General Organic Chemistry

1. Organic chemistry

The study of hydrocarbons and the compounds which would be thought of as their derivative.

2. Nature of covalent bond

A **covalent bond** is formed by the progressive overlapping of two bonding orbitals. For the stable bond formation, the condition is that the electrons should have opposite spins.

3. Sigma Bond (σ)

The molecular orbital formed by the overlapping of two s-atomic orbitals or one s-and one p-orbital is called a **sigma bond**. Overlapping of hybridised orbitals also leads to the formation of sigma bond. σ-bonds are stronger as they result from the effective axial overlapping.

Order of strength of σ-bond :-

(i) $sp^3-sp^3 > sp^3-sp^2 > sp^2-sp^2 > sp^2-sp > sp-sp$ (ii) $sp^3-s > sp^2-s > sp-s$

(iii) $sp^3-p > sp^2-p > sp-p$ (iv) $p-p > s-p > s-s$

The relative energies of different orbitals :-

More is the s-character associated with the orbital less will be its energy $p > sp^3 > sp^2 > sp > s$

4. Pi-bond

The molecular orbital formed by the sideways overlapping of two p-atomic orbitals is called **Pi bond**.

Relative to σ-bond , π-bond is weaker as there is only partial overlapping in the later case.

π-electrons are mobile. Hence π-bond is more reactive as compared to sigma bond. π-bond is always accompanied by the formation of a σ-bond.

5. Hybridisation

In hybridisation phenomenon, the orbitals of different shapes, but almost of equal energies blend up to give the same number of new orbitals of another shape and of identical energies (give stronger, more directional and stable bonds) e.g. sp^3, sp^2, sp

Example :-

(a) $\overset{1}{C}H\equiv\overset{2}{C}-\overset{3}{C}H=\overset{4}{C}H-\overset{5}{C}H_3$ and (b) $\overset{1}{C}H_2=\overset{2}{C}=\overset{3}{C}H-\overset{4}{C}H_3$

(hybridisation state of carbon, number of σ and π-bonds)

(a)	C_1,	C_2,	C_3,	C_4	C_5
	sp,	sp,	sp^2,	sp^2	sp^3
σ	2,	2,	3,	3,	4
π	2,	2,	1,	1,	0
(b)	C_1,	C_2	C_3,	C_4	
	sp^2,	sp,	sp^2,	sp^3	
σ	3,	2,	3,	4	
π	1,	2,	1,	0	

6. Geometry of Carbon

Four valencies of a carbon atom are directed towards the four corners of a regular tetrahedron with carbon atom situated at the centre (Le Bel and vant Hoff, angle 109°28').

The square pyramidal and square planar structures of carbon have not been accepted

7. Bond length

The distance between the nuclei of the two bonded atoms is termed as **bond length** e.g. C–C bond length

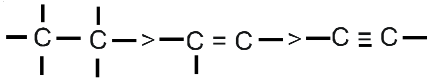
(i) C_2H_6(1.54Å) (ii) C_2H_4 (1.34 Å)

(iii) C_2H_2 (1.20 Å) (iv) C_6H_6 (1.39 Å)

Order of bond length

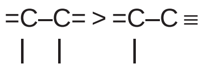
(i) C–C > C–N > C –O (ii) C=C > C=N > C=O

(iii) C≡ C > C ≡ N

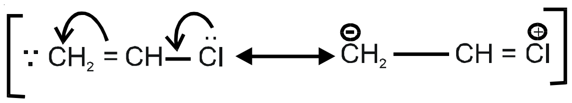
(iv)

$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- > -\underset{|}{C}=C- > -C\equiv C-$

(v) =C=C=> –C ≡ C–

(vi) $>C-C\equiv > C=C=$

(vii)

$=\underset{|}{C}-\underset{|}{C}= \; > \; =\underset{|}{C}-C\equiv$

(viii) C– Cl [in $CH_2Cl - CH_2Cl$] > C – Cl [in CH_2 =CH –Cl]



(C–Cl bond acquires double bond character)

(ix) **C = C bond length** : $CH_2=CH_2>CF_2=CF_2$

[∴ more electronegative atom F is attached to C–atom]

(x) **C–H bond length :** [order]

C —— H > C —— H > C —— H

(sp^3) (s) (sp^2) (s) (sp) (s)

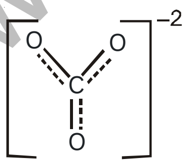
(xi) C —— H > O —— H

(1.08Å) (0.97Å)

(xii) C = C > C = N > C = O

1.34Å 1.29Å 1.22Å

(xiii) C–O bond is same in CO_3^{-2}



(xiv) All the C–C bond distance in benzene are equal [1.39 Å] (resonance). In acetate ion both the C–O bonds are of equal length [1.26 Å] (resonance)

Determination of bond length : X-ray analysis, spectroscopy

8. Bond Dissociation energy

Bond energy may be defined as the energy released when two atoms get bonded or the energy needed to break the bond to form neutral atoms.

Example :

(i) C–C (80 k.cal–mole^{-1}) (ii) C=C (142 k.cal – mole^{-1}) (iii) C≡C (190 k.cal– mole^{-1})

Order of bond energy :-

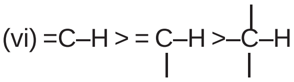
(i) C≡C > C=C>C–C

(ii) H–H > O –H > C–H

(iii) C≡N > C=N > C–N

(iv) C–Cl > C –Br > C–I

(v) C–O (ketone) > C=O [CH_3CHO] > C=O [HCHO]



(vi) =C–H > = C–H >–C–H

(vii) C=O (CO_2) > C=S (CS_2)

(viii) O=O > N = N

(xi) O–H > N –H > C–O > C–N

[110.6] [93.0] [85.5] [73.0] (k.cal-mole^{-1}]

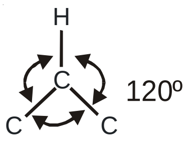
Values of bond dissociation energy

(k.cal mole^{-1})

C–H [99.0]	N=N [100.3]
O–H [110.6]	C=O (CO_2) [192]
N–H [93.6]	C=O (ketone) [179]
C–O [85.5]	C=O [HCHO] [166]
C–Cl [81.1]	C=N [147.2]
C–Br [68.0]	N=O [145.1]
C–I [51.1]	C=S (CS_2) [128]
O–F [45.2]	C≡C [200]
O–Cl [52.1]	C≡N [212.4]
O–Br [48.2]	C=C [142]
C–C [80]	O–O [119]

9. Bond Angle

The angle between two adjacent bonds, in a molecule is known as bond angle, e.g.

Compound		Angle	Number
(i)	acetylene	H–C–C (180°)	two
(ii)	ethylene	H–C–C (120°)	six
(iii)	ethane	H–C–C (109º 28')	twelve
(iv)	benzene		eighteen
(v)	alcohol	R–O–H (105.5°)	one
(vi)	ether	R–O–R (110°)	one

10. Covalent Bond Breaking

(1) Heterolysis, heterolytic fission or heterolytic cleavage

(2) Homolysis, homolytic fission or homolytic cleavage

10.1 Heterolytic Fission

When the covalent bond breaks in such a way that the both the electrons of the bond pair remain with only one of the two atoms, the process is called **heterolysis** or **heterolytic fission** or **ionic fission** or **unsymmetrical fission** or **polar cleavage**.

Heterolysis of a sigma bond forms a cation and an anion as ionic intermediate species.

$$A \vdots : B \longrightarrow \overset{\oplus}{A} + \; :\overset{\ominus}{B}$$

or $$A : \vdots B \longrightarrow \overset{\ominus}{A} : + \overset{\oplus}{B}$$

It is clear that heterolysis of a pi bond should form a bipolar species, as follows.

$$A \overset{\curvearrowright}{=} B \longrightarrow \overset{\oplus}{A} - \overset{\ominus}{B} :$$

10.2 Homolytic Fission

When the covalent bond breaks in such a way that the electrons of the bond pair are distributed between the two atoms i.e. each atom gets a share of one electron, the process is called **homolysis** or **homolytic fission** or **nonionic fission** or **symmetrical fission** or **free radical cleavage**.

Homolysis of a sigma bond forms free radical intermediate species

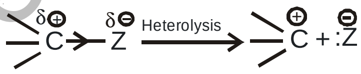
$$A : B \longrightarrow A^{\bullet} + {}^{\bullet}B$$

Homolysis of a pi bond forms a biradial intermediate species

$$A = B \longrightarrow \overset{\bullet}{A} - \overset{\bullet}{B}$$

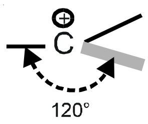
11. Carbocations

When a carbon atom in an organic compound is covalently bonded to a more electronegative atom. Z, the bonding electrons are more shifted towards Z than carbon atom. Therefore, this covalent bond has greater tendency to undergo heterolysis in such a way that the electron pair goes to Z which develops negative charge while carbon atom develops positive charge as shown below



The species formed by heterolysis of a covalent bond in an organic compound and having positively charged carbon atom is known as a **carbocation**

The positively charged carbon atom in an alkyl carbocation has six electrons in its outermost energy level and this carbon atom is in a state of sp^2 hybridisation. Due to sp^2 hybridisation, the geometry around the positive carbon atom is trigonal and the value of bond angles is 120° as shown below.



11.1 Type or carbocations

Carbocations are classified into three categories.

(i) Primary or 1° carbocations

(ii) Secondary or 2° carbocations

(iii) Tertiary or 3° carbocations

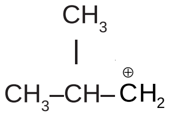
(i) Primary or 1° carbocations have positive charge on primary carbon atom. For example

$\overset{\oplus}{C}H_3$ Methyl carbocation

$CH_3-\overset{\oplus}{C}H_2$ Ethyl carbocation

$CH_3-CH_2-\overset{\oplus}{C}H_2$ n-Propyl carbocation

$CH_3-CH_2-CH_2-\overset{\oplus}{C}H_2$ n-Butyl carbocation



$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-\overset{\oplus}{C}H_2$

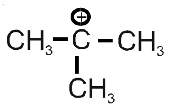
Isobutyl carbocation

(ii) Secondary or 2° carbocations have positive charge on secondary carbon atom. For example

$CH_3-\overset{\oplus}{C}H-CH_3$ Isopropyl carbocation

$CH_3-CH_2-\overset{\oplus}{C}H-CH_3$ sec-Butyl carbocation

(iii) Tertiary or 3° carbocations have positive charge on tertiary carbon atom. For example



$CH_3-\underset{\underset{CH_3}{|}}{\overset{\oplus}{C}}-CH_3$ (tert. Butyl carbocation)

11.2 Stability of Carbocations

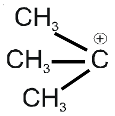
Carbocations are reactive due to positive charge on the carbon atom. Increase in positive charge increases their reactivity and decreases their stability.

11.2.1 Stability of Alkyl Carbocations

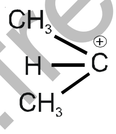
The order of stability of alkyl carbocations is as follows

Tertiary > Secondary > Primary

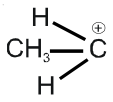
This order of stability is explainable on the basis of increase in the electron-donor (or + I effect due to hyperconjugation) with increase in the number of alkyl groups on the cationic carbon atom. as shown below



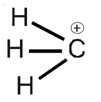
tert-Butyl carbocation (Tertiary)



Isopropyl carbocation (Secondary)



Ethyl carbocation (Primary)



Methyl carbocation (Primary)

11.2.2 Stability of Aryl Carbocations

The increase in the number of phenyl groups on the cationic carbon atom results in tremendous increase in the stability of the aryl carbocations. This is because of resonance due to which the positive charge of carbon atom gets delocalized to o-, p– and o –positions of the benzene rings.

$(C_6H_5)_3\overset{\oplus}{C} > (C_6H_5)_2\overset{\oplus}{C}H > C_6H_5\overset{\oplus}{C}H_2 > CH_2=CH-\overset{\oplus}{C}H_2 > 3° > 2° > 1° > \overset{\oplus}{C}H_3$ (1°)

[Stability $\propto$ No. of resonating structures]

Examples : $\overset{+}{C}H_3$, $CH_3\overset{+}{C}H_2$, $(CH_3)_2\overset{+}{C}H$, $(CH_3)_3\overset{+}{C}$

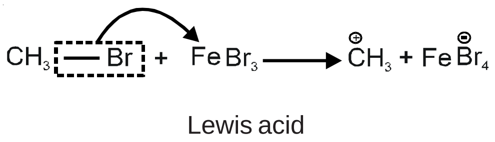
11.3 Formation of carbonium ion

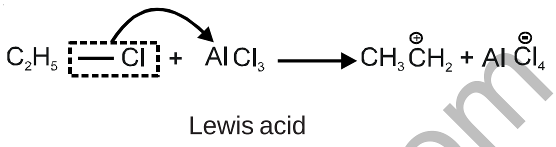
(i) $(CH_3)_3C{-}Cl \rightarrow (CH_3)_3\overset{+}{C} + Cl^-$ [Heterolytic fission]

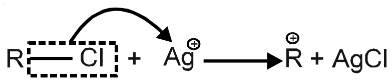
(ii) $CH_3OH \xrightarrow{H^+} CH_3\overset{+}{O}H_2 \xrightarrow{-H_2O} \overset{+}{C}H_3$ [Protonation]

(iii) $CH_3{-}CH=CH_2 \xrightarrow{H^+} CH_3-\overset{+}{C}H-CH_3$ [Protonation]

(iv) Abstraction of halide ion by lewis acid







(v) Removal of N_2 from diazonium cation

Reactions :

(i) Nucleophilic substitution of 3° alkyl halide

(ii) Markownikoff reaction

(iii) Dehydration of alcohols

(iv) Hydrolysis of acetyl chloride

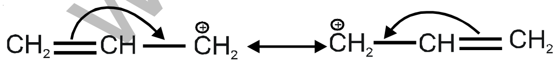
Examples :-

Ethyl alcohol $\xrightarrow[170^\circ]{conc.\ H_2SO_4}$ ethene

Mechanism

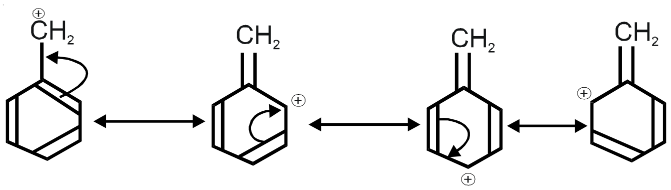
$CH_3{-}CH_2OH \xrightarrow{H^{\oplus}} CH_3{-}CH_2\overset{\oplus}{O}H_2 \xrightarrow{-H_2O} CH_3-\overset{\oplus}{C}H_2 \xrightarrow{-H^{\oplus}} CH_2=CH_2$

Resonance in allyl carbocation :



[Two structures]

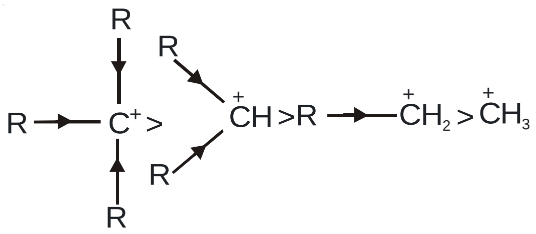
Resonance in benzyl carbocation :



[Four structures]

Obviously benzyl carbocation is more stable as compared to allyl carbocation.

(ii) Stability ∝ Reduction of positive charge on the carbon

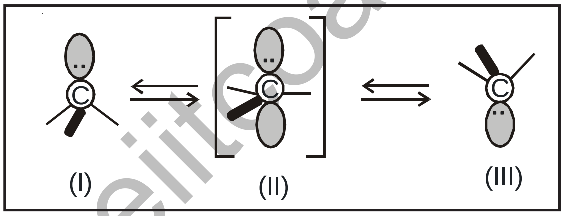


12. Carbanions

When a carbon atom is bonded to a more electron donor atom or group Z. in an organic molecule. The shared pair of electrons is more shifted towards the carbon atom. This bond during chemical reaction can undergo heterolysis in such a way that the electron pair remains with carbon atom and Z does not receive the share of the electron pair. Thus carbon atom acquires a positive charge and Z acquires a negative charge as shown below

$$C \vdots\!-\!Z \rightleftharpoons \overset{\ominus}{C} : + \overset{\oplus}{Z}$$

The organic species obtained as above, having negative charge on carbon atom is known as **carbanion**. The negatively charged carbon atom of a carbanion has eight electrons in its outermost energy level. The carbanion carbon atom of an alkyl carbanion is in a state of sp^3 hybridisation. The geometry of the methyl carbanion is trigonal pyramidal similar to that of ammonia molecule.



12.1 Types of carbanions

(i) Primary Carbanions

$\overset{\ominus}{\ddot{C}}H_3$ Methyl carbanion

$CH_3-\overset{\ominus}{\ddot{C}}H_2$ Ethyl carbanion

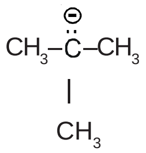
$CH_3-CH_2-\overset{\ominus}{\ddot{C}}H_2$ n-propyl carbanion

(ii) Secondary Carbanions

$CH_3-\overset{\ominus}{\ddot{C}}H-CH_3$ Isopropyl carbanion

$CH_3-CH_2-\overset{\ominus}{\ddot{C}}H-CH_3$ sec-Butyl carbanion

(iii) Tertiary Carbanions



$$CH_3-\underset{\displaystyle CH_3}{\overset{\ominus}{\ddot{C}}}-CH_3$$

tert-Butyl carbanion

12.2 Stability of Carbanions

Carbanions are reactive due to negative charge on the carbon atom. Increase in negative charge increases their reactivity and decreases their stability. Similarly decrease in negative charge decrease the reactivity of the carbanions and increases their stability. If the hydrogen atom present on the negatively charged carbon atom of a carbanion is substituted by an electron-donor group. There is an increase in the electron density on the carbanion carbon and thus decrease in the stability.

$:\overset{\ominus}{C}H_3 > 1° > 2° > 3°$

Examples : $\bar{C}H_3, (CH_3)_2\bar{C}H, CH_3\bar{C}H_2, \bar{C}H_2CHO$

(i) $\overset{\ominus}{C}H_3 > CH_3\overset{\ominus}{C}H_2 > (CH_3)_2\overset{\ominus}{C}H > (CH_3)_3\overset{\ominus}{C}$

Explanation :- Stability of alkyl carbanions can be explained by inductive effect. Greater the number of alkyl group [+ I effect] attached to the carbon atom bearing negative charge, lesser is the stability.

$3° < 2° < 1° < \overset{\ominus}{C}H_3$

(ii) $\overset{\ominus}{C}H_2-NO_2 > \overset{\ominus}{C}H_2-CHO$

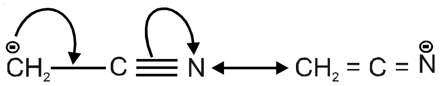
(iii)

(iv) $\overset{\ominus}{C}H_2-CHO > \overset{\ominus}{C}H_3$

(v) $\overset{\ominus}{C}H_2-CH_2-NO_2 > CH_3-\overset{\ominus}{C}H-NO_2 > (CH_3)_2\overset{\ominus}{C}H$

(vi) $F-\overset{\ominus}{C}H_2 > Cl-\overset{\ominus}{C}H_2$

(vii) Resonance exists in $\overset{\ominus}{C}H_2-C\equiv N$, hence it is stable carbanion

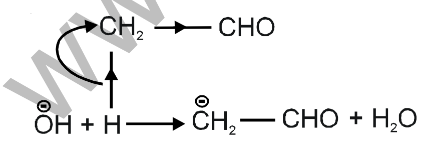

$$\overset{\ominus}{C}H_2-C\equiv N \longleftrightarrow CH_2=C=\overset{\ominus}{N}$$

(viii) Carbanion in which negative charge and double bond are in conjugation

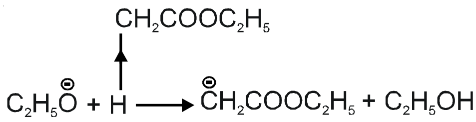
Note : Carbanions are nucleophile

12.3 Formation of Carbanion

(i)


$$\overset{\ominus}{O}H + H-CH_2-CHO \longrightarrow \overset{\ominus}{C}H_2-CHO + H_2O$$

(ii)

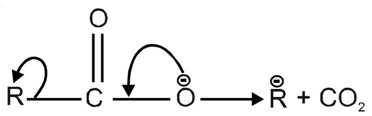

$$C_2H_5\overset{\ominus}{O} + H-CH_2COOC_2H_5 \longrightarrow \overset{\ominus}{C}H_2COOC_2H_5 + C_2H_5OH$$

Reactions :

(i) Aldol condensation (ii) Claisen condensation (iii) Decarboxylation

Example :

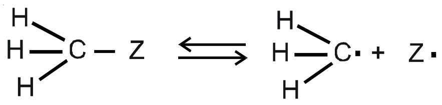
$$RCOOH \xrightarrow{\text{soda-lime}} RH$$


$$R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O} \longrightarrow \overset{\ominus}{R} + CO_2$$

13. Organic Free Radicals

When a carbon atom in an organic compound is covalently bonded to an atom or a group. Z which is electroneutral or very weakly electron-donor or very weakly electron-acceptor. The electron pair of the covalent bond is almost equally shared by C and Z. Such a covalent bond has a tendency to undergo homolysis during chemical reaction to form electroneutral species. Each having one unpaired electron and are known as **free radicals**. The reactive intermediate organic species having an odd or unpaired free electron on a carbon atom is called an **organic free radical**.

Example



Example

$-C^{\cdot}$, $CH_3^{\cdot}$, $(C_6H_5)_3C^{\cdot}$, $CH_2=CH-CH_2^{\cdot}$, $(CH_3)_2CH^{\cdot}$, $CH_3CH_2^{\cdot}$

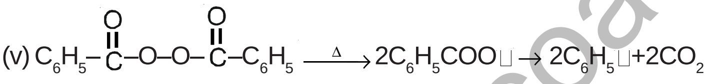
13.1 Formation of free radicals

(i) $Cl_2 \xrightarrow{h\nu} Cl^{\cdot} + Cl^{\cdot}$ [Homolytic fission]

(ii) $CH_3COCH_3 \xrightarrow[140^{\circ}C]{h\nu} CH_3^{\cdot}+CH_3CO \longrightarrow CO + {}^{\cdot}CH_3$

(iii) $(C_2H_5)_4Pb \xrightarrow{140^{o}C} Pb + 4C_2H_5^{\cdot}$

(iv) $CH_3-N=N-CH_3 \rightarrow N_2+2CH_3^{\cdot}$



(v) $C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \xrightarrow{\Delta} 2C_6H_5COO^{\cdot} \rightarrow 2C_6H_5^{\cdot}+2CO_2$

(vi) $Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH + HO^{\cdot}$ [Fenton's reagent]

(vii) $RCOO^- \xrightarrow{anode} RCOO^{\cdot} + e \longrightarrow R^{\cdot} + CO_2$

Salient features

(i) Free radical reactions are catalyzed by light, heat etc.

(ii) Free radical reactions proceed in vapour phase or in nonpolar solvents.

(iii) Free radical reactions are frequently autocatalytic

Reactions

(i) Chlorination of alkanes
(ii) Pyrolysis of alkanes
(iii) Wurtz reaction
(iv) Anti-Markownikoff rule
(v) Kolbe electrolytic synthesis
(vi) Polymerisation initiated by free radical

Example

$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$

Step - I [initiation]

$Cl_2 \longrightarrow Cl^{\cdot} + Cl^{\cdot}$

Step - 2 [propagation]

$CH_4+Cl^{\cdot} \longrightarrow CH_3^{\cdot}+ HCl$ and $CH_3^{\cdot}+Cl_2 \longrightarrow CH_3Cl + Cl^{\cdot}$

Step-3 [termination]

$Cl^{\cdot}+ Cl^{\cdot} \rightarrow Cl_2$ or $CH_3^{\cdot} + CH_3^{\cdot} \rightarrow CH_3-CH_3$ or $CH_3^{\cdot} + Cl^{\cdot} \rightarrow CH_3-Cl$

13.2 Order of stability of free radicals

$(C_6H_5)_3C^{\bullet} > (C_6H_5)_2CH^{\bullet} > C_6H_5CH_2^{\bullet} > CH_2 = CH - CH_2^{\bullet} > 3° > 2° > 1° > CH_3^{\bullet}$

Explanation – Lesser is the bond dissociation energy, greater is the ease with which the free radical is formed (greater its stability)

$CH_3 - H \rightarrow CH_3^{\bullet} + H^{\bullet}$, $\Delta H = 435kJ$

$CH_3 - CH_2 - H \rightarrow CH_3 - CH_2^{\bullet} + H^{\bullet}$, $\Delta H = 411kJ$

$(CH_3)_2CH - H \rightarrow (CH_3)_2CH^{\bullet} + H^{\bullet}$, $\Delta H = 395kJ$

$(CH_3)_3C - H \rightarrow (CH_3)_3C^{\bullet} + H^{\bullet}$, $\Delta H = 381kJ$

It is apparent that 3° free radical is formed easily.

Order of the potential energy of the free radicals

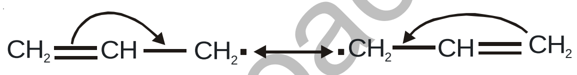
t-butyl < isopropyl < ethyl < methyl

Stability on the basis of resonance

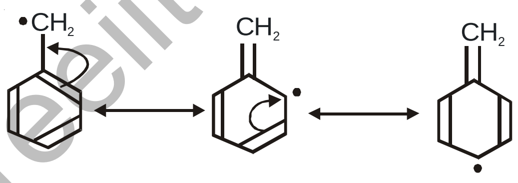
Stability $\propto$ Number of resonating structures

Triphenyl methyl free radical has the maximum number of resonating structures. Hence it is the most stable free radical

Resonance in allyl free radical

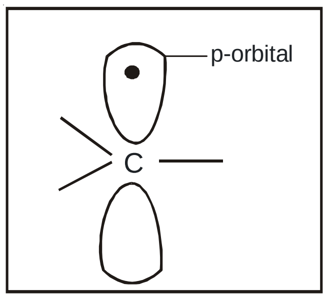


Resonance in benzyl free radical :



13.3 Geometry

(i) Trigonal planar



$(CH_3)_3\dot{C}$ or $(C_6H_5)_3\dot{C}$ $[sp^2]$

(ii) **Planar :** $CH_2 = \dot{C} - CH_3$ $[sp^2]$

(iii) **Free radicals** are electrophiles

14. Intermediate Carbene Species

The central carbon atom of a carbene species is neutral or uncharged. This carbon atom has two sigma bonds and two nonbonding electrons. i.e. there are six electrons or an incomplete octet in its outermost energy level.

$$-\ddot{C}-$$

Partial structure of carbene species

Example-1 : Photolysis of diazomethane forms a carbene species, called methylene intermediate.

$$CH_2N_2 \xrightarrow{h\nu} :CH_2 + N_2$$

Example-2 : Reaction of metallic zinc on methylene dibromide or diiodide also forms methylene intermediate

$$CH_2Br_2 \xrightarrow{h\nu} :CH_2 + ZnBr_2$$

The carbon atom of the methylene intermediate referred to in the above two examples has two bond pairs and two nonbonding electrons. The two odd electrons occupy two separate orbitals and have parallel spins. Therefore such a methylene species may be regarded as a **biradical** that can act as a normal free radical in two steps as follows

(i) $\bullet CH_2 \bullet \quad + \quad \bullet Z \longrightarrow \bullet CH_2 - Z$

Methylene biradical	Free radical	Intermediate free radical

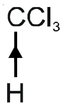
(ii) $\bullet CH_2 - Z \quad + \quad \bullet Z \longrightarrow Z - CH_2 - Z$

Product

Example-3 $CH_2{=}C{=}O \xrightarrow{\Delta} :CH_2 + CO$

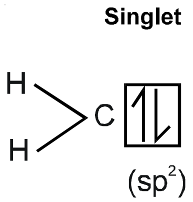
ketene

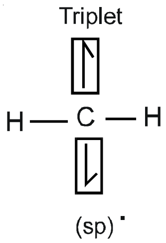
Example-4



$\underset{\underset{H}{\uparrow}}{CCl_3} + OH \rightarrow H_2O + :CCl_3 \;;\; :\bar{C}Cl_3 \rightarrow :\bar{C}l + :CCl_2$ dichlorocarbene

Two forms of carbenes





Reactions

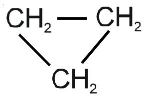
(i) Hofmann carbylamine reaction (ii) Riemer Tiemann reaction

(iii) Formation of cyclopropane from ethene and diazomethane

Example

$$CH_2N_2 \rightarrow :CH_2 + N_2$$

$CH_2{=}CH_2 + :CH_2 \rightarrow$



15. Intermediate Nitrene Species

In a nitrene species the central nitrogen atom is neutral i.e. it bears no charge. This neutral nitrogen atom has one sigma bond and two lone pairs, i.e. a total of six electrons in three pairs in its outermost energy level. In order to complete its octet the nitrogen atom of a nitrene species tries to acquire two electrons from somewhere and form a covalent bond thereby behaves as an electrophile.

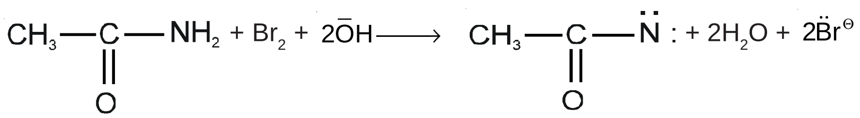
$— \underset{\cdot\cdot}{N}:$

Partial structure Formula of Nitrenes

Example -

Reaction : Hofmann bromide reaction.

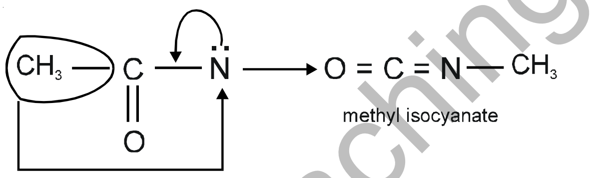
Formation - Amide + bromine + caustic potash



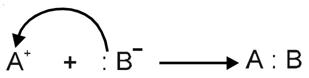
$$CH_3-\underset{\underset{O}{||}}{C}-NH_2 + Br_2 + 2\bar{O}H \longrightarrow CH_3-\underset{\underset{O}{||}}{C}-\ddot{N}: + 2H_2O + 2\ddot{B}r^{\ominus}$$

(Acylnitrene)

Rearrangement



16. Electrophilic And Nucleophilic Reagents



Electrophile Nucleophile

16.1 Electrophile ▶

$$A-B+\overset{\oplus}{X} \rightarrow A-X+\overset{\oplus}{B}$$

$\overset{\oplus}{X}$ - Electrophile

These are positively charged ions or neutral molecules containing electron deficient atom. They are Lewis acids.

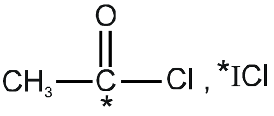
Examples : Positively charged species

$\overset{+}{H}$, $\overset{+}{C}H_3$, H_3O^+, $\overset{+}{N}O_2$, $\overset{+}{N}O$, $\overset{+}{Br}$, $C_6H_5\overset{+}{N}_2$, $CH_3\overset{+}{C}O$, $CH_3\overset{+}{N}_2$

Neutral Species :

$:CH_2$, $C_2H_5\bullet$, $AlCl_3$, BF_3 , $ZnCl_2$, SO_3. $FeCl_3$, Cl, Br, I, $CH_3\bullet$, $SnCl_4$, PCl_3, CO_2, SO_2

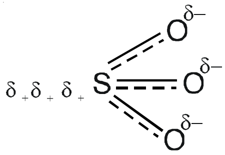
Starred atom :



$$CH_3-\underset{*}{\overset{\overset{O}{||}}{C}}-Cl\ ,\ {}^{*}ICl$$

Note : In *I – Cl , chlorine is more electronegative than iodine [EN(Cl) > EN(I)] as such an electron deficient centre is created on iodine indicated by star.

For SO_3, electrophilic nature can be understood by its structure.



Clearly a positive centre is developed at the site of the sulphur atom.

16.2 Nucleophile

$$A - B + \overset{\ominus}{Y} \longrightarrow A - Y + \overset{\ominus}{B}$$

Y – Nucleophile

These are negatively charged ions or neutral molecule with unshared pair of electrons. They are electron rich or Lewis bases.

Examples - Negatively charged ions

$$\overset{\ominus}{Cl}, \overset{\ominus}{Br}, \overset{\ominus}{I}, \overset{\ominus}{O}H, \overset{\ominus}{C}N, \overset{\ominus}{O}R, R\overset{\ominus}{S}, \overset{\ominus}{C}{\equiv}CH, N\overset{\ominus}{O_2}, HS\overset{\ominus}{O_4}$$

Neutral Species - $\overset{\cdot\cdot}{N}H_3$, $R-\overset{\boxed{\cdot\cdot}}{N}H_2$, $R_2\overset{\boxed{\cdot\cdot}}{N}H$, $R_3\overset{\boxed{\cdot\cdot}}{N}$, $H_2O\boxed{:}$, $R\overset{\boxed{\cdot\cdot}}{O}H$ $R_2O\boxed{:}$, $R_2S\boxed{:}$

Starred atom : $C_2H_5\overset{*}{L}i$, $C_2H_5-\overset{*}{M}gBr$, $NaBH_4$, $\overset{*}{L}iAlH_4$

16.3 Reaction

In fact the reaction is the mutual attack of an electrophile on nucleophile or vice-versa.

electrophile + nucleophile → product

$(CH_3)_3\overset{\oplus}{C} + \overset{\ominus}{O}H \rightarrow (CH_3)_3-OH$

t-butyl alcohol

$\overset{\oplus}{C}H_3 + \overset{\ominus}{C}N \rightarrow CH_3CN$

methyl cyanide

$CH_3-\overset{\oplus}{C}H_2 + :NH_3 \rightarrow CH_3CH_2NH_2 + \overset{\oplus}{H}$

ethylamine

16.4 The strength of electrophile follows the order

(i) $\overset{+}{C}H_3 > CH_3\overset{+}{C}H_2 > (CH_3)_2\overset{+}{C}H > (CH_3)_3\overset{+}{C}$ (ii) $\overset{+}{N}O_2 > \overset{+}{N}O$ (iii) $\overset{+}{Cl} > \overset{+}{Br} > \overset{+}{I}$

16.5 The strength of nucleophile follows the order

(i) $\overset{-}{O}C_2H_5 > \overset{-}{O}H > CH_3CO\overset{-}{O}$ (ii) $I^- < Br^- < Cl^-$ (iii) $CH_3^- > NH_2^- > OH^- > F^-$

16.6 Electrophile and nucleophile at a glance

S.No.	Electrophile	Nucleophile
1.	Accepts the electron pair	Supplies the electrons pair
2.	Electron deficient	Electron rich
3.	Attacks the points of high electron density	Attacks the point of low electron density
4.	Lewis acid	Lewis base
5.	Possesses an empty orbital to receive the electron pair	Possesses an electron pair which is loosely held and can be supplied easily
6.	Usually positively charged species	Usually negatively charged species
7.	Forms an extra bond with the nucleophile	Increases its covalency by one unit

17. Inductive Effect

Electron displacement along a carbon chain due to the presence of an attached substituent is known as inductive effect. It is a permanent effect and decrease rapidly with the length of carbon chain.

$$\underset{4}{C} - \underset{3}{C} - \underset{2}{C} - \underset{1}{C} - Z$$

17.1 Inductive effect is of following types -

(i) Negative Inductive Effector - I Effect

Some atoms or groups have a greater tendency to attract the shared electron of the covalent bond. Such atoms or groups acquire partial negative charge by receiving electron density from the covalent bonds of the chain. Therefore, these are classified as the groups exerting **negative inductive (–I) effect**. For example

$-\overset{\oplus}{N}H_3$, $-\overset{\oplus}{N}R_3$, $-NO_2$, $-C\equiv N$, $-COCl$, $-COOH$

$-CHO$, $-COOR$, $-F$, $-Cl$, $-Br$, $-I$, $-C\equiv CH$

$-CH=CH_2$, $-CO-R$, $-OH$, $-SH$, $-NH_2$, $-NHR$,

$-NR_2$, $-NH-CO-R$, $-CF_3$, $-CCl_3$, etc.

The decreasing order of negative inductive effect of some important atoms and groups is given below

Order of - I effect

$$-\overset{\oplus}{N}H_3 > \overset{\oplus}{N}(CH_3)_3 > -NO_2 > -C\equiv N > -F > -Cl > -Br > -I > -CF_3 > -CCl_3 > -OH > -OCH_3 > -C_6H_5 > -H$$

(ii) Positive Inductive Effect or +I Effect

Some groups are electron donor and therefore acquire partial positive charge by increasing electron density in the covalent bonds of a chain. Such groups exert **positive inductive (+I) effect**. Alkyl radicals are the best examples of this type of groups.

The decreasing order of positive inductive effect of some alkyl groups with respect to hydrogen is given below.

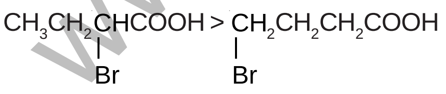
Order of +I Effect

$$\underset{3°}{(CH_3)_3C-} > \underset{2°}{(CH_3)_2CH-} > \underset{1°}{CH_3CH_2-} > \underset{1°}{CH_3-} > H-$$

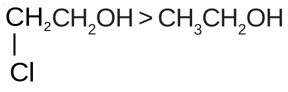
17.2 Examples [applications] :-

(i) $HCOOH > CH_3COOH$

(ii) $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH > CH_3COOH$

(iii) 

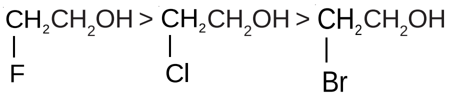
$CH_3CH_2\underset{\underset{Br}{|}}{C}HCOOH > \underset{\underset{Br}{|}}{C}H_2CH_2CH_2COOH$

(iv) 

$\underset{\underset{Cl}{|}}{C}H_2CH_2OH > CH_3CH_2OH$

(v) p-Nitrophenol > Phenol

(vi) $CH_3CH_2OH > (CH_3)_2CHOH > (CH_3)_3COH$

(vii) 

$\underset{\underset{F}{|}}{C}H_2CH_2OH > \underset{\underset{Cl}{|}}{C}H_2CH_2OH > \underset{\underset{Br}{|}}{C}H_2CH_2OH$

(viii) $HCOOH > CH_3COOH > C_2H_5COOH > n\text{-}C_3H_7COOH$

17.3 Order of basic character :-

(i) $NH_3 > ClNH_2$ (ii) $(CH_3)_2NH > CH_3NH_2$ (iii) $C_2H_5NH_2 > C_6H_5NH_2$

17.4 Other examples :-

(i) Order of acid strength : $CH_4 < CH_3I < CH_3Br < CH_3Cl < CH_3F$

(ii) Order of acid strength of β-halo acids

β-fluoroethyl alcohol > β-chloroethyl alcohol > β-bromoethyl alcohol

(iii) Order of acid strength of aromatic alcohols : p-nitrobenzyl alcohol > benzyl alcohol

(iv) Order of acid strength in water

(a) $HCCl_3 > CH_2Cl_2 > CH_3Cl > CH_4$ (b) $HCOOH > CH_3OH > CH_4$

Ex.1 Why is formic acid stronger than acetic acid ?

Sol. In formic acid, COOH group is bonded to the hydrogen atom, which does not exert any inductive effect. In acetic acid, COOH group is bonded to a methyl group, which exerts +I effect. The acetate ion formed due to ionisation of acetic acid is more reactive due to increase in the electron density on oxygen atom. This makes acetate ion more reactive than formate ion. Thus acetate ions react faster with hydrogen ions shifting the equilibrium in backward direction. Thereby decreasing the concentration of hydrogen ions. Therefore acetic acid is weaker than formic acid.

Ex.2 Discuss the decreasing order of acid strength of trihalogenated derivatives of acetic acid.

Sol. The acid strength of the trihalogenated acetic acids increases with increase in the –I effect of the halogen substituents. Three fluorine atoms have greater –I effect than the other three halogens. Therefore trifluoroacetic acid ionises more than the other analogues. Thus, the decreasing order of acid strength is as follows

$$CF_3-COOH > CCl_3-COOH > CBr_3-COOH > CI_3-COOH$$

Ex.3 Discuss the relative order of acid strength of acetic acid and benzoic acid.

Sol. Benzoic acid is a stronger acid than acetic acid. This is because methyl group present in acetic acid has a weak donor (+I) effect and phenyl group present in benzoic acid has a weak acceptor (–I) effect

$$C_6H_5 \leftarrow COOH > CH_3 \rightarrow COOH$$

17.5 Comparison of Base strength

Aliphatic amines are stronger bases than aromatic amines. The basic behaviour of amines is due to availability of lone pair of electrons present on the nitrogen atom. The positive inductive effect of methyl group increases electron density on nitrogen atom, due to which electron pair on nitrogen atoms is more readily available to the attacking acid. Therefore, alkylamines are more basic than ammonia. In aromatic amines, the NH_2 group is bonded to the aromatic ring, which exerts a weak –I effect. That is why, aniline is a weaker base than ammonia.

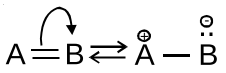
$R \rightarrow NH_2$	>	$H-NH_2$	>	$C_6H_5 \leftarrow NH_2$
(+I effect of R)		(No effect of H)		(–I effect of C_6H_5)

However, the major cause of much lower base strength of aniline than ammonia is resonance. A partial positive charge develops on the nitrogen atom of aniline due resonance, thereby the availability of electron density on nitrogen atom in aniline decreases.

18. Electromeric Effect

Transfer of an electron pair from one location to the other in the structural formula of an organic compound under the influence of a reagent, is known as **electromeric effect**. Electromeric effect is a temporary effect that does not take place of its own, but occurs on the demand of the attacking reagent. This effect vanishes on the completion of the reaction. The electromeric effect is symbolized by a curved arrow (↷). Electromeric effect can normally take place in the following three ways

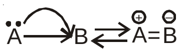
(a) Transfer of pi electron pair to the adjacent atom in the form of nonbonded electron pair



$$A=B \rightleftarrows \overset{\oplus}{A}-\overset{\ominus}{\ddot{B}}$$

In the above representation, the two electrons of the pi bond situated between atoms A and B get transferred to atom B as lone pair.

(b) Transferred of nonbonded electron pair to the same atom in the form of pi electron pair



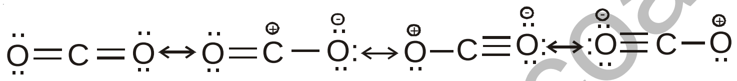
(c) Transfer of pi electron pair to the adjacent atom in the form of pi electron pair

19. Resonance

Many polyatomic molecules and ions having pi bonds can be represented by more than one structural formula,. But none of these structural formulae truly stands for that molecule or ion. because none of them can explain its properties. These hypothetical or nonexistent structural formulae are known as **resonating structures** or **contributing structures** or **canonical structures**. The actual or existent structure is the hybrid of all the canonical structures and is called **resonance hybrid structure**. This property is known as **resonance**, In resonance, the positions of the nuclei of the atoms do not change, but the pi electrons are continuously moving or delocalized. Thus, the delocalization of pi electrons is the cause of resonance. Since the pi electrons constantly move, it becomes more difficult for the reagent to attack then and therefore the molecule or ion undergoing resonance acquires greater stability. This is called **resonance stabilization**.

Ex.1 Indicate resonating structural formulae of carbon dioxide

Sol.

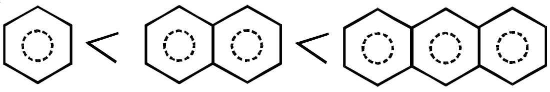


19.1 Resonance Energy

Due to resonance, the per mole energy of the resonance hybrid of a molecule or ion is less than the per mole energy calculated for the most stable of the canonical structures. This energy difference is known as **resonance energy**. Higher the value of resonance energy, greater is the resonance stabilization.

Ex.1 What is the increasing order of resonance stabilization of benzene, naphthalene and anthracene

Sol. The values of resonance energy for benzene, naphthalene and anthracene are 36, 76 and 85 Kcal per mole respectively. It is clear from these values that the resonance stabilisation of naphthalene is more than that of benzene and less than that of anthracene. Thus, the increasing order of resonance stabilisation is as follows.



Benzene Naphthalene Anthracene

19.2 Resonance Effect or Mesomeric Effect (R or M Effect)

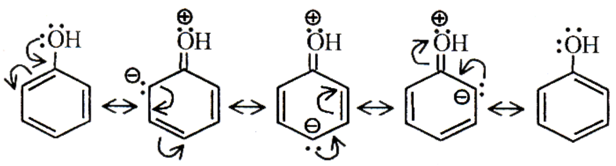
When an atom or a group of atoms or a substituent present in a molecule exerts electromeric displacement of a $\overset{*}{\text{pi}}$ electron pair or a lone pair and thus initiates resonance in the rest of the molecule. The phenomenon is known as **Mesomeric effect or resonance effect**. The electron pair donor substituent is said to exert positive resonance (+R) effect or positive mesomeric (+M) effect. The electron pair acceptor substituents are said to exert negative resonance (–R) or negative mesomeric (–M) effect.

19.2.1 Groups Exerting +R or +M Effect

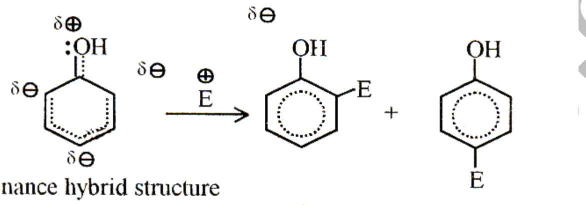
Following are a few examples of the groups exerting positive mesomeric effect.

$-OH$, $-NH_2$, $-OR$, $-NHR$, $-NR_2$, $-O$, $-CH_3$, $-Cl$

If a +M group is present on benzene ring, it increases electron density on o–and p-location, due to which the attacking electrophile largely forms a mixture of o– and p– electrophilic substitution products. Therefore in aromatic electrophilic substitution reactions, the groups exerting +M effect are mainly o- and p- directing, as illustrated below by taking the example of phenol.



Canonical structural formulae



Resonance hybrid structure

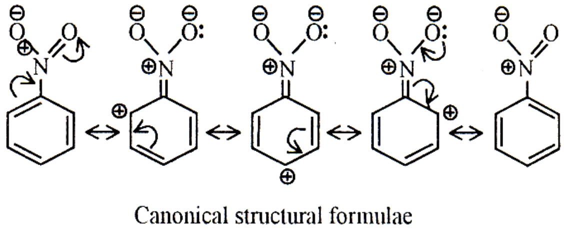
A mixture of *o*- + *p*- S_E products

19.2.2 Groups Exerting –R or –M effect

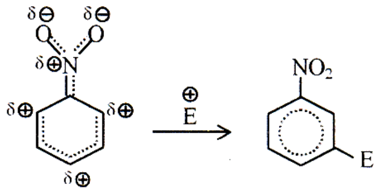
Following are a few examples of groups exerting negative mesomeric effect.

$-NO_2$, $-CN$, $-CHO$, $-COCH_3$, $-COOH$, $-SO_3H$, $-CF_3$, $-CCl_3$

When a substituent exerting –M effect is bonded to the benzene nucleus, it reduces electron density at the ortho and para locations. Therefore, the electrophile cannot attack the positively charged ortho and para positions, but can collide with the electroneutral meta position slowly. Hence, in aromatic electrophilic substitution reactions the groups exerting –M effect exhibit meta-directing influence. This is illustrated below by taking the example of nitrobenzene.



Canonical structural formulae



Resonance hybrid structure

m- S_E product

Few points [M and R effect]

▶ This effect operates in unsaturated molecules in which :

– There is a conjugated system of double bond.

– Negative charge is in conjugation with double (or multiple) bond.

– Lone pair of electron in conjugation with double (or multiple) bond.

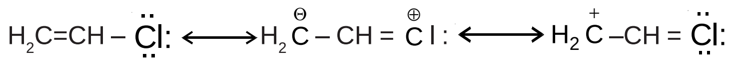
- There is complete transfer of electron pair during the operation
- The reactivity of compounds is affected by the presence of

  $-NO_2$, $-C\equiv N$, $> C = O$, $-\ddot{C}l$, $\ddot{N}H_2$ etc. groups.
- There is relay of π-electron from one end to the other end through a conjugated system of double bond.

Other Illustrations :

Order of stability of canonical forms :

(a) Vinyl chloride :



$$H_2C{=}CH-\ddot{\underset{..}{C}}l{:} \longleftrightarrow H_2\overset{\ominus}{C}-CH=\overset{\oplus}{C}l{:} \longleftrightarrow H_2\overset{+}{C}-CH=\ddot{\underset{..}{C}}l{:}$$

I II III

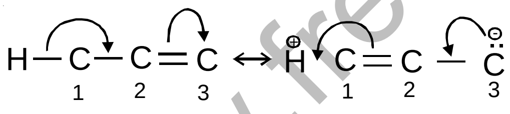
III – least stable	[carbon is electron deficient]
II – less stable	[charge separation]
I – stable	[no charge separation]

∴ III < II < I

20. Hyperconjugation or Baker-Nathan Effect

In an organic molecule, the transfer of a sigma electron pair (heterolysis) or a single electron from a sigma bond (homolysis) may also be responsible for initiation of resonance in the rest of the molecule. This is referred to as **hyperconjugation** or **Baker-Nathan effect**. It was also called **no-bond resonance** because in the canonical structure of the molecule, no bond is shown between the two atoms from where the sigma electrons/s has/have been transferred. It can also be called **σ, π–conjugation** because a sigma electron/s is/are transformed into a pi pair in this type of resonance. However, for the first time, **Mulliken** in 1941 gave the name hyperconjugation to this phenomenon.

Ex.1



(I) (II)

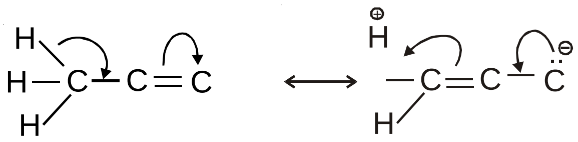
In the above structural part (I) , the sigma electron pair present between H and C–1 atoms shifts between C–1 and C–2 atoms as pi electron pair. Simultaneously, the pi electron pair present between C-2 and C-3 shifts to C-3 as a lone pair. As a result of these electron pair transfers. positive charge develops on hydrogen atom and negative charge develops on C-3 atom. Note that no bond is shown between H and C–1 atom in the canonical structural formula (II)

20.1 Applications of Hyperconjugation

(a) Explanation of Electron Donor Property of Alkyl Radicals

The cause of electron donor effect or +I effect of alkyl radicals is actually hyperconjugation.

Ex.1



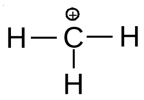
(b) Explanation of Order of Stability of Alkyl Carbocations

The stability of alkyl carbocations decreases in the order 3° > 2° > 1° . For example

$$(CH_3)_3\overset{\oplus}{C} > (CH_3)_2\overset{\oplus}{C}H > CH_3 - \overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3$$

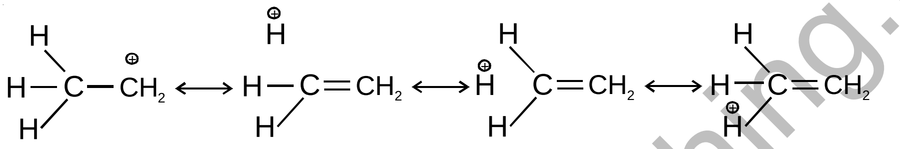
Larger the number of locations for delocalisation of the positive charge in the structural formula of the carbocation, lower is the reactivity or higher is the stability of that carbocation.

Methyl carbocation is least stable amongst alkyl carbocations, because of only one possible location for positive charge. Thus, methyl carbocation has only one structural formula



$$H-\underset{\underset{H}{|}}{\overset{\oplus}{C}}-H$$

Ethyl carbocation is more stable than methyl carbocation, because of four possible locations for its positive charge i.e., one carbon atom and three α-hydrogen atoms. Thus, ethyl carbocation can be represented by the following four structural formulae.



(c) Explanation of Stability of Alkyl Free Radicals

The stability of alkyl free radicals is also similar to that of alkyl carbocations. i.e. 3° > 2° > 1° , because here also methyl, ethyl, isopropyl and tert-butyl free radicals can also be represented by one, four, seven and ten structural formulae. respectively.

$$(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3 - \dot{C}H_2 > \dot{C}H_3$$

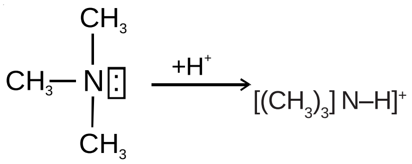
21 Steric hindrance

On account of the presence of bulkier groups at the reaction centre, they cause mechanical interference and with the result that the attacking reagent finds it difficult to reach the reaction site and thus slows down the reaction. This phenomenon is called steric hinderance.

Example :-

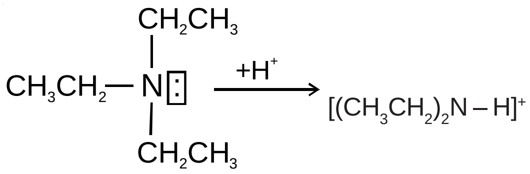
1. $(C_2H_5)_3N\boxed{:}$ is less basic than $(CH_3)_3N\boxed{:}$

Protonation easier : (Smaller size of CH_3 group)



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N}}\boxed{:} \xrightarrow{+H^+} [(CH_3)_3]N-H]^+$$

Protonation difficult : [Bigger size of CH_3CH_2 group]$^+$



$$CH_3CH_2-\underset{\underset{CH_2CH_3}{|}}{\overset{\overset{CH_2CH_3}{|}}{N}}\boxed{:} \xrightarrow{+H^+} [(CH_3CH_2)_2N-H]^+$$

22. Organic Reactions and Mechanism

Types of reaction :-

Organic substrate + Reagent → Product

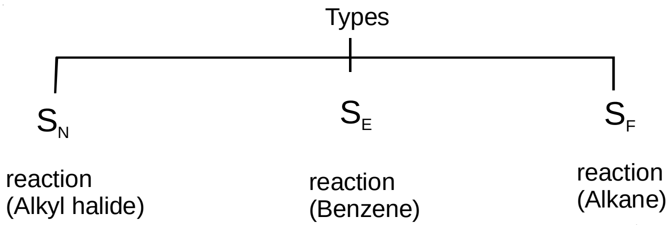
Mainly four types of reactions are

(a) Substitution (b) Addition (c) Elimination (d) Rearrangement or isomerisation

22.1 Substitution Reaction

It involves replacement of one substituent by another

$$A - B + x - y \rightarrow A - x + B - y$$



Example :

S_N , $CH_3Br + CN^- \rightarrow CH_3CN + Br^-$

S_E , $C_6H_6 + Br^+ \rightarrow C_6H_5Br + H^+$

S_E , $CH_4 + Cl_2 \xrightarrow{hv} CH_3Cl + HCl$

22.1.1 S_N reaction or nucleophilic substitution reaction

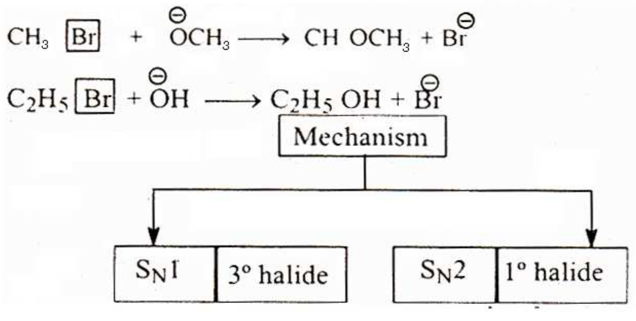
$$\overset{\delta+}{R} \rightharpoonup \overset{\delta-}{X} + \overset{\ominus}{Nu} \rightarrow R - Nu + \overset{\oplus}{X}$$

alkyl halide nucleophile

Here : R– alkyl group X⁻ – leaving group (halide ion)

Nu : attacking species [It is a weaker nucleophile, being conjugate base of hydrohalic acid]

Example :



$CH_3\,\boxed{Br} + \overset{\ominus}{O}CH_3 \longrightarrow CH\ OCH_3 + Br^{\ominus}$

$C_2H_5\,\boxed{Br} + \overset{\ominus}{O}H \longrightarrow C_2H_5\,OH + Br^{\ominus}$

(a) [S_N 1] or unimolecular nucleophilic Substitution Reaction

[substrate–3° or tertiary halide]

Alkaline hydrolysis of tertiary butyl chloride

$$(CH_3)_3\,C{-}Cl + OH^- \rightarrow (CH_3)_3\,C{-}OH + \bar{Cl}$$

Mechanism

Step - 1 (Slow)

$$(CH_3)_3\,C{-}Cl \rightarrow (CH_3)_3\overset{\oplus}{C} + \overset{\ominus}{Cl}$$

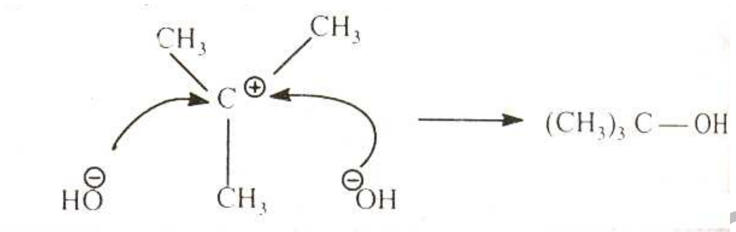
Step - 2 (fast)

$(CH_3)_3\overset{\oplus}{C} + OH^- \rightarrow (CH_3)_3\,C–OH$ t – butyl alcohol

Rate equation :-

V = k [t - butyl halide] Molecularity - 1,

Note :- Here the carbonium ion is planar [sp^2 hybridised] The nucleophile can attack the planar carbonium on either side to give t-butyl alcohol.



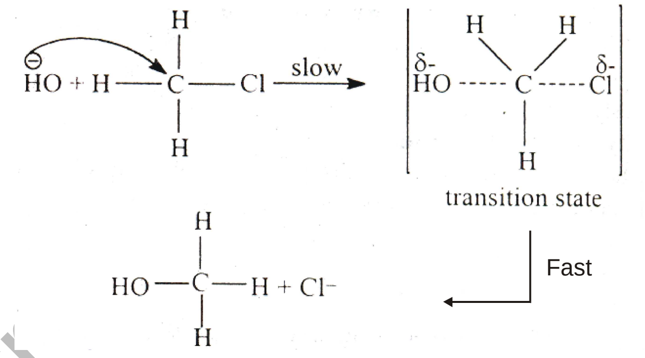
If the three groups attached to positively charged carbon are different than the product will be racemic.

(b) [S_N2] or Bimolecular Nucleophilic Substitution Reaction

[substrate- methyl or 1° halide]

Alkaline hydrolysis of methyl chloride : $CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$

Mechanism : (Concerted one step process)



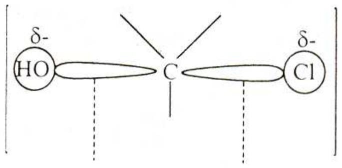
Rate equation : $V = k\,[CH_3Cl]\,[OH^-]$

Molecularity - 2

Note : In the slow or rate determining step two species are taking part. Hence it is a bimolecular reaction. Further OH^- attacks from the rear (back) side and as such **inversion takes place.**

Supposing in place of methyl chloride there is optically active primary halide then the product obtained will be reverse of the original substrate as inversion takes place.

Orbital picture of transition state :



at the point of bond making at the point of bond breaking

(c) S_N 1 or S_N 2 reaction

[Substrate-2° halide]

Non polar medium .... S_N2 reaction

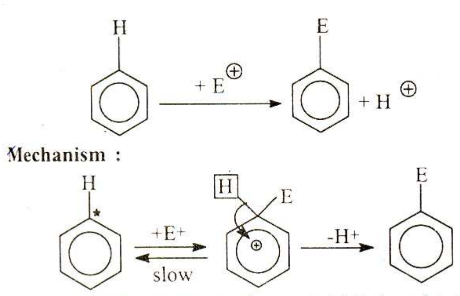
Polar medium .... S_N1 reaction

Transition state and Intermediate

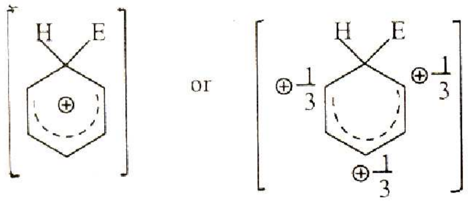
Transition state : A transition state refers to an imaginary state and cannot be isolated (S_N2)

Intermediate : Intermediate is a stable real species and can be isolated under specific condition [S_N1 (carbocation)]

22.1.2 S_E reaction or electrophilic substitution reaction : Benzene usually show electrophilic substitution reaction



Here the starred carbon (in benzene) C^* is in sp^2 hybridisation state. Electrophile attacks and arenium ion is formed as an intermediate.



Since in the rate determining step two species electrophile and benzene participates so it is a **bimolecular reaction.**

Rate = k [benzene]. [electrophile]

Example 1. Methylation of benzene

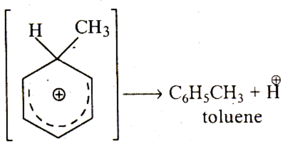
$C_6H_6 \xrightarrow{CH_3Cl\,/\,AlCl_3} C_6H_5CH_3$

Mechanism

Step-1 : $CH_3\text{–}Cl + AlCl_3 \rightarrow \overset{\oplus}{C}H_3 + \overset{-}{A}lCl_4$

Step-2 (Slow)

$CH_3^{\oplus} + C_6H_5 - H \rightarrow$



carbocation (σ-complex intermediate)

Step-3 : $\overset{\oplus}{H} + \overset{\ominus}{AlCl_4} \rightarrow AlCl_3 + HCl$

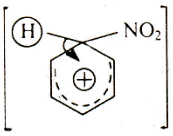
Example 2. Nitration of benzene :

$$C_6H_6 \xrightarrow{HNO_3 / H_2SO_4} C_6H_5NO_2 + H_2O$$

Mechanism :

Step-1 : $2H_2SO_4 + HO - NO_2 \rightarrow \overset{\oplus}{N}O_2 + 2HSO_4^- + H_3\overset{\oplus}{O}$

Step-2 : $\overset{\oplus}{N}O_2 + C_6H_5 - H \longrightarrow$



$\longrightarrow C_6H_5NO_2 + \overset{\oplus}{H}$

(σ–complex)

Step-3 : $\overset{\oplus}{H} + HS\overset{-}{O}_4 \longrightarrow H_2SO_4$

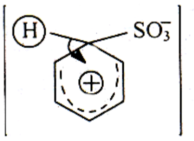
Example 3 : Sulphonation of benzene :

$$C_6H_6 \xrightarrow{conc.H_2SO_4} C_6H_5 - SO_3H + H_2O$$

Mechanism :

Step-1 : $H_2SO_4 \rightleftharpoons H_2O + SO_3$

Step-2 : $SO_3 + C_6H_5 - H \longrightarrow$



$\rightarrow C_6H_5 - S\overset{-}{O}_3 + \overset{\oplus}{H} \rightleftharpoons C_6H_5SO_3H$

(σ–complex)

22.1.3 Free radical substitution

S_F – Chlorination of methane is the example of free radical substitution

Reaction :-

$$CH_4 + Cl_2 \rightarrow CH_3 - Cl + HCl$$

Mechanism :-

(1) Step-1 (Chain initiation step)

$Cl–Cl \xrightarrow{hv} Cl^{\bullet} + Cl^{\bullet}$

(2) Step-2 (Chain propagation step)

$Cl^{\bullet} + CH_4 \rightarrow CH_3^{\bullet} + HCl$

$CH_3^{\bullet} + Cl_2 \rightarrow CH_3Cl + Cl^{\bullet}$

(3) Step-3 (Chain termination step)

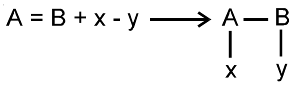
$CH_3^{\bullet} + CH_3^{\bullet} \rightarrow CH_3 - CH_3$

$CH_3^{\bullet} + Cl^{\bullet} \rightarrow CH_3–Cl$

$Cl^{\bullet} + Cl^{\bullet} \rightarrow Cl_2$

22.2 Addition reaction

Addition reaction : Usually unsaturated molecule undergoes addition reaction. In this type of reaction one π-bond is broken and two σ-bonds are formed

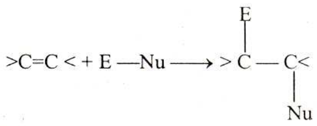


$$A = B + x - y \longrightarrow \underset{x}{A} - \underset{y}{B}$$

[1σ , 1π] [3σ]

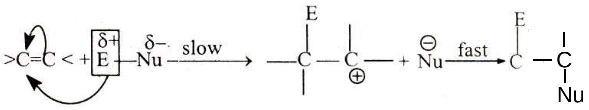
22.2.1 Electrophilic addition reaction

Substrate - Alkene, Alkyne



$$>C=C< + E-Nu \longrightarrow >\overset{E}{C}-\underset{Nu}{C}<$$

Mechanism :



trans-addition

It should be noted that :

– When polar molecular attacks the double bond of alkene, then π-electrons of the double bond shift to one of the carbon atom due to electromeric effect $>C\overset{\frown}{=}C<$, the electrophile attaches to that carbon atom and carbocation is formed

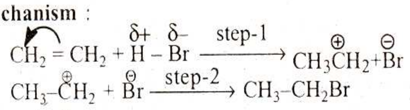
– The nucleophilic part of the reagent attaches to positively charged carbon and forms the end product. This is of course a trans-addition.

– Since the initial attack is of a electrophile this is referred as **electrophilic addition**.

Example 1.

$CH_2 = CH_2 + HBr \rightarrow CH_3–CH_2Br$

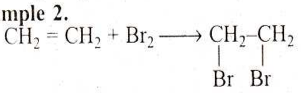
Mechanism :



$$CH_2 = CH_2 + \overset{\delta+}{H} - \overset{\delta-}{Br} \xrightarrow{\text{step-1}} CH_3\overset{\oplus}{C}H_2 + \overset{\ominus}{Br}$$

$$CH_3–\overset{\oplus}{C}H_2 + \overset{\ominus}{Br} \xrightarrow{\text{step-2}} CH_3–CH_2Br$$

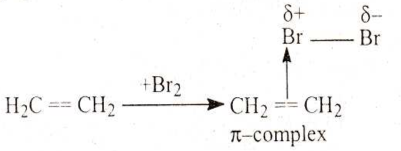
Example 2.



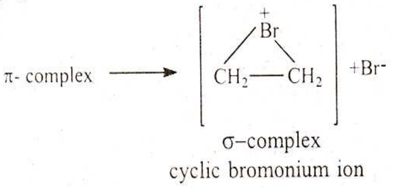
$$CH_2 = CH_2 + Br_2 \longrightarrow \underset{Br}{CH_2}–\underset{Br}{CH_2}$$

Mechanism :

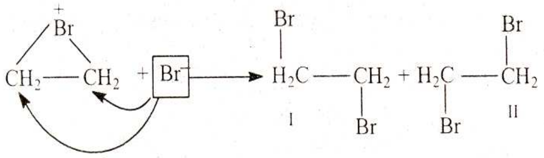
Step–1



Step–2



Step–3

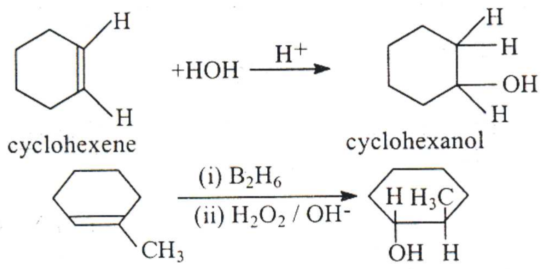


If Br^- attacks first carbon then II product is formed.

If Br^- attacks second carbon then I product is formed. (Here both the products are similar)

Other example :-

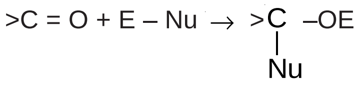
$$CH_2 = CH_2 + H{-}OH \xrightarrow{H^+} CH_3{-}CH_2OH$$



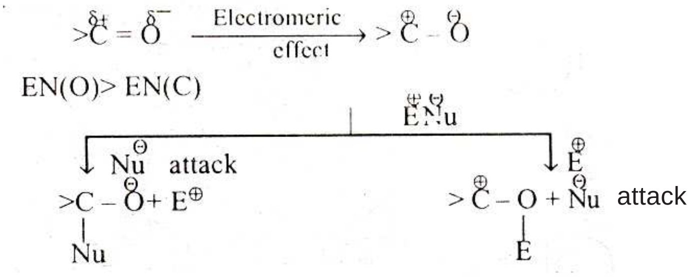
1- methyl cyclohexene trans-2-methyl cyclohexanol

22.2.2 Nucleophilic addition reaction

[Substrate - Aldehyde, Ketone]

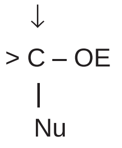
General Mechanism 

$$>C = O + E - Nu \rightarrow \underset{\displaystyle Nu}{\overset{}{>C}}{-}OE$$



Oxygen bearing negative charge more stable (forms)

less stable (does not form)



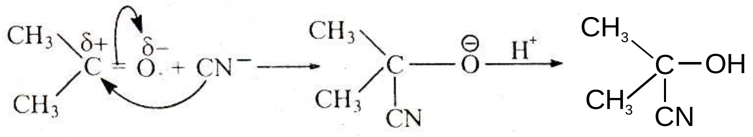
$$\downarrow$$

$$\underset{\displaystyle Nu}{> C} - OE$$

Example :- Addition of HCN at acetone :

Mechanism :

$$HCN \xrightarrow[\text{small quantity}]{\text{Base in}} H^{\oplus} + CN^-$$

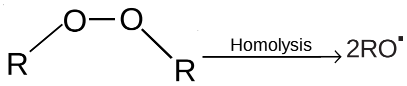


22.2.3 **Free radical addition :** Anti-Markownikoff's reaction- peroxide effect

Addition of HBr to propene in presence of peroxide

$$CH_3-CH=CH_2 + HBr \xrightarrow{\text{Peroxide}} CH_3-CH_2-CH_2Br$$

Mechanism :-



$$R-O-O-R \xrightarrow{\text{Homolysis}} 2RO^{\bullet}$$

(i) Chain initiation :-

$$RO^{\bullet} + HBr \rightarrow ROH + Br^{\bullet}$$

(ii) Chain propagation : (two steps)

$$CH_3-CH=CH_2 + Br^{\bullet} \rightarrow CH_3-\dot{C}H-CH_2Br$$

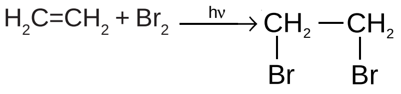
2° free radical

$$CH_3-\dot{C}H-CH_2Br + HBr \rightarrow CH_3-CH_2-CH_2Br + Br^{\bullet}$$

(iii) Chain termination :

$$Br^{\bullet} + Br^{\bullet} \text{ or } 2CH_3-\dot{C}H-CH_2Br \qquad \text{or} \qquad CH_3-\dot{C}H-CH_2Br + Br^{\bullet}$$

Addition of Br_2 to Ethene ;



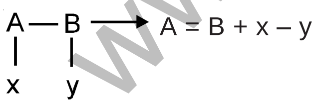
$$H_2C=CH_2 + Br_2 \xrightarrow{h\nu} \underset{Br}{\underset{|}{CH_2}}-\underset{Br}{\underset{|}{CH_2}}$$

Mechanism :

$$Br_2 \xrightarrow{h\nu} 2Br^{\bullet}$$

$$CH_2 = CH_2 + Br\bullet \rightarrow \bullet CH_2-CH_2-Br \xrightarrow{+Br\bullet} Br-CH_2-CH_2-Br$$

22.3 **Elimination reaction :** Elimination is reverse of addition. In this type of reaction two σ–bonds are broken and 1 π bond is formed.



$$\underset{x}{\underset{|}{A}}-\underset{y}{\underset{|}{B}} \longrightarrow A = B + x - y$$

(three σ) (one–σ and one–π) (one–σ)

(i) Dehydration : $CH_3CH_2OH \xrightarrow[170°]{\text{Conc. } H_2SO_4} CH_2=CH_2 + H_2O$

(ii) Dehydrobromination : $CH_3-CH_2Br \xrightarrow{\text{alc. KOH}} CH_2 = CH_2 + HBr$

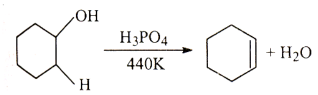
(iii) Debromination : $CH_2Br-CH_2Br \xrightarrow[\Delta]{Zn} CH_2 = CH_2 + ZnBr_2$

$$CH_3CHBr_2 + 2Zn + Br_2CHCH_3 \rightarrow CH_3-CH = CH-CH_3 + 2ZnBr_2$$

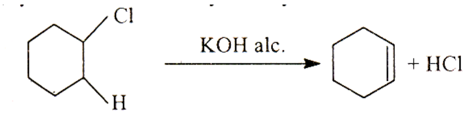
(iv) Dehydrogenation : $CH_3–CH_2OH \xrightarrow[300°]{Cu} CH_3–CHO + H_2$

Examples of Cycloalkenes :

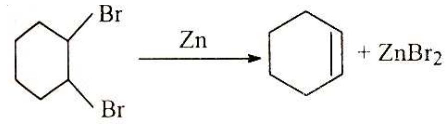
(v) Dehydration of Cyclohexanol :



(vi) Dehydrocholorination of cyclohexylchloride



(v) Debromination of 1,2-dibromocyclohexane

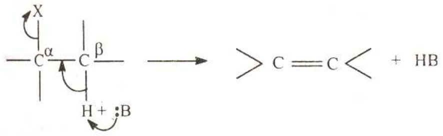


These reactions have been divided into two classes

(1) E2 reaction (2) E1 reaction

22.3.1 E2 reaction : Elimination bimolecular

- Reaction involves one step only
- Base pulls out a proton from the β-carbon atom,
- Simultaneously, a halide ion leaves and the double bond is formed



Rate equation :

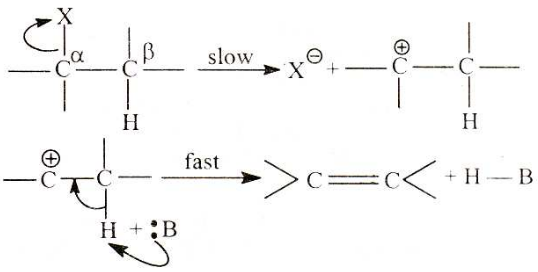
v = k [halide] [:B]

Molecularity - 2

22.3.2 E1 reaction :- Elimination unimolecular

Step-1 Heterolysis of substrate gives carbocation and halide ion (slow)

Step-2 Carbocation gives up proton to a base immediately and alkene is formed

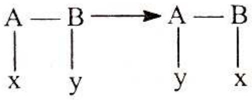


Rate equation :

v = k [RX]

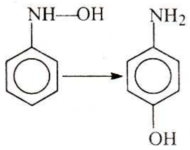
Molecularity - 1

22.4 **Rearrangement reaction :** Substituents change their positions



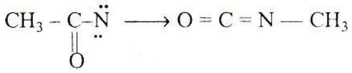
Examples :

(i)



Phenylhydroxylamine p-Amino phenol

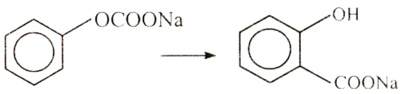
(ii)



$CH_3-\underset{\underset{O}{\|}}{C}-\ddot{N} \longrightarrow O=C=N-CH_3$

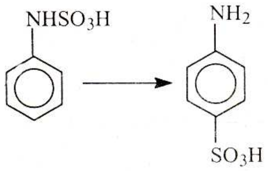
Acetyl nitrene Methyl isocyanate

(iii)



Sodium phenyl carbonate Sodium Salicylate

(iv)



Sulphamic acid Sulphanilic acid

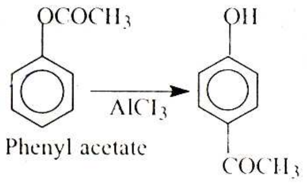
(v) $H-N=C=O \rightarrow N\equiv C-O-H$

Isocyanic acid Cyanic acid

(vi) $CH_3-CH_2-\overset{\oplus}{C}H_2 \rightarrow CH_3-\overset{\oplus}{C}H-CH_3$

1° Carbonium 2° Carbonium

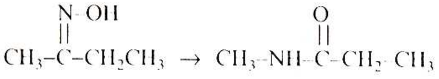
(vii)



Phenyl acetate

p-Hydroxy acetophenone

(viii)



$CH_3-\overset{\overset{N-OH}{\|}}{C}-CH_2CH_3 \rightarrow CH_3-NH-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$

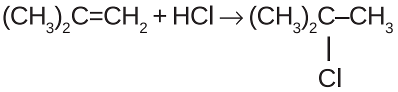
Methyl ethyl ketoxime N–Methyl propionamide

23. Reaction at a glance

Class of compounds	Type
(i) Alkene, alkyne	Electrophilic addition
(ii) Aldehyde, ketone	Nucleophilic addition
(iii) Aldehyde	Nucleophilic substitution
(iv) Aromatic compounds	Electrophilic substitution
(v) Alkane	Free radical substitution

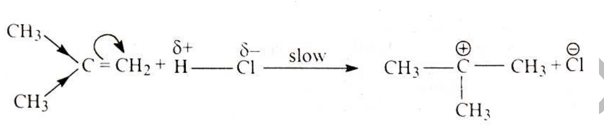
24. Markownikoff's Rule and Peroxide Effect

Markownikoff's Rule : When an unsymmetrical reagent adds to an unsymmetrical unsaturated hydrocarbon, the negative part of the addendum adds on to the carbon containing less number of hydrogen atom.



$$(CH_3)_2C{=}CH_2 + HCl \rightarrow (CH_3)_2\underset{\displaystyle Cl}{\underset{|}{C}}{-}CH_3$$

Mechanism :



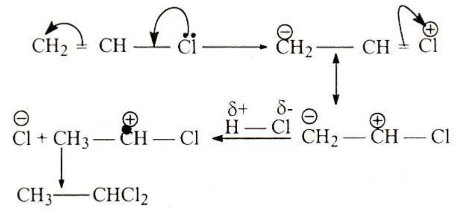
[3° carbonium ion]

$$(CH_3)_2\overset{\oplus}{C}-CH_3+\overset{\ominus}{Cl}\xrightarrow{\text{fast}}(CH_3)_3C{-}Cl$$

Second rule :

In the addition of HCl to vinyl chloride the chlorine, attaches itself to the carbon on which the chlorine atom is already present. $CH_2{=}CHCl + HCl \rightarrow CH_3CHCl_2$

Mechanism :



Peroxide effect :

In the presence of air or peroxides addition of hydrogen bromide to unsymmetrical unsaturated hydrocarbon takes place reverse to that of Markownikoff's rule [Kharash effect]

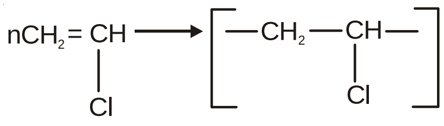
$$(CH_3)_2C = CH + HBr \xrightarrow{\text{peroxide}} (CH_3)_2\,CH{-}CH_2Br$$

It should be noted that HCl and HI do not show peroxide effect.

25. Addition and Condensation Polymers

25.1 **Addition polymerisation :-** Number of monomers unite to produce a macromolecule called **polymer**. The molecular weight of polymer is n times that of monomer [reversible process]

$$nA \rightarrow [-A-]_n$$



$$nCH_2{=}\underset{\displaystyle Cl}{\underset{|}{CH}} \longrightarrow \left[-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-\right]$$

Vinyl chloride [poly vinyl chloride]

Example :

	Monomer	Polymer
(i)	Ethene	Polyethene
(ii)	Acetylene	Benzene
(iii)	Propyne	Mesitylene
(iv)	Vinyl chloride	PVC
(v)	Vinyl acetate	PVA
(vi)	Acrelo nitrile	PAN
(vii)	Styrene	Polystyrene
(viii)	Chloroprene	Neoprene
(ix)	1,3-Butadiene	Buna rubber
(x)	Isoprene	Polyisoprene
(xi)	Formaldehyde	Paraformaldehyde, Trioxane
(xii)	Acetaldehyde	Paraaldehyde, Metaldehyde
(xiii)	Tetra fluoroethene	Teflon
(xiv)	Methyl methacrylate	PMMA

25.2 Condensation Polymerisation

Two or more molecules of different substances unite to give a bigger molecule with the elimination of simple molecules like H_2O, NH_3, HCl etc. (irreversible process)

$$\underset{\text{formaldehyde}}{6HCHO + 4NH_3} \rightarrow \underset{\text{hexa methylene tetraamine or urotropine}}{(CH_2)_6N_4} + 6H_2O$$

Example :

	Substrate	Polymer
(i)	Formaldehyde + phenol	Bakelite
(ii)	Formaldehyde + urea	Urea formaldehyde resin
(iii)	Acetone (+ conc. H_2SO_4)	Mesitylene
(iv)	Acetone (+dry HCl)	Mesityl oxide and phorone
(v)	Adipic acid + hexamethylene diamine	Nylon-66
(vi)	Methyl terephthalate + glycol	Terylene or decron
(vii)	Melamine + formaldehyde	Melmake

IMPORTANT REAGENTS AND TESTS

(1) **Baeyer's Reagent :** Cold and dilute alkaline solution of $KMnO_4$ is known as Baeyer's reagent.

Function : It is used to detect the presence of olefinic double bond (C=C) or triple bond (C≡C)

$$CH_2{=}CH_2 \xrightarrow{O,\, H_2O} CH_2(OH){-}CH_2(OH)$$

ethylene glycol

[pink colour decolurizes]

(2) **Benedict's Solution :** Benedict's solution is a mixture of copper sulphate, sodium carbonate and sodium citrate solution.

Function : For the detection of an aldehydic group [–CHO].

Aldehyde + reagent $\longrightarrow$ red brown precipitate of Cu_2O

$RCHO + 2Cu^{+2} + 5OH^- \rightarrow RCOO^- + 3H_2O + Cu_2O\downarrow$

(3) **Fehling Solution :**

Solution A : Aqueous solution of $CuSO_4$

Solution B : NaOH and aqueous solution of sodium potassium tartarate [Rochelle salt].

Function : For the detection of aldehydic group [–CHO aliphatic].

Equal volumes of A and B solutions are mixed and heated with aldehyde, a red precipitate of Cu_2O appears.

$$RCHO + 2CuO \rightarrow Cu_2O\downarrow + RCOOH$$

(red ppt.)

(4) **Lithium Aluminium Hydride [$LiAlH_4$] :**

Function : As a reductant

$$-CHO \xrightarrow{+2H} CH_2OH$$

$$CO \xrightarrow{+2H} > CHOH$$

$$-COOH \xrightarrow{+4H} > CH_2OH + H_2O$$

$$-CONH_2 \xrightarrow{+4H} > CH_2NH_2 + H_2O$$

$$> C = O \xrightarrow{+4H} > CH_2 + H_2O$$

It does not reduce C=C.

$$CH_3 - CH = CHO \xrightarrow{LiAlH_4} CH_3 - CH = CH - CH_2OH$$

(5) **Bromine :** Br_2 water, Br_2 in acetic acid or Br_2 in CCl_4.

Function : Identify olefinic or acetylenic compounds [C=C or C≡C]

$$CH_2 = CH_2 + Br_2 \xrightarrow{\text{in } CCl_4} CH_2Br - CH_2Br$$

(Red) (colourless)

(6) **Schiff's Reagent** : It is a dilute solution of para–rosaniline hydrochloride or magneta dye decolourised by sulphur dioxide.

Function : For the detection of [–CHO] group.

Schiff's reagent + aldehyde → magneta colour [pink].

(7) **Tollen's Reagent :** Ammonical silver nitrate solution.

Function : For the detection of aliphatic aldehyde [–CHO]

$R{-}CHO + Ag_2O \rightarrow Ag\downarrow + RCOOH$

[silver mirror]

(8) Resin Test :

$$CH_3CHO \xrightarrow{\text{conc. alkali}} \text{yellow resinous type compound}$$

[HCHO does not give this test]

(9) Iodoform Test : NaOH and I_2

Function : For detecting CH_3CO – or CH_3CHOH groups.

$$CH_3COCH_2CH_3 \xrightarrow[\text{NaOH}]{I_2} CHI_3 \text{ [yellow precipitate]}$$

Substances responding iodoform test are :

ethanol, acetone, 2–propanol, lactic acid, acetaldehyde etc.

(10) Lucas Test : Anhydrous $ZnCl_2$ and conc. HCl

Function : For the distinction of 1°, 2°, 3° alcohols.

$$-OH \xrightarrow{\text{reagent}} -Cl \quad \text{[tribidity is formed]}$$

The order of reactivity :

3° (turbidity at once) > 2° (turbidity after 5 minutes) > 1° (turbidity after 30 minutes)

(11) Sulphuric acid H_2SO_4) :

Function : (i) As a dehydrating agent :

$$C_2H_5OH \xrightarrow[170°C]{\text{conc. } H_2SO_4} CH_2 = CH_2 + H_2O$$

$$2C_2H_5OH \xrightarrow[140°C]{\text{conc. } H_2SO_4} C_2H_5OC_2H_5 + H_2O$$

$$HCOOH \xrightarrow{\text{conc. } H_2SO_4} H_2O + CO$$

(ii) As a condensating agent :

$$3CH_3COCH_3 \xrightarrow[\text{distillation}]{\text{conc. } H_2SO_4} \text{mesitylene} + 3H_2O$$

(iii) As a catalyst :

$$CH_3CHO \xrightarrow{\text{conc. } H_2SO_4} \text{paraldehyde (hypnotic)}$$

$$3CH_3 - C \equiv CH \xrightarrow{\text{conc. } H_2SO_4} \text{mesitylene}$$

(iv) Sulphonation :

$$(CH_3)_3CH + H_2SO_4(\text{fuming}) \longrightarrow (CH_3)_3C - SO_2OH$$

2–methyl–2–sulphonic acid

(12) Thionyl chloride [$SOCl_2$] :

Function : For the replacement of –OH group by –Cl atom.

$CH_3OH + SOCl_2 \rightarrow CH_3Cl + SO_2\uparrow + HCl\uparrow$

$CH_3COOH + SOCl_2 \rightarrow CH_3COCl + SO_2\uparrow + HCl\uparrow$

(13) Sulphuryl chloride [SO_2Cl_2] :

Function : For the replacement of H– atom by Cl.

$$RH \xrightarrow[h\nu]{SO_2Cl_2} RCl + SO_2 + HCl$$

$$CH_3COCH_3 \xrightarrow[h\nu]{SO_2Cl_2} CH_3COCH_2Cl + SO_2 + HCl$$

Other reaction :

$(CH_3COO)_2Ca + SO_2Cl_2 \rightarrow 2CH_3COCl + CaSO_4$

(14) Phosphorus pentachloride (PCl_5) :

Function : (i) Replacement of [–OH] by Cl :

$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$

$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$

(ii) [>C = O → > CCl_2]

$> C = O + PCl_5 \rightarrow > CCl_2 + POCl_3$

(iii) Amide into nitrile :

$$CH_3CONH_2 \xrightarrow[(-H_2O)]{PCl_5} CH_3CN$$

(15) Phosphorus pentaoxide (P_2O_5) :

Function : Strong dehydrating agent.

$$2CH_3COOH \xrightarrow[-H_2O]{P_2O_5} \text{acetic anhydride}$$

$$CH_3CONH_2 \xrightarrow[-H_2O]{P_2O_5} CH_3CN$$

(16) Anhydrous zinc chloride ($ZnCl_2$) :

Function : It is a Lewis acid, used as a dehydrating reagent and also for the elimination of HCl.

$$C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O$$

$$C_6H_5OH + NH_3 \xrightarrow[300^\circ]{ZnCl_2} C_6H_5NH_2 + H_2O$$

As a catalyst :

$$C_6H_5OH + NH_3 \xrightarrow[300^\circ]{ZnCl_2} C_6H_5NH_2 + H_2O$$

(17) Anhydrous Aluminium chloride ($AlCl_3$) :

Function : Lewis acid used as a catalyst :

(i) Isomerisation :

$$\text{n–Butane} \xrightarrow[\text{conc. HCl}]{AlCl_3} \text{isobutane}$$

(ii) $CH_2 = CH_2 + CH_3OCl \xrightarrow{AlCl_3} CH_2Cl - CH_2COCH_3$

(iii) $C_2H_5OC_2H_5 + CH_3OCl \xrightarrow{AlCl_3} C_2H_5Cl + CH_3COC_2H_5$

(iv) Friedel Craft reaction :

$$\text{Benzene} \xrightarrow[CH_3Cl]{AlCl_3} \text{toluene}$$

$$\text{Benzene} \xrightarrow[CH_3COCl]{AlCl_3} \text{acetophenone}$$

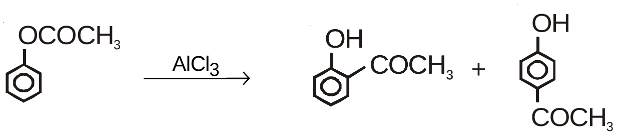
(v) Gattermann Koch synthesis :

$$C_6H_6 + CO + HCl \xrightarrow[\Delta]{AlCl_3} C_6H_5CHO + HCl$$

(vi) Polymerisation :

$$nCH_2 = CH_2 \xrightarrow[\Delta]{AlCl_3} (-CH_2 - CH_2-)_n \text{ Polythene}$$

(vii) Fries rearrangement :



(18) **Zinc–Copper Couple [Zn–Cu couple] :** It is obtained by coating a layer of copper on granular zinc [Zn and $CuSO_4$ solution].

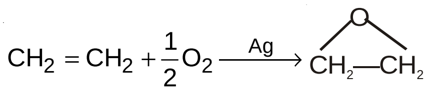
Function : Strong reductant :

$Zn–Cu + 2H_2O \rightarrow Zn(OH)_2 + Cu + 2H$

$Zn – Cu + 2C_2H_5OH \rightarrow Zn(OC_2H_5)_2 + Cu + 2H$

$C_2H_5I \xrightarrow{+2H} C_2H_6 + HI$

(19) **Silver (Ag) :** Various uses of silver are :



$2CHI_3 + 6Ag \rightarrow 6AgI + CH\equiv CH$

$2ClCH_2COOH \xrightarrow[\Delta]{+2Ag}$ succinic acid + 2AgCl

$2CH_3OH + O_2 \xrightarrow[400°C]{Ag} 2HCHO + 2H_2O$

(20) **Tildane Reagent [NOCl] :**

Function : For conversion of $–NH_2$ to –Cl

$C_2H_5NH_2 \xrightarrow{NOCl} C_2H_5Cl + N_2 + H_2O$

(21) **Carbylamine Test :** For the test of primary amine group.

$RNH_2 + CHCl_3 + 3KOH \rightarrow RN\equiv C + 3H_2O + 3KCl$

The smell of isocyanide is most unpleasant and pungent.

(22) **Soda–lime [NaOH/CaO] :**

Function : Useful for decarboxylation.

$RCOOH \xrightarrow{NaOH/CaO} RH$

(23) **Sodium–Boronhydride [$NaBH_4$] :**

Function : As a reductant

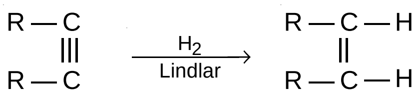
$> CHO \xrightarrow{+2H} –CH_2OH$

$> C = O \xrightarrow{+2H} > CHOH$

Note : It reduces –CHO and >C=O groups only, while –CN, $–NO_2$, $–CONH_2$ groups present in the compound remain unaffected.

(24) **Lindlar's Reagent :** It is a mixture of Pd and $CaCO_3$ rendered inert by lead acetate and quinoline.

Function : It catalyses the specific hydrogenation of alkyne.



$$\begin{array}{c} R—C \\ ||| \\ R—C \end{array} \xrightarrow[Lindlar]{H_2} \begin{array}{c} R—C—H \\ || \\ R—C—H \end{array}$$

cis–alkene

(25) **Sodamide [$NaNH_2$] :** It is a strong base.

Function : For drohalogenation and isomerisation of alkynes.

$$CH_2 = CHBr \xrightarrow[-HBr]{NaNH_2} CH \equiv CH$$

$$CH_3 - C \equiv C - CH_3 \xrightarrow{NaNH_2} CH_3 - CH_2 - C \equiv CH$$

$$C_6H_5Cl + NaNH_2 \xrightarrow{\Delta} C_6H_5NH_2 + NaCl$$

(26) **Copper [Cu] :**

Function : For dehydrogenation :

(i) $$RCH_2OH \xrightarrow[-H_2]{[Cu/300^\circ]} R - CHO$$

$$R_2CHOH \longrightarrow R_2CO + H_2$$

$$(CH_3)_3COH \xrightarrow[-H_2O]{[Cu/300^\circ]} \text{isobutylene}$$

(ii) $$C_6H_5N_2Cl \xrightarrow[HCl]{Cu} C_6H_5Cl + N_2$$

(27) **Alumina [Al_2O_3] :**

Function : As a dehydrating agent.

(i) $$C_2H_5OH \xrightarrow[350-400]{Al_2O_3} \underset{\text{ethene}}{H_2C = CH_2} + H_2O$$

(ii) $$2C_2H_5OH \xrightarrow[240-260^\circ]{Al_2O_3} \underset{\text{diethly ether}}{C_2H_5OC_2H_5} + H_2O$$

(28) **Beilstein's Test :** Halogens in organic compound can be detected by Beilstein's test. It consists of heating the organic substance in contact with pure copper oxide inthe Bunsen flame; the corresponding copper halide is formed, which is volatile, imparts an intense green or bluish–green colour to be mantle of the flame. Urea and thiourea responds to this test.

(29) **Legal's Test [Nitroprusside Test] :** It is a test for acetone. Freshly prepared solution of sodium nitroprusside (5 drops) is added to acetone (5 ml) and sodium hydroxide (1ml.). A ruby red colour is produced which fades to yellow on standing.

(30) **Alcoholic KOH :**

Function : It is used for dehydrohalogenation and isomerisation reaction.

$$R - CH_2 - CH_2Cl \xrightarrow[KOH]{\text{alcoholic}} R - CH = CH_2 + KCl + H_2O$$

$$CH_3 - CH_2 - C \equiv CH \xrightarrow[KOH]{\text{alcoholic}} CH_3 - C \equiv C - CH_3$$

(31) **Nitrous acid [HNO_2] :**

Function: To distinguish between 1°, 2° and 3° amines.

$C_2H_5NH_2 + HNO_2 \rightarrow C_2H_5OH\ (\text{alc.}) + N_2 + H_2O$

$(C_2H_5)_2NH + HNO_2 \rightarrow (C_2H_5)_2N.NO + H_2O$

N–nitroso compound

$(C_2H_5)_3N + HNO_2 \rightarrow (C_2H_5)_3NH.NO_2$

unstable compound

With aromatic amine :

$$C_6H_5NH_2 \xrightarrow[O^\circ C]{HNO_2} C_6H_5N_2Cl$$

benzene diazonium chloride

To identify amino group :

$CH_3CONH_2 + HNO_2 \rightarrow CH_3COOH + N_2 + 2H_2O$

(32) **Sodium [Na] :**

Function : (i) Synthesis of alkane :

$$2CH_3I \xrightarrow[\text{dry ether}]{Na} CH_3 - CH_3$$

(ii) To ascertain the presence of –OH group :

$2CH_3OH + 2Na \rightarrow 2CH_3ONa + H_2\uparrow$

(iii) Synthesis of alkyl benzene :

$$C_6H_5Cl + ClCH_3 \xrightarrow[Na]{ether} C_6H_5 - CH_3$$

(iv) To identify 1–alkyne :

$$CH_3 - C \equiv CH \xrightarrow[180^\circ]{Na} CH_3 - C \equiv CNa + \frac{1}{2}H_2$$

(v) Reduction of organic compounds :

[Na and ethyl alcohol]

$$C_2H_5OH + Na \longrightarrow C_2H_5ONa + H$$

$$C_2H_5I \xrightarrow{+2H} C_2H_6 + HI$$

$$CH_3CN \xrightarrow{+4H} CH_3CH_2NH_2$$

$$CH_3COCl \xrightarrow{+2H} CH_3CHO + HCl$$

(33) **Acetyl chloride and Acetic anhydride :**

Function: Reagent for acetylation.Compounds containing– OH, –NH_2, >NH and SH group give acetyl compound with reagents.

$C_2H_5OH + CH_3COCl \rightarrow CH_3COOC_2H_5 + HCl$

$C_2H_5OH + (CH_3CO)_2O \rightarrow C_2H_5OOCCH_3 + CH_3COOH$

(34) **Lassaigne's Test :** For detecting N, S, P and halogens in organic compound. The organic compound is fused with sodium metal and then extracted with water. The sodium extract is then used to test N, S, P and halogens.

(35) **Benzene–sulphonyl chloride [Hinsberg reagen] : [$C_6H_5SO_2Cl$] :**

For distinction and separation of 1°, 2° and 3° amines.

[1° amine] :

$$C_6H_5SO_2Cl + H_2NCH_3 \xrightarrow{-HCl} C_6H_5SO_2NHCH_3 \xrightarrow{NaOH} \text{soluble}$$

[2° amine] :

$$C_6H_5SO_2Cl + (CH_3)_2NH \xrightarrow{-HCl} C_6H_5SO_2N(CH_3)_2 \xrightarrow{NaOH} \text{insoluble}$$

[3° amine] :

$C_6H_5SO_2Cl + (CH_3)_3N \rightarrow \text{no reaction}$

(36) **Carbonyl chloride or Phosgene [$COCl_2$] :**

Function : It has numerous uses in organic chemistry.

(i) Formation of urea and substituted urea :

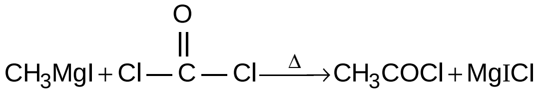
$COCl_2 + 2NH_3 \rightarrow H_2NCONH_2 + 2HCl$

$COCl_2 + 2C_2H_5NH_2 \rightarrow CO(NHC_2H_5)_2 + HCl$

(ii) Formation of benzophenone :

$$2C_6H_6 + COCl_2 \xrightarrow[\Delta]{AlCl_3} C_6H_5COC_6H_5 + 2HCl$$

(iii) Formation of acetyl chloride from Grignard reagent.



$$CH_3MgI + Cl-\overset{\overset{\displaystyle O}{\|}}{C}-Cl \xrightarrow{\Delta} CH_3COCl + MgICl$$

(iv) Formation of diphenyl urea :

$$2C_6H_5NH_2 + COCl_2 \xrightarrow[-2HCl]{\Delta} [C_6H_5NH]_2CO$$

(37) **Jone's Reagent :**

Solution of chromiumtrioxide in dilute sulphuric acid is known as Jone's reagent.

Function : Jone's reagent oxidises primary alcohol to carboxylic acid.

Example :

$$\underset{1-\text{decanol}}{CH_3(CH_2)_8CH_2OH} \xrightarrow[\text{dil.}H_2SO_4]{CrO_3} \underset{93\%}{CH_3(CH_2)_8COOH}$$

(38) **Gilman Reagent :**

Lithium dimethyl copper is called Gilman reagent.

Function : It is used for the preparation of hydrocarbons.

$$(CH_3)_2CuLi + CH_3(CH_2)_8CH_2I \xrightarrow[0^\circ]{\text{ether}} CH_3(CH_2)_8CH_2CH_3 + LiI + CH_3Cu$$

SOME IMPORTANT NAME REACTIONS

1. **Clemmensen Reduction :**

$$R_2CO \xrightarrow[HCl]{Zn(Hg)} R_2CH_2$$

2. **Sabatier and Senderens Reaction :**

$$CH{\equiv}CH \xrightarrow[300^oC]{H_2,(Ni)} CH_2{=}CH_2 \xrightarrow{H_2\ (Ni)} CH_3{-}CH_3$$

3. **Kolbe's Electrolytic Synthesis :**

(For synthesis of alkane, alkene & alkyne)

$$\begin{matrix} CH_3COONa \\ \\ CH_3COONa \end{matrix} \rightarrow CH_3{-}CH_3(\text{anode}) + CO_2$$

$$2Na + H_2O \rightarrow 2NaOH + H_2\ (\text{cathode})$$

4. **Bouveault–Blanc Reduction :**

$$RCO_2R' \xrightarrow{C_2H_5OH,\ Na} RCH_2OH + R'OH$$

5. **Hunsdiecker Reaction :**

$$RCO_2Ag + X_2 \rightarrow RX + CO_2 + AgX$$

6. **Wurtz Reaction :**

$$2R{-}I + 2Na \xrightarrow{\text{dry ether}} R{-}R + 2NaI$$

7. **Aldol Condensation :**

$$CH_3CHO + CH_3CHO \xrightarrow{\text{dil. alkali}} CH_3CH(OH)CH_2CHO$$

8. Cannizzaro's Reaction :

$2HCHO + NaOH \rightarrow HCOONa + CH_3OH$

9. Wurtz–Fitting Reaction :

$C_6H_5Br + CH_3Br + 2Na \xrightarrow{\text{Dry ether}} C_6H_5CH_3 + 2NaBr$

10. Rosenmund's Reaction :

$RCOCl + H_2 \xrightarrow{Pd/BaSO_4} RCHO + HCl$

11. Carbylamine or Isocyanide Reaction :

$RNH_2 + 3KOH + CHCl_3 \rightarrow RNC + 3KCl + 3H_2O$

12. Hofmann's Bromamide Reaction :

$RCONH_2 \xrightarrow{Br_2\ +\ KOH} RNH_2$

13. Curtius Reaction :

$RCON_3 \xrightarrow{\Delta.H_2O} RNH_2$

14. Hell–Volhard–Zelinsky Reaction :

$RCH_2\text{–}CO_2H \rightarrow RCHBr\text{–}CO_2H$

15. Mendius Reaction :

$RCN \xrightarrow{(Na+alc.)\ +\ [4H]} RCH_2NH_2$

16. Reimer–Tiemann Reaction :

Phenol $\xrightarrow{CHCl_3.NaOH}$ Salicyaldehyde

17. Williamson's Synthesis :

$RI + RONa \rightarrow ROR + NaI$

18. Williamson's Continous Etherification Process :

$C_2H_5OH \xrightarrow{H_2SO_4.140^o} C_2H_5OC_2H_5$

19. Reed Reaction :

$C_2H_8 + SO_2 + Cl_2 \rightarrow C_3H_7SO_2Cl + HCl$

20. Stephen's Reaction :

$R\text{—}CN \xrightarrow[+2H]{SnCl_2/HCl} R\text{—}CH{=}NH \xrightarrow{H_2O} RCHO$

21. Lederer–Mannasse Reaction :

Phenol + HCHO $\xrightarrow{\text{dil.NaOH}}$ o– & p– hydroxy benzyl alcohol

22. Schotten–Bauman's Reaction :

[i] $C_6H_5NH_2 + C_6H_5COCl \xrightarrow{NaOH} C_6H_5NHCOC_6H_5 + HCl$

[ii] $C_6H_5OH + C_6H_5COCl \xrightarrow{NaOH} C_6H_5COOC_6H_5 + HCl$

23. Gattermann–Koch Synthesis :

$C_6H_6 \xrightarrow[AlCl_3,\ Cu_2Cl_2]{CO,\ HCl} C_6H_5CHO$

24. Gattermann Synthesis :

$C_6H_5OH \xrightarrow[AlCl_3]{HCN,\ HCl\ \&\ H_2O}$ p–hydroxy benzaldehyde

25. Tischenko Reaction :

$CH_3CHO + CH_3CHO \xrightarrow[AlCl_3]{Al(OC_2H_5)_3} CH_3COOC_2H_5$

26. **Friedel–Crafts Reaction :**

(Alkylation, Acylation etc. of Aromatic compound)

$C_6H_6 + CH_3Cl \xrightarrow{AlCl_3} C_6H_5CH_3 + HCl$

$C_6H_6 + CH_3COCl \xrightarrow{AlCl_3} C_6H_5COCH_3 + HCl$

27. **Kolbe–Schmidt Reaction :**

Sodium phenate + $CO_2 \xrightarrow[130^o]{\text{Under pressure}}$ Sodium salicylate

28. **Phthalein Condensation :**

Phthalic anhydride + Phenol + conc. $H_2SO_4 \rightarrow$ Phenolphthalein

29. **Liebermann's nitroso Reaction :**

Phenol + Sodium nitrite/conc. H_2SO_4 (warmed) → dark green

Colour $\xrightarrow{H_2O}$ Red $\xrightarrow{\text{Alkali}}$ blue,

30. **Etard Reaction :**

$C_6H_5–CH_3 \xrightarrow{CrO_2Cl_2[+2O]} C_6H_5–CHO + H_2O$

31. **Frankland Reaction :**

$CH_3I + 2Zn + CH_3I \xrightarrow{CO_2} (CH_3)_2Zn + ZnI_2$

32. **Perkin Reaction :**

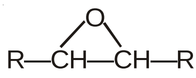
$C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3CO_2K} C_6H_5CH{=}CHCO_2H + CH_3CO_2H$

33. **Wohler's Synthesis :**

$(NH_4)_2SO_4 + KCNO \rightarrow \underset{\text{Urea}}{2NH_4CNO} + K_2SO_4$

34. **Prileschaiv's Reaction :**

$R–CH{=}CH–R' + C_6H_5CO.O_2Na \rightarrow$



$+ C_6H_5CO_2Na$

35. **Gabriel's Phthalimide Reaction :**

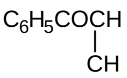
Phthalimide $\xrightarrow{KOH} \xrightarrow{RI} \xrightarrow{H_2O} RNH_2$ + Phthalic acid

36. **Fries rearrangement :**

$CH_3COOC_6H_5 \xrightarrow[\text{Nitrobenzene}]{\text{Anhydrous } AlCl_3}$ o–and p–hydroxyacetophenone

37. **Benzoin Condensation :**

$C_6H_5CHO \xrightarrow[EtOH,\ H_2O]{\Delta,\ CN^-}$



$C_6H_5\underset{\displaystyle CH}{\underset{|}{COCH}}–C_6H_5$ (Benzoin)

38. **Knoevenagel Condensation :**

Benzaldehyde + Malonic ester → Cinnamic acid

39. **Claisen–Schmidt Condensation :**

$C_6H_5CHO + CH_3CHO \xrightarrow{\text{dil. NaOH}} \xrightarrow{\Delta}$ Cinnamaldehyde

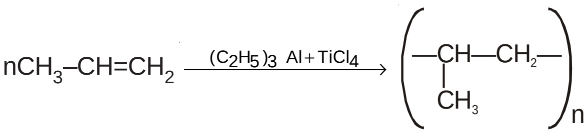
40. **Reformatsky Reaction :**

$C_6H_5CHO + BrCH_2COOC_2H_5 \xrightarrow{Zn} \xrightarrow{H_2O} C_6H_5CHOHCH_2COOC_2H_5$

41. Kucherov's Reaction :

$CH\equiv CH \xrightarrow[\Delta]{Hg^{+2},\ H_3O^+} CH_3CHO$

42. Zeigler–Natta Reaction :



$$nCH_3{-}CH{=}CH_2 \xrightarrow{(C_2H_5)_3\ Al + TiCl_4} \left(-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2- \right)_n$$

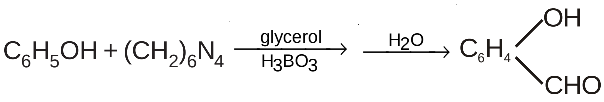
43. Strecker Reaction :

$RX + Na_2SO_3 \rightarrow R{-}SO_3Na + NaX$

44. Gurbet Reaction : [self–condensation)

$C_2H_5OH + H - CH_2 - CH_2OH \xrightarrow[OR^-]{\Delta} CH_3{-}CH_2{-}CH_2{-}CH_2{-}OH$

45. Duff Reaction :



$$C_6H_5OH + (CH_2)_6N_4 \xrightarrow[H_3BO_3]{glycerol} \xrightarrow{H_2O} C_6H_4\begin{matrix} OH \\ CHO \end{matrix}$$

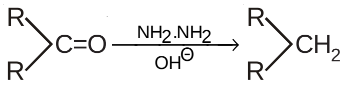
Salisaldehyde (ortho)

46. Arndt–Eistert Reaction :

$RCOCl + CH_2N_2 \xrightarrow{-HCl} \underset{\downarrow -N_2}{RCOCHN_2}$

$RCH_2COOH \xleftarrow{H_3O} R{-}CH{=}C{=}O$

47. Wolf–Kishner Reduction :



$$\begin{matrix} R \\ R \end{matrix}\!\!>C{=}O \xrightarrow[OH^{\ominus}]{NH_2.NH_2} \begin{matrix} R \\ R \end{matrix}\!\!>CH_2$$

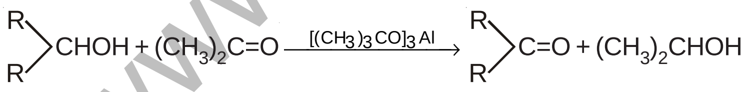
48. Sandmeyer's Reaction :

$C_6H_5N_2Cl \xrightarrow[HBr]{Cu_2Br_2} C_6H_5Br$

49. Schmidt Reaction :

$RCOOH \xrightarrow[\text{hydrazoic acid}]{N_3H,\ \Delta} R{-}NH_2 + CO_2 + N_2$

50 Oppenauer Oxidation :



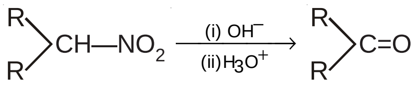
$$\begin{matrix} R \\ R \end{matrix}\!\!>CHOH + (CH_3)_2C{=}O \xrightarrow{[(CH_3)_3CO]_3Al} \begin{matrix} R \\ R \end{matrix}\!\!>C{=}O + (CH_3)_2CHOH$$

51. Wurtz method :

$C_6H_5{-}N{=}C{=}O + 2KOH \rightarrow C_6H_5NH_2 + K_2CO_3$

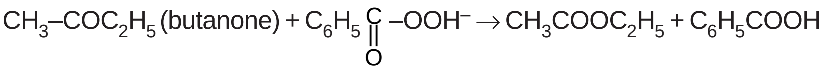
52. Nef Reduction :

$R - CH_2 - NO_2 \xrightarrow[(ii)\,H_3O^+]{(i)\ OH^-} R - CHO$



$$\begin{matrix} R \\ R \end{matrix}\!\!>CH - NO_2 \xrightarrow[(ii)\,H_3O^+]{(i)\ OH^-} \begin{matrix} R \\ R \end{matrix}\!\!>C{=}O$$

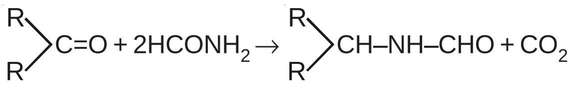
53. Baeyer–Villiger Oxidation :



$$CH_3{-}COC_2H_5\ (\text{butanone}) + C_6H_5\underset{\underset{\displaystyle O}{\|}}{C}{-}OOH^- \rightarrow CH_3COOC_2H_5 + C_6H_5COOH$$

perbenzoic acid

54. Leuckart Reaction :

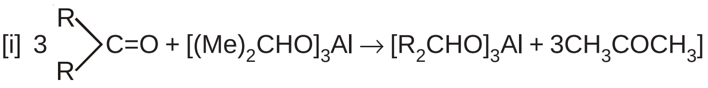


$$R_2C=O + 2HCONH_2 \rightarrow R_2CH\text{–}NH\text{–}CHO + CO_2$$

Formyl compound so obtained gives primary amine on acidic hydrolysis.

55. Meerwein–Ponndorf–Verley Reduction :

The carbonyl compound is heated with aluminium isopropoxide in isopropanol solution. The isopropoxide is oxidised to acetone. Acetone is distilled. The resulting aluminate is then treated with dilute acid to yield the alcohol.



$$[i]\ 3\,R_2C=O + [(Me)_2CHO]_3Al \rightarrow [R_2CHO]_3Al + 3CH_3COCH_3]$$

$$[ii]\ [R_2CHO]_3Al \xrightarrow[HOH]{dil.\ H_2SO_4} 3R_2CHOH$$

56. Ritter Reaction : A method for preparing primary amines containing t–alkyl group.

$$(CH_3)_3C\text{–}OH + HCN + H_2SO_4 \rightarrow (CH_3)_3C\text{–}NH_2$$

t–butyl alcohol [solution in acetic acid]

57. Rasching Process :

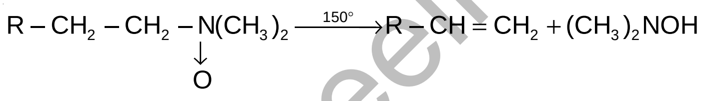
$$C_6H_6 + HCl + \frac{1}{2}O_2 \xrightarrow[250^\circ]{Cu\ -Fe} C_6H_5Cl + H_2O$$

$$C_6H_5Cl + H_2O \xrightarrow[450^\circ]{SiO_2} C_6H_5OH + HCl$$

58. Sommelet Reaction :

$$C_6H_5CH_2Cl + (CH_2)_6N_4 \rightarrow C_6H_5CHO$$

59. Cope Reaction : Amino oxide when heated decomposes to form alkene.

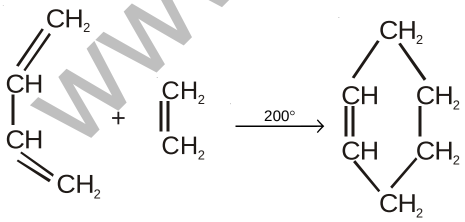


$$R-CH_2-CH_2-\underset{\underset{O}{\downarrow}}{N}(CH_3)_2 \xrightarrow{150^\circ} R-CH=CH_2+(CH_3)_2NOH$$

60. Swarts Reaction :

$$C_2H_5Cl + AgF \xrightarrow{\Delta} AgCl + C_2H_5F$$

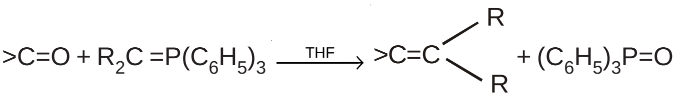
61. Diels–Alder Reaction : It consists the 1,4–addition of the double bond of a suitable dienophile to the two ends of a conjugated diene system.



1,3–butadiene cyclohexene

62. Witting Reactions :

Aldehydes and ketones can be converted into alkenes with the help of phosphoranes.



$$>C=O + R_2C=P(C_6H_5)_3 \xrightarrow{THF} >C=CR_2 + (C_6H_5)_3P=O$$

triphenyl phosphene oxide

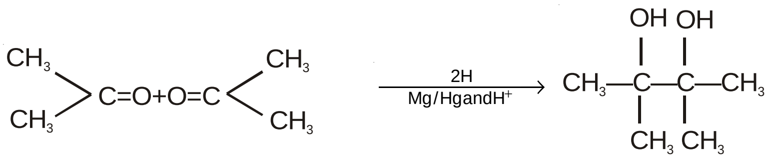
63. Eschweiler – Clark Methylation :

In presence of excess of formaldehyde and formic acid methylation of primary and secondary amines can be easily carried out.

$$C_2H_5NH_2 + CH_2O + HCOOH \xrightarrow{100^\circ C} C_2H_5NHCH_3 + CO_2 + H_2O$$

64. Pinnacole Reaction :

Reduction of acetone with Mg/Hg in acidic medium produces pinnacole.



pinnacole

65. Birnbaum – Simonini Reaction :

When silver salt of fatty acid reacts with iodide produces ester and silver halide is precipitated.

$2RCOOAg + I_2 \rightarrow RCOOR + 2AgI + CO_2\uparrow$

66. Adkene method :

In Adkene method esters are reduced by molecular hydrogen at 280° temperature and 100 atmospheric pressure using copper–chromite as catalyst.

$$CH_3(CH_2)_{10}COOCH_3 + 2H_2 \xrightarrow[280^\circ-300^\circ C, 100\,atm.]{CuO.CuCr_2O_4} CH_3(CH_2)_{10}CH_2OH + CH_3OH$$

67. Patart process :

[Synthesis of methanol]

First of all water–gas is prepared by passing water vapour over red–hot cock.

$$C + H_2O \xrightarrow{\Delta} [CO + H_2]$$

Reduction of water gas produces methanol,

$$[CO + H_2] + H_2 \xrightarrow[4ZnO.CrO_3]{300^\circ} CH_3OH$$

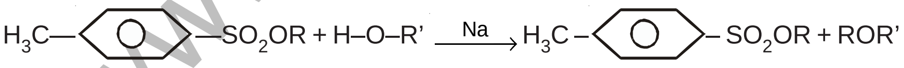
68. Huang – Million Reaction :

Conversion of alkanals and alakanones to alkanes using hydrazine, diethylene glycol and KOH

$$> C = O \xrightarrow{H_2N.NH_2} > C = N - NH_2 \xrightarrow[KOH,\ 200^\circ]{diehylene\ glycol} > CH_2 + N_2$$

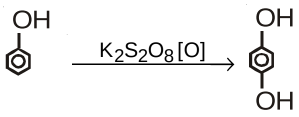
69. Drahowzal Method :

Best method for the preparation of either :



70. Elbs Persulphate Reaction :

Conversion of phenol to quinol by oxidation with potassium persulphate.



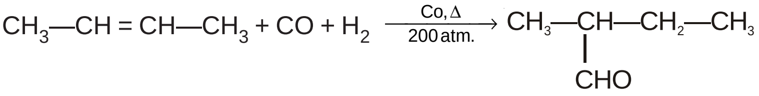
Quinol (hydroquinone)

71. Grove Reaction :

Alcohol to alkyl chloride with HCl and anhydrous $ZnCl_2$

$$R\text{–}OH + HCl \xrightarrow{anhyd.\ ZnCl_2} RCl + H_2O$$

72. Oxo Reaction :



$$CH_3—CH = CH—CH_3 + CO + H_2 \xrightarrow[200\,atm.]{Co,\Delta} CH_3—\underset{\substack{|\\CHO}}{CH}—CH_2—CH_3$$

73. Ullmann Reaction :

$C_6H_5–I + Cu + I–C_6H_5 \rightarrow C_6H_5—C_6H_5 + CuI_2$

74. Mannich Reaction:

$$RCOCH_3 + CH_2O + (CH_3)_2\overset{+}{N}H_2\overset{-}{Cl} \xrightarrow{-H_2O} RCOCH_2CH_2\overset{+}{N}H(CH_3)_2\overset{-}{Cl}$$

NaOH $\downarrow$ –HCl

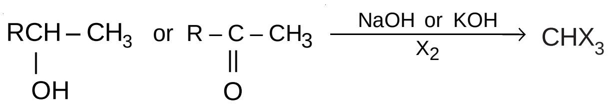
$RCOOCH_2CH_2N(CH_3)_2$

75. Hofmann Mustard Oil Reaction :

$R–NH_2 + CS_2 + HgCl_2 \rightarrow R–N=C=S + HgS + 2HCl$

1° Amine Alkylisothiocyanate

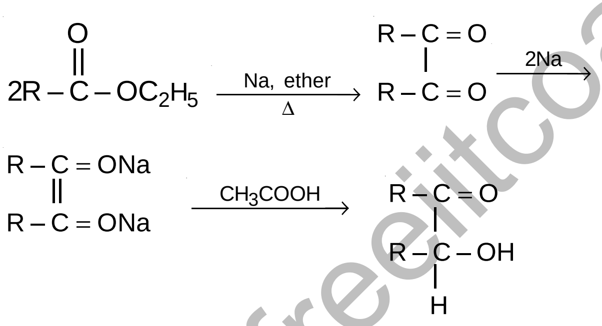
76. Haloform Reaction :



$$\underset{\substack{|\\OH}}{RCH}-CH_3 \text{ or } R-\underset{\substack{\|\\O}}{C}-CH_3 \xrightarrow[X_2]{NaOH\ or\ KOH} CHX_3$$

77. Acylo in condensation :

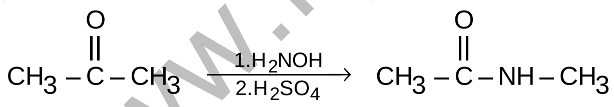
When esters are refluxed with metallic sodium in an aprotic solvent like ether, α–hydroxy ketones are formed. / This reaction is known as acyloin condensation.



$$2R-\overset{\substack{O\\\|}}{C}-OC_2H_5 \xrightarrow[\Delta]{Na,\ ether} \begin{array}{c}R-C=O\\|\\R-C=O\end{array} \xrightarrow{2Na}$$

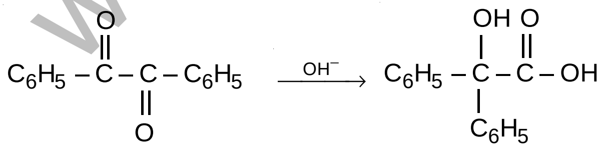
$$\begin{array}{c}R-C=ONa\\\|\\R-C=ONa\end{array} \xrightarrow{CH_3COOH} \begin{array}{l}R-C=O\\\quad|\\R-C-OH\\\quad|\\\quad H\end{array}$$

78. Beckmann rearrangement is:



$$CH_3-\overset{\substack{O\\\|}}{C}-CH_3 \xrightarrow[2.H_2SO_4]{1.H_2NOH} CH_3-\overset{\substack{O\\\|}}{C}-NH-CH_3$$

80. Benzilic acid rearrangement is :

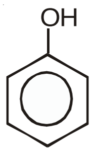
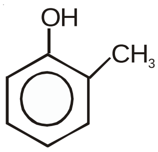
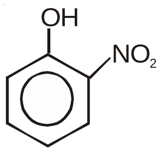
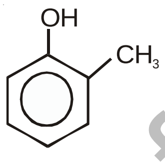
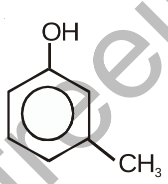
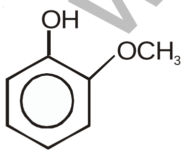
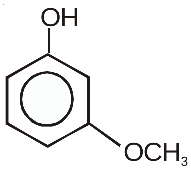


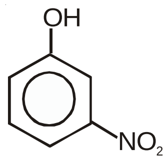
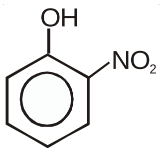
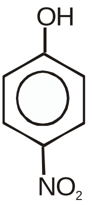
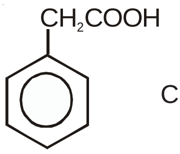
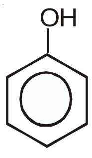
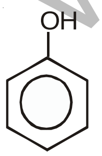
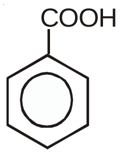
$$C_6H_5-\overset{\substack{O\\\|}}{C}-\underset{\substack{\|\\O}}{C}-C_6H_5 \xrightarrow{OH^-} C_6H_5-\underset{\substack{|\\C_6H_5}}{\overset{\substack{OH\\|}}{C}}-\overset{\substack{O\\\|}}{C}-OH$$

81. Catalytic hydrogenation of azides :

$R—X \xrightarrow{NaN_3} R—N_3 \xrightarrow[pt]{H_2} RNH_2$

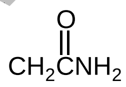
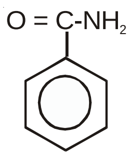
SOME IMPORTANT ORDERS

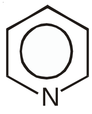
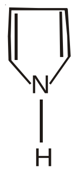
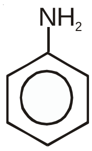
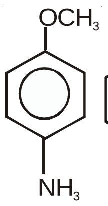
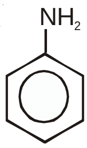
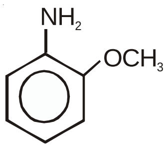
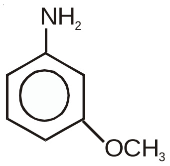
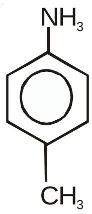
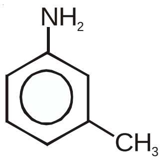
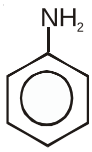
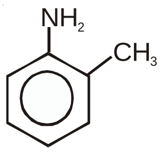
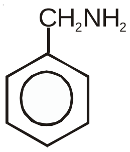
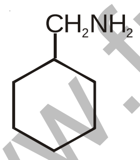
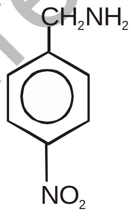
S. No.	Acid Strength	Order	Factor
1.	HCOOH, CH_3COOH, C_6H_5COOH I II III	II < III < I	III resonance stabilised ; II < I by inductive effect
2.	CH_3COOH, CH_3CH_2COOH, $CH_3CH_2CH_2COOH$ I II III	III < II < I	(I_+) Inductive effect
3.	CH_3COOH, $CH_2ClCOOH$; $CHCl_2COOH$ I II III	I < II < III	(I_-) of Cl increases acidic strength
4.	1., 2., 3. chlorobutanoic acid I II III	III < II < I	Farther the (I_-) group, lesser the acid strength
5.	1., 2., 3. methyl pentanoic acid I II III	I < II < III	Farther the (I_+) group (Cl), greater the acid strength
6.	1° 2° 3° isomeric butyl alcohol I II III	III < II < I	(I_+)group (methyl) increases electron density hence acidic nature is decreased.
7.	alkane, alkene and terminal alkynes I II III	I < II < III	acidic nature of C–H bond is sp > sp^2 > sp^3 hybridised carbon
8.	 (I)  (II)  (III)	II < I < III	$–CH_3$ is electron repelling and $–NO_2$ is electron withdrawing
9.	 (I)  (II)  (III)	II < I < III	$–CH_3$ is electron repelling decreases acidic strength of phenol
10.	 (I)  (II)	III < I < II	– do –

11.	   (I) (II) (III)	I < II < III	$-NO_2$ is electron withdrawing; III is more resonance stabilised than I and also than II. In I only inductive effect is operative.
12.	FCH_2COOH, $ClCH_2COOH$, $BrCH_2COOH$ I II III ICH_2COOH IV	I > II > III > IV	Greater the electronegativity (F > Cl > Br > I) greater the (I_-) effect, hence greater the ionisation.
13.	 $CH_2=CHCH_2COOH, CH_3CH_2COOH$ (I) (II) (III)	I > II > III	sp^2 hybridised carbon of I, II are more electronegative hence acid strength is increased Benzylic ($C_6H_5CH_2$) is more stabliised than allylic ($CH_2=CHCH_2$)
14.	$NCCH_2COOH, CH_3COOH, CH_3CH_2COOH$ (I) (II) (III)	I > II > III	$-CN$ is electron withdrawing and $-CH_3$ is electron repelling
15.	CH_3OH CF_3OH CCl_3OH I II III	I < III < II	Inductive effect (electron attracting) of F > Cl > H.
16.	 H_2O CH_3OH (I) (II) (III)	I > II > III	Phenyl is electron withdrawing and phenoxide ion is resonance stablished, $-CH_3$ is electron repelling.
17.	Oxalic acid, succinic acid, malonic acid I II III adipic acid (all dibasic) IV	I > II > III > IV	Effect of one –COOH on the other decreases as its distance between them increases
18.	  CH_3COOH (I) (II) (III)	I < III < II	(I_+) effect in III; resonance effect in benzene nucleus in I,resonance effect in($-COO^-$) and benzene nucleus in II.
19.	o– m– p– I II III toluic acid	III < II < I	$-CH_3$ is electron repelling.
20.	o– m– p– I II III nitrobenzoic acid	II < III < I	$-NO_2$ is electron attracting

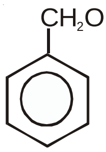
21.	o– I	m– II	p– Hydrocy benzoic acid III	III < II < I	–OH shows electron withdrawing nature at o– and m– and electron repelling at p–.o– isomer due to intramoleculatr bonding in salicylate ion is stronger than m-isomer.
22.	o– I	m– II	p– III methoxy benzoic acid	III < II = I	–do–
23.	o– I	m– II	p– III amino benzoic acid	I < III < II	–NH_2 is electron repelling

Section B

S.No.	**Basic Strength of**	**Order**	**Factor**
1.	NH_3, CH_3NH_2, $(CH_3)_2NH$ I II III	I < II < III	(I_+) effect of CH_3 group increases electron density at N-atom hence basic nature.
2.	OH^-, CH_3COO^- Cl^- I II III (conjugate base of H_2O,CH_3COOH,HCl)	III < II < I	If acid is weak its conjugate base is strong and vice versa.
3.	$CH \equiv C^-$, $CH_2 = CH^-$, $CH_3CH_2^-$ I II III	I < II < III	– do –
4.	1º, 2º, 3º I II III Isomeric butyl alcohol $\underset{\text{base}}{ROH} + \underset{\text{acid}}{HCl} \xrightarrow[\text{(anhydrous)}]{ZnCl_2} \underset{\text{white turbidity}}{RCl} + H_2O$ hence reactivity of alcohol with Lucas reagent ($HCl + ZnCl_2$)	I < II < III	(I_+) effect of alkyl group increases basic nature of alcohol
5.	NH_3, CH_3NH_2, $C_6H_5NH_2$ I II III	III < I < II	(I_+) effect of methyl increases basic nature. (I_-) effect of C_6H_5 (due to conjugation) decreases electron density hence,the basic nature.
6.	$CH_3CH_2NH_2$  $CH_2\overset{O}{\overset{\|}{C}}NH_2$  (I) (II) (III)	I > III > II	$(-\overset{O}{\overset{\|}{C}}-)$ is electron withdrawing decreasing basic nature. In III there is resonance stabilisation along with C = O (cross-conjugation) hence III is more oasic than II.

7.	 (I)  (II)  (III)	I > III > II	lone pair on N is not used in delocalisation of π-electrons in I. In II lone pair of the ring is itself used in delocalisation while that of outside ring in III.
8.	 (I)  (II)  (III)  (IV)	II > III > I > IV	$-OCH_3$ is strong electron donating group. This is due to ortho effect.All the aniline are less basic than p-substituted aniline due to **steric hindrance**
9.	 (I)  (II)  (III)  (IV)	I > II > III > IV	I (Hyper conjugation and induction) II (induction) IV (ortho effect))
10.	$CH_2=CHCH_2NH_2$ I $CH_3CH_2CH_2NH_2$ II $CH\equiv CCH_2NH_2$ III	II > I > III	Electron withdrawing order is : propaargyl > allyl > propyl and thus, electron density is decreased in same order
11.	 (I)  (II)  (III)	II > I > III	In II there is sp^3 hybridised C, In I, sp^2. NO_2 is electron withdrawing.
12.	$CH\equiv CH$, I $CH_2=CH_2$, II CH_3-CH_3 III	I < II < III	Electron withdrawing tendency of C, $sp > sp^2 > sp^3$.

13.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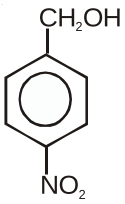
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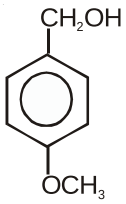
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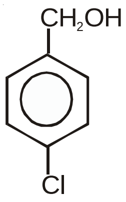

(IV)

III > I > IV > II

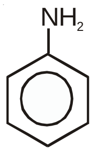
The +ve charge that develops on the benzylic carbon is most effectively delocalised by $-OCH_3$ (electron repelling group)group, order being $OCH_3 > Cl > H > NO_2$ ($-NO_2$ is electron withdrawing)

14. $\underset{I}{CH_3CH_2NH_2}$, $\underset{II}{HOCH_2CH_2NH_2}$, $\underset{III}{OHCH_2CH_2CH_2NH_2}$

I > II > III

Electron withdrawing inductive effect of the OH group decreases the electeon density on N, lowering the basic nature

15.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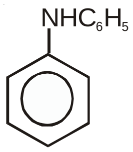
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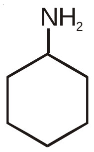
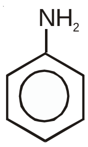
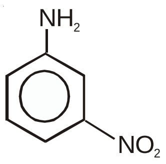

(III)

III > I > II

lone pair on N is used in delocalisation of π-electrons in aromatic amines while cyclohexyl is electeon repelling (III): In II, lone pair on N is used by two benzene ring.

16.


(I)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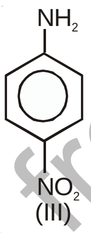
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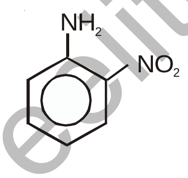
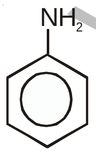

(IV)

I > II > III > IV

NO_2 is electron withdrawing,thus nitro-anilines are less basic than aniline. IV is less basic than III because $-NO_2$ is closer and exerts a stronger inductive effect.

17.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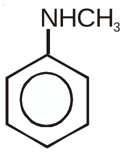
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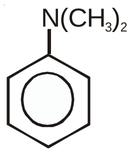
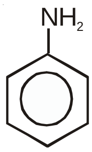
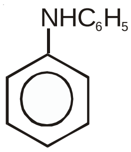

(III)

I < II < III

CH_3 directly attached to N is electron donating hence basic nature is increased.

18.


(I)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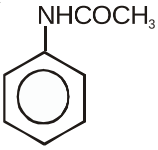
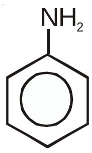

(III)

$I > II > III$ phenyl and $-COCH_3$ are electron withdrawing and $-C_6H_5 < COCH_3$.

19.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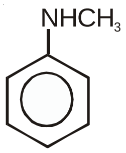
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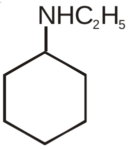
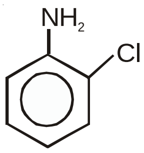

(III)

$I < II < III$ Electron donating nature of $CH_3 < CH_2CH_3$.

20.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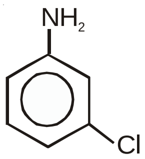
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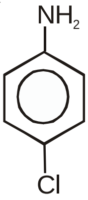
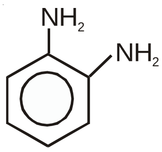
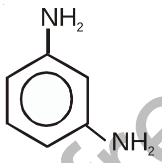

(III)

$I < II < III$ ortho effect in I.

21.


(I)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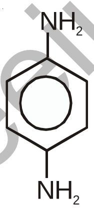

(III)

$I < II < III$ ortho effect in I

22. Cl^- (I), $RCOO^-$ (II), OH^- (III), RO^- (IV), NH_2^- (V)

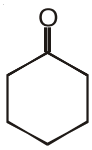
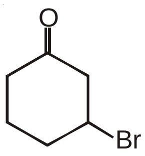
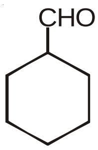
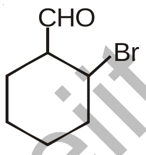
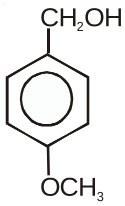
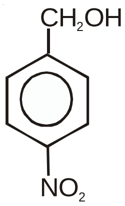
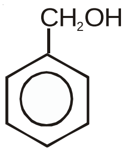
$I < II < III < IV < V$ If acid (HX) is weak its conjugate base (X^-) is strong.

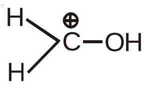
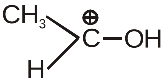
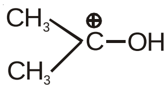
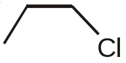
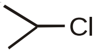
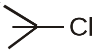
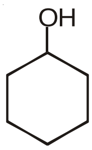
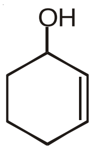
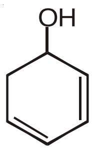
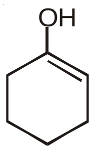
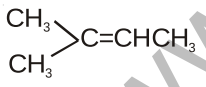
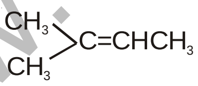
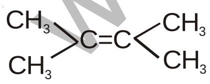
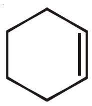
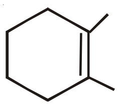
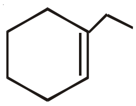
23. NH_3 (I), CH_3NH_2 (II), $(CH_3)_2NH$ (III), $(CH_3)_3N$ (IV)

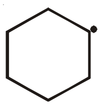
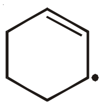
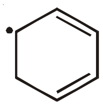
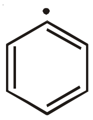
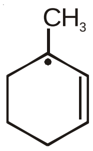
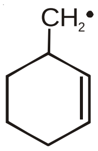
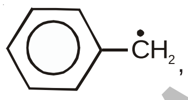
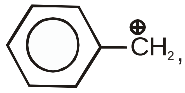
(a) (in aqueous solution) $I < IV < II < III$ (I_+) effect of three methyl groups in 3º amine (IV) alongwith protonation causes steric hindrance hence less basic than 1º and 2º amines

(b) (in gas phase) $I < II < III < IV$ As no of alkyl group increases basicity increases

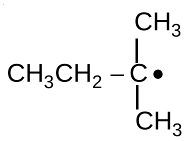
Section C

S.No.	Order of	Order	Factor
1.	Stability of free Radical $CH_3CH_2\overset{\bullet}{C}H_2$ $(CH_3)_2CH\overset{\bullet}{C}H_2$ $(CH_3)_3C\overset{\bullet}{C}H_2$ I II III	I < II < III	Inductive effect is in order 1º < 2º < 3º alkyl group.
2.	Stability of trans-2-butene, cis-2-butene, 1-butene I II III	I > II > III	In cis-isomer steric hindrance decreases stability
3.	Heat of hydrogenation of I, II, III (above)	I < II < III	Greater the stability, smaller the heat of hydrogenation
4.	B.P. of CH_3CH_2OH, CH_3OCH_3 CH_3CH_3 I II III	I > II > III	There is intermolecular H-bonding I. III has weak force of attarction and is most volatile
5.	B.P. of o,m,p-nitro phenol	o < m < p	Intramolecular H-bonding in o-isomer makes it most volatile
6.	Reactivity of ... with Tollen's reagent HCHO CH_3CHO CH_3COCH_3 C_6H_5CHO I II III IV	I > II > IV > III	–CHO group is easily oxidised compared to keto group.
7.	Reactivity of ... with Fehling's solution I. II. III. IV (above)	I > II > IV > III	– do –
8.	Extent of hydration of  (I)  (II)  (III)  (IV)	I < II < III < IV	Aldehydes are more hydrated than ketons. Halide makes C of carbonyl group more electropositive.
9.	Stability of .... carbanion $\overset{\ominus}{C}H_3$ $CH_3\overset{\ominus}{C}H_2$ $(CH_3)_2\overset{\ominus}{C}H$ $(CH_3)_3\overset{\ominus}{C}$ I II III IV	I > II > III > IV	(I_+) effect of alkyl group further increases electron density of $\overset{\ominus}{C}$
10.	Reactivity of .... with HBr :  (I)  (II)  (III)	II < II < I	OCH_3 is electron repelling increasing basic nature of benzyl alcohol hence reactivity with HBr (acid) $–NO_2$ is electron withdrawing hence decreasing basic nature of benzyl alcohol.

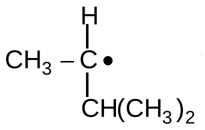
11.	Electrophilic nature of .... for nucleophilic attack  $H_2\overset{\oplus}{C}-OH$ I  $(CH_3)(H)\overset{\oplus}{C}-OH$ II  $(CH_3)_2\overset{\oplus}{C}-OH$ III	I > II > III	CH_3 group decreases +ve charge on C hence nucleophilic attack.
12.	Reactivity of isomeric 1º, 2º, 3º butyl halide towards E2 or E1 (elimination)	1º < 2º < 3º	due to stability of intermediate carbocation ion (1º < 2º < 3º)
13.	Reactivity of .... for S_N1 and S_N2 reaction MeCl (I)  (II)  (III)  (IV)  (V)	S_N1 : I < II < III < IV < V S_N2 I > II > III > IV < V	due to stability of intermediate carbocation due to steric hindrance in 3º in which attack of nucleophile is retarded.
14.	Tendency of 1º, 2º, 3º R–X for S_N and elimination reaction	Elimination 1º < 2º < 3º substitution 1º > 2º > 3º	
15.	Dehydration of  (I)  (II)  (III)  (IV)	IV < I < II < III	Alcohol leading to increases in onjugation due to dehydration is more easily dehydrated.IV isvinylic, hence least
16.	Stability of $CH_2=CH_2$, $CH_3CH=CH_2$, $CH_3CH=CHCH_3$ I II III  $(CH_3)_2C=CHCH_3$ IV  $(CH_3)_2C=CHCH_3$ V  $(CH_3)_2C=C(CH_3)_2$ VI	I < II < III < IV < V < VI	Substituted alkenes are more stable
17.	Stability of  (I)  (II)  (III)	I < III < II	II is more substituted than III

18.	Stability of  (I)  (II)  (III)  (IV)	III > II > I > IV	IV is vinylic while III conjugative, II allylic.
19.	Stability of $CH_2 = \dot{C}H$ (I), $\dot{C}H_2CH = CH_2$ (II),  (III)  (IV)	I < IV < II < III	III is 3º allylic and II is 1º allylic
20.	Cleavage of ...... and reactivity C–F (I), C–Cl (II), C–Br (III), C–I bond (IV)	I < II < III < IV (IV easiest)	B.E. of (C–X)bond is in order C–F > C–Cl > C–Br > C–I
21.	Dehydration of 1º, 2º, 3º isomeric butyl alcohol	1º < 2º < 3º	Greater the basic nature of alcohol,greater the tendency of dehydration.
22.	Boiling points of n butyl amine (I), n-butyl alcohol (II), n-pentane (III)	II > I > III	I, II have H-bonding but electronegativity of O > N hence H-bonding in II > I
23.	Stability of free Radicals $R_3C\bullet$ (I), $R_2\dot{C}H$ (II), $R\dot{C}H_2$ (III), $\dot{C}H_3$ (IV)	I > II > III > IV	(I_+) effect of 'R
24.	Formation of  (I), $R_3\dot{C}$ (II), $R_2\dot{C}H$ (III), $R\dot{C}H_2$ (IV)	I > II > III > IV	greater the stability,easier the formation
25.	Stability and formation of (a)  (I), $(CH_3)_3\overset{\oplus}{C}$ (II), $CH_2{=}CH\overset{\oplus}{C}H_2$ (III)	I > III > II	I and III are resonance stabilised (I_+) effect of methyl group decreases +ve charge.
	(b) $(CH_3)_2\overset{\oplus}{C}H$ (IV), $CH_3\overset{\oplus}{C}H_2$ (V), $\overset{\oplus}{C}H_3$ (VI), $\overset{\oplus}{C}H_2 = \overset{\oplus}{C}H$ (VII)	IV > V > VI > VII	

26. Stability of free radicals



$CH_3CH_2-\overset{CH_3}{\underset{CH_3}{C}}\bullet$



$CH_3-\overset{H}{\underset{CH(CH_3)_2}{C}}\bullet$

$CH_3CH_2\dot{C}H_2$

I II III

III < II < I

(I_+)effect increases stability 1º < 2º < 3º

27. Reactivity of C–H bond (abstraction of H)

$CH_2{=}CH{-}H$, vinylic (I)
$CH_3{-}H$, methyl (II) 1º
$CH_3CH_2{-}H$ (III)
$(CH_3)_2CH{-}H$ 2º (IV)
$(CH_3)_3C{-}H$ 3º (V)
$CH_2{=}CHCH_2{-}H$ (allylic) (VI)

I < II < III < IV < V < VI

Vinyl < methyl 1º < 2º < 3º < allylic

28. Leaving nature (tendency) of .... in S_N reaction

H^-, R^-, MeO^-, OH^-, CN^-, CH_3COO^-
I II III IV V VI

$ROSO_2^-$, $ArSO_3^-$
VII VIII

I < II < III ~ IV < V < VI < VII < VIII

If acid is strong. its conjugate base is weak and greater the leaving tendency

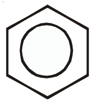
29. Leaving nature of

CH_3COO^-, CCl_3COO^-, PhO^-, $PhSO_3^-$
I II III IV

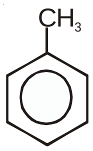
III < I < II < IV

– do –

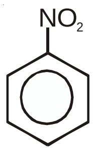
30. Nitration of



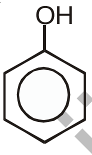
(I)



(II)



(III)



(IV)

III < I < II < IV

$-NO_2$ is deactivating group, $-CH_3$ and –OH activating, but due to lone pair on O in phenol. It is more resonace stbilished for S_E reaction.

31. Rate of esterification of the following acids with MeOH

$MeCH_2COOH$, $Me_2CHCOOH$, Me_3CCOOH,
I II III
Et_3CCOOH, $(i-Pr)_2CHCOOH$
IV V

I > II > III > IV > V

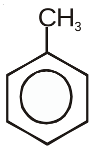
As the size of the substituents on the α–C increases, the tetrahedrally bonded intermediate becomes more crowded and these slower the rate.

32. Relative reactivity of ...... with electrophile in S_E reaction

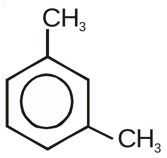
V > III > IV > II > I

$-CH_3$ is o–, p-directing and activating group.

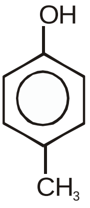
(I)



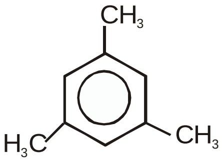
(II)



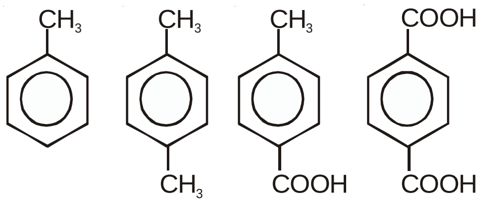
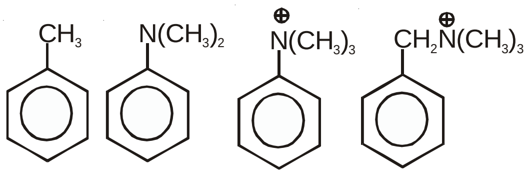
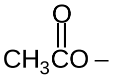
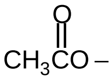
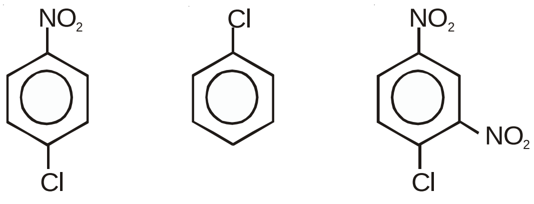
(III)

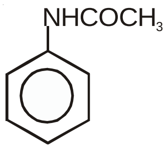
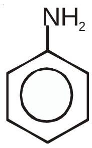
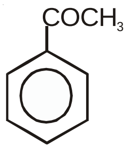
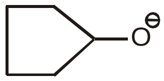


(IV)



(V)

33.	Relative reactivity of .... with electrophile in S_E reaction  (I) (II) (III) (IV)	II > I > III IV	$–CH_3$ is o–. p-directing and activating group while COOH is m–directing and deactivating group.
34.	Relative reactivity of ..... with electrophile in S_E reaction  (I) (II) (III) (III)	II > I > IV > III	As the number of sp^3 hybridised C atoms separeting the ring from the positively charged substituent increases,deactivating effect decreases.
35.	Activating effects on the following o, p– directors –OH, $–O^{\Theta}$,  $CH_3\overset{O}{\overset{\|}{C}}O –$ I II III	II > I > III	$–O^{\Theta}$ is best able to donate electrons thereby giving a very stable uncharged intermediate in  $CH_3\overset{O}{\overset{\|}{C}}O –$ cross conjugation diminished its ability to donate electrons to an arenium ion.
36.	Relative reactivity of .... towards S_N1 reaction benzyl chloride, p-methoxy benzyl chloride I II and p - nitro benzyl chloride III	II > I > III	Intermediates are benzylic cations.CH_3O (electron repelling) provides greater stability through delocalisation while NO_2 (electron attracting) decreases stability
37.	Relative reactivity of ..... towards S_N1 and S_N2 reaction $PHCH_2Cl$ PHCHClMe $PhCClMe_2$ (I) (II) (III) (Ph stands for phenyl, C_6H_5)	S_N1: III > II > I S_N2 III < II < I	S_N1 : 1º < 2º < 3º alkyl halide S_N2 : 3º < 2º < 1º alkyl halide
38.	Relative reactivity of .... with E^+ (electrophile) in S_E reaction  (I) (II) (III)	II > I > III	$–NO_2$ deactivates benzene ring for S_E.

39.	Relative reactivity of .... with E^+ in S_E reactions  (I)  (II)  (III)  (IV)	II > I > IV > III	–$COCH_3$ is deactivating while –NH_2 is activating group –$COCH_3$ attached to N is electron withdrawing hence deactivates –NH_2 group.
40.	Order of S_N2 reactivity of alkoxide nucleophiles Me_3CO^-, MeO^-, $MeCH_2O^-$, Me_2CHO^- I II III IV  V	I < IV < V < III < II	S_N2 reactivity is susceptible to steric hindrance by the nucleophile as well as by the alkyl group
41.	Order of S_N2 reactivity of MeX, RCH_2X, R_2CHX, R_3CX I II III IV	IV < III < II < I	Due to R groups electron density at carbon atom increases hence attack of nucleophile is retarded.
42.	Order of S_N1 reactivity of I II III IV (above)	I < II < III < IV	C–X bond breaks in slow step (order being 3º > 2º > 1º alkyl halide)
43.	Hyperconjugation effect in $CH_3CH=CH_2$ I $CH_3CH_2CH=CH_2$ II  $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CHCH=CH_2$ III $(CH_3)_3CCH=CH_2$ IV	I > II > III > IV	greater the number of H at α–C wrt. allylic, greater the hyper conjugation
44.	Reactivity of halogens (x_2) for a given type of abstraction of H(say 1º)	$F_2 > Cl_2 > Br_2 > I_2$	B.E. of I_2 in maximum
45.	Extent of hydration of CH_3COCH_3, CH_3COCH_2Cl, CH_3CHO I II III $ClCH_2CHO$ IV	I < II < III < IV	Aldehyde is more hydrated than ketone. Cl is electron attracting producing positive charge at C of carbonyl group hence attack of H_2O (hydration) is increased
46.	Leaving tendency of .... in S_N reaction NH_2^-, RO^-, OH^-, $RCOO^-$, Cl^- I II III IV V	I < II ~ III < IV < V	If base is weaker, Its leaving tendency is higher.
47.	Hydrolysis tendency of CH_3COCl, CH_3CONH_2, $CH_3COOC_2H_5$, I II III $(CH_3CO)_2O$ IV	II < III < IV < I	Cl^-, NH_2^-, $^-OC_2H_5$. CH_3COO^- are replaced by OH^- in hydrolysis; weaker the base greater the leaving nature.
48.	Reactivity of .... NH_3 with CH_3COCl, CH_3COOH, $CH_3COOC_2H_5$, $(CH_3CO)_2O$ I II III IV	II < III < IV < I	NH_2^- replaces X^- (Cl^-, OH^-, $^-OC_2H_5$, CH_3COO^-) weaker the X^-, greater the leaving nature.