CHAPTER 24

ORGANIC REACTIONS

24.1 INTRODUCTION

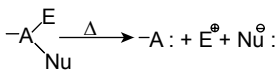
Organic reaction belongs to following categories:

1. Elimination reaction
2. Addition reaction
3. Substitution reaction
4. Rearrangement reaction
5. Condensation reaction
6. Disproportionation reaction

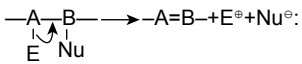
24.2 ELIMINATION REACTION

If two groups are removed from a substrate molecule, then the reaction is termed as elimination reaction. Depending upon the relative position of leaving groups, they are classified into four categories.

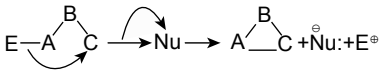
(i) **α–elimination reaction:** If both leaving group are present on same atom of substrate molecule, then the reaction is termed as α-elimination. This reaction always results in the formation of carbenes and nitrenes which are unstable and therefore this reaction is always endothermic.



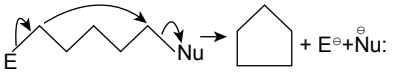
(ii) β-**elimination reaction:** If leaving groups are present on the adjacent atom of a substrate molecule, then the reaction is termed as β-elimination. Mostly elimination reaction belongs to this category. In such a reaction, there occurs loss of two sigma bond and gain of one π-bond and therefore product system is less stable than that of reactant system and therefore this reaction is always endothermic.



(iii) γ-**elimination reaction:** If leaving groups are present on alternate atom of a substrate molecule, then the reaction is termed as γ-elimination. γ-elimination always results in the formation of cyclo-propyl ring which is a strained structure. This reaction is also endothermic.



(iv) δ **or higher order elimination:** If leaving groups are present on (1, n) position of a substrate molecule where n ≥ 4, then the reaction is termed as δ or higher-order elimination.
This elimination always results in the formation of either a conjugated product or a cyclic ring, If a conjugated product is obtained as a product, then it is termed as conjugate elimination (here, n ≥ 4 and always even) for cyclic ring (n ≥ 4; and can be odd or even)



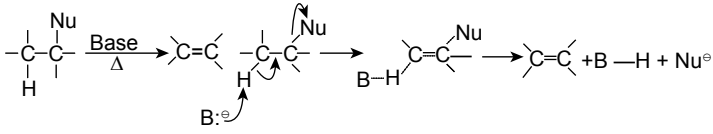
β-Elimination reaction: It is further classified into three categories.

1. Bimolecular elimination reaction (E_2)
2. Unimolecular elimination reaction
   (a) E_1 reaction (carbocationic elimination) (b) E_1 cb reaction (carbanionic elimination)
3. Pyrolytic elimination reaction

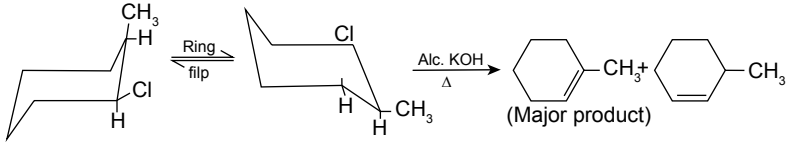
Bimolecular elimination reaction (E_2): When a substrate molecule having a good nucleofuge and having atleast one β-hydrogen w.r.t. nucleofuge, is heated with strong base then elimination product alkene or alkyne is obtained.

Reaction proceeds in a single step and therefore involved in the formation of a transitition state.

Transition state produced during the reaction must acquire anti-periplanar arrangement in which five atoms including base atom lie in one plane and both leaving groups must be exactly anti to each other.

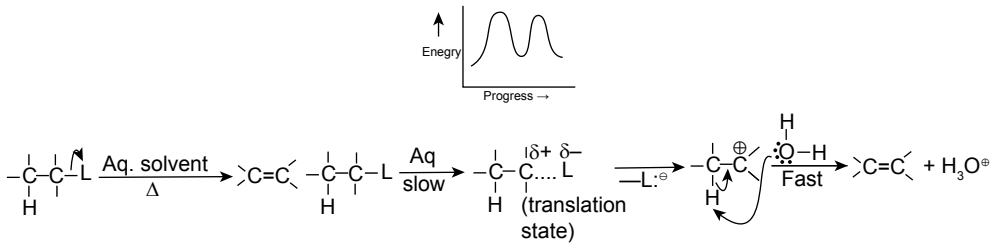


1. **Characteristics of E_2 reaction:** Rate of reaction depends upon substrate concentration as well as base concentration or both. Therefore, reaction follows second-order kinetics.
2. Since reaction proceeds in single step, whose molecularity is 2, therefore reaction is termed as bimolecular elimination reaction.
3. Presence of good leaving group on substrate increases its reactivity towards E_2 reaction.
   R–F < R–Cl < R–Br < R–I
4. Since reaction rate depends upon base concentration therefore by considering high concentration of strong base, E_2 reaction is favourable.
5. Reaction best proceeds in polar aprotic or less polar solvents.
6. Rearrangement is impossible during the reaction.
7. Reaction has very high kinetic isotope effect.
   E.g., $CH_3–CH_2–Cl \xrightarrow[\Delta]{\text{Alc. KOH}} CH_2=CH_2 + KCl + H_2O$
   $CD_3–CD_2–Cl \xrightarrow[\Delta]{\text{Alc. KOH}} CD_2=CD_2 + KCl + DOH$
   first reaction system is seven times more reactive than the second reaction system under similar conditions.
8. Both leaving groups must be exactly anti to each other, e.g., in case of cyclo-hexyl substrate in order to participate in E_2 mechanism, both leaving groups must be present at the axial position in chair conformation rather than equatorial position.



II **Uni molecular elimination reaction:** It is further classified into two categories.

1. E_1 reaction **(carbocationic elimination)**: When a substrate molecule having a good nucleofuge leaving group is heated in a polar protic solvent, then elimination product is obtained.
   Reaction proceeding through the formation of carbocation reaction inter mediate is the slowest step.



24.2.1 Characteristics

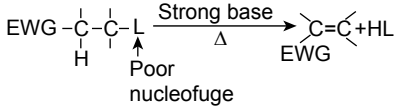
1. In slowest step of E_1 reaction, only substrate molecule is present therefore reaction follows first order kinetics.
2. Since slowest step of reaction is independent from base concentration therefore, E_1 reaction is favourable in presence of low base concentration or when weak base is involved.
3. Presence of good nucleofuge increases the reactivity of substrate towards E_1 reaction.
4. Reaction best proceeds in a polar protic solvent because it favours the formation of transition state as well as stabilizes the carbocation intermediate.
5. Rearrangement is always possible in E_1 reaction.

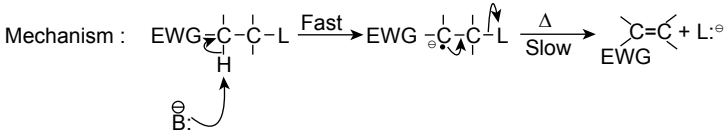
24.3 E_1 CB REACTION (CARBANIONIC ELIMINATION)

In this reaction removal of electrofuse mostly hydrogen occurs first from substrate nuclecude which results in the formation of carbanion intermediate followed by the removal of nucleofuge in a slowest step to gives elimination product.

24.3.1 Conditions for E_1 cb

1. Substrate molecule must have a poor nucleofuge.
2. β-carbon with respect to nucleofuge must have atleast one H.
3. Reaction must proceed in presence of a strong base.
   In E_1 cb electrofuge is removed first resulting in the formation of carbanion followed by removal of nucleofuge in a slowest step to give elimination product.





General elimination rules: The following four rules are taken into consideration for this purpose.

1. **Saytzeff's rule (Zaitsev's rule):** According to this rule, during elimination reaction, hydrogen is always removed from that β-carbon which possess minimum number of hydrogen atoms. Under such conditions, formation of more stable substrate alkene occurs, which is more stable because of hyper conjugation.

Note:

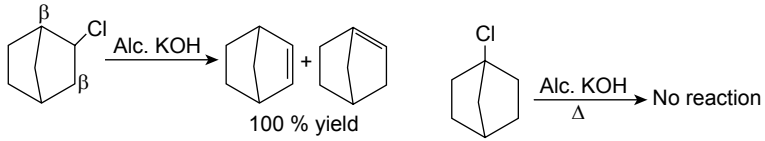
Saytzeff's rule is followed in all E_1 reactions and in majority of E_2 reactions.

2. **Hofmann's rule, i.e., Anti-Saytzeff's rule**
   According to this rule, if reaction condition is favourable, then H is removed from that β-carbon with respect to nucleofuge which posses more number of hydrogen atoms.

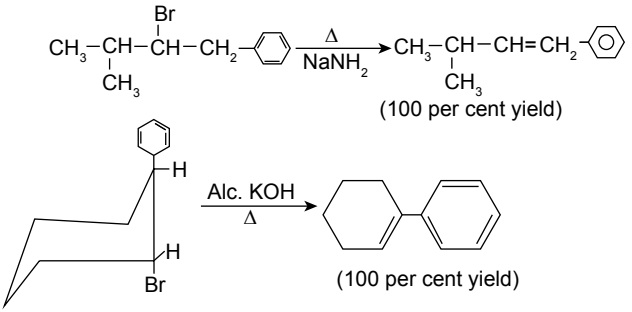
Note:

Hofmann's rule is followed in some E_2 reaction and in all E_{1cb} reactions as well as in pyorolytic elimination reaction.

3. **Bredt's rule**
   According to this rule, no matter reaction follows whatsoever mechanism a multiple bond never go to the bridge head carbon of a bridged bicyclic compound unless excellent nucleofuge is present or ring size is large enough.

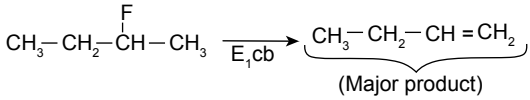


4. **Conjugation rule:** According to this rule, no matter a reaction follows whatsoever the mechanism is if a substrate molecule already possess a multiple bond then newly formed multiple bond is produced in such a manner that it is present in conjugation with old multiple bond. This rule is followed even in those cases where stereochemistry is unfavourable.

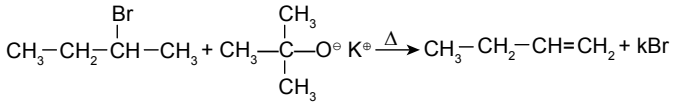


E_2 reaction where Hofmann's rule is followed:

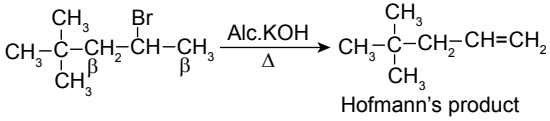
1. **De-hydrohalogenation of alkyl halide** having poor nucleofuge produces Hofmann's product as the major product



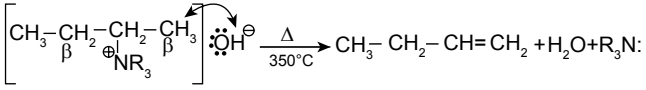
2. **If a bulky base is involved in a E_2 reaction,** then Hofmann's product is the major product.



3. **If γ-carbon w.r.t. nucleofuge is quaternary**, then Hofmann's product is the major product.



4. If a substrate molecule contains bulky leaving group, then Hofmann's product is the major product.
Hofmann's degradation: When quaternary ammonium hydroxide having atleast one hydrogen at β-carbon is heated at 350°C, alkene is obtained according to Hofmann's elimination rule.

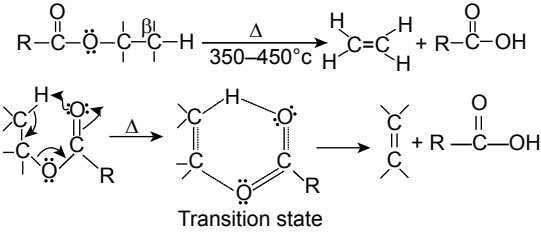


Pyrolytic elimination: This elimination is given by a very small family of organic compounds like ester, xanthate and amine oxides. This reaction proceeds in a gaseous phase at high temperature, (usually above the boiling point of the substrate) and does not involve any catalyst. Reaction is example of syn elimination because it proceeds through the formation of a cyclic transition state.

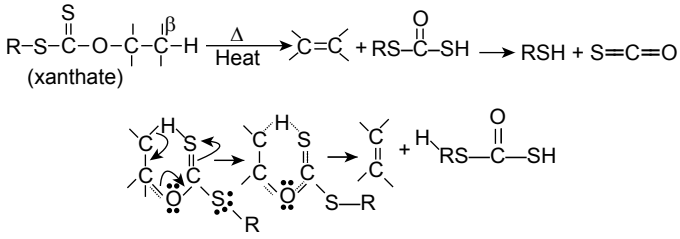
Reaction always follows Hofmann's elimination rule.

24.3.2 Pyrolysis of ester

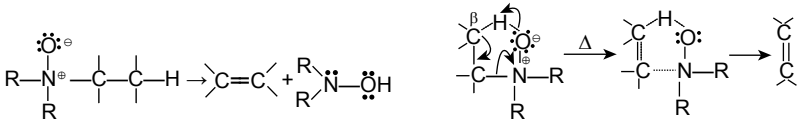
1. When ester containing atleast one β-hydrogen on the alkyl group attached with oxygen atom is heated at 350– 450°C, alkene is obtained.
Mechanism



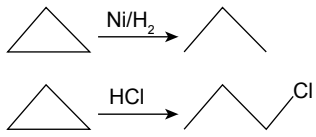
2. **Pyrolysis of xanthates:** When xanthate having atleast one β-hydrogen on alkyl group attached with oxygen atom is heated at 200–300°C, alkene is obtained.



3. **Pyolysis of amine oxide:** When amine oxide having atleast one β-hydrogen on alkyl group attached with N atom is heated at 150–250°C, alkene is obtained.



Addition reaction: A substrate molecule having a multiple bond can participate in addition reaction except cyclopropane. Cyclopropane is the only substrate which possess no multiple bond; still, it can participate in addition reaction because of presence of angular strain.



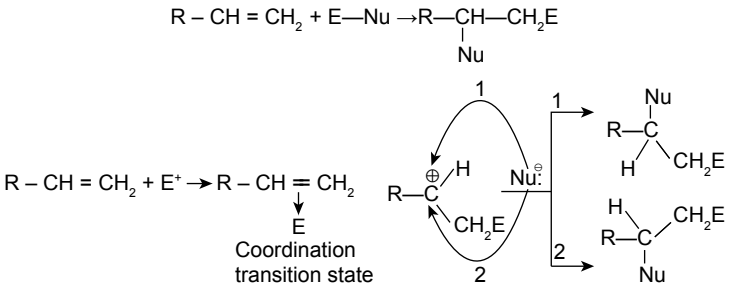
In addition reaction, there occurs loss of one π bond and gain of two σ-bonds, therefore, product system is more stable than that of reactant system due to which reaction is always exothermic.

Depending upon the type of reagents involved in slowest step, addition reaction reactions are classified into three categories:

(i) Electrophilic addition: This reaction is mainly given by alkene and alkyne.

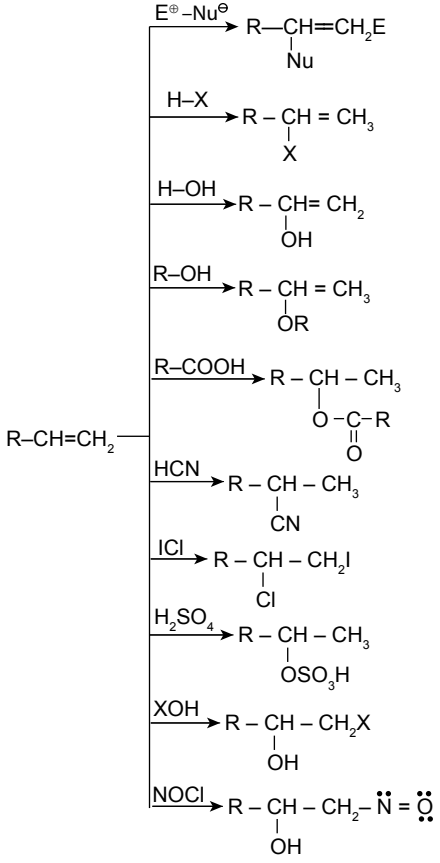
- In general, reaction proceeds in two steps through the formation of carbocation intermediate.
- Due to formation of carbocation intermediate, rearrangement is possible during the reaction.
- If the reagent involved is a weak electroyte like water, alcohol, HCN, etc. then reaction is catalysed by some Lewis acid or some protonic acids.
- If substrate and reagent both are unsymmetrical, then reaction follows Markownikoff's addition rule and is an example of Regio; Selective reaction.
  All addition reaction which follow either markownikoff's rule and elimination reaction which follow saytzeff and anti Saytzeff's rule are example of Regio -Selective reaction.

24.4 GENERAL REACTION MECHANISM

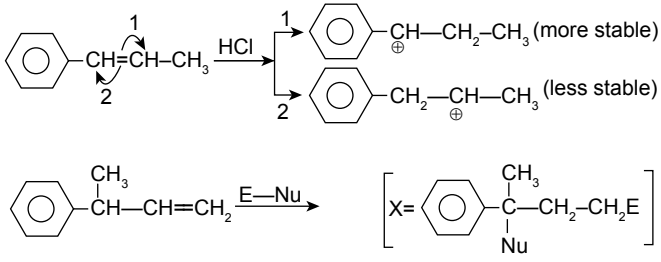


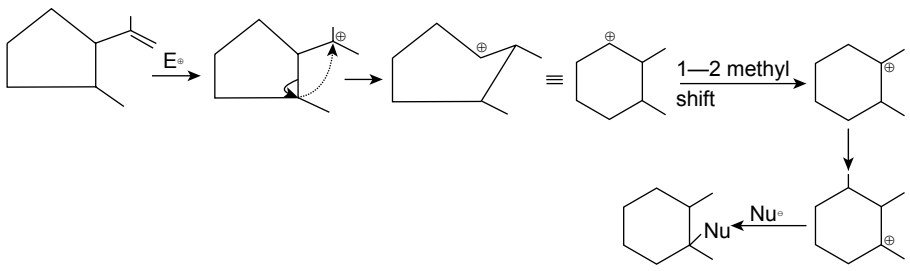
24.4.1 Markownikoff's Rule

Old statement: If both substrate and reagent are unsymmetrical, then positive part of the reagent is attached with that part of multiple bond which possess more number of hydrogen atom.



Modern statement: If both reagent and substrate are unsymmetrical, then attack of electrophile occurs in such a manner that the formation of more stable carbocation occur.

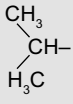
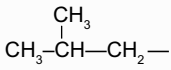
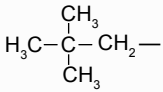
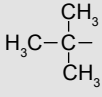
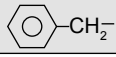




Nucleophilic substitution reaction: When part of a substrate is replaced by nucleophilic part of reagent, then reaction is termed as nucleophilic substitution substrate. In nucleophilic substitution, involved is either neutral or positively charged whereas substrate reagent involved is either neutralor negatively charged.

Factors affecting Nucleophlic substitution reaction

Structural feature of substrate: Branching present at α or β-carbon of the substrate w.r.t. nucleofuse decreases its reactivity towards S_N2 reaction because of increase in steric hindrance $R - L + Nu^{\ominus} : \rightarrow R - Nu + L^{\ominus}$

Alkyl part of Substrate	Relative reaction rate
1. C_2H_5-	1
2. CH_3-	30
3. $CH_3-CH_2-CH_2-$	0.4
4. 	0.025
5. 	0.03
6. $CH_3-CH_2-CH_2-CH_2-$	~0.4
7. 	10^{-5}
8. 	0
9. $CH_2=CH-CH_2-$	40
10. 	120

Branching present at γ or δ carbon creates steric effect but not hindrance.

1. Branching present at α or β-carbon increases the reactivty of substrate towards S_N1 reaction.
2. Unsaturation present at β-carbon or heteroatom containing lone pair of electron present on α-carbon increases the reactivity of substrate towards S_N1 reaction.

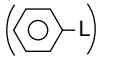
$$CH_3-CH_2-CH_2-L << CH_2=CH-CH_2-L << CH_3-\ddot{N}H-CH_2-L$$

3. Presence of strong electron with – drawing group on α-carbon of substrate increases its reactivity towards S_N2 mechanism.

$$CH_3-CH_2-CH_2-L << CH_3-\overset{\overset{O}{\|}}{C}-CH_2-L < O_2N-CH_2-L$$

Strong electron withdrawing group increases the charge intensity on α-carbon due to which attraction for nucleophile increases.

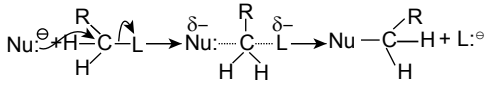
4. Unsaturation present at α-carbon may increase or decrease the reactivity of substrate towards nucleophilic substitute reaction.

Vinyl ($CH_2 = CH - L$) and aryl 

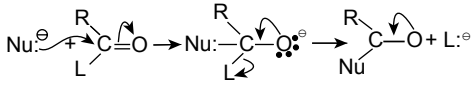
Substrates are almost inert toward nucleophilic substitution reaction.

Comparative study between nucleophilic acyl substitution and aliphatic nucleophilic substitution:

Nucleophilic acyl substitution



Aliphatic nucleophilic substitution



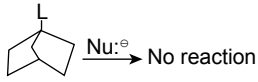
Acyl substrates $(R-\overset{\overset{O}{\|}}{C}-L)$ are more reactive than that of alkyl substrate ($R - CH_2 - L$) because of the following facts.

S. No.	Nucleophilic acyl substitution	Aliphatic nucleophilic substitution
1.	During the attack of nucleophile cleavage of a weak π-bond occur	During the attack of nucleophile cleavage of a strong σ bond occurs
2.	Carbon of aryl substrate is more electron deficient; therefore, offers more attraction for nucleophile.	Carbon of alkyl substrate is less electron deficient; therefore, offers less attraction for nucleophile
3.	Substrate molecule is planar and therefore offers less steric hindrance	Substrate molecule is tetrahedral, i.e., nonplanar and therefore offers more steric hindrance
4.	Reaction involves the formation of a tetrahedral intermediate which is more stable	Reaction involves the formation of transition state which is less stable

$$CH_3-\overset{\overset{O}{\|}}{C}-Cl > CH_3-CH_2-Cl \text{ and } CH_3-\overset{\overset{O}{\|}}{C}-O-CH_3 > CH_3-CH_2-O-CH_3$$

$$R-\overset{\overset{O}{\|}}{C}-X > R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R > RCOOR > RCOOH > R-\overset{\overset{O}{\|}}{C}-NH_2$$

5. Leaving groups present on bridged carbon of bridged bicyclic compound are always inert towards any kind of nucleophilic substitution.



Nature and concentration of nucleophilic: In slowest step of S_N1 reaction, nucleophile is not involved and therefore rate of S_N1 reaction is independent from the nature and concentration of nucleophile.If nucleophile is weak and its concentration is low, then S_N1 mechanism is favourable. In most of the S_N1 reactions solvent molecule acts as a nucleophile itself.

Since S_N2 reaction proceeds through a single step, therefore the rate of reaction depends upon the nature as well as identity of nucleophile, i.e., if nucleophile is strong and its concentration is high, then S_N2 mechanism is favourable. Nucleophillicity depends upon

1. In polar protic solvents like water, alcohol, etc. nucleophilicity $\propto \frac{1}{\text{Extent of hydration}}$

$$\text{Extent of hydration} \propto \frac{1}{\text{Size of nucleophilic atom}}$$

2. Polarizability of nucleophilic atom: Nucleophilicity ∝ polarizability of nucleophilic atom

Nature of leaving group: Presence of good nucleofuse increases the reactivity of substrate torwards S_N1 and S_N2 reactions.

Leaving tendency of nucleofuse, i.e., nucleofusity $\propto \frac{1}{\text{Basicity}}$

Therefore, we can say that weakest bases are best nucleofuses. Order of necleofusity

$$CF_3-SO_3^{\ominus} > H_3C-C_6H_4-SO_3^{\ominus} > CH_3-SO_3^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$$

Nature of solvent used: This is a very important factor. Some reactions may not proceed due to improper selection of solvent only.

Selection of solvent towards S_N1 reaction

Substate	Transition State Product	Stabilization of Transition State w.r.t. Substrate in Polar Protic Solvent	Effect on Reaction State
1. (R – L)	$R^{\delta+}\cdots L^{\delta-}$	More	Increases
2. $R-L^{\oplus}$	$R^{\delta+}\cdots\cdots L^{\delta+}$	Less	Decreases

Selection of solvent towards S_N2 reaction

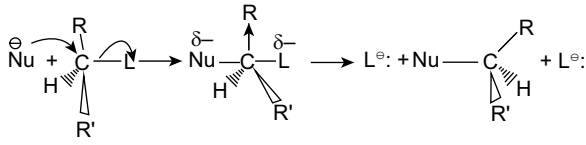
Reactant System	Transition State Produced	Stabilization of Transition State w.r.t Reactant in Polar Protic Solvent.	Effect on Reaction State
1. R – L + Nu	$\overset{\delta+}{Nu}\cdots\cdots R\cdots\cdots \overset{\delta-}{L}$	More	Increases
2. $R-L+Nu^{\ominus}$	$\overset{\delta-}{Nu}\cdots\cdots R\cdots\cdots \overset{\delta-}{L}$	Less	increases

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

On the basis of the above facts, we can conclude that for SN' 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.

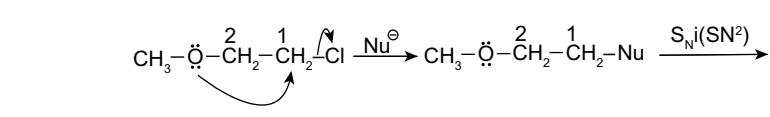
Mechanism involved in nucleophilic substitution reaction :

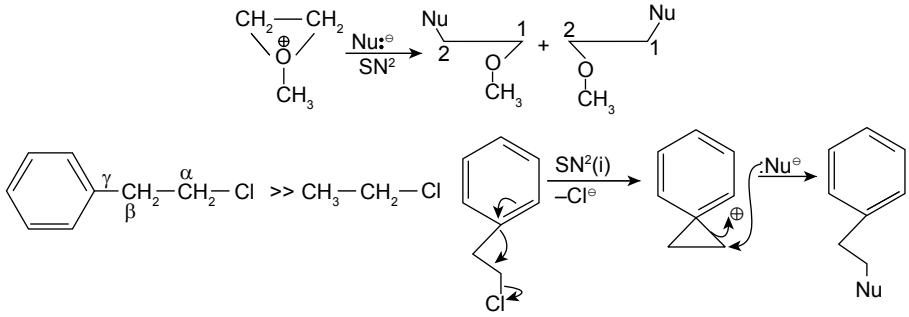
S_N2 reaction: When a substrate molecule having a good nulceofuge is treated with a nucleophile, Where attack of nucleophile occurs from opposite side to that of leaving group, then there occurs the formation of a pentavalent transition which gets converted into inverted product if leaving group is directly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



24.5 CHARACTERISTICS OF S_N2 REACTION

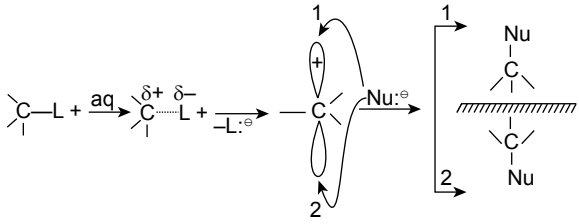
1. Since reaction completes in a single step, therefore rate of reaction depends upon the concentration of substrate and nucleophile due to which reactions follows second-order kinetics r = K [R – L] [base]
2. Presence of good nucleofuse increases the reactivity of substrate towards S_N2 reaction.
3. If nucleophile is strong and its concentration is high, then S_N2 reaction is favourable.
4. S_N2 reaction best proceeds in a polar aprotic solvent like acetone, DMSO, DMF, etc.
5. If leaving group is directly attached with a chiral carbon, then during the reaction Walden inversion takes place.
6. Primary substrate where β-carbon is primary or secondary and secondary substrate where β-carbon is primary always follows S_N2 path but secondary substrate where β-carbon is secondary follows S_N1 or S_N2 path depending upon other reaction condition.
7. Substrate molecule having hetero atom containing lone pair of electron at β-carbon or containing unsaturated γ-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.





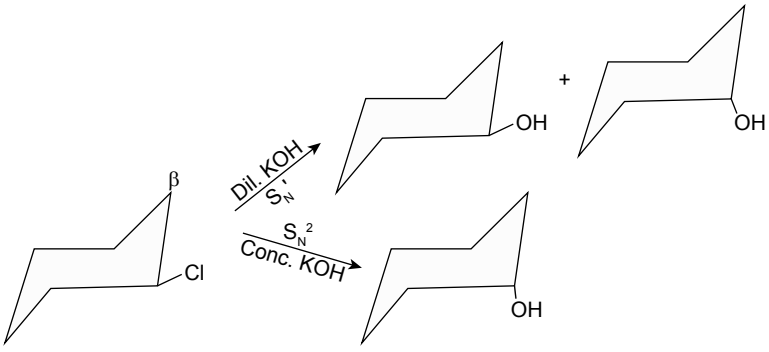
Uni molecular Nucleophilic substitution: S_N1 Reaction

When a substrate molecule having a good nucleofuse 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



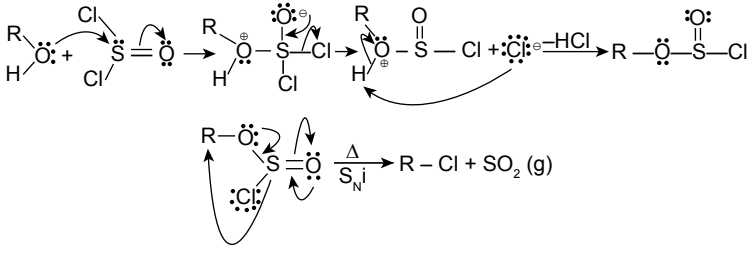
24.5.1 Characteristics of S_N1 Reaction

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 nucleofuse increases the reactivity of substrate towards S_N1 reaction.
3. If nucleophile is weak or its concentration is low, then S_N1 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 β-carbon is tertiary or quaternary always follow S_N1 mechanism.
6. Tertiary substrate always follows S_N1 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 S_N1 and S_N2 mechanisms.
9. If nucleofuge is present on bridgehead carbon of bridged bicyclic compound, then such substrates are inert towards both S_N1 and S_N2.
10. In majority of SN' 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_Ni)

In some nucleophilic susbstitution 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_Ni a part of leaving group attacks the carbon of substrate by detaching itself from the leaving group.

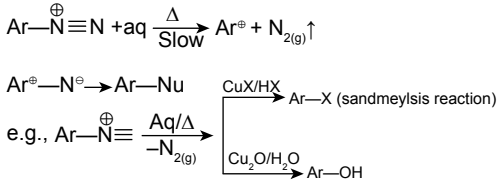


In Darzen's method, $SOCl_2$ can be replaced by $COCl_2$. However, in case of $COCl_2$ yield of product produced is poor S_N1, S_N2' and S_Ni'

If substrate used is allylic and reaction conditions are corresponding to S_N1, S_N2 and S_Ni respectively, then formation of product occurs through allylic shift. During the formation of this product, S_N1', S_N2', S_Ni' mechanisms are observed.

Unimolecular aromatic nucleophilic substitution (ArS_N')

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.

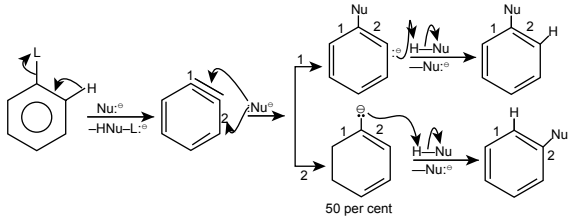


2. $Ar—SO_3^{\ominus}\ Na^{\oplus} + Na^{\oplus}Nu^{\ominus} \xrightarrow{\Delta} Ar—Nu + Na_2SO_3$

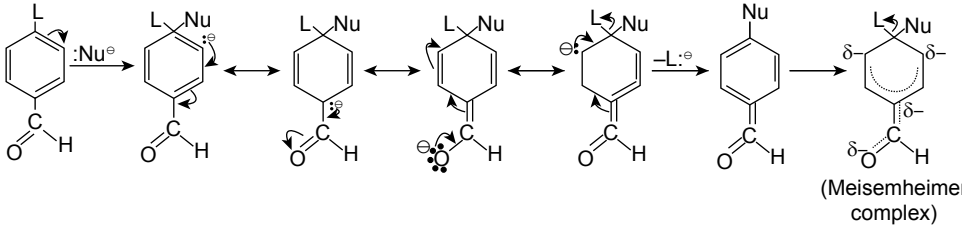
Bimolecular aromatic nucleophilic substitution (ArS_N2)

Following two mechanism are observed in this case:

1. **Benzyne intermediate formation mechanism:** This mechanism is observed in those cases where
   (i) Substrate molecule has atleast one ortho hydrogen w.r.t. nucleofuse
   (ii) There is no EWG at ortho or para position w.r.t. nucleofuge
   (iii) 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, flourine 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, HIO_3, etc. are used.

$$R-H+X_2 \xrightarrow[\text{or } \Delta]{\text{UV light}} R-X+HX$$

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

1. **Reactivity of halogen involved:** As the reactivity of halogen increases, extent of multiple substitution also increases.
   $F_2 > > > Cl_2 > > Br_2 > > > > I_2$
   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.
2. **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.

Initiation step: $X\!-\!X \rightarrow 2X$

Propagation step: $R\!-\!H \rightarrow X \rightarrow R + H\!-\!X\ ;\ \Delta H_1$

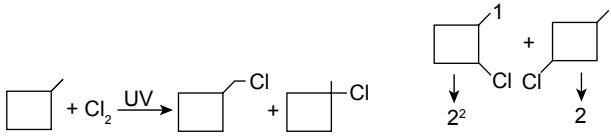
$R + X\!-\!X \rightarrow R\!-\!X + X\ ;\ \Delta H_2$

	F_2	Cl_2	Br_2	I_2
ΔH_1	< 0	< 0	> 0	> 0
ΔH_2	< 0	> 0	< 0	< 0
ΔH_{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 subsitution.
  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° – H : 2° – H : 1° – H : 5 : 3.8 : 1
  For bromination, relative reactivity of hydrogen is 3° – H : 2° – H : 1° – 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 $\propto \dfrac{1}{\text{Reactivity of halogen involved}}$
- Reactivity of H being substituted depends upon the stability of free radical produced per cent yield of a product produced towards halogenation $= \dfrac{\text{Total reactivity of H being substituted}}{\text{Total reactivity of all hydrogen}} \times 100$

  Total reactivity of a particular hydrogen = (number of that type of H) × 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.

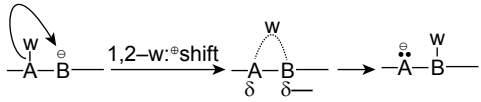
Among aryles, presence of EDG increases its migratory aptitude, which presence of EWG decreases its migratory aptitude.

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

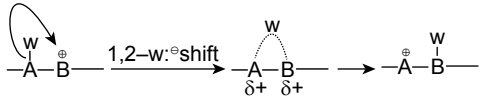
1. **Intermolecular rearrangement:** If during a rearrangement reaction migrating group is detached completely from the substrate molecule and then either it reattaches with the same molecule or attaches with some other molecule then reaction is termed as intermolecular rearrangement.
   Such reactions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

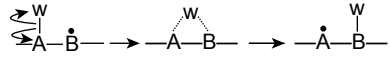
1. **Nucleophilic rearrangement:** If migration terminus of the substrate is electron deficient (due to +ve charge or incomplete octet or presence of d or f-orbitals), then nucleophilic rearrangement takes places and most rearrangement reactions belong to this category.



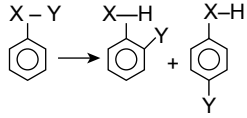
2. **Electrophilic rearrangement:** If migration terminus is electron rich, then this rearrangement takes place. It is rearrangement and is observed rarely.



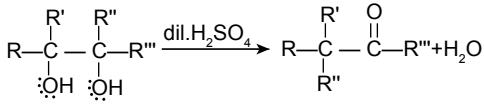
3. **Free radical rearrangement:** If migration terminus contains unpaired electron, then free radical rearrangement takes place. This rearrangement is observed rarely.



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 seperated or partially separated from substrate and thus it is included in both inter and intra molecular rearrangement).

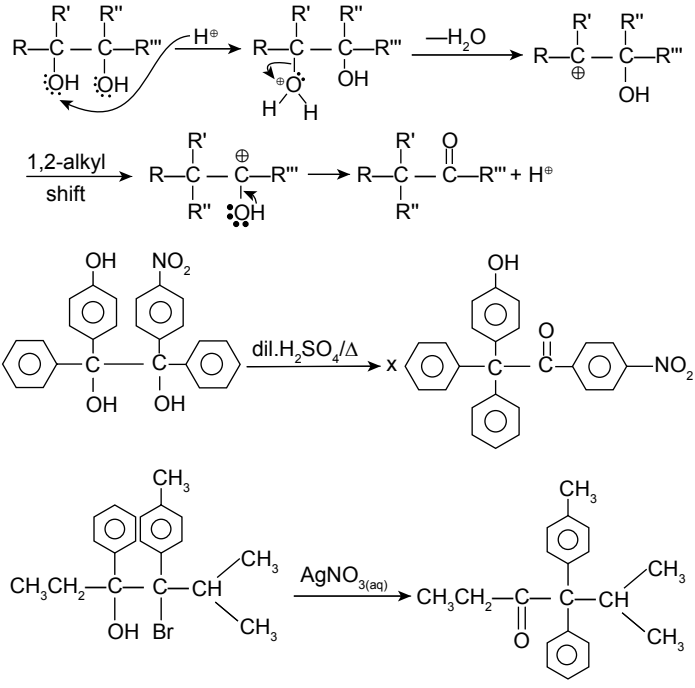


5. **Carbon to carbon rearrangement reaction:** If migration origin migration terminates and both are carbon atoms, then rearrangement reaction belongs to this category.
6. **Pinnacol Pinnacolone reaction:** When vic diol (also called pinna col) is treated with dilute H_2SO_4, it undergoes rearrangement to produce a ketone, also called pinnacolone.

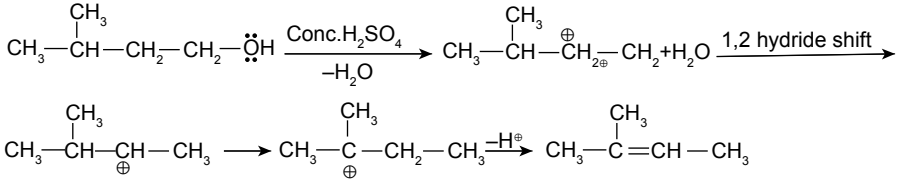


In this reaction, bromohydrin can also participate on treatment with aq. $AgNO_3$ solution and hydroxylamine can participate on treatment with nitrous acid.

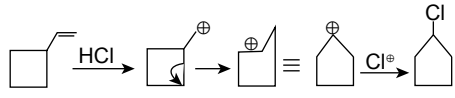
- During the reaction, protonation of that hydroxyl group occurs first corresponding to which directly formed carbocation is more stable.



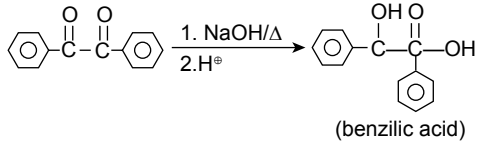
2. Wagner Meerwein rearrangement or Retro pinnacol rearrangement
This rearrangement is observed in those E_1 reactions where carbocation intermediate produced undergoes rearrangement to form more stable carbocation. In Wagner Meerwein rearrangement, migratory aptitude of hydride is maximum.



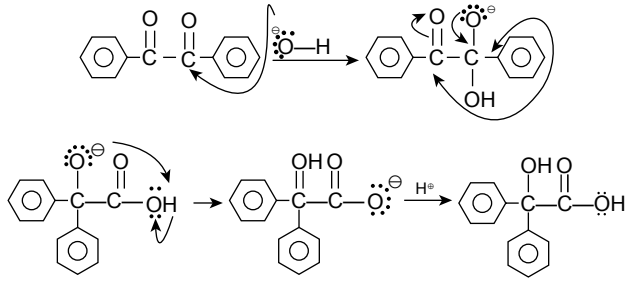
3. Demzanov rearrangement: This rearrangement is observed in those reactions where carbocation, carbene or nitrene intermediate undergo ring expansion or ring contraction to produce final product.



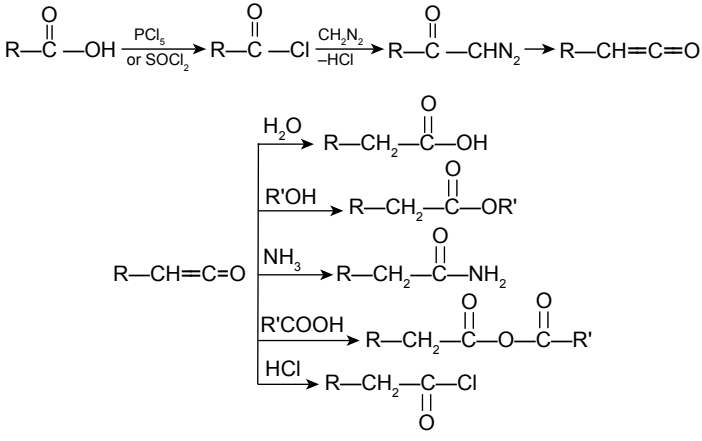
4. Allylic rearrangement: This rearrangement is observed in those reactions where formation of product occurs by allylic shift of substrate. It is observed in S_N1', S_N2' and in S_Ni' mechanism.



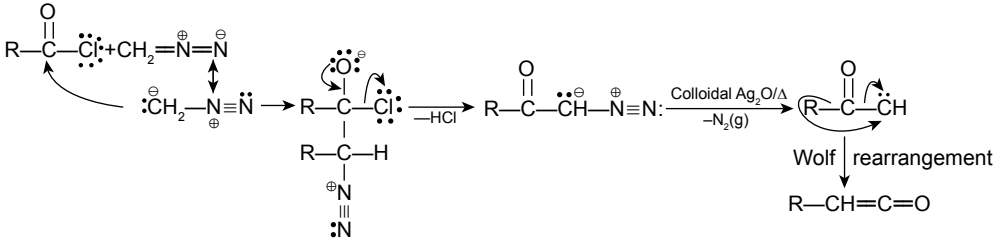
5. **Benzillic rearrangement:** When aromatic α-diketone also called benzil, is treated with alkali like NaOH and KOH, followed by acidification, benzilic acid is obtained.
During the reaction attack of OH^- ion occur on that carbonyl carbon which is more e^- deficient.



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 Ag_2O 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.

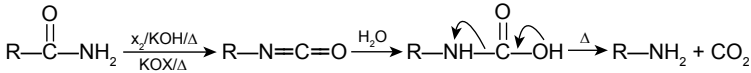


Mechanism:

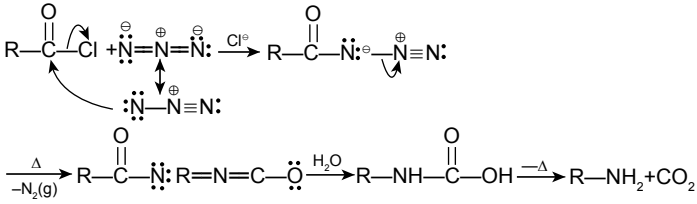


1. **Carbon-to-nitrogen rearrangement:** If migration origin is carbon and nitrogen terminus is nitrogen, then rearrangement reaction belongs to this category.

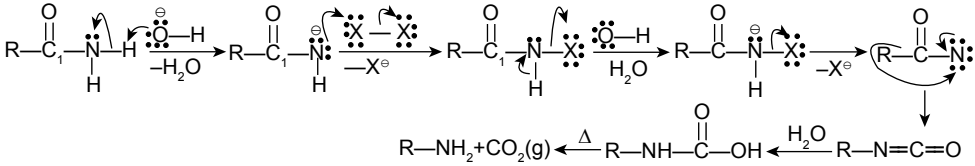
Hoffmann's bromamide synthesis: When un substituted amide is treated with halogen along with alkali or metal hypohalite, formation of alkyl isocyanate occurs which on hydrolysis produces primary amine with the evaluation of CO_2.



Mechanism:

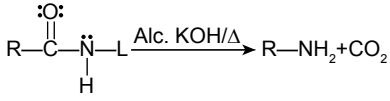


Mechanism:

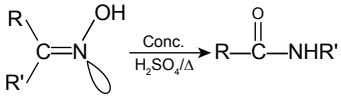


2. **Curtius rearrangement:** When acid halide is treated with metal azide, acyl azide is obtained, which on heating gets converted into isocyanate with a good yield. Then, isocyanate undergoes hydrolysis to produce primary amine with evolution of N_2 gas.

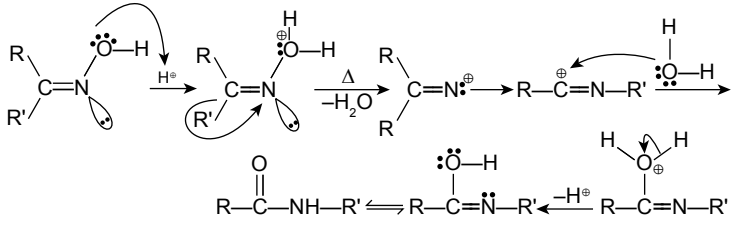
3. **Lossen rearrangement:** When substituted amide containing a good nucleofuge and hydrogen attached with N atom, is treated with a strong base, it undergoes elimination to produce isocyanate which on hydrolysis gives primary amine and CO_2.



4. **Bakemann's rearrangement:** When ketoxime is heated with dehydrating agent like conc. H_2SO_4, H_3PO_4, dry HCl, P_2O_5, Al_2O_3, BF_3, etc. it undergoes rearrangement to produce substituted amide during the reaction, alkyl group which is present anti to that of –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.



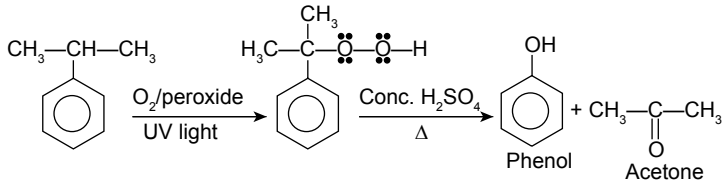
Mechanism:



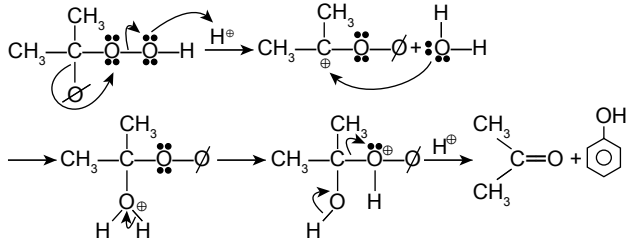
3. **Carbon to oxygen rearrangement:**

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

When cumene hydroperoxide is treated with conc. H_2SO_4, it undergo rearrangement to produce phenol and acetone, where cumene hydroperoxide is prepared by treating cumene, i.e., isopropyl benzene with oxygen air an in 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: $R-\overset{O}{\overset{\|}{C}}-O-R' + R''-\overset{O}{\overset{\|}{C}}-O-H$

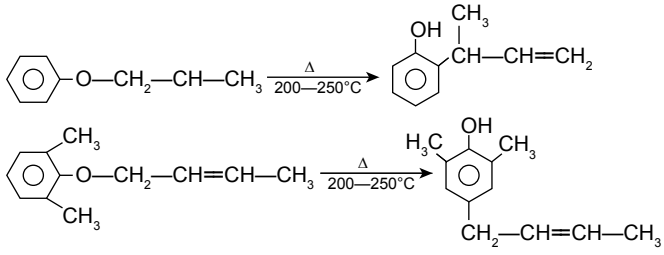
During the reaction, migration of that alkyl group occurs from C to O which possess highest migratory aptitude. During the reaction, ester produced may be involved in trans-esterification reaction with the acid present on product side. However, trans-esterification process is pH dependent. Due to trans-esterification, 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

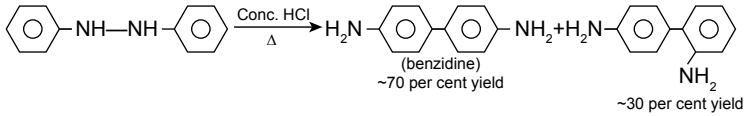
When allyl aryl ether is heated at 200–250°C, in absence of catalyst, ortho and para–allyl phenol is obtained, paramigration occurs only when both orthopositions are blocked.

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.



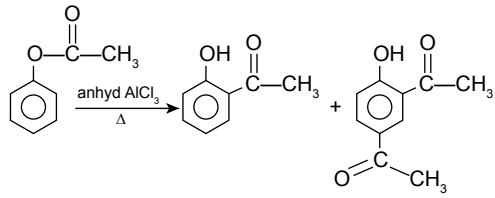
24.8 BENZIDINE REARRANGEMENT

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 $AlCl_3$, 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) **Favorskii rearrangement:**

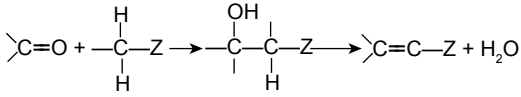
When α-ahalogenated ketone is treated with aqueous alkali or with alcoholic metal alkoxide or with $NaNH_2/NH_3(\ell)$ it gets converted into carboxylic acid, ester and acid amide respectively.

If ketone used is cyclic, then ring contraction occurs; however, if it is acyclic, then chain shortening of principle chain occurs.

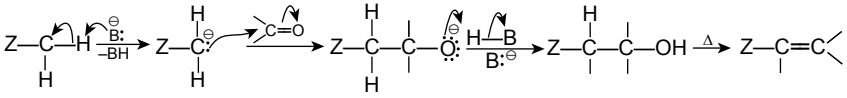
24.10 CONDENSATION REACTION

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 α-hydrogen which is sufficiently an acidic reaction to proceed in presence of base as a catalyst.

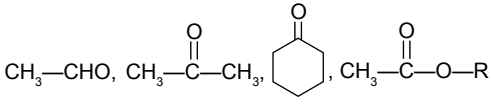
General reaction:



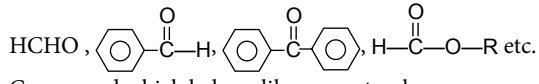
Reaction mechanism:



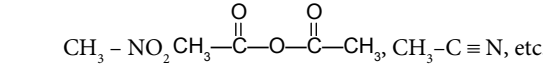
Compound which can act as substrate and reagent both in condensation reaction, are



Compounds which behave like substrate only are



Compound which behave like reagent only are

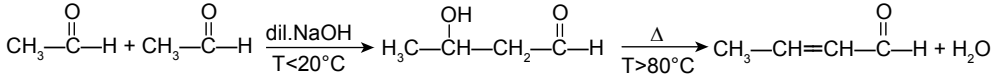


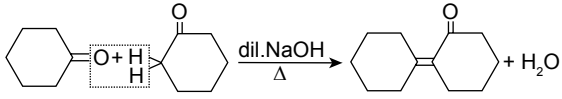
24.11 ALDOL CONDENSATION

When a carbonyl compound containing at least two α-hydrogen is heated with dil. alkali, at low temperature, i.e., < 20°C, formation of addition product aldol occurs which undergoes dehydration at high temperature, > 80°C to produce, α, β unsaturated carbonyl compound.

24.11.1 Classification of Aldol Condensation

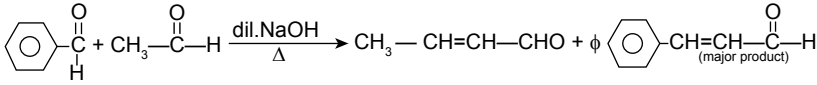
Self-aldol condensation: When reaction occurs between two molecules of same carbonyl compound, then reaction is termed as self-aldol condensation



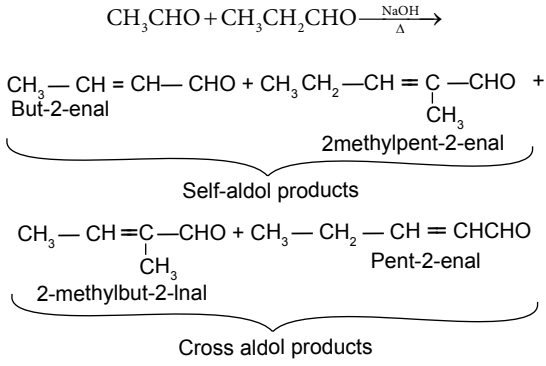


Cross aldol condensation: This reaction takes place between two different carbonyl compound where cross product is always a major product.

Case I: If only one of them possess α-hydrogen:

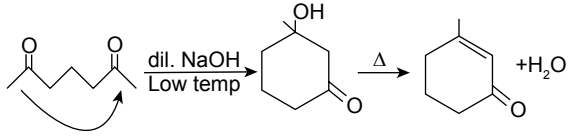


Case II: When both contain α-hydrogen: Under such a condition, four products are produced out of which two are cross condensation products and two are self-condensation products.

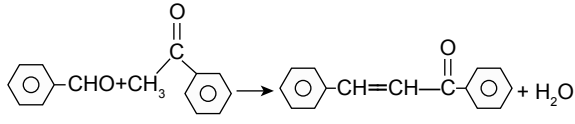


Intramolecular aldol condensation, i.e., cyclization via aldol condensation

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.



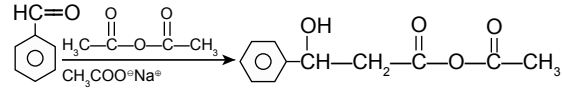
Claisen Schmidt's condensation: Cross aldol condensation between aromatic aldehydes and aliphatic or mixed ketone is called Claisen Schmidt's condensation.



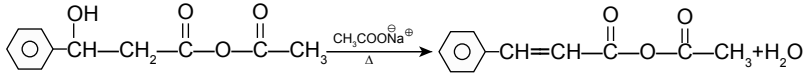
24.12 PERKIN'S CONDENSATION

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

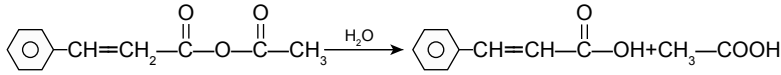
Step 1: In this step, nucleophilic addition occurs between aromatic aldehyde with acid anhydride.



Step 2: Dehydration of nucleophillic addition product occurs to produce α, β-unsaturated acid anhydride.



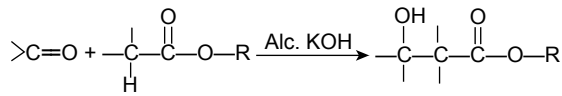
Step 3: In this step, hydrolysis of dehydrated product takes place, which results in the formation of α, β-unsaturated acid.



24.13 STOBBE CONDENSATION

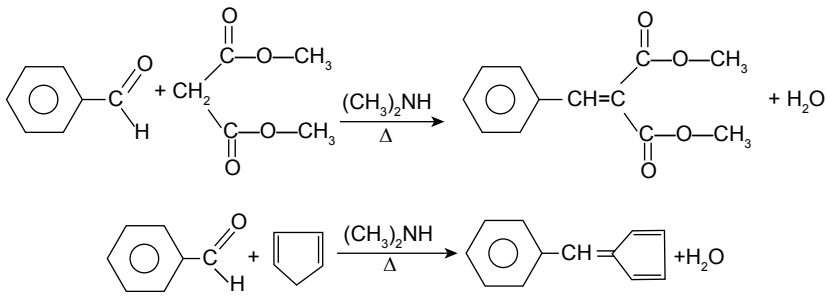
This reaction taken place between a carbonyl compound which may or may not have α-hydrogen and ester having atleast one α-hydrogen. Reaction is catalysed by strong passes such as alc. KOH, metal akoxide, $NaNH_2$, etc.

Product of the reaction is β-hydroxy ester which may or may not be dehydrated to produce α, β-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.

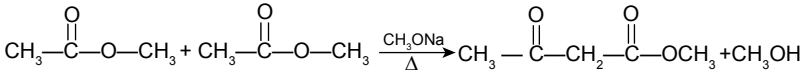


24.15 CLAISEN CONDENSATION

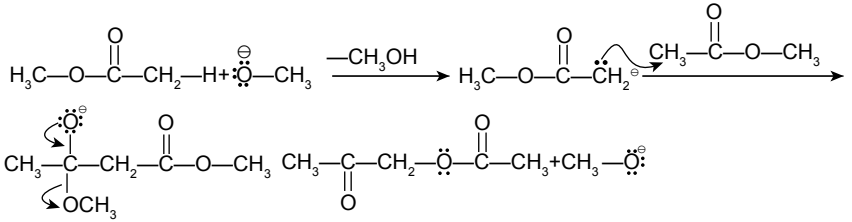
When an ester containing atleast one α-hydrogen is treated either with the same molecule or with some other ester molecule in presence of strong base like metal alkoxide $NaNH_2$, etc. β-keto ester is obtained. Reaction is further classified into two categories.

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

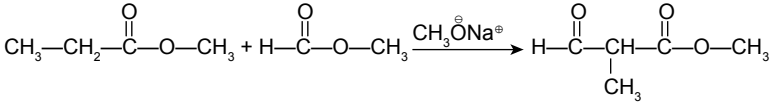
(i) **Intermolecular claisen condensation:** This reaction takes place between two molecules of ester whether they are same or different. It is further classified into two categories:
(a) Self-Claisen condensation: When reaction occurs between same ester molecules



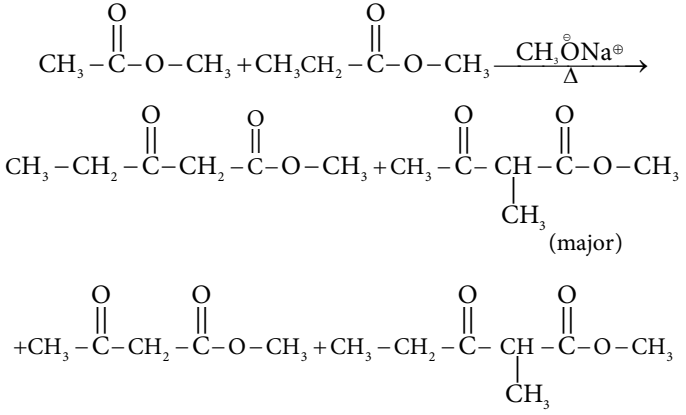
Mechanism



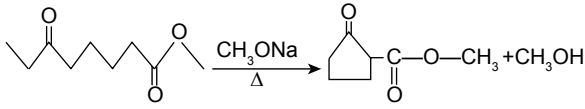
(b) Cross Claisen condensation:
Case I: If only one of when possess α-hydrogen



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



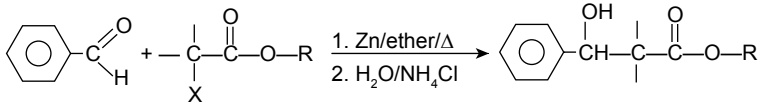
(ii) Intramolecular claisen condensation: It is also called Diechmann condensation or cyclization via claisen condensation. This reaction is given by diesters when they are treated with metal alkoxide or $NaNH_2$. During the reaction, 5 or 6 membered ring is produced.



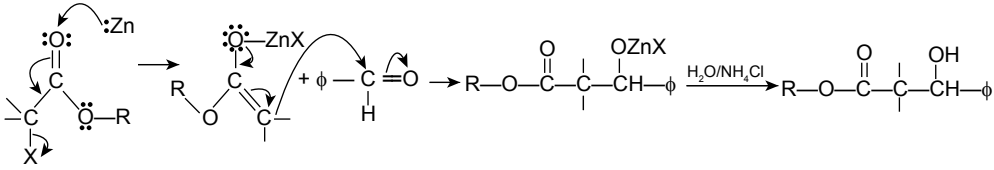
24.16 REFORMATSKY REACTION

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

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

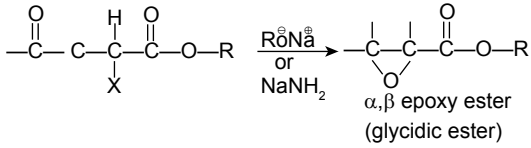


Mechanism:



24.17 DARZEN'S GLYCIDIC ESTER CONDENSATION

When a carbonyl compound containing α-hydrogen or not is heated with α-halogenated ester containing atleast one α-hydrogen in presence of strong base α,β-epoxy ester, also called glycid ester, is produced.

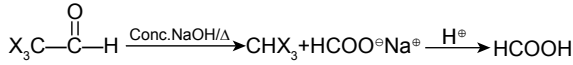


Disproportionation reaction: In a disproportionation reaction, same species undergo oxidation and reaction simultaneously.

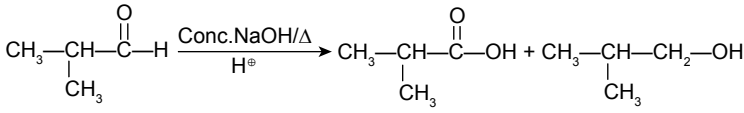
24.18 CANNIZZARO REACTION

When an aldehyde containing no α-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 α-hydrogen; still, it cannot participate in Cannizzaro reaction under similar conditions to produce haloform.



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

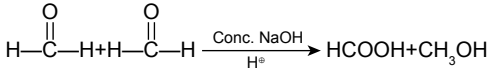


Reaction further classified into two categories:
(a) Intermolecular Cannizzaro reaction
(b) Intra-molecular Cannizzaro reaction or internal cannizzaro reaction.

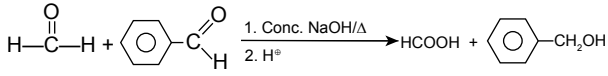
24.19 INTERMOLECULAR CANNIZZARO REACTION

This reaction takes place between two molecules of aldehyde having no α-hydrogen.

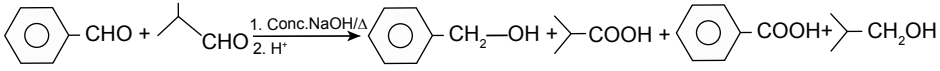
(i) Self-Cannizzaro reaction: When same aldehyde molecule is used during reaction.



(ii) Cross Cannizzaro Reaction: It two different molecules of aldehyde are used.
Case I: If one of them is formaldehyde, then HCHO always undergo oxidation.

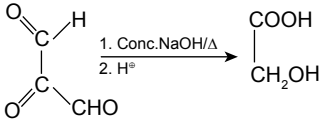


Case II: If none of them is HCHO, then mixture of the product is obtained.

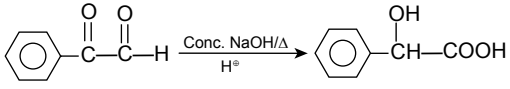


24.20 INTRAMOLECULAR CANNIZZARO REACTION OR INTERVAL CANNIZZARO REACTION

(i) **Internal self Cannizarro reaction:**
This reaction is given by dialdehyde containing no α-hydrogens.

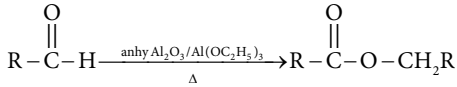


(ii) **Internal cross canizaaro reaction:**
This reaction is given by keto aldehyde containing no α-hydogen where aldehyde is always converted into carboxylic acid by oxidation, whereas keto group undergo reduction.



24.21 TISHCHENKO REACTION

When aldehyde containing α-hydrogen or not is treated with anhydrous Al_2O_3, or with $(C_2H_5O)_3Al$, or with some other Lewis acid catalyst, ester is obtained.



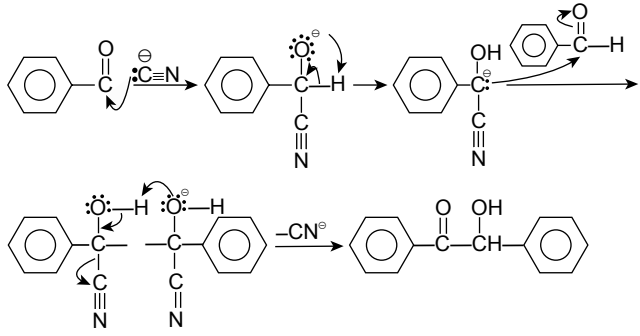
Reaction is also termed as extended Cannizzaro reaction on the basis of final products, produced.

If aldehyde used is aromatic, then reaction best proceed in complexes like $Na_2[Fe(CO)_4]$.

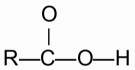
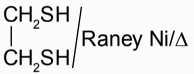
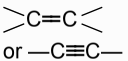
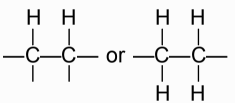
During the reaction, oxidation of that aldehyde occurs which combines with Lewis acid catalyst, whereas the other aldehyde undergo reduction.

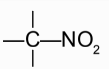
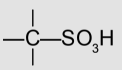
24.22 BENZOIN CONDENSATION

When an aromatic aldehyde is treated with alcohol in aqueous KCN, aromatic α-hydroxy ketone also called benzoin is obtained which gives positive test with Tollen's, Bendict's, and Fehling's reagent though having no aldehydic group.

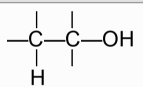
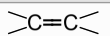
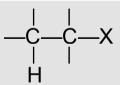
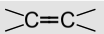
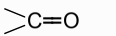
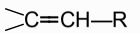
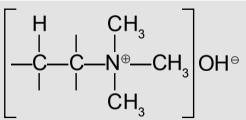
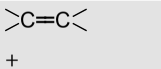


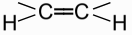
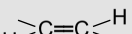
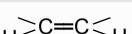
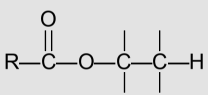
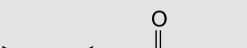
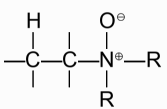
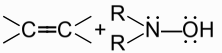
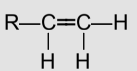
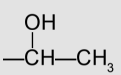
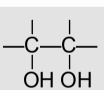
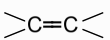
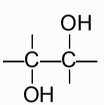
24.23 ALKANE

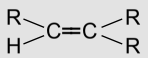
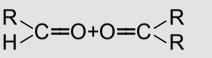
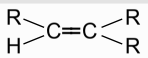
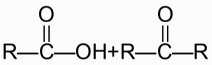
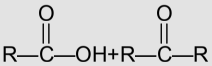
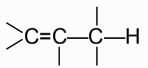
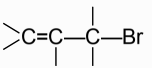
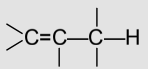
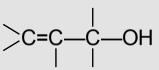
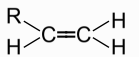
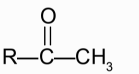
S. No.	Reactants	Reagents	Products	Mechanism involved	Name of reaction
1.		NaOH/CaO/Δ	R–H	Carbanion formation	Decarboxylation
2.	R – X	$R_2'CuLi$ (Gilmann's regent)	R – R′	Nucleophilic substitution (S_N2)	Corey-house synthesis
3.	2R – X	Na/dry ether	R – R	Free radical and ionic mechanism	Wurtz reaction
4.	R – COOK	H_2O/electrolysis	R – R	Free radical mechanism	Kolbe's electrolytic method
5.		Zn–Hg/HCl	R – CH_2 – R	Reduction	Clemmensen reduction
6.		NH_2NH_2/KOH/glycol/Δ	R – CH_2 – R	Reduction	Wolf-Kishner reduction
7.			R – CH_2 – R	Reduction	Mozingo method
8.	2R – X	Zn/C_2H_5OH or ether	R – R	Nucleophilic substitution	Frankland's reaction
9.	R – X	Zn/CH_3COOH or Zn/HCl or Zn–Cu/C_2H_5OH	R – H	_____	Reduction of alkyl halide
10.	R – X	$LiAlH_4$ or $NaBH_4$ or Ph_3SnH	R – H	Nucleophilic substitution	Reduction of alkyl halide
11.		H_2/Ni or H_2/Pt or Raney Ni		Adsorption	Hydrogenation of alkene or alkyne

S. No.	Reactants	Reagents	Products	Mechanism involved	Name of reaction
12.	R – X or R – OH	HI/red P	R – CH_3	_____	Reduction
13.	Be_2C or Al_4C_3	H_2O	CH_4	Neutralization	Hydrolysis of carbide
14.	n-hexane	$V_2O_5/Cr_2O_3 - Al_2O_3/500°C$		Free radical mechanism	Aromatization
15.		Conc. HNO_3/Conc. H_2SO_4/500°C		Free radical substitution	Nitration of alkane
16.		Conc. H_2SO_4 or fuming H_2SO_4/500°C		Free radical substitution	Sulphonation of alkane

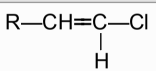
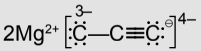
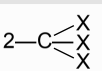
24.24 ALKENE

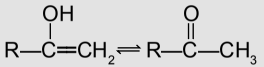
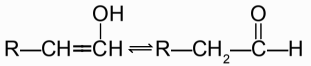
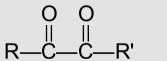
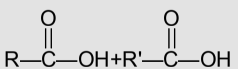
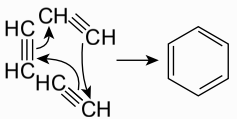
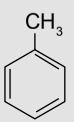
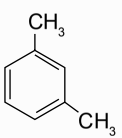
S. No.	Reactants	Reagents	Products	Mechanism involved	Name of reaction
1.		Conc. H_2SO_4/Δ or P_2O_5/Δ or $AlCl_3/\Delta$		Elimination (E_1)	Dehydration of alcohol
2.		Alc. KOH/Δ or $RONa/\Delta$ or $NaNH_2/\Delta$		Elimination (E_2)	Dehydrohalogenation
3.		$Ph_3P = CH - R$		Nucleophilic addition elimination	Wittig reaction
4.		Δ	 + $(CH_3)_3N + H_2O$	Elimination (E_2)	Hofmann's degradation

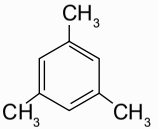
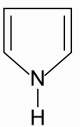
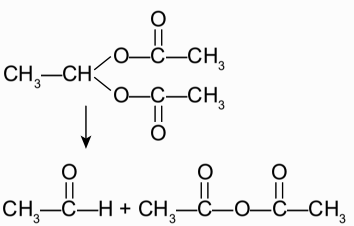
S. No.	Reactants	Reagents	Products	Mechanism involved	Name of reaction
5.	$-C \equiv C-$	1. B_2H_6/THF 2. CH_3COOH		Syn-addition reaction	Hydroboration-reduction
6.	$-C \equiv C-$	$Na/NH_{3(l)}$ or $Li/NH_{3(l)}$		Anti-addition	Birch reduction
7.	$-C \equiv C- + H_2$	$Pd/CaCO_3/BaSO_4$ or quinoline (Lindlar's catalyst) or Ni_2B (P-2 catalyst)		Syn-addition reaction	Syn-hydrogenation
8.		Δ/400°C		Pyrolytic elimination	Pyrolysis of ester
9.		Δ/200°C		Pyrolytic elimination	Cope elimination
10.		Dil. H_2SO_4		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.		Cold, dil. alkaline $KMnO_4$ (Bayer's reagent) or $OsO_4/NaHSO_3/H_2O$		Syn-addition reaction	Syn-hydroxylation
13.		Peroxy acid/H_2O/ $OH^{\ominus}$		Prileschaev reaction	Anti-hydroxylation

S. No.	Reactants	Reagents	Products	Mechanism involved	Name of reaction
14.		$O_3/Zn/H_2O$		_____	Reductive ozonolysis
15.		$DMSO_3/H_2O$			Oxidative ozonolysis
16.		Dil. alk $KMnO_4/\Delta$ or $K_2Cr_2O_7/H^+/\Delta$		Oxidation	Oxidative cleavage of alkene
17.		$NBS/CCl_4/UV$ light		Free radical substitution	Allylic bromination
18.		SeO_2/CH_2Cl_2		Free radical mechanism	Allylic oxidation
19.		1. $PdCl_2/H_2O$ 2. $CuCl_2$/air/Δ		_____	Wacker's process

24.25 ALKYNE

S. No.	Reactants	Reagents	Products	Mechanism involved	Name of reaction
1.		$NaNH_2/\Delta$	$R - C \equiv CH$	E_2	Dehydrohalogenation reaction
2.		H_2O	$H–C\equiv CH + Ca(OH)_2$	Neutralization reaction	Hydrolysis of carbide
		H_2O	$CH_3 - C \equiv CH$	Neutralization reaction	Neutralization reaction
3.		Ag powder/Δ	$—C \equiv C—$	Elimination	Dehalogenation of gem trihalide

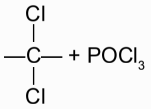
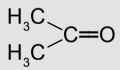
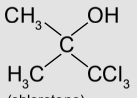
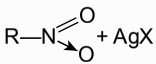
S. No.	Reactants	Reagents	Products	Mechanism involved	Name of reaction
4.	R – C ≡ C – H	1. $HgSO_4/H_2SO_4$ 2. $NaBH_4$		Nucleophillic addition (Markownikoff rule)	Oxymercuration-demercuration (anti-addition)
5.	R – C ≡ C – H	**1.** B_2H_6/THF/ **2.** $H_2O/OH^{\ominus}$		Syn-addition (anti-Markownikoff's rule)	Hydroboration – oxidation
6.	R – C ≡ C – R′	$O_3/Zn/H_2O$ or $DMSO_3/H_2O$	 R–COOH + R′–COOH	Reductive oxidative	Ozonolysis Ozonolysis
7.	CH≡CH+CH≡CH	$CuCl/NH_4Cl/\Delta$	CH_2=CH–C≡CH	Addition reaction	Reductive coupling
8.	R – C = C – R′	Dil. alk $KMnO_4/\Delta$ or $K_2Cr_2O_7/H^{\oplus}/\Delta$		Oxidation	Oxidative cleavage of alkyne
9.	3CH≡CH	Red hot cu tube		Free radical coupling	Pyrolysis of alkyne
10.	CH_3–C≡CH + 2CH≡CH	Red hot cu tube		Free radical coupling	Pyrolysis of alkyne
11.	$2CH_3$–C≡CH + CH ≡ CH	Red hot cu tube		Free radical coupling	Pyrolysis of alkyne

S. No.	Reactants	Reagents	Products	Mechanism involved	Name of reaction
	$3CH_3–C\equiv CH$	Red hot cu tube		Free radical coupling	Pyrolysis of alkyne
	$4CH\equiv CH$	Red hot cu tube		Free radical coupling	Pyrolysis of alkyne
	$2CH\equiv CH + H_2S$	Red hot cu tube		Free radical coupling	Pyrolysis of alkyne
	$2CH\equiv CH + NH_3$	Red hot cu tube		Free radical coupling	Pyrolysis of alkyne
	$2CH\equiv CH + CH_3NH_2$	Red hot cu tube		Free radical coupling	Pyrolysis of alkyne
12.	$CH\equiv CH$	$AsCl_3/Hg^{2+}$	$CH(Cl)=CH-AsCl_2$ (Lewisite) (poisonous gas) Highly poisonous gas	----------	----------
13.	$CH\equiv CH$	CH_3COOH/Hg^{2+}		Nucleophilic addition	----------

S. No.	Reactants	Reagents	Products	Mechanism involved	Name of reaction
14.	CH≡CH	$CO + H_2O/Ni(CO)_4$	$CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}OH$ (acrylic acid)	Nucleophilic addition	----------
15.	R—C≡C—H	$AgNO_3/NH_4OH$	R—C≡C—Ag (grey ppt.)	----------	Silver mirror test
16.	R—C≡C—H	$CuCl/NH_4OH$	R—C≡C—Cu (red ppt.)	----------	
17.	R—C≡C—H	$AuCl/NH_4OH$	R—C≡C—Au (golden ppt.)	----------	Analytical test of terminal alkyne

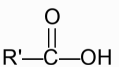
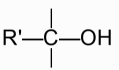
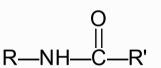
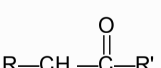
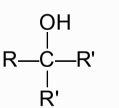
24.26 ALKYL HALIDE

S.No	Reactants	Reagent	Products	Mechanism involved	Name of reaction
1.	$-\overset{|}{\underset{|}{C}}-H$	X_2/UV light X=–Cl, –Br, –F	$-\overset{|}{\underset{|}{C}}-X+HX$	Free radical substitution	Halogenation of alkane
2.	$-\overset{|}{\underset{|}{C}}-H$	I_2/HNO_3	$-\overset{|}{\underset{|}{C}}-I$	Free radical substitution	Iodination of alkane
3.	$-\overset{|}{\underset{|}{C}}-X;X=Br,Cl$	NaI/Acetone	$-\overset{|}{\underset{|}{C}}-I$	Nucleophilic substitution	Finkelstein reaction
4.	$R-\overset{\overset{O}{\|}}{C}-O-Ag$	$X_2/CCl_4/\Delta$	R-X + AgX + CO_2	Free radical substitution	Borodine Hunsdiecker reaction
5.	R–OH	$PX_3/PX_5/HX$	R–X	Nucleophilic substitution	Halogenation of alcohol
6.	R–X X=–Cl, –Br	AgF or Hg_2F_2 or CoF_3	R–F	Nucleophilic substitution	Swarts reaction

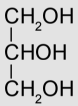
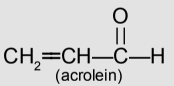
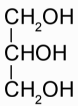
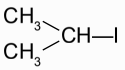
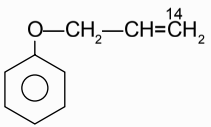
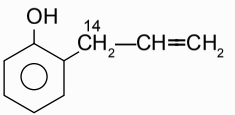
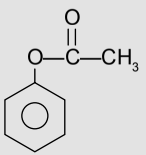
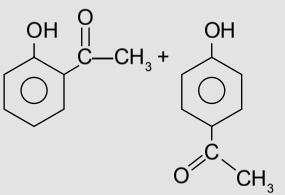
S.No	Reactants	Reagent	Products	Mechanism involved	Name of reaction
7.		PCl_5		----------	Halogenation of carbonyl compound
8.	R—OH	$SOCl_2$	$R—Cl + SO_2 + HCl$	Internal nucleophilic substitution (S_Ni)	Darzen's method
9.	$CHCl_3$	HNO_3	$C(NO_2)Cl_3 + H_2O$ Nitrochloroform or chloropicrin or tear gas	Electrophilic substitution	----------
10.		$CHCl_3/KOH/\Delta$	 (chloretone) (soporific in nature)	Nucleophilic addition	----------
11.	$CHCl_3$	O_2/Sunlight	$COCl_2$ (phosgene) poisonous gas	Oxidation	----------
12.	R—X	KCN(alc)	R—CN + KX	Nucleophilic substitution	----------
13.	R—X	AgCN(alc)	R—NC + AgX	Nucleophilic substitution	----------
14.	R—X	KNO_2 (alc)	R—O—N = O + KX	Nucleophilic substitution	----------
15.	R—X	Ag—O—N = O		Nucleophilic substitution	----------
16.	R—X	NH_3(alc)	$R—NH_2+R_2NH+R_3N$	Nucleophilic substitution	Hyproning ammonolysis

S.No	Reactants	Reagent	Products	Mechanism involved	Name of reaction
17.	R—X	$NaOH_{(aq)}$	R—OH	Nucleophilic (S_N^2) substitution	_____
18.	R—X	$Ag_2O_{(moist)}$	R—OH	Nucleophilic (S_N^1) substitiution	_____

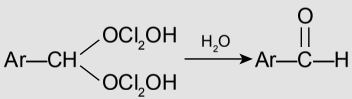
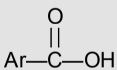
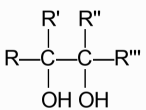
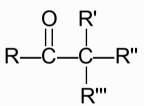
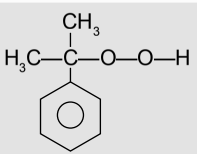
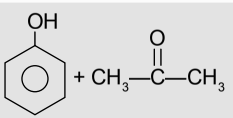
24.27 ALCOHOL AND ETHER

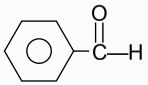
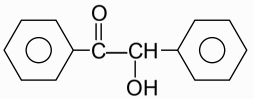
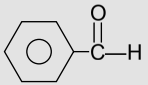
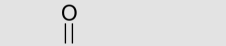
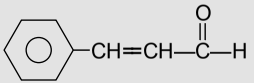
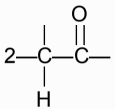
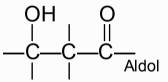
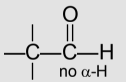
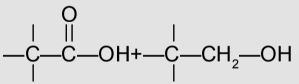
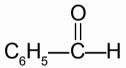
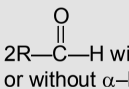
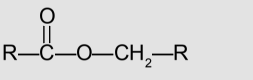
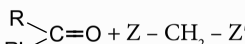
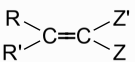
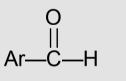
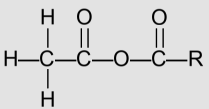
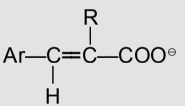
S.No	Reactants	Reagent	Products	Mechanism involved	Name of reaction
1.	R′–MgX	$O=C=O/H_3O^{\oplus}$		Nucleophilic addition	----------
		$>C=O/H_3O^{\oplus}$		Nucleophilic addition	----------
		$R–N=C=O/H_3O^{\oplus}$		Nucleophilic addition	----------
		$R–CH=C=O/H_3O^{\oplus}$		Nucleophilic addition	----------
		 L = –OR, –X, –OCOR			----------
2.	R–L L=–Br, –I, $-OSO_2R$, etc	$R'O^{\ominus}\ Na^{\oplus}$	R – O – R’	Nucleophilic substitution	Williamson synthesis
3.	2RX	Ag_2O/Δ	R–O–R + 2AgX	Nucleophilic substitution	----------

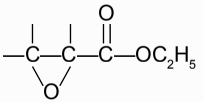
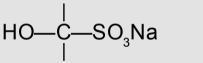
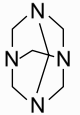
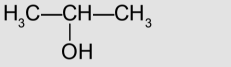
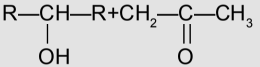
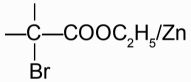
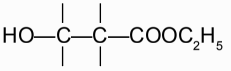
S.No	Reactants	Reagent	Products	Mechanism involved	Name of reaction
4.	$R–CH_2–OH$	Jones reagent (CrO_3/H_2SO_4) or H_2CrO_4/acetone	$R—\overset{O}{\overset{\|\|}{C}}—H$	Oxidation	----------
	$R—\underset{\|}{\overset{\|}{CH}}—OH$ (R)	Sarret's reagent (CrO_3/C_5H_5N) Collin's reagent (PCC/CH_2Cl_2) MnO_2, etc	$\begin{matrix}R\\R\end{matrix}\!\!>\!C=O$	Oxidation	----------
5.	$R–CH_2–OH$	Cu/Δ	$—\overset{O}{\overset{\|\|}{C}}—H$	Oxidation	Dehydrogenation
	$\begin{matrix}R\\R\end{matrix}\!\!>\!CH—OH$	Cu/Δ	$>C=O$	Oxidation	Dehydrogenation
	$R—\underset{\|}{\overset{R}{\overset{\|}{C}}}—OH$ (R)	Cu/Δ	Alkene	Oxidation	Dehydration
6.	$>C=O$	$NaBH_4$, $LiACH_4$	$>CH—OH$	Reduction	_____
7.	$—\underset{OH}{\overset{\|}{C}}—\underset{OH}{\overset{\|}{C}}—$	HIO_4 or $Pb(OAc)_4$	$>C=O + O=C<$	Oxidation	Oxidative cleavage of glycol (malaprade oxidation)
8.	$CH_3—\overset{O}{\overset{\|\|}{C}}—$ or $CH_3—\overset{OH}{\overset{\|\|}{CH}}—$	I_2/NaOH or NaOI or $NaIO_3$ or $IO^{\ominus}$ or $IO_3^{\ominus}$	$CHI_3 + —\overset{O}{\overset{\|\|}{C}}—ONa$	----------	Iodoform test
9.	R–O–R'	HI/Δ	R–OH + R'–I	Nucleophilic substitution	----------
		$HI_{(excess)}/\Delta$	R–I + R'–I	Nucleophilic substitution	----------
10.	R—OH	$NaBr/H_2SO_4$ or HBr	R—Br	Nucleophilic substitution	----------

S.No	Reactants	Reagent	Products	Mechanism involved	Name of reaction
11.	R—OH	KI/H_3PO_4 or HI	R—I	Nucleophilic substitution	----------
12.	R—OH	HCl/anhyd $ZnCl_2$ (Lucas reagent)	R—Cl	Nucleophilic substitution	Groove's process
13.		Conc. H_2SO_4 or $KHSO_4/\Delta$	 (acrolein)	Dehydration reaction	----------
14.		3HI 5HI	$CH_2{=}CH{-}CH_3{-}I$ 	Nucleophilic substitution	----------
15.		Δ/200–250°C		Rearrangement reaction	Claisen rearrangement
16.		Anhydrous $AlCl_3/\Delta$		Rearrangement reaction	Fries rearrangement

24.28 ALDEHYDE AND KETONE

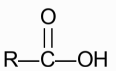
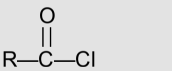
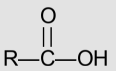
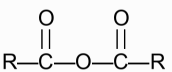
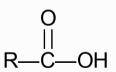
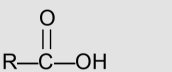
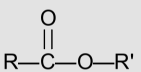
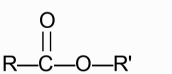
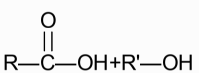
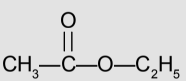
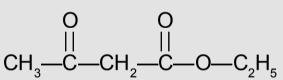
S.No	Reactants	Reagent	Products	Mechanism Involved	Name of Reaction
1.		$R–Li_{(excess)}/H_3O^{\oplus}$		Nucleophilic addition	----------
2.	–C≡C–	SeO_2		Oxidation	Methylene oxidation
		SeO_2		Oxidation	
3.	$Ar–CH_3$	CrO_2Cl_2/H_2O/ Pyridine		Oxidation	Etard's reaction
		$KMnO_4/\Delta$		Oxidation	----------
4.		$Pd/BaSO_4$/Quincline/ Boiling xylene		Partial reduction	Resenmund's reaction
5.	R—CN	1. $SnCl_2/HCl$ 2. H_3O^+		----------	Stephen's reduction
6.		Dil. H_2SO_4/Δ		Rearrangement reaction	Pinnacol – Pinnacolone rearrangement
7.		Dil. H_2SO_4		Rearrangement reaction	Cumene-hydroperoxide rearrangement

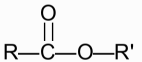
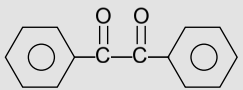
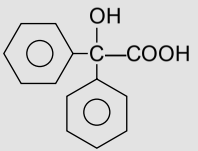
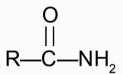
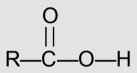
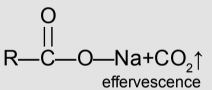
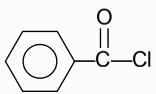
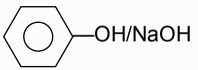
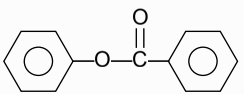
S.No	Reactants	Reagent	Products	Mechanism Involved	Name of Reaction
8.		Alc. aq. KCN/Δ		Disproportionation	Benzoin condensation
9.				Condensation	Cross aldol condensation
10.		Dil. NaOH/Cold		Nucleophilic addition	Aldol addition
11.		1. Conc. NaOH/Δ 2. $H^{\oplus}$		Disproportionation	Cannizzaro reaction
12.		1.  2. $H^{\oplus}$	$C_6H_5-CH_2-OH + HCOO^{\ominus}$	Disproportionation	Cross Cannizzaro reaction
13.		$Al(OEt)_3$		Disproportionation	Tischenko reaction
14.	 (active methylene compound)	$NaOH_{(aq)}$ or R_2NH or R_3N		Condensation	Knovengel's reaction
15.		 $R-CH_2-COOK$		Nucleophilic addition, then dehydration and then hydrolysis	Perkin's condensation

S.No	Reactants	Reagent	Products	Mechanism Involved	Name of Reaction
16.		C_2H_5ONa		Condensation	Darzen's glycidic ester condensation
17.		$NaHSO_3$	 (White crystalline adduct)	Nucleophilic addition	Bisulphite addition (characteristics test)
18.		NH_3	 Hexamethylene tetraamine	Nucleophilic addition	Urotropine formation (urinary antiseptic)
19.				Oxidation reduction	Meerwein - Ponndorf - Verley reduction or oppenauer oxidation
20.		1.  2. H_2O/NH_4Cl		Condensation	Reformatsky reaction
21.		NH_2–Z		Condensation	---------
		NH_2–NH_2		Axime formation	Hydrazone formation
		NH_2–OH			---------

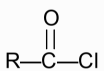
S.No	Reactants	Reagent	Products	Mechanism Involved	Name of Reaction
22.	$>C=O$	NH_2–R	$>C=N—R$	_____	Imine formation
		NH_2–NH– ϕ	$>C=N—NH—\phi$	_____	Phenylhydrazone
		NH_2–NH–$CONH_2$	$>C=N—NH—CONH_2$	_____	Semi carbazone

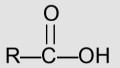
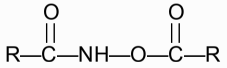
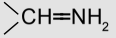
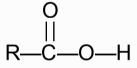
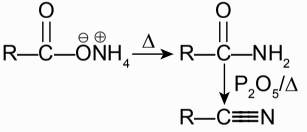
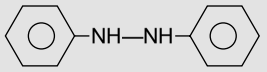
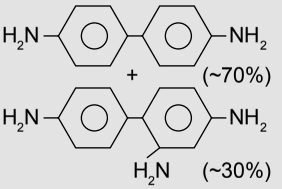
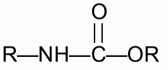
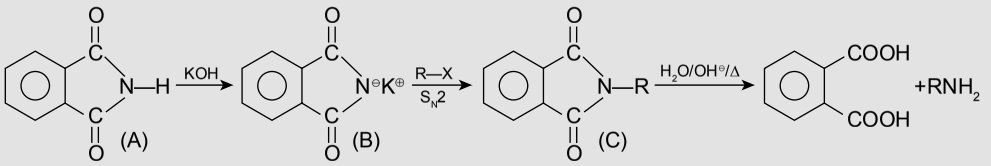
24.29 CARBOXYLIC ACIDS AND THEIR DERIVATIVES

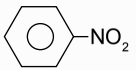
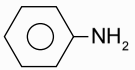
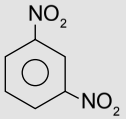
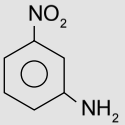
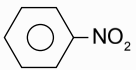
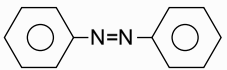
S.No	Reactants	Reagent	Products	Mechanism involved	Name of reaction
23.	R – CN	H^+/H_2O		----------	Hydrolysis
24.		$H_2O/H^{\oplus}$ or $OH^{\ominus}$		Nucleophilicacyl substitution	Hydrolysis
25.		$H_2O/H^{\oplus}$		Nucleophilic acyl substitution	Hydrolysis
26.		R' – OH/$H^{\oplus}$		Nucleophilic acyl substitution	Fischer-Spier synthesis
27.		$H_2O/H^{\oplus}$ or $OH^{\ominus}$		Nucleophillic acyl substitution	De-esterification
28.	 Ester containing α–H	C_2H_5ONa		Nucleophilic acyl substitution	Claisen condensation

S.No	Reactants	Reagent	Products	Mechanism involved	Name of reaction
29.		 or H_2SO_5 or BF_3/H_2O_2		Rearrangement reaction	Baeyer–Villiger oxidation
30.		1. Conc. KOH or NaOH 2. H^+		Rearrangement reaction	Benzillic rearrangement
31.		$Br_2/KOH/\Delta$	$R–NH_2$	Rearrangement reaction	Hofmann's bromamide synthesis
32.		$NaHCO_3$		Salt formation	Analytical test of carboxylic acid
33.				Nucleophilic acyl substitution	Schotten–Baumann reaction

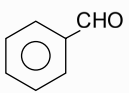
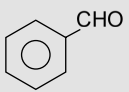
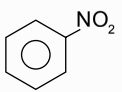
24.30 AMINES AND NITRO COMPOUNDS

S.No	Reactants	Reagent	Products	Mechanism involved	Name of Reaction
1.		1. NaN_3/Δ 2. H_2O	$R–NH_2 + CO_2$	Nucleaphilic acyl substitution then Rearrangement	Curtius rearrangement

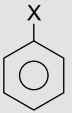
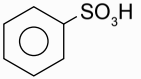
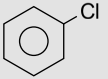
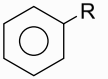
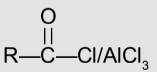
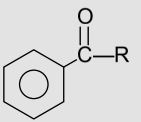
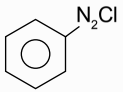
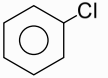
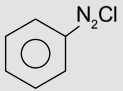
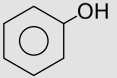
S.No	Reactants	Reagent	Products	Mechanism involved	Name of Reaction
2.		1. $N_3H/H^{\oplus}$ 2. H_2O	$R–NH_2 + CO_2$	Rearrangement reaction	Schmidt's rearrangement
3.		1. $OH^{\ominus}/\Delta$ 2. H_2O	$R–NH_2 + CO_2$	Rearrangement reaction	Lossen rearrangement
4.		1. NH_3 2. H_2/Ni		Nucleophilic addition elimination	Reductive amination
5.		NH_3/Δ		Nucleophilic substitution	----------
6.		Conc. HCl or H_2SO_4		Rearrangement reaction	Benzidine rearrangement
7.	R – N = C = O	R–OH		Addition	Alcohololysis
8.	R–C≡N	$R–CH_2–NH_2$	Na/C_2H_5OH	Reduction	Mendius reduction
9.	$R–NH_2$ or $Ar–NH_2$	$CHCl_3$/alc. KOH	R–NC or Ar–NC	Carbene addition	Carbyl amine test
10.					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.		NH_3/H_2S or $(NH_4)_2S_X$		Selective reduction	--------
13.		$LiAlH_4$		Reduction reaction	---------

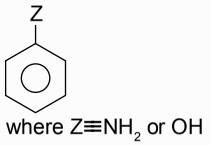
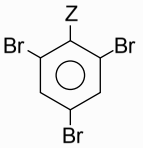
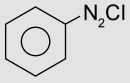
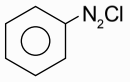
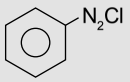
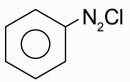
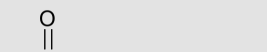
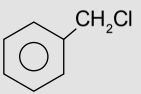
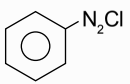
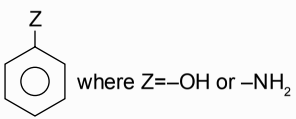
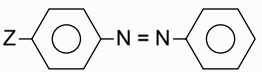
24.31 AROMATIC COMPOUNDS

S.No	Reactants	Reagent	Products	Mechanism Involved	Name of Reaction
1.		1. HCN/HCl/$AlCl_3$ 2. H_2O		ArSE	Gattermann–aldehyde synthesis
2.		CO/HCl/$AlCl_3$		ArSE	Gattermann–koch formylation
3.		Conc. HNO_3/Conc. H_2SO_4		ArSE	Nitration

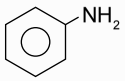
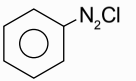
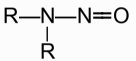
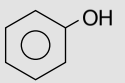
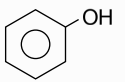
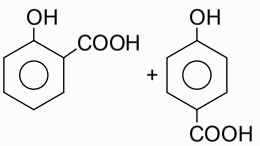
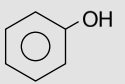
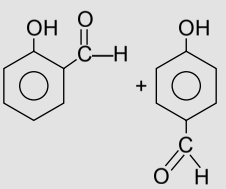
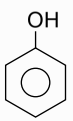
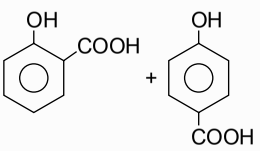
ArSE → Electrophilic aromatic substitution
ArSN → Nucleophilic aromatic substitution

S.No	Reactants	Reagent	Products	Mechanism Involved	Name of Reaction
4.		X_2/CS_2 or FeX_3		ArSE	Halogenation
5.		Conc. H_2SO_4 or fuming H_2SO_4		ArSE	Sulphonation
6.		Cl_2/Fe		ArSE	Chlorination
7.		$RCl/AlCl_3$		ArSE	Friedel Craft alkylation
8.				ArSE	Friedel Craft acylation
9.		Cu/HCl		ArSN	Gettermann's reaction
10.		$H_2O/H^{\oplus}$ or $Cu_2O/H_2O/\Delta$		ArSN	----------

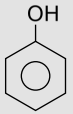
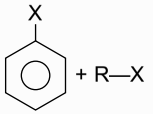
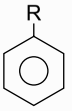
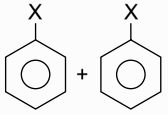
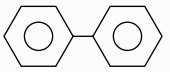
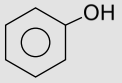
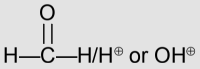
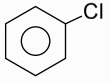
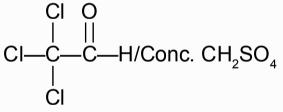
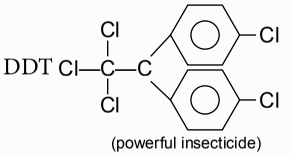
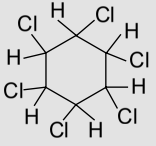
ArSE → Electrophilic aromatic substitution
ArSN → Nucleophilic aromatic substitution

S.No	Reactants	Reagent	Products	Mechanism Involved	Name of Reaction
11.		Br_2/H_2O		ArSE	Bromination
12.		HBF_4 or BF_3/HF		ArSN	Balze–Schiemann reaction
13.		CuX/HX, where X = Cl, Br, CN		ArSN	Sandmeyer's reaction
14.		KI		ArSN	----------
15.		H_3PO_2/Δ		ArSN	Deamination
16.				ArSE	Chloromethylation or Blance reaction
17.				ArSE	Diazocoupling
18.	2Ar–I	Cu/Δ	Ar–Ar	----------	Ullmann reaction

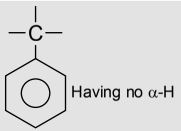
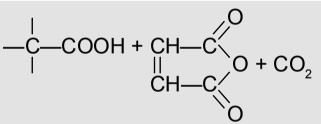
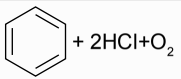
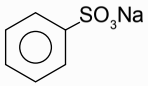
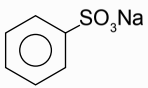
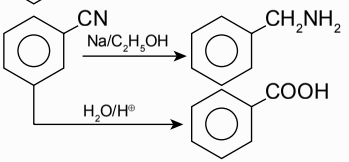
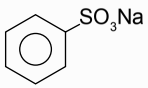
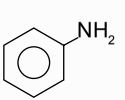
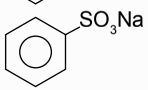
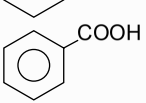
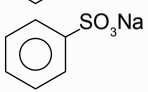
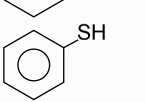
ArSE → Electrophilic aromatic substitution
ArSN → Nucleophilic aromatic substitution

S.No	Reactants	Reagent	Products	Mechanism Involved	Name of Reaction
19.	 $R–NH_2$ R–NH–R	$NaNO_2/HCl/0\text{-}5°C$ $NaNO_2/HCl$ $NaNO_2/HCl$	 R—OH 	-------- --- ArSN ArSE	Diazotization
20.		Zn dust		Reduction	----------
21.		**1.** $CCl_4/NaOH_{(aq)}$ **2.** $H^{\oplus}$		----------	Reimer-Tiemann reaction
22.		**1.** $CHCl_3/NaOH_{(aq)}$ **2.** $H^{\oplus}$		_____	Reimer-Tiemann reaction
23.		**1.** $CO_2/NaOH_{(aq)}$ **2.** $H^{\oplus}$		ArSE	Kolbe-Schmidt's reaction

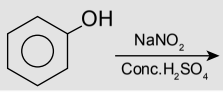
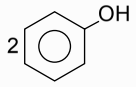
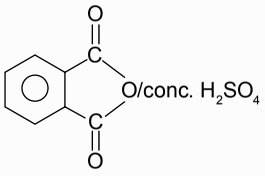
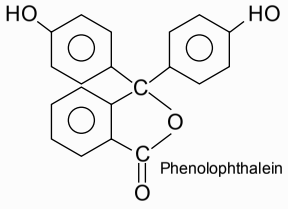
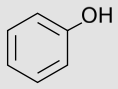
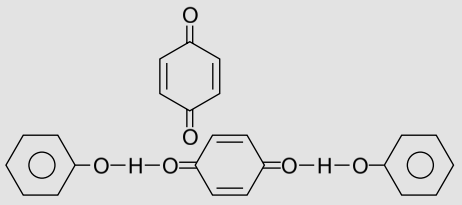
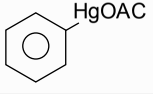
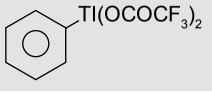
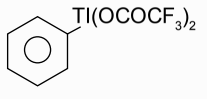
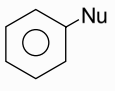
ArSE → Electrophilic aromatic substitution
ArSN → Nucleophilic aromatic substitution

S.No	Reactants	Reagent	Products	Mechanism Involved	Name of Reaction
24.		Neutral $FeCl_3$ in C_2H_5OH	$(C_6H_5–O)_3Fe$ reduction violet colour	---------- ----	Analytical test for enol form
25.		Na/dry ether		Free radical mechanism	Wurtz–Fittig reaction
		Na/dry ether		Free radical mechanism	Fittig reaction
26.			Bakelite (cross-linked polymer)	ArSE	Laderer–Manase reaction
27.			 (powerful insecticide)	ArSE	DDT formation
28.		Cl_2/diffused sunlight	 Gammaxene or lindane	Addition	----------

ArSE → Electrophilic aromatic substitution
ArSN → Nucleophilic aromatic substitution

S.No	Reactants	Reagent	Products	Mechanism Involved	Name of Reaction
29.		$Na/NH_{3(l)}$ or C_2H_5OH		Free radical addition	Birch reduction
30.		$KMnO_4/\Delta$ or $K_2Cr_2O_7/\Delta$ (vigorous heating)		---------	Oxidation
31.		$CuCl_2/\Delta$	$C_6H_5Cl + 2H_2O$	--------	Raschig method
32.		**1.** 2NaOH/350°C/high P **2.** $H^{\oplus}$		ArSN	Dow's process
33.		1. NaOH/Δ 2. $HCl_{(aq)}$		ArSN	----------
		1. NaCN/Δ		ArSN	---------- ----------
		$NaNH_2/\Delta$		ArSN	----------
		1. HCOONa/Δ 2. dil. HCl		ArSN	----------
		NaSH/Δ		ArSN	

ArSE → Electrophilic aromatic substitution
ArSN → Nucleophilic aromatic substitution

S.No	Reactants	Reagent	Products	Mechanism Involved	Name of Reaction
34.		deep green blue colour ----- red colour ------ deep blue colour			Liebermann's nitroso–test
35.				ArSE	----------
36.		O_2(air)/CrO_3/CrO_2Cl_2		Oxidation	----------
37.		$Hg(OAC)_2/H^+$		ArSE	Mercuration
38.		$Tl(OCOCF_3)_3/H^+$		ArSE	Thalluation
39.		$M^+Nu^{\ominus}/H_2O$ where $\overset{\oplus}{M}Nu^{\ominus}$ may be KOH or KSH or $NaNH_2$, etc.		ArSN	-------

ArSE → Electrophilic aromatic substitution
ArSN → Nucleophilic aromatic substitution