}{\underset{\text{C}}{\text{C}}}-\text{R}'$ $\text{R}-\text{COOH} + \text{R}'-\text{COOH}$	Reductive oxidative	Ozonolysis Ozonolysis:
7.	$\text{CH}\equiv\text{CH}+\text{CH}\equiv\text{CH}$	$\text{CuCl}/\text{NH}_4\text{Cl}/\Delta$	$\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$	Addition reaction	Reductive coupling
8.	$\text{R}-\text{C}\equiv\text{C}-\text{R}'$	Dil. alk $\text{KMnO}_4/\Delta$ or $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+/\Delta$	$\text{R}-\overset{\text{O}}{\underset{\text{C}-\text{OH}}{\text{C}}}-\text{R}'$	Oxidation	Oxidative cleavage of alkyne
9.	$3\text{CH}\equiv\text{CH}$	Red hot cu tube		Free radical coupling	Pyrolysis of alkyne
10.	$\text{CH}_3-\text{C}\equiv\text{CH} + 2\text{CH}\equiv\text{CH}$	Red hot cu tube		Free radical coupling	Pyrolysis of alkyne
11.	$2\text{CH}_3-\text{C}\equiv\text{CH} + \text{CH}\equiv\text{CH}$	Red hot cu tube		Free radical coupling	Pyrolysis of alkyne

S. No.	Reactants	Reagents	Products	Mechanism involved	Name of reaction
1.	$3\text{CH}_3-\text{C}\equiv\text{CH}$	Red hot cu tube		Free radical coupling	Pyrolysis of alkyne
2.	$4\text{CH}\equiv\text{CH}$	Red hot cu tube	 	Free radical coupling	Pyrolysis of alkyne
3.	$2\text{CH}\equiv\text{CH} + \text{H}_2\text{S}$	Red hot cu tube		Free radical coupling	Pyrolysis of alkyne
4.	$2\text{CH}\equiv\text{CH} + \text{NH}_3$	Red hot cu tube		Free radical coupling	Pyrolysis of alkyne
5.	$2\text{CH}\equiv\text{CH} + \text{CH}_3\text{NH}_2$	Red hot cu tube		Free radical coupling	Pyrolysis of alkyne
6.	$\text{CH}\equiv\text{CH}$	$\text{AsCl}_3/\text{Hg}^{2+}$	$\text{CH}-\text{Cl} \text{ (Lewisite)}$ $\text{CH}-\text{AsCl}_2 \text{ (poisonous gas)}$	Highly poisonous gas	
7.	$\text{CH}\equiv\text{CH}$	$\text{CH}_3\text{COOH}/\text{Hg}^{2+}$		Nucleophilic addition	
8.	$\text{CH}\equiv\text{CH}$		$\text{CH}_3-\text{C}(=\text{O})-\text{CH}_3 + \text{CH}_3-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-\text{CH}_3$		

S. No.	Reactants	Reagents	Products	Mechanism involved	Name of reaction
14.	$\text{CH} \equiv \text{CH}_\downarrow$	$\text{CO} + \text{H}_2\text{O}/\text{Ni}(\text{CO})_4$	$\text{CH}_2=\overset{\text{O}}{\underset{\text{acrylic acid)}}{\text{C}}-\text{OH}$	Nucleophilic addition	
15.	$\text{R}-\text{C}\equiv\text{C}-\text{H}$	$\text{AgNO}_3/\text{NH}_4\text{OH}$	$\text{R}-\text{C}\equiv\text{C}-\text{Ag}$ (grey ppt.)		Silver mirror test
16.	$\text{R}-\text{C}\equiv\text{C}-\text{H}$	$\text{CuCl}/\text{NH}_4\text{OH}$	$\text{R}-\text{C}\equiv\text{C}-\text{Cu}$ (red ppt.)		
17.	$\text{R}-\text{C}\equiv\text{C}-\text{H}$	$\text{AuCl}/\text{NH}_4\text{OH}$	$\text{R}-\text{C}\equiv\text{C}-\text{Au}$ (golden ppt.)		Analytical test of terminal alkyne

## 24.26 ALKYL HALIDE

S.No	Reactants	Reagent	Products	Mechanism involved	Name of reaction
1.	$\begin{array}{c}   \\ -\text{C}-\text{H} \\   \end{array}$	$\text{X}_2/\text{UV light}$ $\text{X}=-\text{Cl}, -\text{Br}, -\text{F}$	$\begin{array}{c}   \\ -\text{C}-\text{X}+\text{HX} \\   \end{array}$	Free radical substitution	Halogenation of alkane
2.	$\begin{array}{c}   \\ -\text{C}-\text{H} \\   \end{array}$	$\text{I}_2/\text{HNO}_3$	$\begin{array}{c}   \\ -\text{C}-\text{I} \\   \end{array}$	Free radical substitution	Iodination of alkane
3.	$\begin{array}{c}   \\ -\text{C}-\text{X} : \text{X}=\text{Br}, \text{Cl} \\   \end{array}$	$\text{NaI}/\text{Acetone}$	$\begin{array}{c}   \\ -\text{C}-\text{I} \\   \end{array}$	Nucleophilic substitution	Finkelstein reaction
4.	$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{O}-\text{Ag} \end{array}$	$\text{X}_2/\text{CCl}_4/\text{A}$	$\text{R}-\text{X} + \text{AgX} + \text{CO}_2$	Free radical substitution	Borodine Hunsdiecker reaction
5.	$\text{R}-\text{OH}$	$\text{PX}_3/\text{HX}$	$\text{R}-\text{X}$	Nucleophilic substitution	Halogenation of alcohol
6.	$\text{R}-\text{X} : \text{X}=-\text{Cl}, -\text{Br}$	$\text{AgF}$ or $\text{Hg}_2\text{F}_2$ or $\text{CoF}_3$	$\text{R}-\text{F}$	Nucleophilic substitution	Swarts reaction

S.No	Reactants	Reagent	Products	Mechanism involved	Name of reaction
7.	$\begin{matrix} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{R}' \end{matrix}$	$\text{PCl}_5$	$\begin{matrix} \text{Cl} \\   \\ -\text{C}- + \text{POCl}_3 \\   \\ \text{Cl} \end{matrix}$	-----	Halogeneration of carbonyl compound
8.	$\text{R}-\text{OH}$	$\text{SOCl}_2$	$\text{R}-\text{Cl} + \text{SO}_2 + \text{HCl}$	Internal nucleophilic substitution ( $\text{S}_{\text{N}}\text{i}$ )	Darzen's method
9.	$\text{CHCl}_3$	$\text{HNO}_3$	$\text{C}(\text{NO}_2)\text{Cl}_3 + \text{H}_2\text{O}$ Nitrochloroform or chloropicrin or tear gas	Electrophilic substitution	-----
10.	$\begin{matrix} \text{H}_3\text{C} \\   \\ >\text{C}=\text{O} \\   \\ \text{H}_3\text{C} \end{matrix}$	$\text{CHCl}_3/\text{KOH}/\Delta$	$\begin{matrix} \text{CH}_3 & \text{OH} \\   &   \\ \text{H}_3\text{C} & \text{CCl}_3 \\ (\text{chloform}) & \\ (\text{soapstone in nature}) & \end{matrix}$	Nucleophilic addition	-----
11.	$\text{CHCl}_3$	O <sub>2</sub> /Sunlight	COCl <sub>2</sub> (phosgene) poisonous gas	Oxidation	-----
12.	$\text{R}-\text{X}$	KCN(alc)	$\text{R}-\text{CN} + \text{AgX}$	Nucleophilic substitution	-----
13.	$\text{R}-\text{X}$	AgCN(alc)	$\text{R}-\text{NC} + \text{AgX}$	Nucleophilic substitution	-----
14.	$\text{R}-\text{X}$	$\text{KNO}_4$ (alc)	$\text{R}-\text{O}-\text{N}=\text{O} + \text{KX}$	Nucleophilic substitution	-----
15.	$\text{R}-\text{X}$	$\text{Ag}-\text{O}-\text{N}=\text{O}$	$\text{R}-\text{N}=\text{O} + \text{AgX}$	Nucleophilic substitution	-----
16.	$\text{R}-\text{X}$	$\text{NH}_3$ (alc)	$\text{R}-\text{NH}_2 + \text{R}_2\text{NH} + \text{R}_2\text{N}$	Nucleophilic substitution	Hyproning ammonolysis

S.No	Reactants	Reagent	Products	Mechanism involved	Name of reaction
17.	R-X	NaOH <sub>(aq)</sub>	R-OH	Nucleophilic (S <sub>N</sub> <sup>2</sup> ) substitution	
18.	R-X	Ag <sub>2</sub> O <sub>(moist)</sub>	R-OH	Nucleophilic (S <sub>N</sub> <sup>1</sup> ) substitution	

### 24.27 ALCOHOL AND ETHER

S.No	Reactants	Reagent	Products	Mechanism involved	Name of reaction
1.	R'-MgX	O=C=O/H <sub>3</sub> O <sup>⊕</sup>	$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{OH} \end{array}$	Nucleophilic addition	
		>C=O/H <sub>3</sub> O <sup>⊕</sup>	$\begin{array}{c}   \\ \text{R}'-\text{C}-\text{OH} \end{array}$	Nucleophilic addition	
		R-N=C=O/H <sub>3</sub> O <sup>⊕</sup>	$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{NH}-\text{C}-\text{R}' \end{array}$	Nucleophilic addition	
		R-CH=CH <sub>2</sub> /H <sub>3</sub> O <sup>⊕</sup>	$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{CH}_2-\text{C}-\text{R}' \end{array}$	Nucleophilic addition	
		$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{L}-\text{H}_3\text{O}^+ \end{array}$	$\begin{array}{c} \text{OH} \\   \\ \text{R}-\text{C}-\text{R}' \\   \\ \text{R}' \end{array}$	Nucleophilic addition	
2.	R-L L=Br <sub>2</sub> -I, -OSO <sub>2</sub> R, etc	R'O <sup>⊖</sup> Na <sup>⊕</sup>	R-O-R'	Nucleophilic substitution	Williamson synthesis
3.	2RX	Ag <sub>2</sub> O/Δ	R-O-R + 2AgX	Nucleophilic substitution	

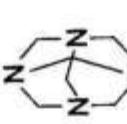
S.No	Reactants	Reagent	Products	Mechanism involved	Name of reaction
4.	$\text{R}-\text{CH}_2-\text{OH}$	Jones reagent ( $\text{CrO}_3/\text{H}_2\text{SO}_4$ ) or $\text{H}_2\text{CrO}_4/\text{acetone}$	$\begin{matrix} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{matrix}$	Oxidation	
	$\begin{matrix} \text{R} &   \\ & \text{C}-\text{OH} \\ &   \\ & \text{R} \end{matrix}$	Sarret's reagent ( $\text{CrO}_3/\text{C}_2\text{H}_5\text{N}$ ) Collin's reagent ( $\text{PCC}/\text{CH}_2\text{Cl}_2$ ) $\text{MnO}_2$ , etc	$\begin{matrix} \text{R} & >\text{C}=\text{O} \\ &   \end{matrix}$	Oxidation	
5.	$\begin{matrix} \text{R}-\text{CH}_2-\text{OH} \\ \text{R}>\text{CH}-\text{OH} \\   \\ \text{R}-\text{C}-\text{OH} \\   \\ \text{R} \end{matrix}$	$\text{Cu}/\Delta$	$\begin{matrix} \text{O} \\ \parallel \\ -\text{C}-\text{H} \end{matrix}$	Oxidation	Dehydrogenation
		$\text{Cu}/\Delta$	$>\text{C}=\text{O}$	Oxidation	Dehydrogenation
6.	$>\text{C}=\text{O}$	$\text{NaBH}_4, \text{LiAlCH}_4$	$>\text{CH}-\text{OH}$	Reduction	
7.	$\begin{matrix}   &   \\ -\text{C}-\text{C}- \\   &   \\ \text{OH} & \text{OH} \end{matrix}$	$\text{HIO}_4$ or $\text{Pb(OAc)}_4$	$>\text{C}=\text{O} + \text{O}=\text{C}<$	Oxidation	Oxidative cleavage of glycol (malaprade oxidation)
8.	$\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-$ or $\text{CH}_3-\overset{\text{OH}}{\underset{\parallel}{\text{C}}}-$	$\text{I}_2/\text{NaOH}$ or $\text{NaOI}$ or $\text{NaIO}_3$ or $\text{IO}^\ominus$ or $\text{IO}_3^\ominus$	$\begin{matrix} \text{O} \\ \parallel \\ \text{CH}_3+\text{C}-\text{ONa} \end{matrix}$		Iodoform test
9.	$\text{R}-\text{O}-\text{R}'$	$\text{HI}/\Delta$	$\text{R}-\text{OH} + \text{R}'-\text{I}$	Nucleophilic substitution	
		$\text{HI}_{(\text{excess})}/\Delta$	$\text{R}-\text{I} + \text{R}'-\text{I}$	Nucleophilic substitution	
10.	$\text{R}-\text{OH}$	$\text{NaBr}/\text{H}_2\text{SO}_4$ or $\text{HBr}$	$\text{R}-\text{Br}$	Nucleophilic substitution	

S.No	Reactants	Reagent	Products	Mechanism involved	Name of reaction
11.	R—OH	KI/H <sub>3</sub> PO <sub>4</sub> or HI	R—I	Nucleophilic substitution	
12.	R—OH	HCl/anhyd ZnCl <sub>2</sub> (Lucas reagent)	R—Cl	Nucleophilic substitution	Groove's process
13.	CH <sub>2</sub> OH CHOH CH <sub>2</sub> OH	Conc. H <sub>2</sub> SO <sub>4</sub> /Δ	CH <sub>2</sub> =CH—C(=O)H (acrolein)	Dehydration reaction	
14.	CH <sub>2</sub> OH CHOH CH <sub>2</sub> OH	3HI	CH <sub>2</sub> =CH—CH <sub>3</sub> —I CH <sub>3</sub> >CH—I CH <sub>3</sub>	Nucleophilic substitution	
15.			OH   C <sup>14</sup> H <sub>2</sub> —CH=CH <sub>2</sub>	Rearrangement reaction	Claisen rearrangement
16.		Δ/200–250°C	OH   C(=O)CH <sub>3</sub>   O—C(=O)CH <sub>3</sub>	Rearrangement reaction	Fries rearrangement

## 24.28 ALDEHYDE AND KETONE

S.No	Reactants	Reagent	Products	Mechanism Involved	Name of Reaction
1.	$\text{R}-\overset{\text{O}}{\underset{  }{\text{C}}}-\text{O}-\text{H}$	$\text{R}-\text{Li}_{(\text{excess})}/\text{H}_3\text{O}^+$	$\text{R}-\overset{\text{O}}{\underset{  }{\text{C}}}-\text{R}$	Nucleophilic addition	
2.	$-\text{C}\equiv\text{C}-$ $\text{O}$ $-\overset{\text{O}}{\underset{  }{\text{C}}}-\text{CH}_2-$	$\text{SeO}_2$	$\begin{array}{c} \text{O} \quad \text{O} \\    \quad    \\ \text{C}-\text{C} \\    \quad    \\ \text{O} \quad \text{O} \\    \quad    \\ \text{C}-\text{C} \end{array}$	Oxidation	Methylene oxidation
3.	$\text{Ar}-\overset{\text{O}}{\underset{  }{\text{C}}}-\text{CH}_3$	$\text{SeO}_2$	$\begin{array}{c} \text{O} \quad \text{O} \\    \quad    \\ \text{C}-\text{C} \\    \quad    \\ \text{O} \quad \text{O} \\    \quad    \\ \text{C}-\text{C} \end{array}$	Oxidation	Etard's reaction
4.	$\text{Ar}-\overset{\text{O}}{\underset{  }{\text{C}}}-\text{H}$	$\text{CrO}_2\text{Cl}_2/\text{H}_2\text{O}/$ Pyridine	$\begin{array}{c} \text{O} \quad \text{O} \\    \quad    \\ \text{Ar}-\text{CH}-\text{OCl}_2\text{OH} \\    \quad    \\ \text{O} \quad \text{O} \\    \quad    \\ \text{C}-\text{H} \end{array}$	$\xrightarrow{\text{H}_2\text{O}}$ Oxidation	Resenmund's reaction
5.	$\text{R}-\overset{\text{O}}{\underset{  }{\text{C}}}-\text{X}$	$\text{KMnO}_4/\Delta$	$\begin{array}{c} \text{O} \\    \\ \text{Ar}-\overset{\text{O}}{\underset{  }{\text{C}}}-\text{OH} \\    \\ \text{O} \\    \\ \text{C}-\text{H} \end{array}$	Oxidation	Stephen's reduction
6.	$\text{R}-\overset{\text{O}}{\underset{  }{\text{C}}}-\text{CN}$	$\text{Pd/BaSO}_4/\text{Quincline}/$ Boiling xylene	$\begin{array}{c} \text{O} \\    \\ \text{R}-\overset{\text{O}}{\underset{  }{\text{C}}}-\text{H} \\    \\ \text{O} \\    \\ \text{C}-\text{H} \end{array}$	Partial reduction	Pinnacol - Pinnacolone rearrangement
7.	$\text{R}'\overset{\text{O}}{\underset{  }{\text{C}}}\text{R}''$	1. $\text{SnCl}_4/\text{HCl}$ 2. $\text{H}_3\text{O}^+$	$\begin{array}{c} \text{O} \\    \\ \text{R}'\overset{\text{O}}{\underset{  }{\text{C}}}\text{R}'' \\    \\ \text{R}'' \end{array}$	Rearrangement reaction	Cumene-hydroperoxide rearrangement

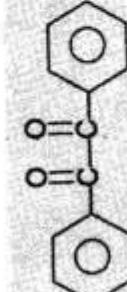
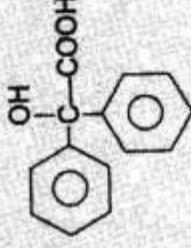
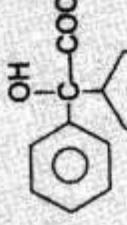
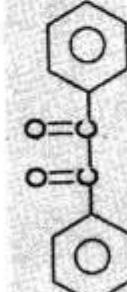
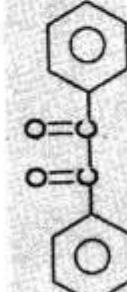
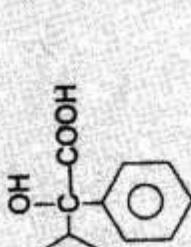
S.No	Reactants	Reagent	Products	Mechanism Involved	Name of Reaction
8.		Alc. aq. KCN/ $\Delta$		Disproportionation	Benzoin condensation
9.		$\text{H}_3\text{C}-\overset{\text{O}}{\underset{\text{C}-\text{H}}{\text{C}}}-\text{H}/\text{NaOH}_{(\text{aq})}/\Delta$		Condensation	Cross aldol condensation
10.		Dil. NaOH/Cold		Nucleophilic addition	Aldol addition
11.		1. Conc. NaOH/ $\Delta$ 2. $\text{H}^{\oplus}$		Disproportionation	Cannizzaro reaction
12.		1. $\text{H}-\overset{\text{O}}{\underset{\text{C}-\text{H}}{\text{C}}}-\text{H}/\text{Conc.NaOH}/\Delta$ 2. $\text{H}^{\oplus}$		Disproportionation	Cross Cannizzaro reaction
13.		$\text{Al(OEt)}_3$		Disproportionation	Tischchenko reaction
14.	$\text{R}'>\text{C}=\text{O} + \text{Z} - \text{CH}_2 - \text{Z}'$ (active methylene compound)	$\text{NaOH}_{(\text{aq})}$ or $\text{R}_2\text{NH}$ or $\text{R}_3\text{N}$		Condensation	Knowles's reaction
15.		$\text{R}-\text{CH}_2-\text{COOK}$		Nucleophilic addition, then dehydration and then hydrolysis	Perkin's condensation

S.No	Reactants	Reagent	Products	Mechanism Involved	Name of Reaction
16.	$\text{C}(=\text{O})\text{Cl} + \text{CH}_2=\text{COOC}_2\text{H}_5$	$\text{C}_2\text{H}_5\text{ONa}$	$\begin{array}{c} \text{O} \\    \\ \text{C}-\text{C}-\text{CH}_2-\text{COOC}_2\text{H}_5 \end{array}$	Condensation	Darzen's glycidic ester condensation
17.	$>\text{C}=\text{O}$	$\text{NaHSO}_3$	$\begin{array}{c} \text{O} \\    \\ \text{C}-\text{C}-\text{SO}_3\text{Na} \end{array}$ (White crystalline adduct)	Nucleophilic addition	Bisulphite addition (characteristics test)
18.	$\begin{array}{c} \text{H} \\   \\ >\text{C}=\text{O} \end{array}$	$\text{NH}_3$	 Hexamethylene tetraamine	Nucleophilic addition	Urotropine formation (urinary antiseptic)
19.	$\begin{array}{c} \text{R} \\   \\ >\text{C}=\text{O} \\   \\ \text{R} \end{array}$		$\begin{array}{c} \text{H}_3\text{C}-\text{CH}(\text{OH})-\text{CH}_3 \\   \\ \text{R}-\text{CH}-\text{R}+\text{CH}_2-\text{C}(=\text{O})-\text{CH}_3 \\   \\ \text{OH} \end{array}$ $\text{Al}[\text{OCH}(\text{CH}_3)_2]_3$	Oxidation reduction	Meerwein - Ponndorf - Verley reduction or Oppenauer oxidation
20.	$>\text{C}=\text{O}$		1. $\begin{array}{c} \text{C}-\text{COOC}_2\text{H}_5/\text{Zn} \\   \\ \text{Br} \end{array}$ 2. $\text{H}_2\text{O}/\text{NH}_4\text{Cl}$	Condensation	Reformatsky reaction
21.	$>\text{C}=\text{O}$		$\begin{array}{c} \text{NH}_2-\text{NH}_2 \\   \\ >\text{C}=\text{N}-\text{Z} \end{array}$ $\begin{array}{c} \text{NH}_2-\text{NH}_2 \\   \\ >\text{C}=\text{N}-\text{OH} \end{array}$	Condensation Axime formation Hydrazone formation	

S.No	Reactants	Reagent	Products	Mechanism Involved	Name of Reaction
22.	$>\text{C}=\text{O}$	$\text{NH}_2-\text{R}$ $\text{NH}_2-\text{NH}-\phi$ $\text{NH}_2-\text{NH}-\text{CONH}_2$	$>\text{C}=\text{N}-\text{R}$ $>\text{C}=\text{N}-\text{NH}-\phi$ $>\text{C}=\text{N}-\text{NH}-\text{CONH}_2$	— — —	Imine formation Phenylhydrazone Semi carbazole

## 24.29 CARBOXYLIC ACIDS AND THEIR DERIVATIVES

S.No	Reactants	Reagent	Products	Mechanism involved	Name of reaction
23.	$\text{R}-\text{CN}$	$\text{H}^+/\text{H}_2\text{O}$	$\begin{matrix} \text{O} \\    \\ \text{R}-\text{C}-\text{OH} \end{matrix}$	— — —	Hydrolysis
24.	$\begin{matrix} \text{O} \\    \\ \text{R}-\text{C}-\text{Cl} \end{matrix}$	$\text{H}_2\text{O}/\text{H}^\oplus$ or $\text{OH}^\ominus$	$\begin{matrix} \text{O} \\    \\ \text{R}-\text{C}-\text{OH} \end{matrix}$	Nucleophilic acyl substitution	Hydrolysis
25.	$\begin{matrix} \text{O} \\    \\ \text{R}-\text{C}-\text{O}-\text{C}-\text{R} \end{matrix}$	$\text{H}_2\text{O}/\text{H}^\oplus$	$\begin{matrix} \text{O} \\    \\ \text{R}-\text{C}-\text{OH} \end{matrix}$	Nucleophilic acyl substitution	Hydrolysis
26.	$\begin{matrix} \text{O} \\    \\ \text{R}-\text{C}-\text{OH} \end{matrix}$	$\text{R}'-\text{OH}/\text{H}^\oplus$	$\begin{matrix} \text{O} \\    \\ \text{R}-\text{C}-\text{O}-\text{R}' \end{matrix}$	Nucleophilic acyl substitution	Fischer-Spiersynthesis
27.	$\begin{matrix} \text{O} \\    \\ \text{R}-\text{C}-\text{O}-\text{R}' \end{matrix}$	$\text{H}_2\text{O}/\text{H}^\oplus$ or $\text{OH}^\ominus$	$\begin{matrix} \text{O} \\    \\ \text{R}-\text{C}-\text{OH}+\text{R}'-\text{OH} \end{matrix}$	Nucleophilic acyl substitution	De-esterification
28.	$\begin{matrix} \text{O} \\    \\ \text{CH}_3-\text{C}-\text{O}-\text{C}_2\text{H}_5 \end{matrix}$ Ester containing $\alpha$ -H	$\text{C}_2\text{H}_5\text{ONa}$	$\begin{matrix} \text{O} \\    \\ \text{CH}_3-\text{C}-\text{O}-\text{C}_2\text{H}_5 \end{matrix}$	Nucleophilic acyl substitution	Claisen condensation

S.No	Reactants	Reagent	Products	Mechanism involved	Name of reaction
29.	$R>C=O$ $R>C=O$	$\begin{array}{c} O \\    \\ R-C-O-O-H \end{array}$ or $H_2SO_5$ or $BF_3H_2O_2$	$\begin{array}{c} O \\    \\ R-C-O-R' \end{array}$	Rearrangement reaction	Baeyer–Villiger oxidation
30.		1. Conc. KOH or NaOH 2. $H^+$		Rearrangement reaction	Benzilic rearrangement
31.		$Br_2/KOH/\Delta$	$R-NH_2$	Rearrangement reaction	Hofmann's bromamide synthesis
32.		$NaHCO_3$	$\begin{array}{c} O \\    \\ R-C-O-Na^+CO_2^- \\ \text{effervescence} \end{array}$	Salt formation	Analytical test of carboxylic acid
33.		$NaOH/NaOH$		Nucleophilic acyl substitution	Schotten–Baumann reaction

### 24.30 AMINES AND NITRO COMPOUNDS

S.No	Reactants	Reagent	Products	Mechanism involved	Name of Reaction
1.	$\begin{array}{c} O \\    \\ R-C-Cl \end{array}$	1. $NaN_3/\Delta$ 2. $H_2O$	$R-NH_2 + CO_2$	Nucleophilic acyl substitution then Rearrangement	Curtius rearrangement

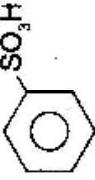
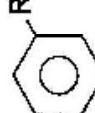
S.No	Reactants	Reagent	Products	Mechanism involved	Name of Reaction
2.	$\begin{matrix} \text{O} \\    \\ \text{R}-\text{C}-\text{OH} \end{matrix}$	1. $\text{N}_3\text{H}/\text{H}^+$ 2. $\text{H}_2\text{O}$	$\text{R}-\text{NH}_2 + \text{CO}_2$	Rearrangement reaction	Schmidt's rearrangement
3.	$\begin{matrix} \text{O} \\    \\ \text{R}-\text{C}-\text{NH}-\text{O}-\text{C}-\text{R} \end{matrix}$	1. $\text{OH}^{\ominus}/\Delta$ 2. $\text{H}_2\text{O}$	$\text{R}-\text{NH}_2 + \text{CO}_2$	Rearrangement reaction	Lossen rearrangement
4.	$\begin{matrix} \text{O} \\    \\ \text{R}-\text{C}-\text{O}-\text{C}-\text{R} \end{matrix}$	1. $\text{NH}_3$ 2. $\text{H}_2/\text{Ni}$	$\text{>CH=NH}_2$	Nucleophilic addition elimination	Reductive amination
5.	$\begin{matrix} \text{O} \\    \\ \text{R}-\text{C}-\text{O}-\text{H} \end{matrix}$	$\text{NH}_3/\Delta$	$\begin{matrix} \text{O} \\    \\ \text{R}-\text{C}-\overset{\oplus}{\text{ONH}_4} \xrightarrow{\Delta} \text{R}-\overset{\ominus}{\text{C}}-\text{NH}_2 \\ \downarrow \text{P}_2\text{O}_5/\Delta \\ \text{R}-\text{C}\equiv\text{N} \end{matrix}$	Nucleophilic substitution	-----
6.	$\begin{matrix} \text{O} \\    \\ \text{R}-\text{C}-\text{O}-\text{C}-\text{R} \end{matrix}$	Conc. $\text{HCl}$ or $\text{H}_2\text{SO}_4$	$\begin{matrix} \text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2 \\ + (\sim 70\%) \\ \text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2 \\ \text{H}_2\text{N} (\sim 30\%) \end{matrix}$	Rearrangement reaction	Benzidine rearrangement
7.	$\text{R}-\text{N}=\text{C}=\text{O}$	$\text{R-OH}$	$\text{R}-\text{NH}-\overset{\oplus}{\text{C}}(\text{OR})-\text{OR}$	Addition	Alcohololysis
8.	$\text{R}-\text{C}\equiv\text{N}$	$\text{Na/C}_2\text{H}_5\text{OH}$	$\text{R}-\text{CH}_2-\text{NH}_2$	Reduction	Mendius reduction
9.	$\text{R}-\text{NH}_2$ or $\text{Ar-NH}_2$	$\text{CHCl}_3/\text{alc. KOH}$	$\text{R}-\text{NC}$ or $\text{Ar-NC}$	Carbene addition	Carbyl amine test
10.	$\begin{matrix} \text{O} \\    \\ \text{R}-\text{C}-\text{N}-\text{C}-\text{R} \end{matrix}$	$\text{KOH}$	$\begin{matrix} \text{O} & \text{O} \\    &    \\ \text{R}-\text{C}-\text{N}^{\oplus}-\text{C}-\text{R} & \text{C}-\text{N}-\text{R} \\    &    \\ \text{O} & \text{O} \\ \text{(A)} & \text{(B)} \end{matrix} \xrightarrow{\text{H}_2\text{O}/\text{OH}^{\ominus}/\Delta} \text{C}_6\text{H}_4-\text{COOH} + \text{RNH}_2$	$\begin{matrix} \text{O} \\    \\ \text{R}-\text{C}-\text{N}^{\oplus}-\text{C}-\text{R} \\    \\ \text{O} \\ \text{(C)} \end{matrix}$	Gabriel - Phthalimide synthesis

S.No	Reactants	Reagent	Products	Mechanism involved	Name of Reaction
11.		Sn/HCl or Zn/HCl or Fe/HCl		Reduction reaction	
12.		NH3/H2S or (NH4)2Sx		Selective reduction	
13.		LiAlH4		Reduction reaction	

### 24.31 AROMATIC COMPOUNDS

S.No	Reactants	Reagent	Products	Mechanism Involved	Name of Reaction
1.		1. HCN/HCl/AlCl3 2. H2O		ArSE	Gattermann-aldehyde synthesis
2.		CO/HCl/AlCl3		ArSE	Gattermann-koch formylation
3.		Conc. HNO3/Conc. H2SO4		ArSE	Nitration

ArSE → Electrophilic aromatic substitution  
 ArSN → Nucleophilic aromatic substitution

S.No	Reagents	Products	Mechanism Name of Involved Reaction
4.	$X_2CS_2$ or $FeX_3$		ArSE
5.	Conc. $H_2SO_4$ or fuming $H_2SO_4$		Sulphonation
7.	$Cl_2/AlCl_3$		Friedel-Crafts alkylation
8.	$Cl_2/AlCl_3$		Friedel-Crafts acylation
9.	$Cu/HCl$		Getermann's reaction
10.	$N_2Cl$ or $Cu_2O/H_2O/A$		ArSN

ArSE → Electrophilic aromatic substitution  
 ArSN → Nucleophilic aromatic substitution

S.No	Reactants	Reagent	Products	Mechanism Involved	Name of Reaction
11.		$\text{Br}_2/\text{H}_2\text{O}$		ArSE	Bromination
12.		$\text{HBF}_4$ or $\text{BF}_3/\text{HF}$		ArSN	Balze-Schiemann reaction
13.		$\text{CuX}/\text{HX}$ , where $\text{X} = \text{Cl}, \text{Br}, \text{CN}$		ArSN	Sandmeyer's reaction
14.		KI		ArSN	-----
15.		$\text{H}_3\text{PO}_4/\Delta$		ArSN	Deamination
16.		$\text{H}-\overset{\text{O}}{\underset{\text{C}-\text{H}}{\text{C}}}+\text{HCl}/\text{anhyd ZnCl}_2$		ArSE	Chloromethylation or Blance reaction
17.				ArSE	Diazocoupling
18.	$2\text{Ar-I}$	$\text{Cu}/\Delta$		Ar-Ar	Ullmann reaction

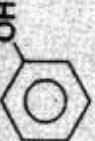
ArSE  $\rightarrow$  Electrophilic aromatic substitution  
 ArSN  $\rightarrow$  Nucleophilic aromatic substitution

S.No	Reactants	Reagent	Products	Mechanism Involved	Name of Reaction
19.		NaNO <sub>2</sub> /HCl/0-5°C NaNO <sub>2</sub> /HCl NaNO <sub>2</sub> /HCl		-----	Diazotization
	R-NH <sub>2</sub> , R-NH-R	R-OH R-N—N=O		---	ArSN
20.		Zn dust		Reduction	-----
21.		1. CCl <sub>4</sub> /NaOH <sub>(aq)</sub> 2. H <sup>⊕</sup>	 	-----	Reimer-Tiemann reaction
22.		1. CHCl <sub>3</sub> /NaOH <sub>(aq)</sub> 2. H <sup>⊕</sup>	 	-----	Reimer-Tiemann reaction
23.		1. CO <sub>2</sub> /NaOH <sub>(aq)</sub> 2. H <sup>⊕</sup>	 	ArSE	Kolbe-Schmidt's reaction

ArSE → Electrophilic aromatic substitution  
 ArSN → Nucleophilic aromatic substitution

S.No	Reactants	Reagent	Products	Mechanism Involved	Name of Reaction
24.		Neutral $\text{FeCl}_3$ in $\text{C}_2\text{H}_5\text{OH}$	$(\text{C}_6\text{H}_5\text{-O})_2\text{Fe}$ reduction violet colour	-----	Analytical test for enol form
25.	+ $\text{R}-\text{X}$	Na/dry ether		Free radical mechanism	Wurtz-Fittig reaction
26.	+	Na/dry ether		Free radical mechanism	Fittig reaction
27.		$\text{H}-\text{C}(=\text{O})-\text{H}/\text{H}^\oplus \text{ or } \text{OH}^\ominus$	Bakelite (cross-linked polymer)	ArSE	Ladener-Manase reaction
28.		$\text{Cl}-\text{C}(=\text{O})-\text{H}/\text{Conc. CH}_2\text{SO}_4$		DDT formation	DDT formation (powerful insecticide)
					Addition

$\text{ArSE} \rightarrow$  Electrophilic aromatic substitution  
 $\text{ArSN} \rightarrow$  Nucleophilic aromatic substitution

S.No	Reactants	Reagent	Products	Mechanism Involved	Name of Reaction
29.		Na/NH <sub>(3,0)</sub> or C <sub>2</sub> H <sub>5</sub> OH		Free radical addition	Birch reduction
30.	 Having no α-H	KMnO <sub>4</sub> /Δ or K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> /Δ (vigorous heating)			Oxidation
31.	 + 2HCl + O <sub>2</sub>	CuCl <sub>2</sub> /Δ			Raschig method
32.		1. 2NaOH/350°C/high P 2. H <sup>+</sup>		ArSN	Dow's process
33.	 SO <sub>3</sub> Na	1. NaOH/Δ 2. HCl <sub>(aq)</sub>		ArSN	
	 SO <sub>3</sub> Na	1. NaCN/Δ		ArSN	
	 SO <sub>3</sub> Na	H <sub>2</sub> O/H <sup>+</sup>		ArSN	
	 SO <sub>3</sub> Na	NaNH <sub>2</sub> /Δ		ArSN	
	 SO <sub>3</sub> Na	1. HCOONa/Δ 2. dil. HCl		ArSN	
	 SO <sub>3</sub> Na	NaSH/Δ		ArSN	

ArSE → Electrophilic aromatic substitution  
 ArSN → Nucleophilic aromatic substitution

S.No	Reactants	Reagent	Products	Mechanism Involved	Name of Reaction
34.		$\text{NaNO}_2$ $\xrightarrow{\text{Conc. H}_2\text{SO}_4}$	deep green blue colour red colour deep blue colour		Liebermann's nitroso-test
35.		$\text{O}/\text{conc. H}_2\text{SO}_4$		ArSE	
36.		$\text{O}_2(\text{air})/\text{CrO}_3/\text{CrO}_2\text{Cl}_2$		Oxidation	
37.		$\text{Hg(OAc)}_2/\text{H}^+$		ArSE	Mercuration
38.		$\text{Ti(OCOCF}_3)_2/\text{H}^+$		ArSE	Thalluation
39.		$\text{Ti(OCOCF}_3)_2$		ArSN	

ArSE → Electrophilic aromatic substitution  
 ArSN → Nucleophilic aromatic substitution

**BIOMOLECULES****25.1 DEFINITION OF CARBOHYDRATES**

Optically active polyhydroxy aldehydes or polyhydroxy ketones or compounds which give such compounds on hydrolysis are called carbohydrates.

**25.2 CLASSIFICATION OF CARBOHYDRATES**

They are of three types.

**25.2.1 Monosaccharides**

- Simplest carbohydrates which cannot be hydrolyzed into simpler compounds belongs to this category.
- E.g., glucose, mannose, galactose, ribose, etc. There are 20 naturally occurring monosaccharides.

**25.2.2 Oligosaccharides**

- Carbohydrates which give 2 to 10 monosaccharide units on hydrolysis are called oligosaccharides.
- E.g., sucrose, lactose, maltose, etc.

**25.2.3 Polysaccharides**

- Carbohydrates which on hydrolysis give large number of monosaccharide units after hydrolysis are called polysaccharides.
- E.g., cellulose, starch, glycogen, etc.

**25.2.4 Reducing and Non-reducing Sugars**

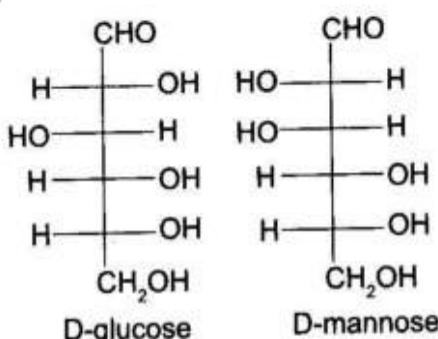
If a carbohydrate possesses hemiacetal group at anomeric carbon then it is called reducing sugar; however, if an acetal group is present at anomeric carbon it is called non-reducing sugar. All monosaccharides are reducing sugars, whereas disaccharides such as maltose, lactose, etc. are reducing sugars.

### 25.3 ANOMERS

Pair of cyclic optical isomers which differ in configuration only around C<sub>1</sub> atom are called anomers.  
E.g., α-D-glucopyranose and β-D-glucopyranose.

### 25.4 EPIMERS

Pair of optical isomers which differ in configuration around any one C atom are called epimers.  
E.g., D-glucose and D-mannose are C<sub>2</sub> epimers. All anomers are epimers but the converse is not always true. All epimers are diastereomers.

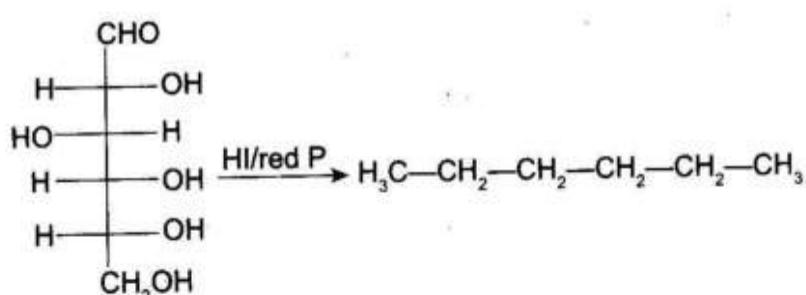


#### 25.4.1 Preparation of Glucose (Also Called Dextrose, Grape Sugar)

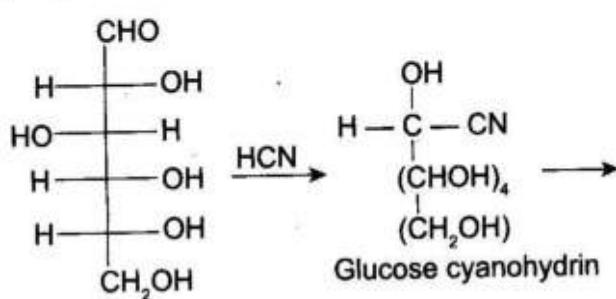
1. From sucrose:  $C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{Sucrose}]{H^+ \text{ or } \text{Invertase}} C_6H_{12}O_6 + C_6H_{12}O_6$  Glucose Fructose
2. From starch:  $(C_6H_{10}O_5)_n + nH_2O \xrightarrow[\text{Sucrose or cellulose}]{H^+, 393K, 2-3atm} nC_6H_{12}O_6$  Glucose

### 25.5 STRUCTURAL ANALYSIS OF GLUCOSE

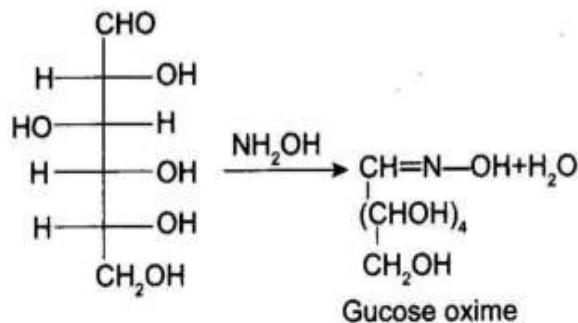
- (i) Presence of 6 carbons linked directly



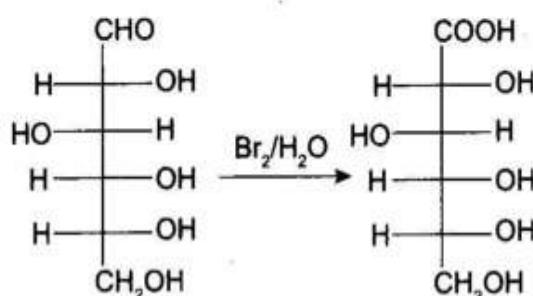
- (ii) Presence of carboxyl group in open chain structure



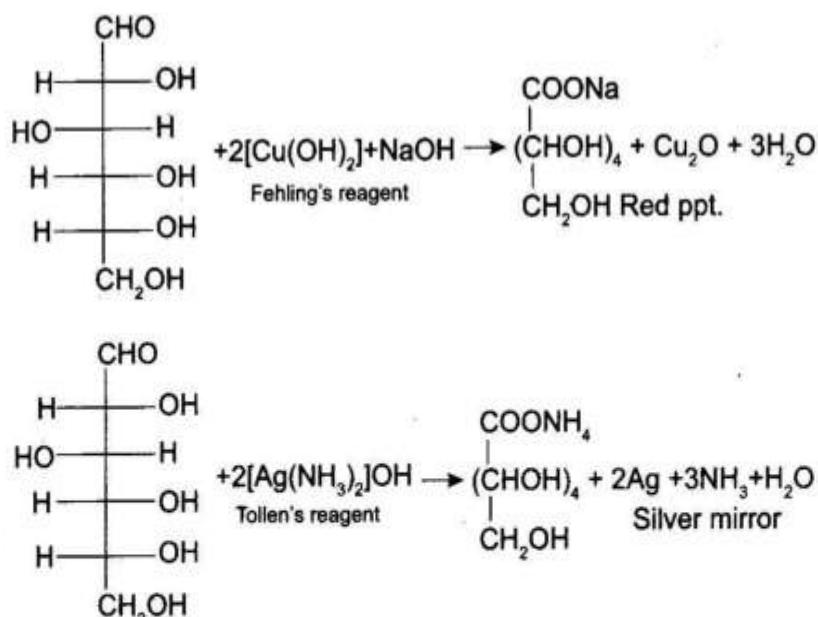
(iii) Presence of carbonyl group in open chain structure.



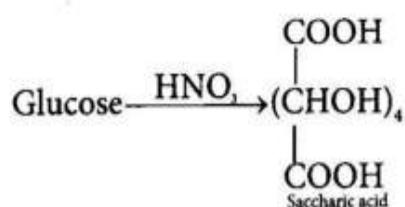
(iv) Glucose discharges the reddish brown colour of  $\text{Br}_2/\text{H}_2\text{O}$ . This indicates that it possesses  $\text{-C}(=\text{O})-\text{H}$  group.



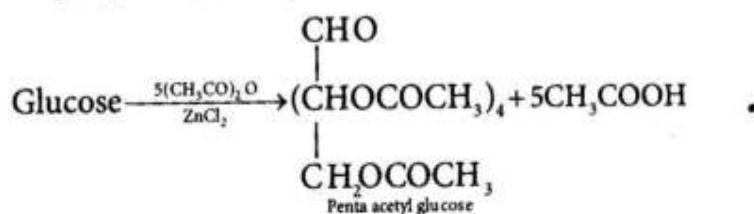
(v) Glucose is a reducing sugar, this is confirmed by treating it with Fehling's reagent and Tollen's reagent.



(vi) Presence of primary alcoholic group in glucose

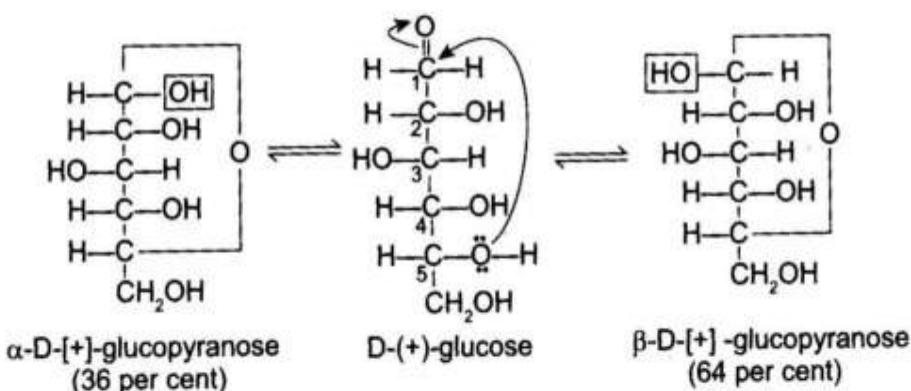


(vii) Presence of pure OH group on adjacent carbon.

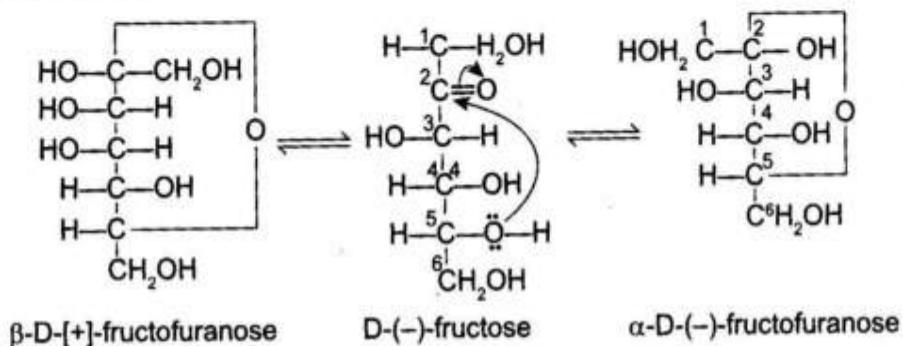


(viii) **Presence of ring structure:** Glucose does not give Schiff's test and does not react with sodium bisulphite and  $\text{NH}_3$ . Pentaacetyl glucose does not react with hydroxyl amine. This shows the absence of  $-\text{CHO}$  group and hence the presence of ring structure.

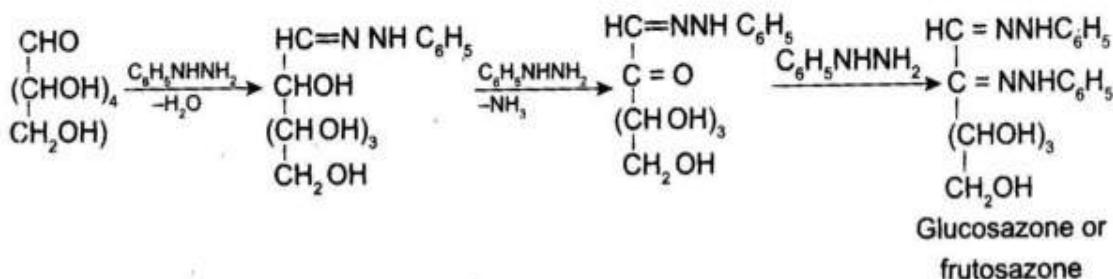
## 25.6 CYCLIC STRUCTURE OF GLUCOSE



## 25.7 CYCLIC STRUCTURE OF FRUCTOSE



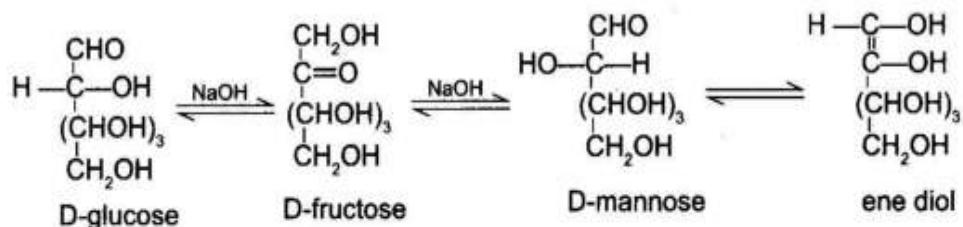
## 25.8 REACTION OF GLUCOSE WITH PHENYL HYDRAZINE FORMATION OF OSAZONE



Glucose and fructose give the same osazone because the reaction takes place at C<sub>1</sub> and C<sub>2</sub> only.

## 25.9 LOBRY DE BRUYN VAN EKENSTEIN REARRANGEMENT

Glucose, fructose and mannose are interconvertible because of formation of ene diol intermediate. This explains why fructose acts as a reducing sugar.



- Aldoses can be distinguished from ketones by  $\text{Br}_2/\text{H}_2\text{O}$  as aldoses discharge the colour of  $\text{Br}_2/\text{H}_2\text{O}$  but ketones does not.

## 25.10 MUTAROTATION

Slow but spontaneous change in specific rotation of an optically active pure compound is called mutarotation. E.g.,  $\alpha$ -D-glucose with specific rotation  $[\alpha]_D = +111^\circ$  and  $\beta$ -D-glucose with specific rotation  $[\alpha]_D = +19.2^\circ$ . When either form is dissolved in water and allowed to stand, the specific rotation of the solution changes slowly and reaches a constant value of  $+52.5^\circ$ .

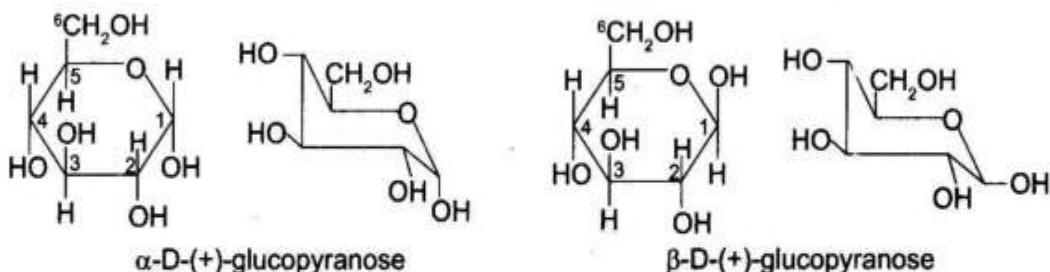
$\alpha$ -D-glucose = open chain form =  $\beta$ -D-glucose.

$$[\alpha] = 111^\circ \quad [\alpha] = +52.5^\circ \quad [\alpha] = +19^\circ$$

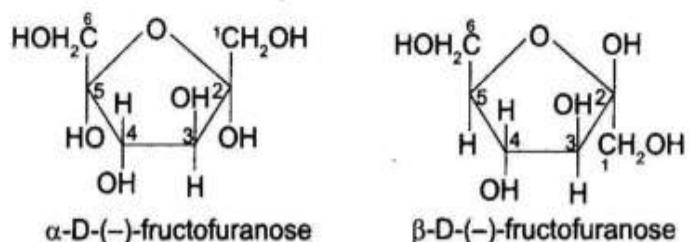
## 25.11 HAWORTH PROJECTION

Ring structure of glucose and fructose is also represented in terms of Haworth projection. Six-membered ring is called pyranose ring, whereas five-membered ring is called furanose ring.

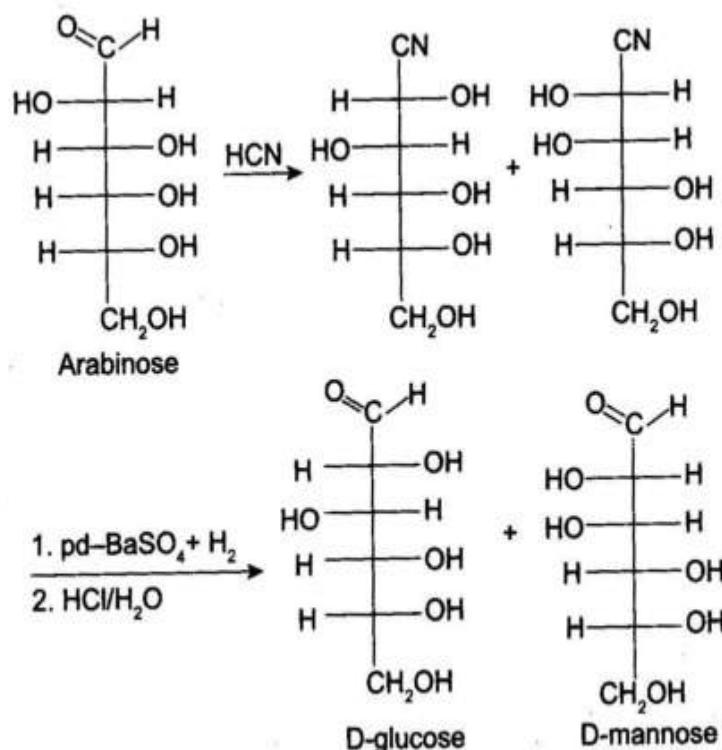
**In Haworth projection:** Groups projected to the right in the Fischer projection are written below the plane and those to the left are written above the plane. Haworth projection of glucose:



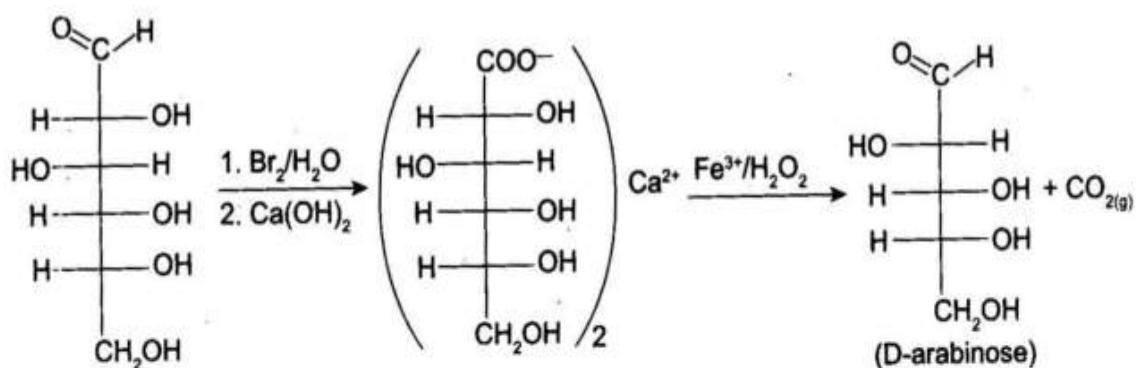
### 25.11.1 Haworth Projection for Fructose



### 25.11.2 Kiliani-Fischer Synthesis



### 25.11.3 Ruff Degradation

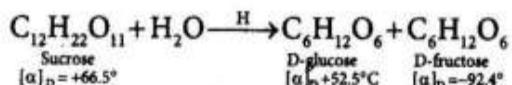


## 25.12 GLYCOSIDIC LINKAGE

The oxide linkage formed by the loss of a water molecule when two monosaccharides are joined together through oxygen atom is called glycosidic linkage.

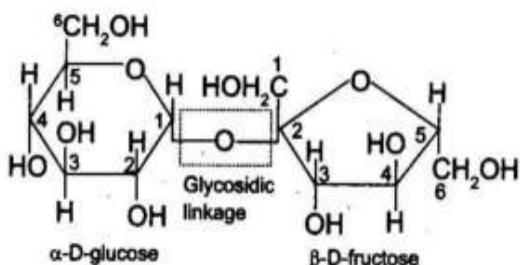
### 25.12.1 Sucrose (Invert Sugar)

Sucrose is dextrorotatory but on hydrolysis it gives dextrorotatory glucose and laevorotatory fructose and the mixture is laevorotatory because laevo rotation of fructose dominates over dextro rotation of glucose.



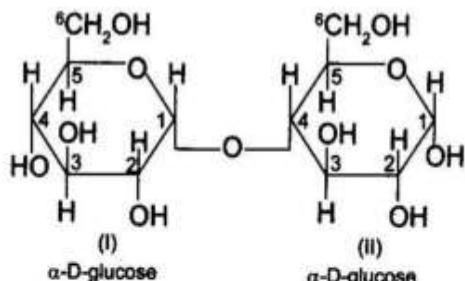
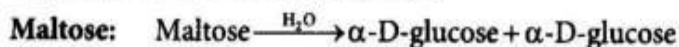
Sucrose is a non-reducing sugar because the two monosaccharide units are held together by a glycosidic linkage between C<sub>1</sub> of α-glucose and C<sub>2</sub> of β-fructose. Since the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non-reducing sugar.

### 25.12.2 Haworth Projection of Sucrose



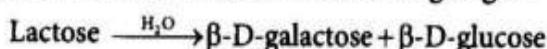
### 25.13 MALTOSE

**Maltose** is composed of two  $\alpha$ -D-glucose units in which C<sub>1</sub> of one glucose is linked to C<sub>4</sub> of another glucose unit. The free aldehyde group can be produced at C<sub>1</sub> of second glucose in solution and as it shows reducing properties it is a reducing sugar.

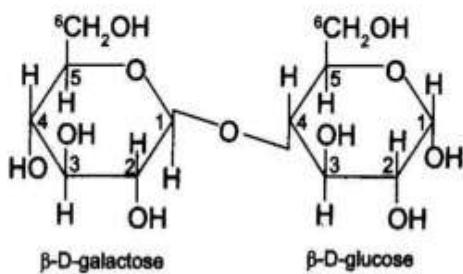


### **25.14 LACTOSE (MILK SUGAR)**

It is composed of  $\beta$ -D-galactose and  $\beta$ -D-glucose. The linkage is between C<sub>1</sub> of galactose and C<sub>4</sub> of glucose. Hence it is also a reducing sugar.



### Haworth projection of lactose



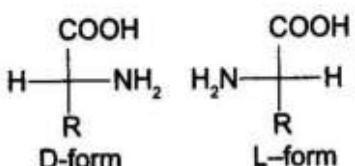
## 25.15 STARCH

It is a polymer of  $\alpha$ -glucose and consists of two components, amylose and amylopectin.

Amylose	Amylopectin
It is water soluble	It is water insoluble
<b>A long unbranched chain polymer</b>	<b>A branched chain polymer</b>
Contains 200–1000 $\alpha$ -D-(+)-glucose units held by linkages involving C1–C4 glycosides.	It is a branched chain polymer of $\alpha$ -D-glucose units in which chain is formed by C1–C4 glycosidic linkage, whereas branching occurs by C1–C6 glycosidic linkage.
<b>It constitutes about 15–20% of starch</b>	<b>It constitutes about 80–85 per cent of starch</b>

## 25.16 AMINO ACIDS

Compounds containing both amino and carboxylic group are called amino acids. In protein chemistry, only  $\alpha$ -amino acids are involved. Most naturally occurring amino acids have L-configuration. Except glycine, all other naturally occurring  $\alpha$ -amino acids are optically active.



## 25.17 ESSENTIAL AMINO ACIDS

Those amino acids which cannot be synthesized in the body and must be obtained through diet are known as essential amino acids. Examples: Valine, leucine, etc.

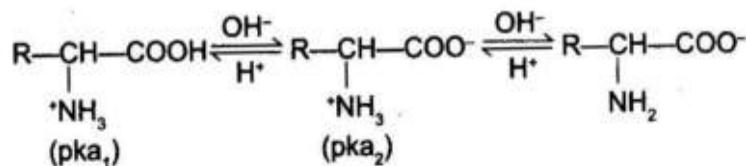
### 25.17.1 Non-essential Amino Acids

The amino acids which can be synthesized in the body are known as non-essential amino acids. Examples: Glycine, alanine, etc.

**Classification of amino acids:** Amino acids containing equal number of amino and carboxylic groups are neutral, whereas those containing greater number of carboxylic groups than amino groups are acidic and vice versa for basic amino acids.

### 25.17.2 Zwitter Ion form of Amino Acids

Amino acids behave like salts rather than simple amines or carboxylic acids. This behaviour is due to the presence of both acidic (carboxyl group) and basic (amino group) groups in the same molecule. In aqueous solution, the carboxyl group can lose a proton and amino group can accept a proton, giving rise to a dipolar ion known as zwitter ion. This is neutral but contains both positive and negative charges. In zwitter ionic form, amino acids show amphoteric behaviour as they react both with acids and bases.



### 25.17.3 Isoelectronic Point

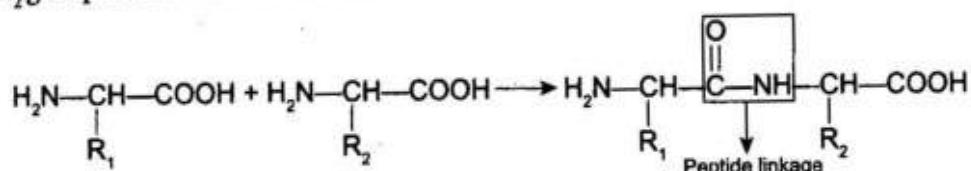
The pH at which the dipolar ion exists as a neutral ion and does not migrate to either electrode cathode or anode is called isoelectronic point.  $pI = \frac{pK_{a_1} + pK_{a_2}}{2}$

#### 25.17.4 Proteins

Proteins are the polymers of  $\alpha$ -amino acids and they are connected to each other by peptide bond or peptide linkage. A polypeptide with more than hundred amino acid residues, having molecular mass higher than 10,000 u is called a protein.

### 25.17.5 Peptide Linkage

Peptide linkage is an amide linkage formed by condensation reaction between -COOH group of one amino acid and -NH<sub>2</sub> group of another amino acid.



### 25.17.6 Classification of Proteins

**Primary structure of proteins:** The sequence of amino acids is said to be the primary structure of a protein.

**Secondary structure of proteins:** It refers to the shape in which long polypeptide chain can exist. Two different types of structures known are:

### **1. $\alpha$ -Helix structure of protein:**

- It exists when R-group is large.
  - Right-handed screw with the NH group of each amino acid residue H-bonded to Diagram = O of adjacent turn of the helix.
  - Each turn of the helix has approximately 3.6 amino acids and a 13-membered ring is formed by H-bonding.
  - The repeat distance of  $\alpha$ -helix is 5.4 Å.

## 2. $\beta$ -pleated sheet structure:

- Exists when R group is small.
  - In this conformation, all peptide chains are stretched out to nearly maximum extension and then laid side by side which are held together by hydrogen bonds. The repeat distance in  $\beta$ -pleated sheet structure is equal to 7 Å.

**Tertiary structure of proteins:** It represents the overall folding of the polypeptide chain, i.e., further folding of the 2° structure.

Types of bonding which stabilize the 3° structure:

- |  |                                    |
|--|------------------------------------|
| (i) Disulphide bridge (-S - S-)                            | (ii) H-bonding - (C = O ... H - N) |
| (iii) Salt bridge (COO <sup>-</sup> ... +NH <sub>3</sub> ) | (iv) Hydrophobic interactions      |
| (v) Van der Waal's forces                                  |                                    |

Fibrous proteins	Globular proteins
When the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, then fibre-like structure is formed.	This structure results when the chains of polypeptides coil around to give a spherical shape.
Such proteins are generally insoluble in water.	They are usually soluble in water.
Examples: keratin (present in hair, wool, silk) and myosin (present in muscles), etc.	Examples: Insulin and albumin.

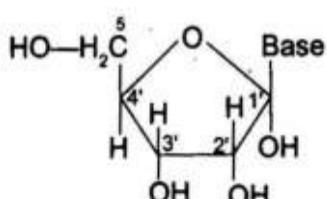
**Quaternary structure of proteins:** Some of the proteins are composed of two or more polypeptide chains referred to as subunits. The spatial arrangement of these subunits with respect to each other is known as quaternary structure of proteins.

## 25.18 DENATURATION OF PROTEINS

The loss of biological activity of proteins when a protein in its native form is subjected to physical change like change in temperature or chemical change like change in pH. This is called denaturation of protein. Examples: coagulation of egg white on boiling, curdling of milk, etc.

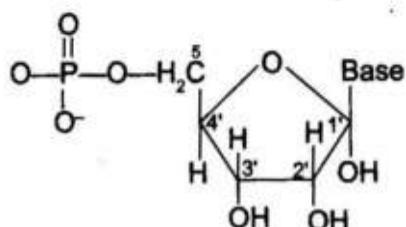
## 25.19 NUCLEOSIDE

It consists of pentose sugar β-D-ribose or β-D-2-deoxyribose and bases like purine or pyrimidine.



## 25.20 NUCLEOTIDE

It consists of nucleoside and phosphate group where phosphate is present at C5.



## 25.21 NUCLEIC ACIDS (OR POLYNUCLETIDES)

Long chain polymers of nucleotides. Nucleotides are joined by phosphodiester linkage between 5' and 3' C atoms of a pentose sugar.

### 25.21.1 Two Types of Nucleic Acids

Deoxyribonucleic Acid (DNA)	Ribonucleic Acid (RNA)
It has a double stranded $\alpha$ -helix structure in which two strands are coiled spirally in opposite directions.	It has a single stranded $\alpha$ -helix structure.
Sugar present is $\beta$ -D-2-deoxyribose	Sugar present is $\beta$ -D-ribose
Bases:	Bases:
Purine bases: Adenine (A) and guanine (G)	Purine bases: Adenine (A) and Guanine (G)
Pyrimidine bases: Thymine (T) and cytosine (C)	Pyrimidine bases: Uracil (U) and cytosine (C)
It occurs mainly in the nucleus of the cell.	It occurs mainly in the cytoplasm of the cell.
It is responsible for transmission for heredity characters.	It helps in protein synthesis.

## 25.22 DOUBLE HELIX STRUCTURE OF DNA

- It is composed of 2 right handed helical polynucleotide chains coiled spirally in opposite directions around the same central axis.
- The two strands are anti-parallel, i.e., their phosphodiester linkage runs in opposite directions.
- Bases are stacked inside the helix in planes perpendicular to the helical axis.
- Two strands are held together by H-bonds ( $A = T$ ,  $G \equiv C$ ).
- The two strands are complementary to each other because the hydrogen bonds are formed between specific pairs of bases. Adenine forms hydrogen bonds with thymine, whereas cytosine forms hydrogen bonds with guanine.
- Diameter of the double helix is 2 nm and repeat distance is equal to 3.4 nm.

### 25.22.1 Charagoff's rule

- Total amount of purine ( $A + G$ ) = Total amount of pyrimidine ( $C + T$ ).

### 25.22.2 Vitamins

Vitamins are organic compounds required in the diet in small amounts to perform specific biological functions for normal maintenance of optimum growth and health of the organism.

### 25.22.3 Classification of vitamins

Vitamins are classified into two groups depending upon their solubility in water or fat.

Fat Soluble Vitamins	Water Soluble Vitamins
These vitamins are soluble in fat and oils but insoluble in water.	These vitamins are soluble in water.
<b>They are stored in liver and adipose (fat storing) tissues</b>	<b>Water soluble vitamins must be supplied regularly in diet because they are readily excreted in urine and cannot be stored (except vitamin B<sub>12</sub>) in our body.</b>
Examples: Vitamin A, D, E and K	Examples: Vitamin C, B group vitamins

### 25.22.4 Important vitamins, their sources and their deficiency

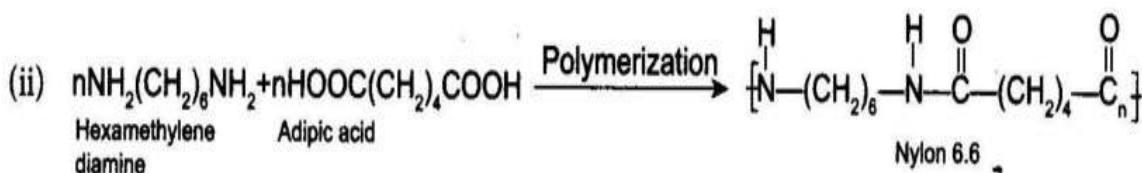
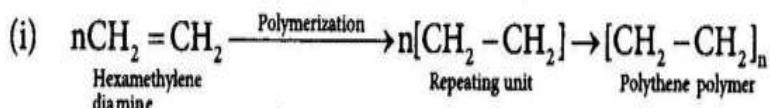
Name of Vitamin	Source	Deficiency Diseases
Vitamin A	Fish liver oil, carrots, butter and milk	Night blindness (hardening of cornea of eye)
Vitamin B1 (thiamine)	Yeast, milk, green vegetables and cereals	Beri beri (loss of appetite, retarded growth)
Vitamin B2 (riboflavin)	Milk, egg white, liver, kidney	Cheilosis (fissuring at corners of mouth and lips), digestive disorders and burning sensation of the skin.
Vitamin B <sub>6</sub> (pyridoxine)	Yeast, milk, egg yolk, cereals and grams	Convulsions
Vitamin B12	Meat, fish, egg and curd	Pernicious anaemia (RBC deficient in haemoglobin)
Vitamin C (ascorbic acid)	Citrus fruits, amla and green leafy vegetables	Scurvy (bleeding gums)
Vitamin D	Exposure to sunlight, fish and egg yolk	Rickets (bone deformities in children) and osteomalacia (soft bones and joint pain in adults)
Vitamin E	Vegetable oils like wheat germ oil, sunflower oil, etc.	Increased fragility of RBCs and muscular weakness
Vitamin K	Green leafy vegetables	Increased blood clotting time

POLYMER

## 26.1 INTRODUCTION

The word ‘polymer’ is coined from two Greek words: poly means many and mer means unit or part. These are also referred to as **macromolecules**, which are formed by joining of repeating structural units on a large scale. The repeating structural units are derived from some simple and reactive molecules known as monomers and are linked to each other by covalent bonds. This process of formation of polymers from respective monomers is called **polymerization**.

E.g., the transformation of ethene to polythene and interaction of hexamethylene diamine and adipic acid leading to the formation of nylon 6,6 are examples of two different types of polymerization reactions.



### **26.1.1 Molecular Weight of Polymer**

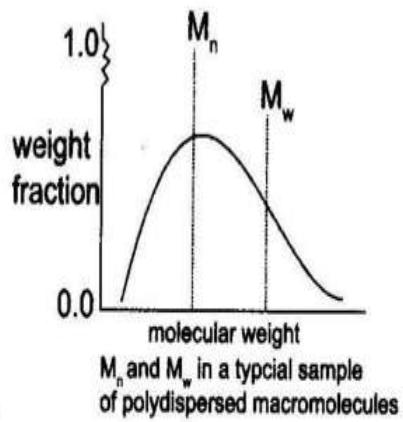
Polymer sample contains chains of varying lengths and hence its molecular mass is always expressed as an average. The molecular mass of polymer can be determined by chemical and physical methods.

**Two experimentally determined values are common:**  $M_n$ , the number average molecular weight and  $M_w$  weight average molecular weight  $M_w$ : It is the average of molecular masses of individual

$$\text{macromolecules } \bar{m}_n = \frac{\sum_i N_i M_i}{\sum_i N_i} \text{ where } N_i = \bar{m}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \text{ number}$$

of molecules of molecular masses  $M_i$ .

The ratio of mass average to the number average is called polydispersity index, e.g., If  $\frac{M_w}{M_n} = 1$ , monodisperse polymer



## 26.2 CLASSIFICATION OF POLYMERS

There are several ways of classification of polymers based on some special considerations. The following are some of the common classifications of polymers:

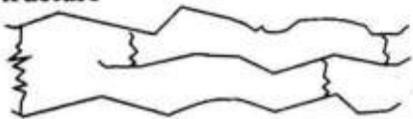
### 26.2.1 Classification Based on Source

Under this type of classification, there are three subcategories.

Natural polymers	These polymers are found in plants and animals. Examples are proteins, cellulose, starch, some resins and rubber.
Semi-synthetic polymers	Cellulose derivatives as cellulose acetate (rayon) and cellulose nitrate, etc. are the usual examples of this subcategory.
Synthetic polymers	A variety of synthetic polymers as plastic (polythene), synthetic fibres (nylon 6,6) and synthetic rubbers (Buna - S).

### 26.2.2 Classification Based on Structure of Polymers

There are three different types based on the structure of the polymers.

Linear Polymers	Branched Chain Polymers	Cross linked or Network Polymers
These polymers consist of long and straight chains.	These polymers contain linear chains having some branches	These are usually formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains,
E.g., high density polythene, polyvinyl chloride, etc.	E.g., low density polythene, etc.	E.g., bakelite, melamine, etc.
structure 	These are depicted as follows: 	Structure 

### 26.2.3 Classification Based on Mode of Polymerization

Polymers can also be classified on the basis of mode of polymerization into two sub groups.

Addition Polymers	Condensation Polymers
The addition polymers are formed by the repeated addition of monomer molecules possessing double or triple bonds, e.g., the formation of polythene from ethene and polypropene from propene.	The condensation polymers are formed by repeated condensation reaction between two different bi-functional or tri-functional monomeric units. In these polymerization reactions, the elimination of small molecules such as water, alcohol, hydrogen chloride, etc. take place. The examples are terylene (dacron), nylon 6, 6, nylon 6, etc.

Addition Polymers	Condensation Polymers
<p>Addition polymers formed by the polymerization of a single monomeric species are known as <b>homopolymers</b>, e.g., polythene</p> $n\text{CH}_2 = \text{CH}_2 \xrightarrow[\text{Ethane}]{\text{Polythene}} -(\text{CH}_2 - \text{CH}_2)_n - \text{Homopolymer}$ <p>The polymers made by addition polymerization from two different monomers are termed as <b>copolymers</b>, e.g., Buna-S, Buna-N, etc.</p> $\begin{array}{c} n\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 + n\text{C}_6\text{H}_5\text{CH} = \text{CH} \rightarrow \\ \text{1,3-butadiene} \qquad \qquad \qquad \text{Styrene} \\ \\ \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH} \Big) _n - \\ \text{Buna-S: Butadiene-styrene copolymer (Buna-S)} \end{array}$	<p>For example, nylon 6, 6 is formed by the condensation of hexamethylene diamine with adipic acid.</p> $\begin{array}{c} n\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2 + n\text{HOOC} \\ (\text{CH}_2)_4\text{COOH} \longrightarrow \\ \left[ \text{NH}(\text{CH}_2)_6\text{NHCO}(\text{CH}_2)_4\text{CO} \right] + n\text{H}_2\text{O} \\ \text{Nylon 6, 6} \end{array}$

#### 26.2.4 Classification Based on Molecular Forces

	Definition	Examples
Elastomers	<p>These are rubber-like solids with elastic properties. In these elastomeric polymers, the polymer chains are held together by the weakest intermolecular forces.</p> <p>The examples are buna-S, buna-N, neoprene, etc.</p>	$\left( \text{CH}_2 - \underset{\text{Cl}}{\overset{ }{\text{C}}} = \text{CH} - \text{CH}_2 \right)_n$ <p>Neoprene</p>
Fibres	<p>Fibres are the thread-forming solids which possess high tensile strength and high modulus. These characteristics can be attributed to the strong intermolecular forces like hydrogen bonding. The examples are polyamides (nylon 6, 6), polyesters (terylene), etc.</p>	$\left( \begin{array}{c} \text{H} & \text{H} & \text{O} & \text{O} \\   &    & &   \\ \text{N}-[\text{CH}_2]_6-\text{N}-\text{C}[\text{CH}_2]_4-\text{C}- & & & \end{array} \right)_n$ <p>Nylon 6, 6</p>
Thermo-plastic polymer	<p>These are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. Some common thermoplastics are polythene, polystyrene, polyvinyls, etc.</p>	$(-\text{CH}_2 - \underset{\text{PVC}}{\overset{\text{Cl}}{\overset{ }{\text{C}}}} \text{H})_n -$
Thermo-setting polymers	<p>These polymers are cross-linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused. Some common examples are bakelite, urea-formaldehyde resins, etc.</p>	$\left( \begin{array}{c} \text{O}-\text{H} & \text{O}-\text{H} \\   &   \\ \text{CH}_2 & \text{CH}_2 \end{array} \right)_n$ <p>Bakelite</p>

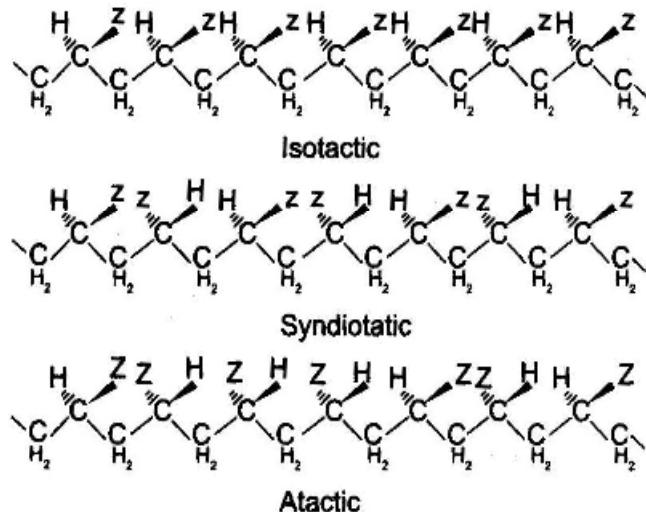
**Note:**

Order of strength of intermolecular forces

Thermoset > fibres > thermoplastic > elastomers

### 26.2.5 Classification of Polymer on the Basis of Stereo Chemistry

If the polymer chain is drawn in a zig-zig fashion each of substituent group (Z) will necessarily be located above or below the plane defined by the carbon chain. Consequently, we can identify three configurational isomers of such polymers. If all the substituents lie on one side of the chain the configuration is called **isotactic**. If the substituents alternate from one side to another in a regular manner of configuration is termed **syndiotactic**. Finally, a random arrangement of substituent groups is referred to as **atactic**. Examples of these configurations are shown here.



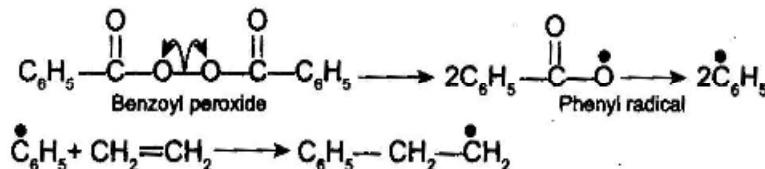
## 26.3 CLASSIFICATION BASED ON GROWTH POLYMERIZATION

### 26.3.1 Addition Polymerization or Chain Growth Polymerization

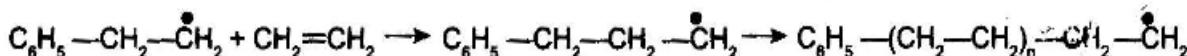
In this type of polymerization, the molecules of the same monomer or different monomers add together on a large scale to form a polymer. The monomers used are unsaturated compounds, e.g., alkenes, alkadienes and their derivatives. Product of each step is a reaction intermediate.

- (i) **Free radical chain growth polymerization:** A variety of alkenes or dienes and their derivatives are polymerized in the presence of a free radical generating initiator (catalyst) like benzoyl peroxide, acetyl peroxide, tert-butyl peroxide, etc. For example, the polymerization of ethene to polythene consists of heating or exposing to light a mixture of ethene with a small amount of benzoyl peroxide initiator.

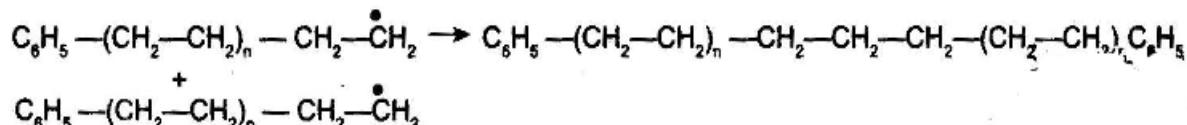
#### Chain initiation steps



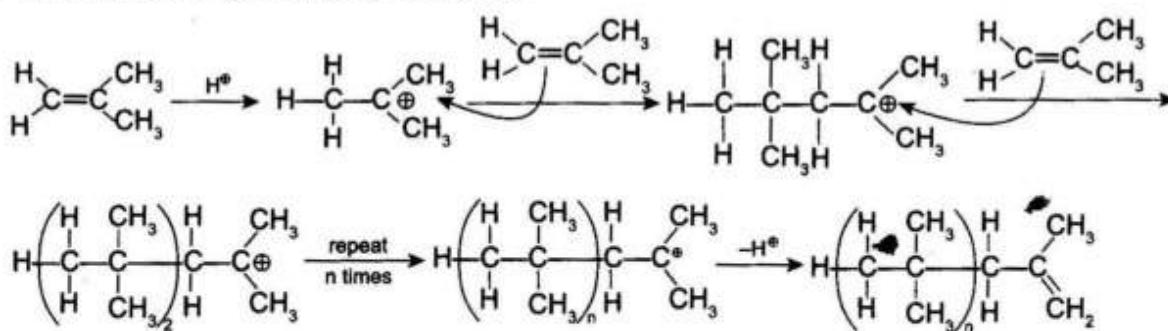
#### Chain propagating step



**Chain terminating step:** For termination of the long chain, these free radicals can combine in different ways to form polythene. One mode of termination of chain is shown as under.



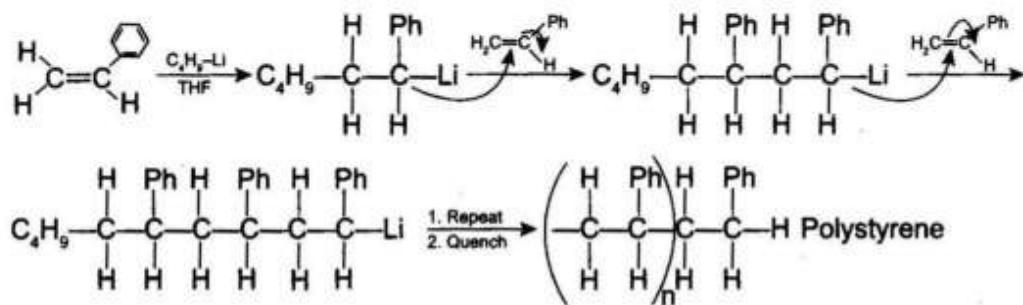
## (ii) Cationic chain-growth polymerization



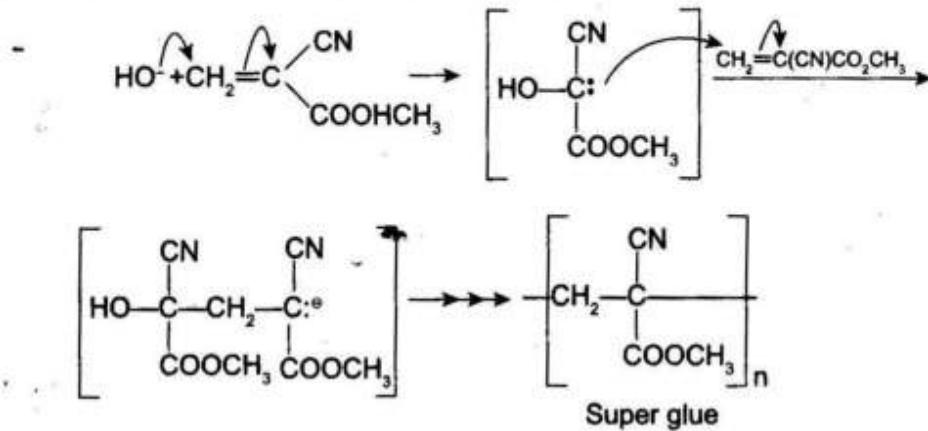
Polymerization of isobutylene (2-methylpropene) by traces of strong acids is an example of cationic polymerization. The polyisobutylene product is a soft rubbery solid. This process is similar to radical polymerization, as demonstrated by the following equations. Chain growth ceases when the terminal carbocation combines with a nucleophile or loses a proton, given a terminal alkene (as shown here). Monomers bearing cation stabilizing groups, such as alkyl, phenyl or vinyl can be polymerized by cationic processes. These are normally initiated at low temperature in methylene chloride solution. Strong acids, such as  $\text{HClO}_4$ , or Lewis acids containing traces of water serve as initiating regents. At low temperatures, chain transfer reactions are rare in such polymerizations, so the resulting polymers are clearly linear (unbranched).

## (iii) Anionic chain growth polymerization.

Only monomers having anion stabilizing substituents, such as phenyl, cyano or carbonyl are good substrates for this polymerization technique. Many of the resulting polymers are largely isotactic in configuration, and have high degrees of crystallinity.



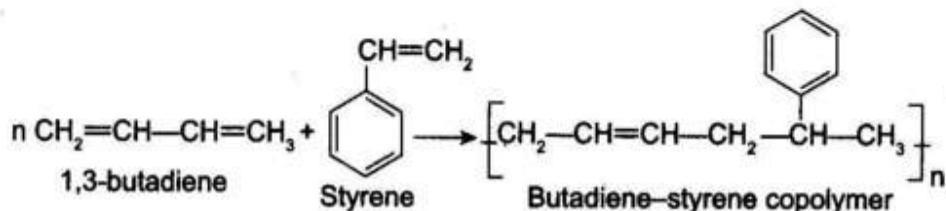
Species that have been used to initiate anionic polymerization include alkali metals, alkali amides, alkyl, lithiums and various electron sources. A practical application of anionic polymerization occurs in the use of superglue. This material is methyl 2-cyanoacrylate  $\text{CH}_2=\text{C}(\text{CN})\text{CO}_2\text{CH}_3$ . When exposed to water, amines or other nucleophiles, a rapid polymerization of this monomer takes place,



Name(s)	Polymer	Monomer	Properties	Uses
Polyethylene low density (LDPE)	$-\left[CH_2 - CH_2\right]_n -$	Ethylene $CH_2 = CH_2$	Soft, waxy solid	Film wrap, plastic bags
Polyethylene high density (HDPE)	$-\left[CH_2 - CH_2\right]_n -$	Ethylene $CH_2 = CH_2$	Rigid, translucent solid	Electrical insulation bottles, toys
Polypropylene (PP) different grades	$-\left[CH_2 - \overset{CH_n}{C} - Cl\right]_n -$	Propylene $CH_2 = CHCH_3$	Actactic soft, elastic solid isotactic hard, strong solid	Similar to LDPE carpet, upholstery
Poly(vinyl chloride) (PVC)	$-\left[CH_2 - \overset{CH_n}{C} - CH_3\right]_n -$	Vinyl chloride $CH_2 = CHCl$	Strong rigid solid	Pipes, riding flooring
Poly(vinylidene chloride) Saran A)	$-\left[CH_2 - CCl_2\right]_n -$	Vinylidene chloride $CH_2 = CCl_2$	Dense, high-melting solid	Seat cover, films
Polystyrene (PS)	$-\left[CH_2 - \overset{CH_n}{C} - C_6H_5\right]_n -$	Styrene $CH_2 = CHC_6H_5$	Hard, rigid, clear solid soluble in organic solvents	Toys, cabinet packaging (foamed)
Polyacrylonitrile (PAN, Orion, Acrilan)	$-\left[CH_2 - \overset{CH_n}{C} - CN\right]_n -$	Acrylonitrile $CH_2 = CHCN$	High-melting solid soluble in organic solvents	Rugs, blankets clothing
Polytetrafluoroethylene (PTFE, Teflon)	$-\left(CF_2 - CF_2\right)_n -$	Tetrafluoroethylene $CF_2 = CF_2$	Resistant, smooth solid	Non-stick surfaces electrical insulation
Poly(methyl methacrylate) (PMMA, lucite, plexiglas)	$-\left[CH_2 - CO_2 CH_3\right]_n -$	Methyl methacrylate $CH_2 = C(CH_3)CO_2 CH_3$	Hard, transparent solid	Lighting covers, signs skylights
Poly(vinyl acetate) (PVAc)	$-\left[CH_2 - CHOCOCH_3\right]_n -$	Vinyl acetate $CH_2 = CHCOCOCH_3$	Soft, sticky solid	Latex paints, adhesives
Cis-Polyisoprene Natural rubber	$-\left[CH_2 - CH=C(CH_3) CH_2\right]_n -$	Isoprene $CH_2 = CH - C(CH_3) = CH_2$	Soft, sticky solid	Requires vulcanization for practical use
Polychloroprene (cis + trans) (Neoprene)	$-\left[CH_2 - CH= \overset{Cl}{C} - CH_2\right]_n -$	Chloroprene $CH_2 = CHCCl=CH_2$	Tough, rubbery solid	Synthetic rubber oil resistant

### 26.3.2 Condensation Polymerization

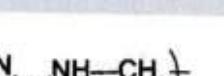
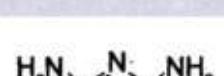
This type of polymerization generally involves a repetitive condensation reaction between two bi-functional monomers. These polycondensation reactions may result in the loss of some simple molecules as water, alcohol, etc. and lead to the formation of high molecular mass condensation polymers. In these reactions, the product of each step is again a bi-functional species and the sequence of condensation goes on. Since, each step produces a distinct functionalized species and is independent of each other, this process is also called as step growth polymerization. The formation of terylene or dacron by the interaction of ethylene glycol and terephthalic acid is an example of this type of polymerization.



Some important condensation polymerization reactions characterized by their linking units are described below:

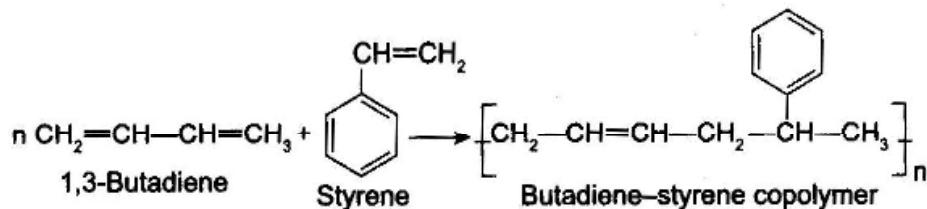
#### 26.3.2.1 Some Condensation Polymers

Formula	Type	Monomer	Uses
$-\text{[CO(CH}_2)_4\text{CO-OCH}_2\text{CH}_2\text{O]}_n-$	Polyester	$\text{HO}_2\text{C-(CH}_2)_4\text{-CO}_2\text{H}$ + $\text{HO-CH}_2\text{CH}_2\text{-OH}$	Outwear because of high tenacity
	Polyester Dacron Mylar	Para $\text{HO}_2\text{C-C}_6\text{H}_4\text{-CO}_2\text{H}$ + $\text{HO-CH}_2\text{CH}_2\text{-OH}$	Curtains, shirts, dresses
	Polyester	Meta $\text{HO}_2\text{C-C-C}_6\text{H}_4\text{-CO}_2\text{H}$ + $\text{HO-CH}_2\text{CH}_2\text{-OH}$	Coating, adhesives, msealants
$-\text{[CO(CH}_2)_5\text{NH]}_n-$	Polyamide Nylon-6 Perlon		Gears, fittings, bearings
$-\text{[CO(CH}_2)_4\text{CO-NH(CH}_2)_6\text{NH]}_n-$	Polyamide Nylon-6, 6	$\text{HO}_2\text{C-(CH}_2)_4\text{-CO}_2\text{H}$ + $\text{H}_2\text{N-(CH}_2)_6\text{-NH}_2$	Airbags, tyres, ropes
$\{\text{CO(CH}_2)_8\text{CO-NH(CH}_2)_6\text{NH}\}_n$	Nylon-6, 10	$\text{HOOC-(CH}_2)_8\text{-COOH}$ (sebacic acid) + $\text{H}_2\text{N-(CH}_2)_6\text{-NH}_2$	To make bristles and brushes
	Polyamide Kevlar	Para $\text{HO}_2\text{C-C}_6\text{H}_4\text{-CO}_2\text{H}$ + Para $\text{H}_2\text{N-C}_6\text{H}_4\text{-NH}_2$	Ropes, fabric sheets, body armor

Formula	Type	Monomer	Uses
	Polyamide Nomex	Meta HO <sub>2</sub> C-C <sub>6</sub> H <sub>4</sub> -CO <sub>2</sub> H + Meta H <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> -NH <sub>2</sub>	Protective fabrics, garments, insulation
	Melamine Polymer, i.e., melmac	 Melamine HCHO Formaldehyde	Manufacture of unbreakable crockery

### 26.3.3 Copolymerization

Copolymerization is a polymerization reaction in which a mixture of more than one monomeric species is allowed to polymerize and form a copolymer. The copolymer can be made not only by chain growth polymerization but by step growth polymerization also. It contains multiple units of each monomer used in the same polymeric chain. For example, a mixture of 1, 3-butadiene and styrene can form a copolymer.



Copolymers have properties quite different from homopolymers. For example, butadiene-styrene copolymer is quite tough and is a good substitute for natural rubber. It is used for the manufacture of autotires, floortiles, footwear components, cable insulation, etc.

### **Some Useful Copolymers**

Monomer A	Monomer B	Copolymer	Uses
$\text{H}_2\text{C}=\text{CHCl}$	$\text{H}_2\text{C}=\text{CCl}_2$	Saran	Films and fibers
$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	$\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$	SBR Styrene butadiene rubber	Tyres
$\text{H}_2\text{C}=\text{CHCN}$	$\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$	Nitrile rubber	Adhesives hoses
$\text{H}_2\text{C}=\text{C}(\text{CH}_3)_2$	$\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$	Butyl rubber	Inner tubes
$\text{F}_2\text{C}=\text{CF}(\text{CF}_3)$	$\text{H}_2\text{C}=\text{CHF}$	Viton	Gaskets

#### **Natural Rubber**

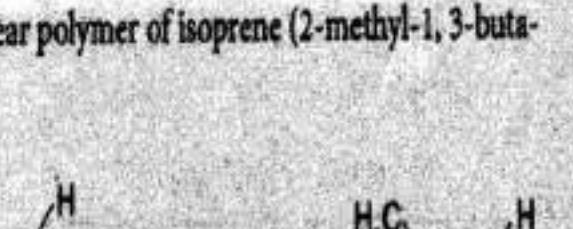
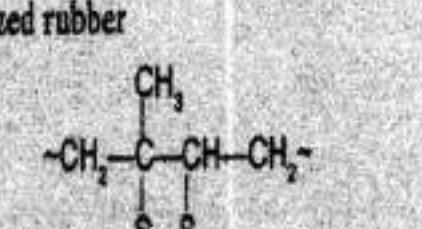
It becomes soft at high temperature ( $>335\text{ K}$ )

It is brittle at low temperatures ( $<283\text{ K}$ )

## Vulcanized Rubber

It does not become soft at high temperature ( $>335\text{ K}$ )

**It does not become brittle at low temperature ( $<283$  K).**

Natural Rubber	Vulcanized Rubber
It has high water absorbing capacity.	It does not absorb water.
It is soluble in non-polar solvents and it is non-resistant to attack by oxidizing agents.	It is not soluble in non-polar solvent and is resistant to attack by oxidizing agent.
It is manufactured from rubber latex which is a colloidal dispersion of rubber in water.	It is prepared by heating a mixture of raw rubber with sulphur and appropriate additives at temperature between 373 and 415 K.
It is a linear polymer of isoprene (2-methyl-1,3-butadiene)	Vulcanized rubber
	
Various chains are held together by weak Van der Waal's forces and hence it exhibits elastic properties.	Sulphur forms double bonds at the reactive sites of double bonds and rubber gets stiffened.

**Note:**

Trans-polyisoprene, i.e., trans-2-methyl-1, 3-butadiene is termed as gutta-percha.

## 26.4 SYNTHETIC RUBBERS

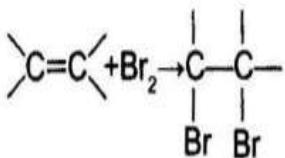
Synthetic rubber is any vulcanizable rubber like polymer, which is capable of getting stretched to twice its length. However, it returns to its original shape and size as soon as the external stretching force is released. Thus, synthetic rubbers are either homopolymers of 1, 3-butadiene derivatives or copolymers of 1, 3-butadiene or its derivatives with another unsaturated monomer. Some synthetic rubbers are neoprene, buna-N rubber.

## ANALYTICAL TEST OF ORGANIC COMPOUNDS

### 27.1 ALKENE AND ALKYNE

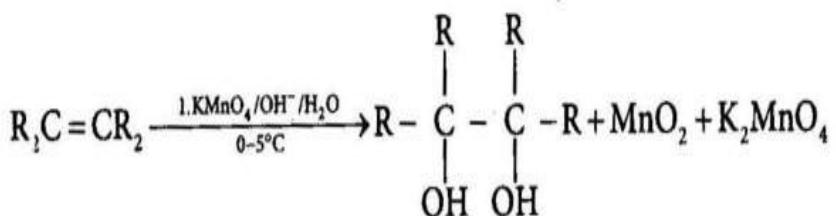
#### 27.1.1 Bromine Water Test

In this test the alkene or alkyne reacts with  $\text{Br}_2$  to form an alkyl dibromide, which causes the orange-brown of the  $\text{Br}_2$  to disappear. This will be immediate with alkenes, but may take a short while with alkynes. Activated aromatic rings give a false positive in this test.



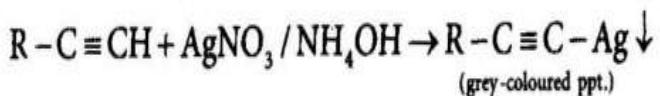
#### 27.1.2 Baeyer's Reagent

In this test the alkene or alkyne is oxidized to a diol (alkene) or diketone (alkyne), which uses up the purple permanganate solution and produces manganese dioxide, a brown precipitate. It may also give a positive test for aryl amines, aldehydes, and alcohols, which can also be oxidized.

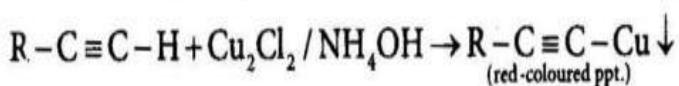


#### 27.1.3 Metal alkynide Test

When terminal alkyne is treated with ammonical  $\text{AgNO}_3$ , to produce silver alkynide



When terminal alkyne is treated with ammonical  $\text{Cu}_2\text{Cl}_2$  to produce red-coloured ppt.

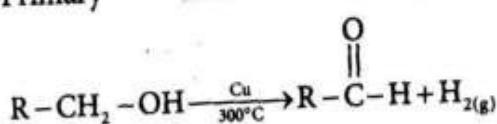


## 27.2 ALCOHOL

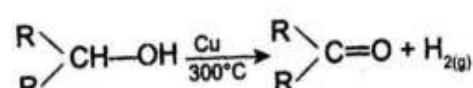
### 27.2.1 Dehydrogenation Test

When alcohol vapours are passed through red hot Cu at 300°C, they react differently

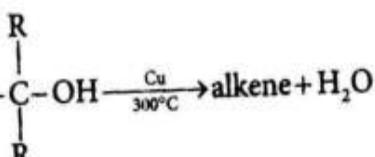
(a) Primary alcohol undergoes dehydrogenation to produce aldehyde



(b) Secondary alcohol also undergoes dehydrogenation to produce ketone



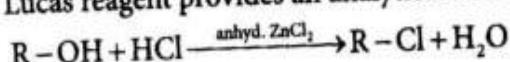
(c) Tertiary alcohol undergoes dehydration to produce alkene



### 27.2.2 Lucas Test

In this method, alcohol is treated with equimolar mixture of anhydrous  $\text{ZnCl}_2$  and Conc. HCl also called Lucas reagent at room temperature to produce alkyl chloride.

Lucas reagent provides an analytical test to distinguish primary, secondary and tertiary alcohol.

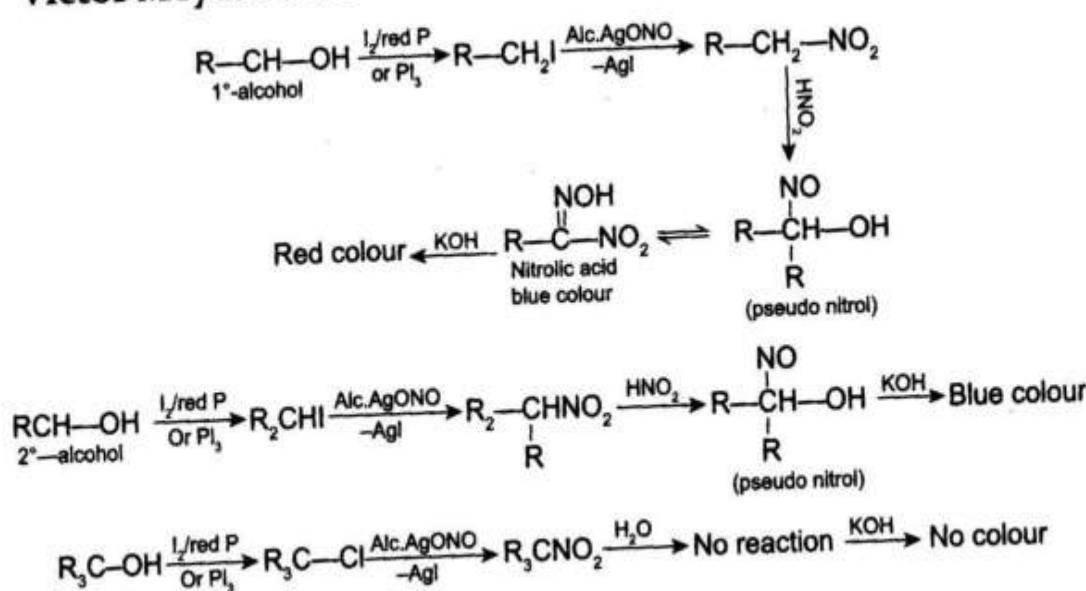


1. Tertiary alcohol gives white turbidity immediately.
2. Secondary alcohol gives white turbidity in few minutes.
3. Primary alcohol do not give white turbidity at room temperature.

#### Note:

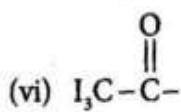
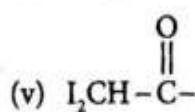
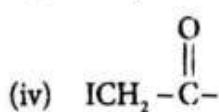
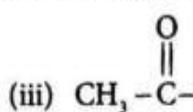
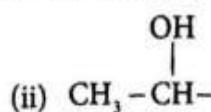
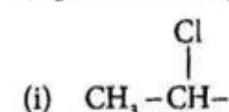
Though benzyl or allyl alcohol are primary still they produce white turbidity immediately due to high stability of carbonation produced during the reaction.

### 27.2.3 Victor Meyer's Test

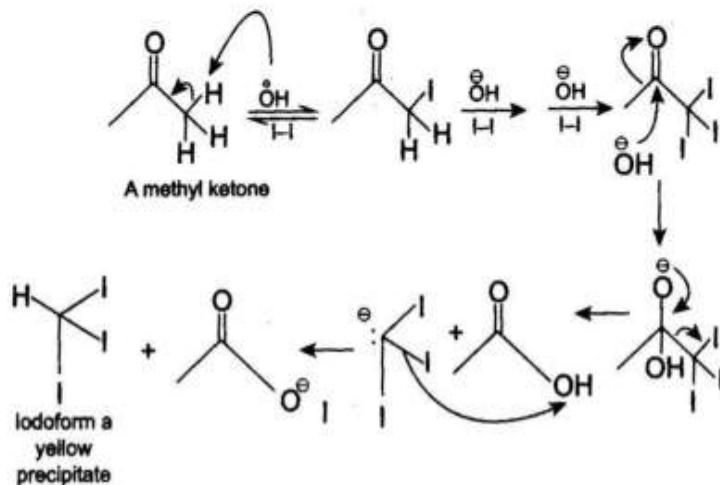


### 27.2.4 Iodoform Test

Compound which give +ve iodoform test have any one of the following structural features:

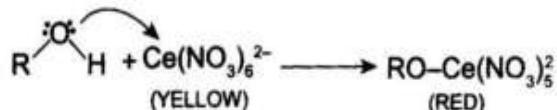


When a compound having any one of the above structural feature is treated with  $\text{I}_2$  in presence of alkali like  $\text{NaOH}$  or  $\text{KOH}$  or  $\text{Ca}(\text{OH})_2$ , etc. iodoform as a yellow precipitate is obtained.



### 27.2.5 Ceric Ammonium Nitrate Test

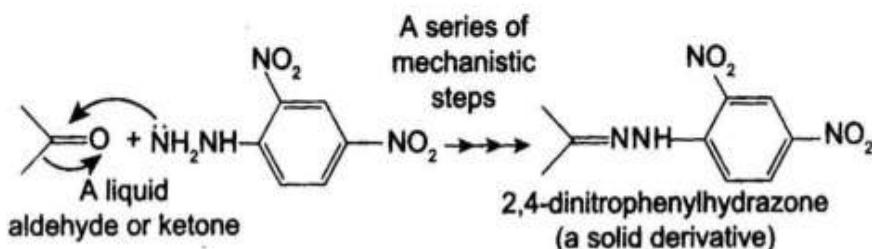
Alcohols react with ceric nitrate reagent to produce a colour change (yellow to red), whereas carbonyl compounds do not react. Note that changing the groups attached to certain inorganic ions such as  $\text{Ce}^{4+}$  results in a change to the electronic structure, which results in a colour change. Production of a magenta color therefore indicates the presence of an alcohol group.



## 27.3 ALDEHYDE AND KETONE

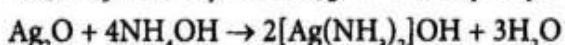
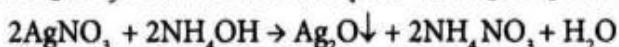
### 27.3.1 2,4-DNP Test

Aldehydes and ketones react with 2,4-dinitrophenylhydrazine reagent to form yellow, orange, or reddish-orange precipitates, whereas alcohols do not react. Formation of a precipitate therefore indicates the presence of an aldehyde or ketone. The precipitate from this test also serves as a solid derivative.

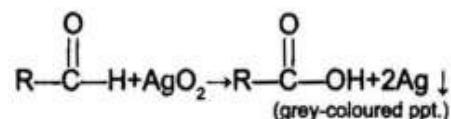


### 27.3.2 Tollen's Test

When  $\text{AgNO}_3$  is treated with  $\text{NH}_4\text{OH}$ , white precipitate of  $\text{Ag}_2\text{O}$  is produced.



Tollen's reagent due to this complex dissolves again in solution.  $2[\text{Ag}(\text{NH}_3)_2]\text{OH} \xrightarrow{\Delta} \text{Ag}_2\text{O} + \text{H}_2\text{O} + 4\text{NH}_3$

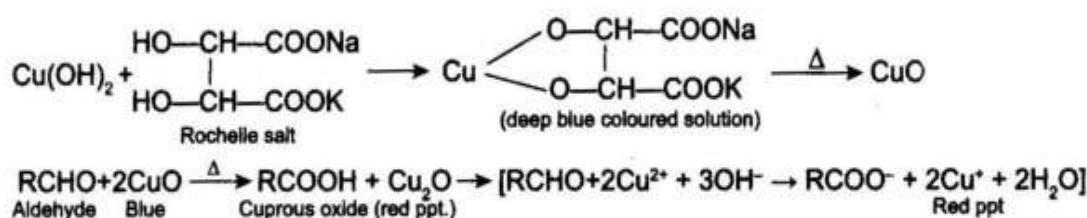
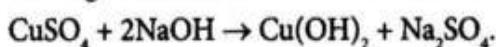
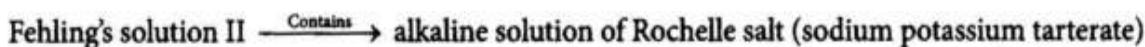
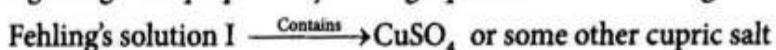


Compounds which give positive test with Tollen's reagent are:

- |                      |                     |                                |
|----------------------|---------------------|--------------------------------|
| (i) Aldehydes        | (ii) $\text{HCOOH}$ | (iii) $\alpha$ -hydroxy ketone |
| (iv) $\text{CHCl}_3$ | (v) Terminal alkyne | (vi) Hydroxyl amine            |

### 27.3.3 Fehling's Test

Fehling's reagent is prepared by mixing equal volume of Fehling's solution I and Fehling's solution II.



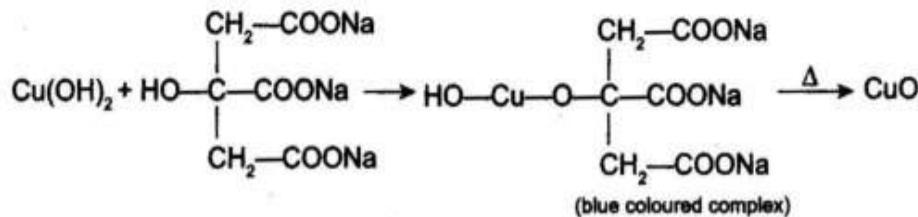
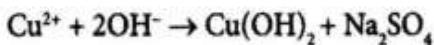
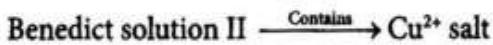
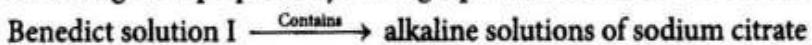
Compounds which give +ve test with Fehling's reagent are:

- |                         |                     |                                 |
|-------------------------|---------------------|---------------------------------|
| (i) Aliphatic aldehydes | (ii) $\text{HCOOH}$ | (iii) $\alpha$ -hydroxyl ketone |
| (iv) $\text{CHCl}_3$ ,  | (v) Terminal alkyne |                                 |

Fehling's reagent can be used to distinguish between aliphatic and aromatic aldehydes.

### 27.3.4 Benedict's Test

Benedict's reagent is prepared by mixing equal volume of Benedict solution I with Benedict solution II.

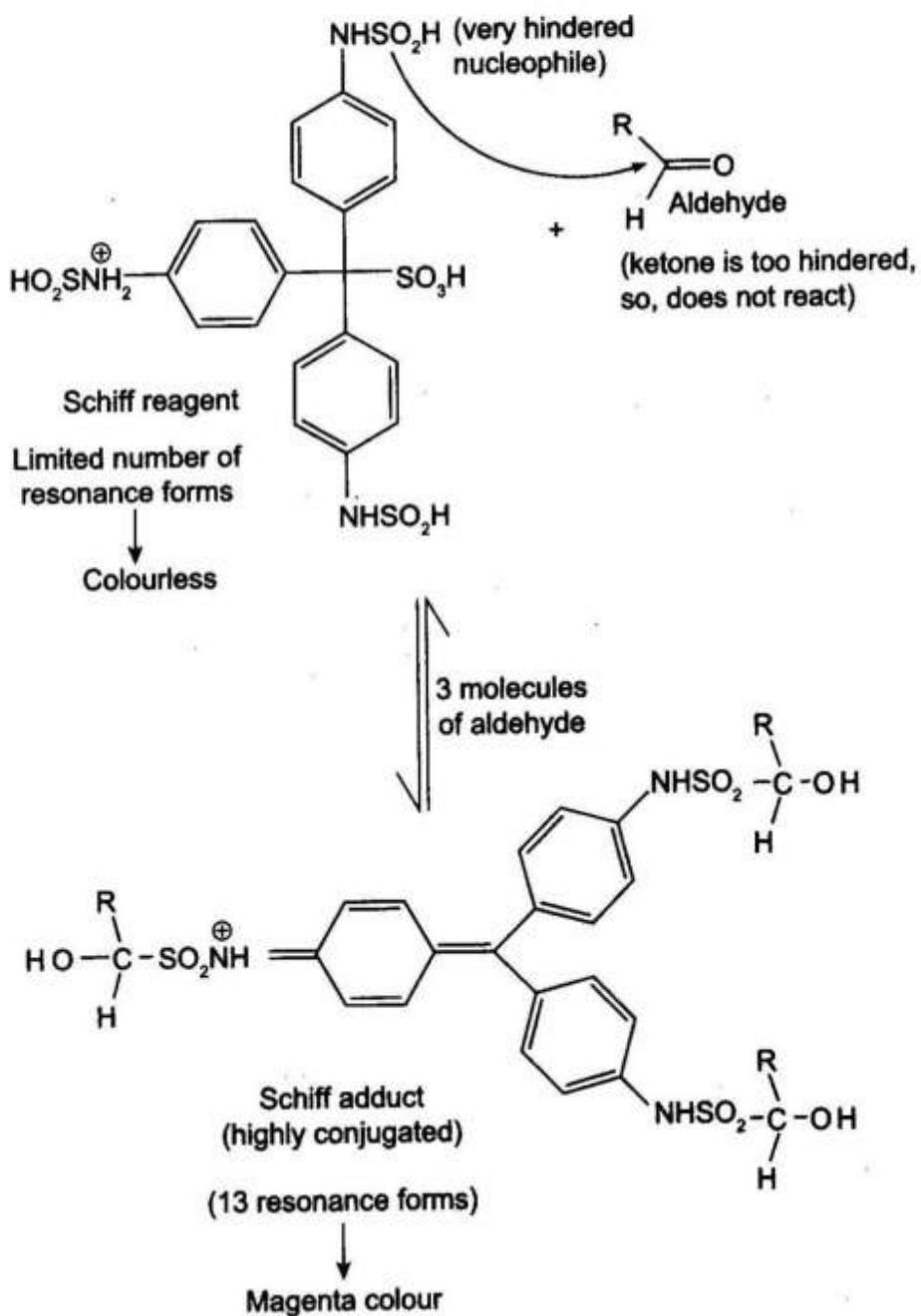


- All compounds which give positive test with Fehling's reagent also give similar test with Benedict's reagent.

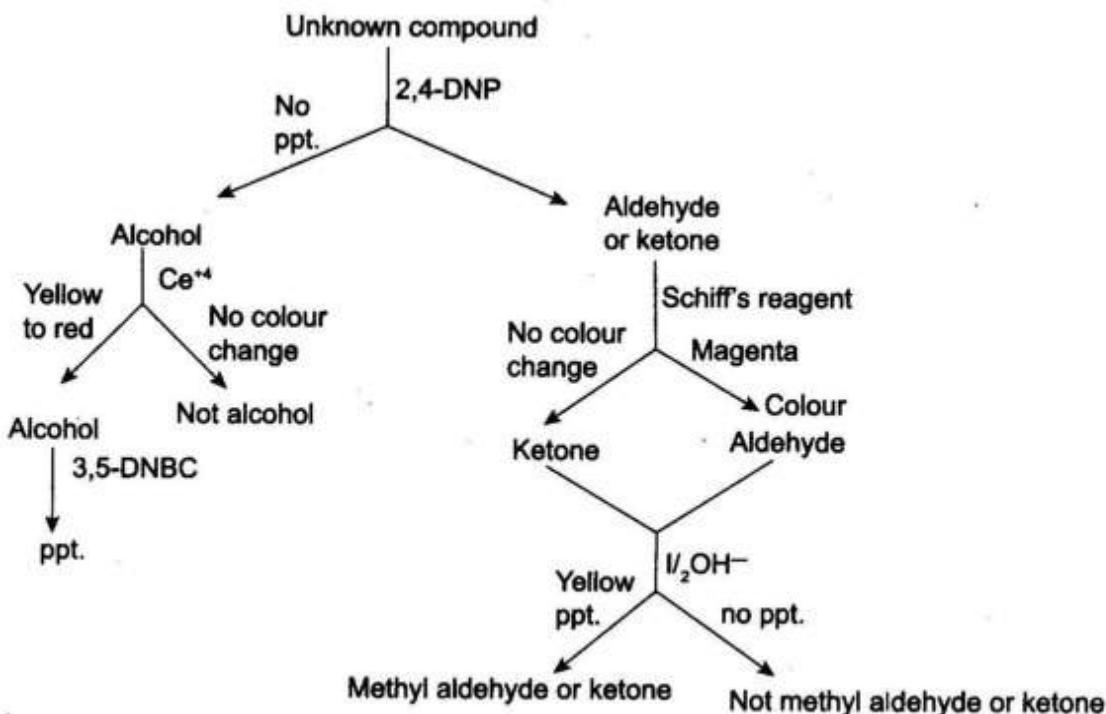
### 27.3.5 Schiff's Test

The Schiff's reagent acts as a nucleophile that adds to the carbonyl group of an aldehyde. Because this nucleophile is extremely bulky, a ketone, which is more sterically crowded than an aldehyde at the carbonyl carbon, does not react with Schiff's reagent, and thus does not produce the magenta color. Production of the magenta colour therefore indicates that the unknown compound is an aldehyde and not a ketone. Note that, generally, more extended systems of conjugation lead to coloured compounds, whereas the Schiff reagent itself has a limited system of conjugation, the adduct with an aldehyde has an extended system of conjugation, resulting in a highly coloured compound.

Schiff's test for aldehydes



## Identification of an unknown organic compound

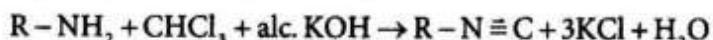


where 3,5 - DNHC is 3, 5-dinitrobenzoyl chloride.

## 27.4 AMINES

### 27.4.1 Carbyl Amine Test

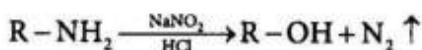
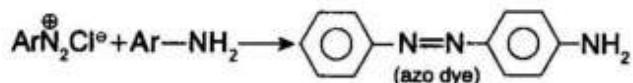
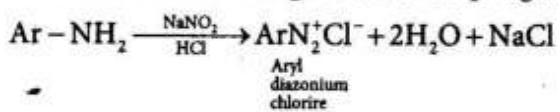
When primary amine whether it is aliphatic or aromatic is treated with CHCl<sub>3</sub> and alcoholic KOH a bad smelling compound isocyanide is produced.



#### 27.4.1.1 Azo dye test

When aliphatic primary amine is treated with HNO<sub>2</sub> or NaNO<sub>2</sub> Conc. HCl at low temperature it undergoes diazotization to produce colourless alcohols.

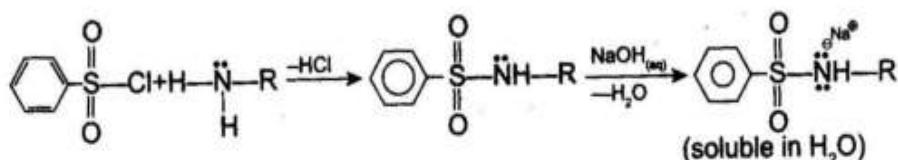
However, when aromatic primary amine is treated with NaNO<sub>2</sub> and or Conc. HCl at 0–5°C. An aryl diazonium salt which undergoes diazo coupling with aromatic amine to produce coloured azo dye.



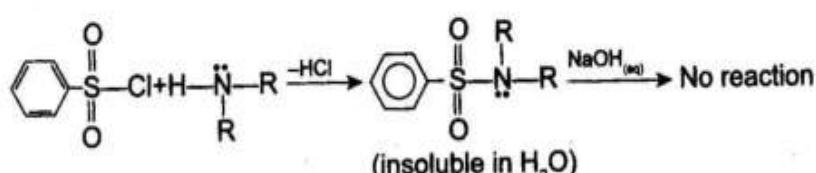
#### 27.4.2 Hinsberg's Test

In this method amine mixture is treated with Hinsberg's reagent, i.e.,  $C_6H_5SO_2Cl$ . (Benzene sulphonyl chloride) where they react differently.

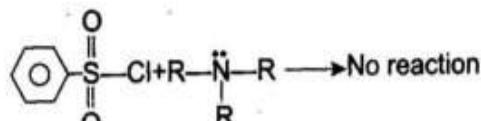
Primary amine reacts with Hinsberg's reagent to produce a substituted sulphonamide which is soluble in aq. alkali.



Secondary amine reacts with Hinsberg's reagent to produce N, N-dialkyl sulphonamide which is insoluble in aq. alkali.



Tertiary amine does not react at all with Hinsberg's reagent.



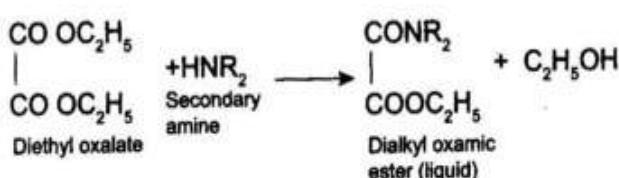
### 27.4.3 Hofmann's Test

In this method, amine mixture is treated with Hofmann's reagent, i.e., ethyl oxalate where they react differently.

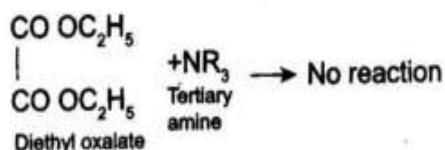
- Primary amine reacts with Hofmann's reagent to produce a substituted oxamide which is a crystalline solid.



- ◆ Secondary amines reacts with Hofmann's reagent to produce N, N – dialkyl oxamic ester which is a high boiling liquid.

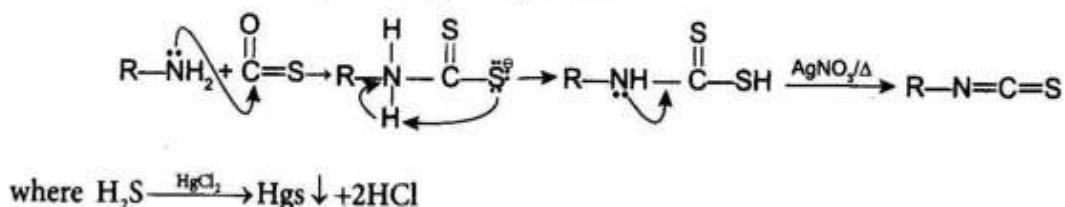


- ♦ Tertiary amine does not react at all with Hoffmann's reagent



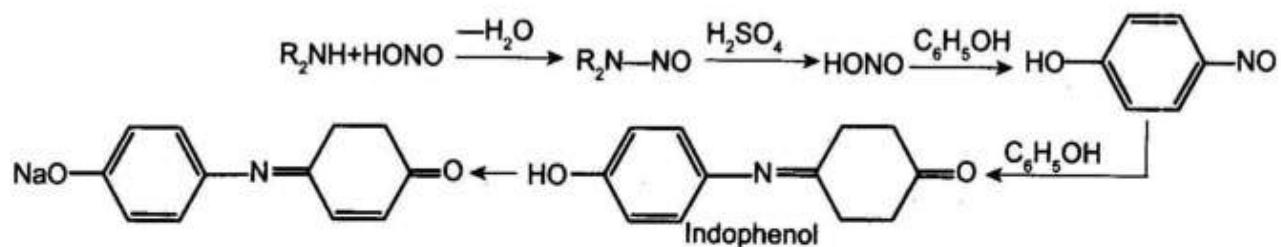
### 27.4.4 Hofmann's Mustard Oil Test

When primary amine is treated with  $\text{CS}_2$ , then N-alkyl dithiocarbamic acid is produced which on decomposition with  $\text{AgNO}_3$  and  $\text{HgCl}_2$  produces alkyl isothiocyanate, an oily compound having mustard oil smell along with formation of black precipitate of  $\text{HgS}$ . Secondary and tertiary amines do not give this test and therefore this is a confirmatory test of a primary amine.



### 27.4.5 Liebermann's Nitroso Test

This test is given only by  $2^\circ$  amine whether it is aliphatic or aromatic.  $2^\circ$  amine is converted into nitroso amine by treating the amine with  $\text{HNO}_2$ . On warming with phenol and Conc.  $\text{H}_2\text{SO}_4$  brown on red colour is formed at first which changes to blue then to green colour changes to red on dilution and further to greenish blue or violet on treatment with alkali.

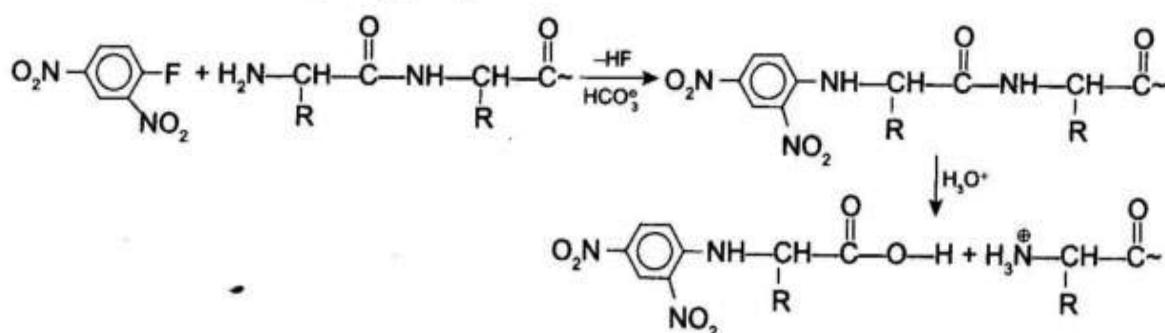


## 27.5 PROTEIN CHEMISTRY

### 27.5.1 Sanger's Test

When 2,4-dinitro-fluoro-benzene (DNFB) is treated with polypeptide in a solution, an aromatic nucleophilic substitution takes place involving the free amine group of the N-terminal residue.

Subsequent hydrolysis of the polypeptide gives, a mixture of amino acids in which N-terminal amino acid bear a label of 2,4-dinitrophenyl group.



### 27.5.2 Ninhydrin Test

When a protein is treated with ninhydrin, a violet or purple-coloured anion is produced.