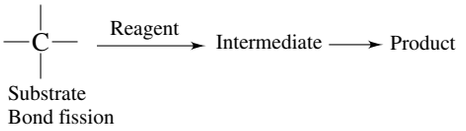
CHAPTER 3

General Organic Chemistry

MECHANISMS OF REACTIONS



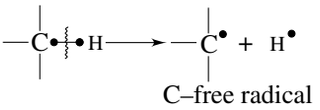
BREAKING OF COVALENT BOND (BOND FISSION)

The fission of a covalent bond can take place in two ways depending upon the nature of the given compound, the nature of attacking reagent and the reaction conditions.

(1) Homolytic fission or homolysis.

(2) Heterolytic fission or heterolysis.

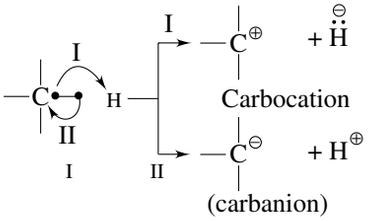
(1) Hemolytic bond fission (Homolysis): Such fission in which bond pair is equally distributed in between respective atoms, which leads the formation of free radical is known as homolysis.



Favorable conditions

1. When the EN difference between two atoms is zero or near zero.
2. Reaction is carried out at high temp. ($T \geq 500°$)
3. In presence of sunlight.
4. When reagent is radical.
5. In presence of peroxide or tetraethyl lead (TEL)
6. In presence of Non-polar solvent.
7. In gaseous phase of reacting mixture.

(2) Heterolytic bond fission (Heterolysis): Such fission in which bond pair completely transfers towards one of the atoms, which leads the formation of ions is known as heterolysis.



Favorable conditions

(1) When EN difference between two atoms is very high.

(2) Reaction is carried out at low temp.

(3) In presence of ionic reagent.
(4) In presence of polar solvents.
(5) In liquid phase of reacting mixture.

Note: Energy needed for heterolysis is always greater than energy needed for homolysis.

Attacking Reagent

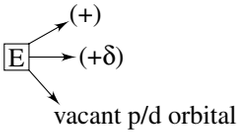
Most of the attacking reagent can be classified as follows:

(1) Electrophiles
(2) Neucleophiles
(3) Ambiphiles
(4) Free Radicals

(1) Electrophiles:

- They are e^- loving species.
- They are e^- deficient reagent.
- They are e^- pair acceptor from any donor.
- They are also behave as Lewis acid.

Identification:



Some of the electrophiles are listed below:

Type-I: +vely charged electrophile (E^+)

All cation except cation of IA, IIA, H_3O^+, $NH_4^{\oplus}$

$\overset{\oplus}{H}$, $\overset{\oplus}{C}H_3$, $\overset{\oplus}{C}l$, $\overset{\oplus}{N}O_2$, $N\overset{\oplus}{O}$, $S\overset{\oplus}{O}_3H$, etc.

Type-II: Neutral electrophile

(i) Vacant p orbital $BeCl_2$, BF_3, $AlCl_3$, $\ddot{C}H_2$, $\ddot{C}Cl_2$, etc.
(ii) Vacant d orbital $SnCl_2$,$SnCl_4$, $ZnCl_2$, $FeBr_3$, $SbCl_5$, etc

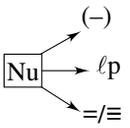
Type-III: After bond break

(i) Like YZ_n type molecule EN(y) < E.N.(z), $n \geq 2$
CO_2, CCl_4, NF_3, SO_3, etc
(ii) Halogen molecule Br–Br, Cl–Cl, I–I

(2) Neucleophiles:

- They are nucleus loving species.
- They are e^- rich reagent.
- They are e^- pair donor to any acceptor.
- They also behave as Lewis base.

Identification:



Some of the Neucleophiles are listed below:

Type-I: (–)vely charged nucleophile (nu)

All anions $\overset{\ominus}{H}$, $\overset{\ominus}{C}H_3$, $\overset{\ominus}{O}H$, $\overset{\ominus}{F}$, $\overset{\ominus}{N}H_2$, $\overset{\ominus}{N}_3$, $CH{\equiv}\overset{\ominus}{C}$, $R–COO^-$, etc.

Type-II: Neutral nucleophile

(i) Compound with the atom having at least one ℓp.

$H_2\ddot{O}$, $\ddot{N}H_3$, $\ddot{P}H_3$, CH_3–OH, CH_3–NH_2

(ii) Compound with the atom having π-bond

Alkene/Alkyne type R – CH = CH_2, R–C ≡ CH, Benzene, etc.

Type-III: All organometallic compounds

R Mgx, R_2 Zn, R_2LiCu, ete.

Type-IV: *Ambident nucleophile:* two or more nucleophilic site in a molecule.

$C \equiv \overset{\ominus}{N}$, $N\overset{\ominus}{O}_2$, $S\overset{\ominus}{O}_3$, NH_2OH, etc.

(3) Ambiphiles: Such reagent which behave both as electrophile as well nucleophile is known as ambiphile.

Organic substance in which carbon-atom directly attaches with highly EN atom with multiple bond behaves as ambiphile.

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3,\ CH_3-C\equiv N,\ CH_3-\underset{\underset{O}{\|}}{C}-Cl,\ CH_3-\underset{\underset{O}{\|}}{C}-NH_2,\ \text{etc.}$$

(4) Free Radicals:

- They are neutral species.
- They are e^- deficient reagent.
- They consist of unpaired e^- or odd e^-
- They are highly reactive.
- Requirement of one electron form completing their octet.

$\dot{H}$, $\dot{C}H_3$, $\dot{C}\ell$, R–$COO^{\bullet}$, $O\dot{H}$, etc.

REACTION INTERMEDIATES

In the study of organic chemistry following intermediates are important.

(i) Carbocation
(ii) Carbanion
(iii) Carbon free radical
(iv) Carbene
(v) Nitrene

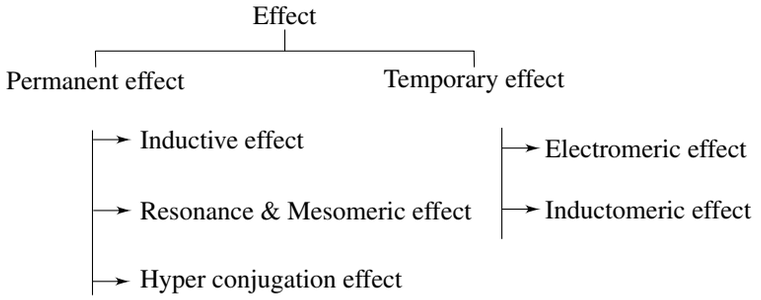
Carbocation, Carbanion and Carbon free radical are of following type

Property	Carbocation	Carbanion	Carbon free radical
Representation			
Bond fission	Heterolysis	Heterolysis	Homolysis
Electrical nature	Positive	Negative	Neutral
Number of electrons in valence shell	6	8	7
Hybridisation	sp^2	sp^3	sp^2
Shape	Planar	Pyramidal	Planar
Number of unpaired e(n)	0	0	1
Magnetic moment ($\mu = \sqrt{n(n+2)}$ B.M.)	0	0	1.73 BM
Magnetic nature	Diamagnetic	Diamagnetic	Paramagnetic
Reagent	Electrophile	Nucleophile	Electrophile

• Carbene and Nitrene each are of following two types:

Property	Singlet carbene	Triplet carbene	Singlet nitrene	Triplet nitrene
Representation	 –C–	 –C– 	 –N	 –N 
Electrically nature	Neutral	Neutral	Neutral	Neutral
Number of electrons in valence sheet	6	6	6	6
Hybridisation	sp^2	sp	sp^2	sp
Shape	V-shape	Linear	Linear	Linear
Stability	Less	More	Less	More

FACTORS INFLUENCING THE COVALENT BOND



INDUCTIVE EFFECT (I-EFFECT)

$\delta_0 \quad \delta\delta\delta_+ \; \delta\delta_+ \quad \delta_+$
$C_4—C_3—C_2—C_1—Z \; \{EN© < EN(z)\}$
(Source)

- Due to partial displacement of bond pair towards more EN atom, polarisation of carbon chain takes place, known as I effect.
- Cause → due to difference in E.N.

Characteristics

1. It is a permanent effect.
2. It is a weak effect because only partial charge develops.
3. It is operated by σ bond (works in between σ bond).
5. Shifted bond pair never loses parent orbital.
6. I–effect is distance dependent.

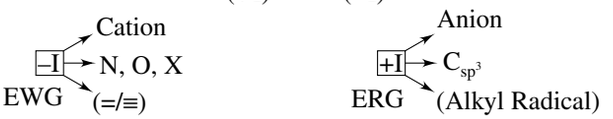
+I EFFECT/–I EFFECT

1. **+I effect:** Such atom/group which repels σ electrons as compared to H-atom are +I group and observed effect is +I effect.
   - +I effect showing group ⇒ Electron repelling group (E.R.G.)
2. **–I effect:** Such atom/group which attracts σ electrons as compared to H-atom are –I group and observed effect is –I effect.
   - –I effect showing group ⇒ Electron withdrawing group. (E.W.G.)

Identification:

Trick: $E.N.(Csp^3) < E.N(z)$

$(+I) \qquad (-I)$



–I series.

$-\overset{\oplus}{N}F_3 > \overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3 > -\overset{\oplus}{S}R_2 > -NO_2 > -C \equiv N > -COOH > -COOR > -CH = O > -F >$

$-OR > -OH > Cl > Br > I > -NH_2 > -C \equiv CH > Phenyl > -CH = CH_2 > H.$

+I series: $= \overset{\ominus}{N}H_2 > O^{\ominus} > -COO > R-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}(3°) > R-\underset{(2°)}{\overset{\overset{R}{|}}{CH}} -> R-\underset{(1°)}{CH_2} -> -CH_3 > T > D > H$

Application of I effect:

1. **Stability of reaction intermediate:**

   Stability of $-\overset{|}{C}^{\oplus} \propto +I \propto \frac{1}{-I}$

   Stability of $-\overset{|}{C}^{\ominus} \propto -I \propto \frac{1}{+I}$

   Stability of $-\overset{|}{C}^{\bullet} \propto +I \propto \frac{1}{-I}$

   trick → Like to Like stability

   $-\overset{|}{\underset{|}{C}}^{\oplus}$ $+I$ Stability↑

   $-\overset{|}{\underset{|}{C}}^{\oplus}$ $-I$ Stability↑

Note: I factor works only when bonding nature of charged atom is same (EN same)

2. **Acidic Strength:**

   According to Bronsted theory

   Acidic strength ∝ stability of anion

   Acidic strength $\propto -I \propto \frac{1}{+I}$

   Acid strength ↑ Ka ↑ Pk_a ↓ PH ↓

3. **Basic Strength:**

   Basic strength $\propto +I \propto \frac{1}{-I}$

   Base strength ↑ k_b ↑ Pk_b ↓ PH ↑

   Some facts:

   - I effect works only when source group is same.
   - Between strength and distance, distance must be preferred over strength.
   - Between strength and number of –I group, number must be preferred over strength.

Basic strength of 1°/2°/3° amine

Due to steric hindrance of three alkyl group, donation of lone pair becomes difficult so that it is less basics (basic strength decreases) **As per NCERT**

In aqueous solution

(i) $R = -CH_3$

$2° > 1° > 3° > NH_3$

(ii) $R = -C_2H_5$

$2° > 3° > 1° > NH_3$

In vapour state

$3° > 2° > 1° > NH_3$

Note: If medium is not given then basic strength is compared only in aqueous solution.

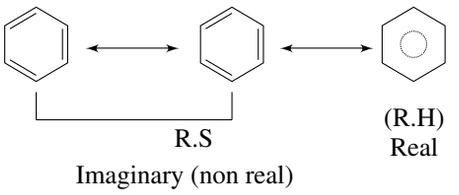
RESONANCE AND MESOMERIC EFFECT

Such hypothetical phenomena in which one of the substance can be represented by more than one imaginary structure known as resonance.

Permanent electron delocalisation of π-bond in nuclear framework or carbon chain is known as resonance.

→ These imaginary non-real structures are known as resonating strength (R.S) or canonical structure.

→ One of the real structure formed by contribution of all canonical form known as resonating hybrid (R.H).



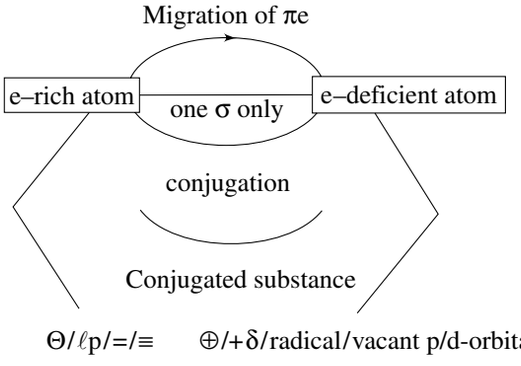
Cause: It is due to de-localisation of $\pi - e^-$ in conjugate substance.

Condition for resonance:

(1) Molecule or its part must be planar i.e., participating atom lies in same plane.

(2) Molecule must be in conjugation.

- When e^- rich and e^- deficient atoms are separated by only one σ-bond, then such atoms are said be in conjugation.
- Such substance which consists of at least 2-conjugated atoms is known as conjugated substance.
- In conjugate substance, migration of πe from e–rich to e–deficient atom takes place, is known as de-localisation



- Double/triple bond may be e^- rich or e^- deficient depending upon nature of other part.

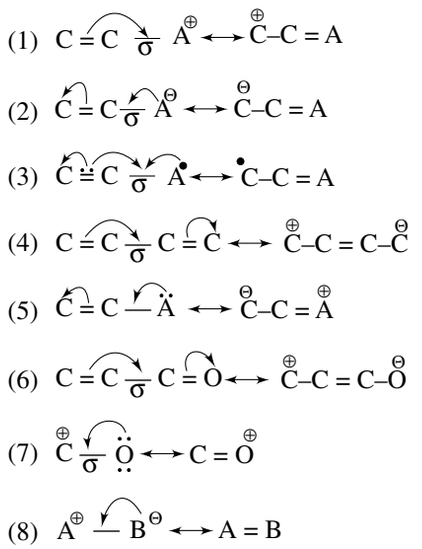
(1) **Rules for directing arrow in resonance:**

(1) π-electron migrates towards cation during resonance.

(2) Anion electron migrates towards π-bond during resonance.

(3) Homolytic cleavage of π-bond takes place if radical show resonance.

(4) Lone pair electron migrates towards π-bond.



Properties of resonating structures:

(1) Resonating structures (R.S.) are imaginary structures, so they can't be isolated.

(2) Resonating hybrid (R.H.) is the real structure so that it can be isolated.

(3) R.H can be formed by equal or unequal contribution of individual R.S.

(4) The whole property of conjugate substance can be explained by only R.H.

(5) R.S can explain the properties according to their contributed proportion.

(6) Conjugate substance is always represented by most contributed R.S.

(7) There is no equilibrium that exists between R.S.

(8) R.S can be separated by the symbol (↔)

(9) The stability of R.H is always greater than any individual R.S

(10) In R.H, πe^- is distributed equally throughout the conjugated part.

Delocalised πe

e^- of π-bond or negative charge or ℓp takes part in conjugation known as delocalized πe

(i) When more than one π bond or lone pair of same atom is present in conjugation then only one of them takes part in delocalisation

(ii) When positive, negative, ℓp, radical is present in conjugation in addition with π bond then only π-π conjugate predominantly takes place

Hint: At conjugate atom: $1\ell p \Rightarrow 2\pi e$, 1 (–) $\Rightarrow 2\pi e$, $1(\bullet) \Rightarrow 1\pi e$, $1(=) \Rightarrow 2\pi e$

Stability of resonating structure:

Generally stability of R.S $\propto$ Contribution

(1) More the covalent bond more stable is R.S.

(2) Neutral molecule is more stable than ionic molecule if octet is complete.

(3) Complete octet of each atom is highly stable R.S.

(4) Negative charge is more preferred on high electro negative atom and positive charge is preferred on less electronegative atom.

(5) Charge separation means heterolytic cleavage which is highly unstable and known as heterovalent R.S.

(6) Similar charge at neighbour position is highly unstable and opposite charge is stable at neighbour position.

Note: Those R.S. having same stability, same potential energy, same contribution towards resonating hybrid are known as equivalent resonating structure.

Mesomeric effect: Permanent delocalisation of π-e of a functional group to the single bond is known as mesomeric effect.

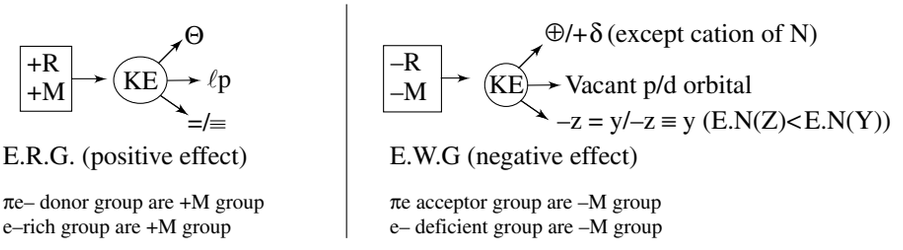
Cause: De-localisation of πe^- in conjugate substance.

Characteristic:

1. It is permanent effect.
2. It is a strong effect because real charge develops.
3. It is operated by π-bond (πe).
4. M-effect is a distance independent.
5. M-effect works in only conjugate substance.

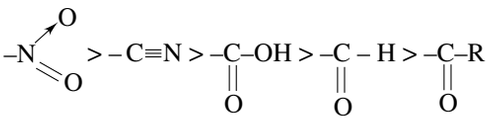
<u>+M/–M effect</u>

(1) Identification

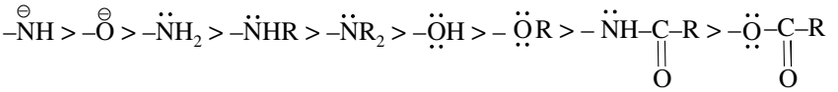


KE (Key element) ⇒ Atom is directly attached with conjugate part.

- Order of –M-effect of some standard species is:



- Order of +M-effect of some standard species is:

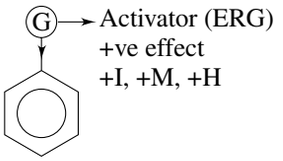


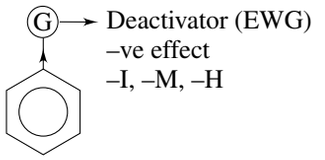
Comparison of M and I effect:

Mesomeric effect	**Inductive effect**
(1) This operates on π-bond	(1) This operate on σ-bond
(2) Distance independent	(2) Distance dependent
(3) It is more dominant because of complete charge	(3) It is less dominant because of partial charge
(4) In benzene M-effect is applicable at only ortho/ para positions	(4) In benzene I-effect is applicable at all 3-ortho-meta, para position
(5) Resonance is a stabilising effect	(5) In neutral molecule inductive effect is destabilising effect
(6) M-effect work only in conjugate substance	(6) I-effect works in both conjugate and non-conjugate substance

Note: In Halogen (–Cl, –Br, –I) , –N = O, etc. –I-effect dominants over +M-effect.

Activator/deactivator: Such groups which increase the e^- density of benzene ring are known as activators and those which decrease the e^- density of benzene ring are known as deactivators.





Overall M and I effect i.e., ERG/EWG

Group at Benzene ring		Effect	Overall effect	Activator and De-activator	Directive Nature for Ar–SE
1.	$-\overset{\ominus}{N}H, -\overset{\ominus}{O}$	+M, +I	positive effect/ERG	Activator	O/P director
2.	$-\ddot{O}H, -\ddot{N}H_2$ $-NH-\overset{\overset{O}{\|\|}}{C}-R, -O-\overset{\overset{O}{\|\|}}{C}-R$	+M, –I +M > –I	positive effect/ERG	Activator	O/P director
3.	$-CH=CH_2$ $-C_6H_5$	+M, –I (+M > –I)	positive effect/ERG	Activator	O/P director
4.	Alkyl $-CH_3$,$-C_2H_5$	+H, +I	positive effect/ERG	Activator	O/P director
5	–X, (F, Cl, Br, I) –N=O	+M, –I –I > + M	negative effect/EWG	De-activator	O/P director
6.	$-NO_2$, – CH = O –CN, – COOH	–M,–I	negative effect/EWG	De-activator	Meta director
7.	$-CCl_3$, $-CF_3$	–H,–I	negative effect/EWG	De-activator	Meta director
8.	$-\overset{\oplus}{N}R_3$, $-\overset{\oplus}{N}H_3$	Only –I	negative effect/EWG	De-activator	Meta director

Strength of activator (ERG):

$$\underset{\text{Strong activator}}{\underbrace{-\overset{\ominus}{N}H > \overset{\ominus}{O} > -NR_2 > -NH_2 > -OH}} > \underset{\text{Moderate activator}}{\underbrace{-OR > -NH-\overset{\overset{O}{\|}}{C}-R > -O-\overset{\overset{O}{\|}}{C}-R}} > \underset{\text{Weak activator}}{\underbrace{\text{alkyl} > \text{phenyl} > H}}$$

Strength of deactivator (EWG):

$$\underset{\text{Strong De-activator}}{\underbrace{-\overset{\ominus}{N}H_3 > \overset{\ominus}{-}NO_2 > CF_3 > -CCl_3}} > \underset{\text{Moderate De-activator}}{\underbrace{-CN > -SO_3H - CH=O > -COOH}} > \underset{\text{Weak De-activator}}{\underbrace{-F > -Cl > -Br > -I > H}}$$

Application of Resonance:

(1) Hybridisation: When negative charge or ℓp atom is present in conjugation, such atoms are always in sp^2 hybridised state.

(2) Bond length/bond energy/bond strength:

$$\text{Bond length of single bond} \propto \frac{1}{\text{Resonance}}$$

$$\text{Bond length of double bond} \propto \text{Resonance}$$

$$\text{Bond length} \propto \frac{1}{\text{bond energy}} \propto \frac{1}{\text{bond strength}}$$

(3) Resonance energy: Energy is released whenever localised electron interconverts into delocalised electron.

(4) Aromaticity:

(I) Aromatic substances: Such substances which fulfill the following conditions are known as aromatic substance.

(a) Molecule must be cyclic

(b) Ring must be planar

(c) Continuous conjugation throughout ring

(d) Obey Huckel rule

$\boxed{4n + 2 = \pi e}$

{n = 0, 1, 2, 3 ...} s

- Aromatic substances are diamagnetic in nature.

(II) Anti-aromatic substances:

(a) Molecule must be cyclic

(b) Ring must be planar

(c) Continuous conjugation throughout ring

(d) $\boxed{4n = \pi e^-}$

{n = 1, 2, 3…}

- Anti-aromatic substances are paramagnetic in nature.

(III) Non-aromatic substances: Such cyclic substances which are neither aromatic nor anti-aromatic, are non-aromatic substances.

Stability order of cyclic substances:

Aromatic > Non-Aromatic > Anti-aromatic

Annulene: Such monocyclic substances in which alternate single and double bond are present in a ring, are known as Annulene.

Annulene (4)

Annulene (6)

Annulene (8)

Annulene [8], [10], [12] are non-planar due to repulsion between adjacent H-atom.

(5) Stability of reaction intermediate:

Profile-1: In different type of conjugation

(1) Conjugate substance is more stable than non-conjugate substance, except antiaromatic substance.

(2) In conjugate substance

Stability ∝ Resonance ∝ Number of R.S ∝ Number of conjugated position

(3) When negative, positive, ℓ.p, are aromatically stablised then such conjugate substances are most stable even that less Number of R.S

(4) Equally contributed R.S. containing conjugate substance is more stable even that less Number of R.S

- Aromatic stable substance > conjugate substance (equal contributor) > conjugate substance (unequal contributor) > non-conjugate substance

Profile-2: In same type of conjugation

$$\text{Stability of } -\overset{|}{\underset{|}{C}}{}^{\oplus} / -\overset{|}{\underset{|}{C}}{}^{\bullet} \propto \text{ERG (+ve)} \propto \frac{1}{\text{EWG (–ve)}}$$

Stability of $-\overset{|}{\underset{|}{C}}^{\ominus} \propto$ EWG (–ve effect) $\propto \dfrac{1}{\text{ERG (+ve effect)}}$

(6) Acidic strength

Profile-1: In different type of conjugation

Acidic strength $\propto$ stability of anion

Acidic strength $\propto$ Delocalisation (Resonace)

Profile-2: In same type of conjugation

Acidic strength $\propto$ EWG(negative) $\propto \dfrac{1}{\text{ERG(positive)}}$

(7) Basic strength

Profile-1: In different type of conjugation

Basic strength $\propto$ e^--donating tendency

Base strength $\propto \dfrac{1}{\text{Delcalisation of } \ell p \text{ (Resonance)}}$

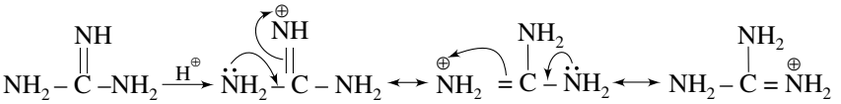
Profile-2: In same type of conjugation

Base strength $\propto$ ERG $\propto \dfrac{1}{\text{EWG}}$

Profile-3: Base strength of guanidine

Guanidine is most basic nitrogenous organic substance

Explanation:



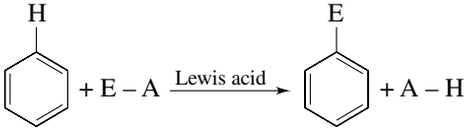
3 equal contributor canonical form
Most stable cation

Basic strength $\propto$ stability of conjugate cation

(8) Aromatic Electrophilic Substitution Reactions

The reactions in which one or more hydrogen atoms of the benzene ring are replaced by an electrophile are called electrophilic aromatic substitution reactions.

These reactions are of the general type shown below:



EFFECT OF SUBSTITUENTS ON REACTIVITY AND ORIENTATION

When substituted benzene undergo electrophilic attack, groups already on the ring affect both the rate of the reaction and the site of attack therefore substituent groups affect both reactivity and orientation in electrophilic aromatic substitutions.

We can divide substituent groups into two classes according to their influence on the reactivity of the ring. Those that cause the ring to be more reactive than benzene itself we call activating groups. Those that cause the ring to be less reactive than benzene we call deactivating groups.

Theory of Orientation

A group attached to benzene has a directing influence on the electrophilic substitution reaction. Two types of groups have been classified based on their orientation effects.

Activating Group

A group that releases electrons to benzene ring is an activating group. It directs the incoming electrophile to *ortho* or *para* position. Examples include

Strongly activating: $-NH_2$, $-NHR$, $-NR_2$, $-OH$, $-OCH_3$

Moderately activating: $-NHCOCH_3$, $-OCOCH_3$

Weakly activating: $-CH_3$, $-CH{=}CH_2$, $-C_6H_5$

Deactivating Group

A group that withdraws electrons from benzene is a deactivating group. It directs the incoming electrophile to *meta* position. Examples include

Strongly deactivating: $-\overset{+}{N}(CH_3)_3$,$-NO_2$, $-CN$, $-SO_3H$

Moderately deactivating $-CHO$, $-COR$, $-COOR$, $-COOH$, $-COCl$

*Weakly deactivating: F, –Cl, –Br, –I (*o/p* director)

Mode of Orientation

Case-I: Activating Groups: Ortho para Directors

Case-II: Deactivating Groups: Meta Directors

Case-III: Halo Substituents: Deactivating Ortho-Para Directors

EFFECT OF SUBSTITUTENTS ON REACTIVITY

In presence of different substituents on benzene ring, rate of reaction increased or decreased is known as substitution effect.

$$\text{Reactivity of ArsE} \propto \text{Activating power} \propto \frac{1}{\text{Deactivating power}}$$

Aromatic Electrophilic Substitution Reactions of Polysubstituted Benzene

What happens when two or more substituent groups are attached to the benzene ring? Where is the electrophile likely to attack? Some qualitative rules have been formulated to answer this question.

(i) The most activating group will control orientation.

(ii) No substitution occurs between two meta substituents because of crowding.

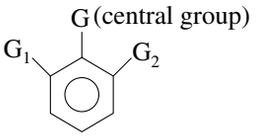
(iii) When both groups are meta directors, it is difficult to introduce third group.

Reactions of aromatic substance are following Reaction:

Reaction	Reagent	$E^{\oplus}$
Chlorination	$Cl_2/FeCl_3$ Cl_2/Fe	$Cl^{\oplus}$
Nitration	HNO_3/H_2SO_4	$\overset{\oplus}{N}O_2$
Sulphonation	Conc. H_2SO_4	SO_3 Neutral
Friedel–Craft reaction	$R{-}Cl/AlCl_3$ $R{-}\underset{\underset{O}{\|\|}}{C}{-}Cl/AlCl_3$	$R^{\oplus}$ $R{-}C^{\oplus}{=}O$

(9) Ortho effect:

(1) SIR effect (Steric inhibition of resonance)



Due to maximum repulsion by G_1 and G_2 groups, central group G comes out of the plane of benzene ring so that group G can't participate in resonance with ring is known as SIR or ortho effect

Condition for SIR effect:

(1) Central group 'G' must be bulky.

Bulky group → –COOH, $-SO_3H$, $-\overset{\overset{O}{\|}}{C}-Cl$, $-\overset{\overset{O}{\|}}{C}-NH$, CMe_3, $-NR_2$, $-NO_2$, –Br, – I, etc.

Smaller group → –OH, $-OCH_3$, $-NH_2$, $-CH_3$, –F, –Cl, etc.

(2) G_1 and G_2 may or may not be bulky but must be occupied at both the ortho positions of G

Note: For –COOH, $-SO_3H$, presence of only one group at ortho-position is sufficient for SIR effect.

- Ortho substituted benzoic acid is more acidic because its conjugate base will be more stable due to steric crowding.

Steric Inhibition in protonation (S.I.P.)

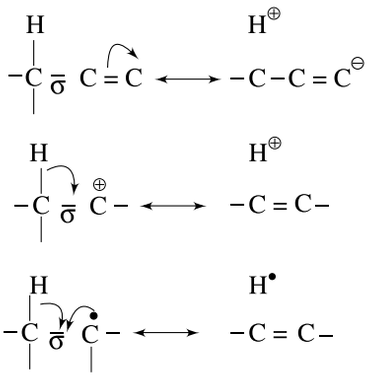
- Only for basic strength.
- Ortho substituted aniline are weaker bases because their conjugate acids are unstable due to van der Waal repulsion.
- Exception: No SIP effect is observed in case of OCH_3 group only.

Hyperconjugation effect (H-effect):

Backer Nathan effect (No bond Resonance)

When at least one C–H bond is separated by only one σ bond with π bond/ positive charge/ radical then delocalisation σ bond of C–H takes place is known as H-effect or σ–π conjugation.

Types of hyperconjugation:



- Order of effectiveness M > H > I

Some facts:

- Allylic hydrogen and benzylic hydrogen are more reactive due to hyper conjugation.
- In alkene or alkyne bond length are not ideal single bond having double bond character and vice-versa.
- Saytzeff rule will be explained by hyperconjugation because more the substituted alkene more stable because of more α-hydrogen.
- Hyperconjugation can be applied on alkene, alkyne, cation and radical.

+H effect: Alkyl group increases e-density of benzene ring by the delocalisation of σ bond

Power of +H group

(i) In different alkyl group

+H power ∝ Number of α-H

$CH_3- > CH_3-CH_2- > (CH_3)_2-CH- > (CH_3)_3-C-$

(ii) In isotopic hydrogen

$-CH_3 > -CD_3 > -CT_3$

Reverse Hyperconjugation (–H effect)

–H group ⇒ $-CZ_3$

Ex. $-CF_3$, $-CF_3$, $-CCl_3$, $-C(NO_3)_3$

Application of hyper conjugation:-

(1) Stability

(i) Stability of alkenes ∝ Number of α-H

(ii) Stability of alkyl carbocations ∝ Number of α-H

(iii) Stability of alkyl free radical ∝ Number of α-H

(2) Heat of hydrogenation

$CH_2=CH_2 + H_2 \rightarrow CH_3-CH_3$

(1) ΔH (HOH) ∝ Number of π-bond

(2) If number of π-bonds is same

$$\Delta H \text{ (HOH)} \propto \frac{1}{\text{stability of alkene}}$$

(3) Heat of combustion

$CH_2=CH_2 + O_2 \rightarrow 2CO_2 + 2H_2O$

(1) ΔH (HOC) ∝ Number of C & H

(2) If number of carbons is same

$$\Delta H \text{ (HOC)} \propto \frac{1}{\text{stability of alkene}}$$

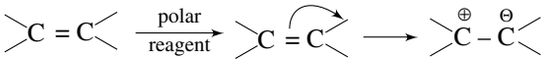
ELECTROMERIC EFFECT

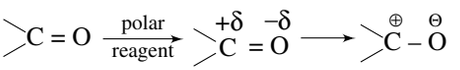
Condition: Compound must have π bond

–C=C–, –C≡C–, –C=O, –C≡N, etc.

- The effect involving the complete transfer of shared pair of electrons of pi bond in the presence of polar reagent is known as electromeric effect (E effect).

  It is a temporary effect and is brought into play instantaneously at the demand of the attacking reagent. However, as soon as the attacking reagent is removed, original electronic condition is restored.





Nucleophilicity (Strength of Nucleophile): The relative reactivity of nucleophile is known as nucleophilicity.

Nucleophilicity can be compared as given below:

(1) A negatively charged nucleophile is always a more reactive nucleophile than its conjugate acid. Thus HO^- is a better nucleophile than H_2O and RO^- is better than ROH.

(2) In a group of nucleophiles in which the nucleophilic atom is the same or belong to same period,

$$\boxed{\text{Nucleophilicities} \propto \text{Basicities}}$$

(3) In a group of nucleophiles in which the nucleophilic atom is the same and the category of anion is also same then,

$$\boxed{\text{Nucleohilicities} \propto \frac{1}{\text{steric hindrance}}}$$

(4) In a group of nucleophiles in which the nucleophilic atom is the different, then nucleophilicities are depends upon nature of solvent:

(i) In Polar Protic Solvents $\boxed{\text{Nucleophilicities} \propto \text{Size}}$

(ii) In Polar Aprotic Solvents $\boxed{\text{Nucleohilicities} \propto \frac{1}{\text{Size}}}$

Relative Nucleophilicity in Protic solvents:

$$SH^- > CN^- > I^- > OH^- > N_3^- > Br^- > CH_3CO_3^- > Cl^- > F^- > H_2O$$

Leaving Groups(or nucleofuge): In alkyl halides the leaving group is the halogen substituent – it leaves as a halide ion. To be a good leaving group the substituent must be able to leave as a relatively stable, weakly basic molecule or ion.

$$Nu:^- + R - L \rightarrow R - Nu + :L^-$$

SOLVED EXAMPLE

1. Which of the following compounds easily undergoes homolytic bond fission?

(1) CH_3–Cl (2) CH_3–CH=O

(3) H–O–O–H (4) NH_2–CH_3

Sol. **[3]**

H–O–O–H

Due Least E.N. difference.

2. Which of the following represents the mode of hybridisation sp^2–sp^2–sp–sp from left to right?

(1) CH_2=CH–C≡N (2) HC≡C–C≡CH

(3) CH_2=C=C=CH_2 (4) CH_2=CH–CH=CH_2

Sol. **[1]**

CH_2=CH–C≡N

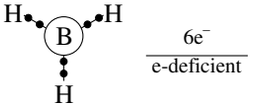
sp^2 sp^2 sp sp

3. Which of the following is an electron deficient molecule?

(1) CH_3CH_3 (2) BH_3

(3) SiH_4 (4) PH_3

Sol. **[2]**



4. One of the following pairs represents a set of nucleophile:

(1) CN^- and NH_3 (2) $AlCl_3$ and Cl^-

(3) H^+ and H_2O (4) Br^+ and $\ddot{C}\,Cl_2$

Sol. **[1]**

e-rich species are nucleophile (refer key concept.)

5. The decreasing order of –I effect of the following is:

I. $H_3N^{\oplus}$ **II.** NO_2

III. CN **IV.** COOH

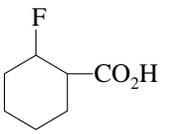
(1) I > II > III > IV (2) II > I > III > IV

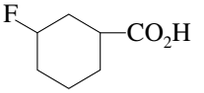
(3) I > II > III > IV (4) II > I > IV > III

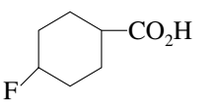
Sol. **[1]**

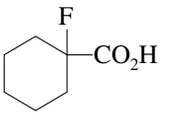
$\underset{\text{cation}}{-NH_3^+} > -NO_2 > -CN > -COOH$ $\xrightarrow[\downarrow -I \text{ effect}]{}$ (refer key concept.)

6. Which of the following has highest K_a value?

(1) 

(2) 

(3) 

(4) 

Sol. **[4]**

Acidic strength ∝ –I Power ∝ K_a

Also –I power decresed as distance increses

7. Which of following has lowest pK_a value?

(1) $Cl–CH_2–CO_2H$ (2) $Cl–\underset{\displaystyle Cl}{\underset{|}{CH}}–CO_2H$

(3) $Cl_3C–CO_2H$ (4) $CH_3–CO_2H$

Sol. **[3]**

Acidic strength $\propto -I \propto K_a \propto \frac{1}{pK_a}$

As number of –I group increases, –I power further increases hence pK_a value decreases.

8. Arrange the following compound in order of decreasing acidity

$CH_3–CH_2–OH\,(\alpha); CH_3–CH_3–\overset{\oplus}{O}H_2(\beta); CH_3–O–CH_3\,(\gamma)$

(1) $\alpha > \beta > \gamma$ (2) $\beta > \alpha > \gamma$

(3) $\gamma > \beta > \alpha$ (4) $\alpha > \gamma > \beta$

Sol. **[2]**

$$\underset{\text{acid Strength} \downarrow}{\underline{\text{Cation} > \text{Alcohol} > \text{ether}}}$$

9. Amongst the amines $C_6H_5NH_2$ (I), CH_3NH_2 (II), $(CH_3)_2NH$ (III) and $(CH_3)_3N$ (IV) the order of basicity (in aqueous medium) is–

(1) I < IV < II < III (2) IV < III < II < I

(3) I < II < III < IV (4) II < III < IV < I

Sol. **[1]**

$\underset{\substack{\ell p \text{ delocalised}\\ \text{least basic}}}{C_6H_5–NH_2(I)}$ $\underbrace{\underset{(1°)}{CH_2–NH_2(II)}\ \underset{(2°)}{(CH_3)_2NH(III)}}_{\ell p\text{-localised more basic}}$ $\underset{(3°)}{(CH_3)_3N(IV)}$

Also as per N.C.E.R.T result if R = $–CH_3$

Basic strength 2° > 1° > 3°

Hence order of basic strength in aqueous solution

(I) < (IV) < (II) < (III)

10. The order of decreasing stability of the anions

$\underset{I}{(CH_3)_3C^-}$ $\underset{II}{(CH_3)_2CH^-}$ $\underset{III}{CH_3CH_2^-}$ $\underset{IV}{C_6H_5CH_2^-}$ is–

(1) I > II > III > IV (2) IV > III > II > I

(3) IV > I > II > III (4) I > II > IV > III

Sol. **[2]**

$$\underset{\substack{\text{Resonance}\\ \text{Stability}}}{(IV)} > \underbrace{(III) > (II) > (I)}_{\substack{+I \text{ Power} \uparrow\\ \text{Stability of Carbanion} \downarrow}}$$

11. In the formate ion $(H—\overset{\displaystyle O}{\overset{\|}{C}}—O^-)$, the two carbon-oxygen bonds are found to be equal. This is because

(1) the formate ion $HCOO^-$ is obtained by the removal of a proton from HCOOH

(2) the carbon atom in $HCOO^-$ is sp^2 hybridised

(3) the formate ion is a tautomeric mixture of

$H—\overset{\displaystyle O}{\overset{\|}{C}}—O^-$ and $O=\overset{\ominus}{C}—OH$

(4) the formate ion is a resonance hybrid of the two equivalent resonance structures

$H—\overset{\displaystyle O}{\overset{\|}{C}}—O^-$ and $H—\overset{\displaystyle O^{\ominus}}{\overset{|}{C}}=O$

Sol. **[4]**

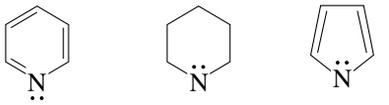
$H–\overset{\displaystyle O}{\overset{\|}{C}}–O^- \longleftrightarrow H–\overset{\displaystyle O^-}{\overset{|}{C}}=O$

(Resonance)

Equal contributor

Resonating hybrid $\Rightarrow$ $H—\overset{\displaystyle O^{\delta-}}{\overset{\|}{C}}—O^{\delta-}$

12. The hybridisation states of the nitrogen atoms at in pyridine, piperidine and pyrrole are respectively:

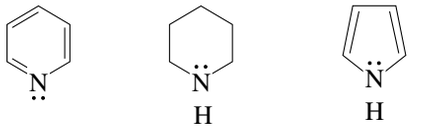


Pyridine Piperidine Pyrrole

(1) sp^2, sp^3 and sp^2 (2) sp^2, sp^3 and sp^3

(3) sp^3, sp^3 and sp^3 (4) sp^2, sp^2 and sp^2

Sol. **[1]**

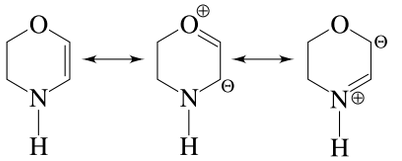


Pyridine Piperidine Pyrrole

sp^2 sp^3 sp^2

(ℓp delocalised)

13.



(I) (II) (III)

The least stable canonical structure among these is:

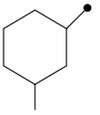
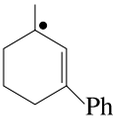
(1) I (2) II

(3) III (4) all are equally stable

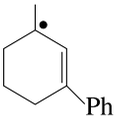
Sol. **[2]**

→ In (II) Str., more EN atom carries positive charge, less stable

14. Which one of the following is most stable?

(1) 
(2) 
(3) 
(4) 

Sol. **[3]**



Resonance & 3α – H(+H Effect)

most stable

15. Pyridine is less basic than triethyl amine because:

(1) Pyridine has aromatic character

(2) Nitrogen in pyridine is sp^2 hybridised

(3) Pyridine is a cyclic system

(4) Lone pair of nitrogen is delocalised in pyridine

Sol. **[4]** ℓp of N in pyridine is de-localised so that it is less basic than triethyl amine.

16. Which is an aromatic compound?

(1) 
(2) 
(3) 
(4) 

Sol. **[2]**

 4n=8 Anti Aromatic ;  4n + 2 = 6 Aromatic ;

 Non planar non aromatic ;  non planar non aromatic

17. Which of the following is the strongest nucleophile?

(1) $EtO^{\ominus}$
(2) $\overset{\ominus}{O}H$
(3) $\overset{\ominus}{C}N$
(4) $I^{\ominus}$

Sol. **[1]**

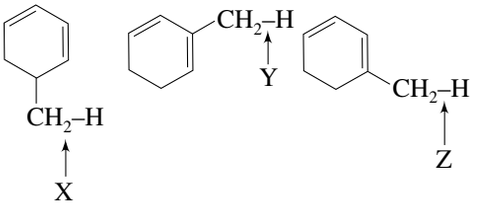
Nucleophilicity is parallel to basicity

Acidity : HI > HCN > H_2O > EtOH

Basicity and nucleophilicity:

$I^{\ominus} < \overset{\ominus}{C}N < \overset{\ominus}{O}H < EtO^{\ominus}$

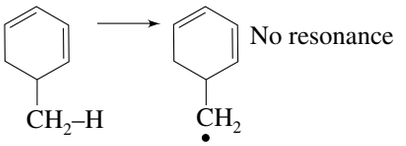
18. Which of the following is the correct order for bond energy for C–H bonds in these compounds?

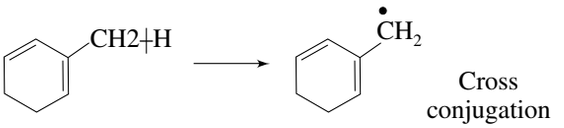


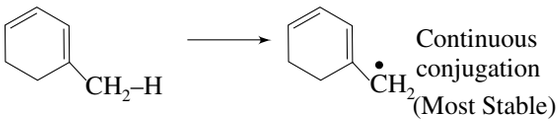
(1) Y > Z > X
(2) X > Z > Y
(3) X > Y > Z
(4) Z > X > Y

Sol. **[3]**

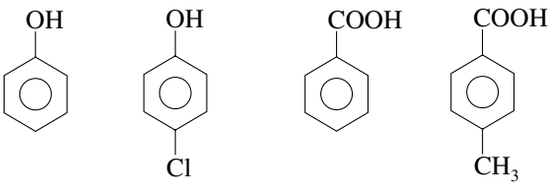
$$\text{Bond energy} \propto \frac{1}{\text{stablity of free radical}}$$





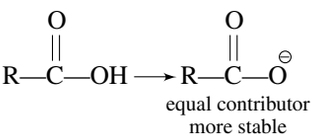


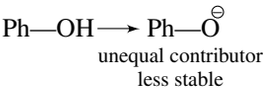
19. The correct order of decreasing acidity of the compounds is:



(1) III > IV > II > I
(2) IV > III > I > II
(3) III > II > I > IV
(4) II > III > IV > I

Sol. **[1]**





Acidic strength ∝ stability of anion

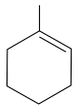
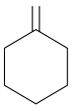
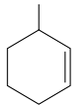
Thus R—COOH > Ph–OH (Acid strength)

when functional group (source group) is same

Acid strength ∝ EWG ∝ $\frac{1}{\text{ERG}}$

Hence III > IV > II > I

20. Compare heat of hydrogenation of the following:

(i)  (ii)  (iii) 

(1) i > ii > iii (2) iii > ii > i

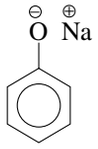
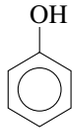
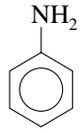
(3) ii > i > iii (4) ii > iii > i

Sol. **[2]**

ΔH Heat of hydrogenation

$$\propto \frac{1}{\text{sterbility of alkene}} \propto \frac{1}{\text{number } \alpha - H}$$

21. Compare rate of EAS

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

(1) a > b > c > d (2) a > c > b > d

(3) c > a > b > d (4) c > b > a > d

Sol. **[2]**

Rate of Ar – $S_E \propto$ ERG

ERG power ($-O^{\ominus}$ > – NH_2 > –OH)

22. Which among the following statements are incorrect?

(1) $\ddot{C}F_2$ is more stable than $\ddot{C}Cl_2$

(2) $\ddot{C}Cl_2$ is more stable than $\ddot{C}Br_2$

(3) singlet $\ddot{C}H_2$ is more stable than triplet $\ddot{C}H_2$

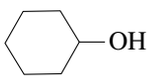
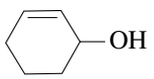
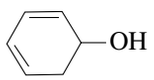
(4) Singlet $\ddot{C}H_2$ has planar geometry

Sol. **[3]**

:CF_2 > **:**CCl_2 > **:**CBr_2 > **:**Cl_2 ⟶ Stability

Triplet $\ddot{C}H_2$ is more stable than singlet $\ddot{C}H_2$. Hence it is incorrect.

23. Identify the correct order of the ease of dehydration of the following compounds.

 I  II  III

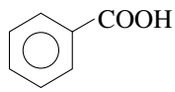
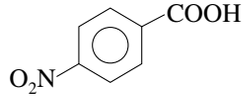
(1) I > II > III (2) III > II > I

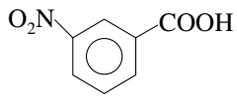
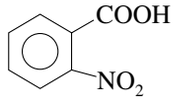
(3) I > III > II (4) III > I > II

Sol. **[2]**

Rate of dehydration ∝ stability of carbocation

24. Which of the following compounds has the highest pK_a value?

(1)  (2) 

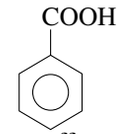
(3)  (4) 

Sol. **[1]**

When functional. group (–COOH) same

Acidic strength ∝ EWG ∝ $\frac{1}{pKa}$

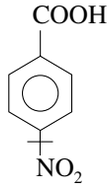
Acid strength ∝ $K_a \propto \frac{1}{pKa}$



no effect

less Acidic

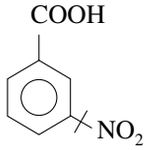
pKA ↑



–M

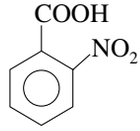
–I dist. ↑

$(EWG)_2$



Meta position only

–I $(EWG)_3$

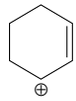
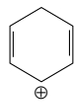


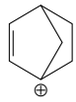
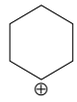
–Mda

–I ↑ dist. ↓

$(EWG)_1$

25. Least stable carbocation amongst following is:

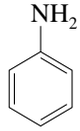
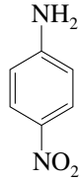
(1)  (2) 

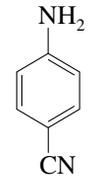
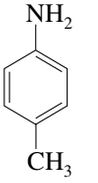
(3)  (4) 

Sol. **[3]**

→ Due to Bredt's rule +ve charge cannot be placed at the bridgehead carbon.

26. Consider the following compounds:

(I)  (II) 

(III)  (IV) 

Arrange these compounds in decreasing order of their basicity:

(1) I > II > III > IV (2) II > III > I > IV

(3) IV > I > III > II (4) IV > I > II > III

Sol. **[3]**

Base strength $\propto$ + M, +I $\propto \frac{1}{-M, -I}$

27. Which of the following has highest leaving group ability?

(1) $\overset{\ominus}{N}H_2$ (2) $H_3C-\underset{\underset{O}{\|}}{C}-O^{\ominus}$

(3) $\overset{\ominus}{O}CH_3$ (4) $I^{\ominus}$

Sol. **[4]**

Leaving ability $\propto$ acid strength of conjugate acid

$\propto \frac{1}{\text{base strength of anion}}$

$\rightarrow$ HI is most acidic hence I^- is good leaving group

28. What is the decreasing order of stability of the ions?

(I) $H_3C-HC^{+}-CH_3$ (II) $H_3C-HC^{+}-O-CH_3$

(III) $H_3C-HC^{+}-\underset{\underset{O}{\|}}{C}-CH_3$

(1) I > II > III (2) II > III > I

(3) III > I > II (4) II > I > III

Sol. **[4]**

$CH_3-\overset{+}{C}H-CH_3$

Incomplete octet and less EN carbon atom carries +ve charge, Hence more stable than III but less stable than II

$CH_3-\overset{+}{C}H-\ddot{O}CH_3 \leftrightarrow CH_3-CH=\overset{+}{O}-CH_3$

Complete octet (Most stable)

$CH_3-\overset{\oplus}{C}H-\underset{\underset{O}{\|}}{C}-CH_3 \leftrightarrow CH_3-CH=\underset{\underset{O^{+}}{|}}{C}-CH_3$

Incomplete octet and more EN oxygen atom carries +ve charge hence less stable

Therefore correct stability after is:

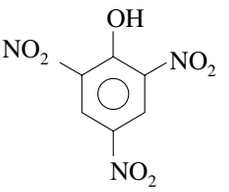
(II) > (I) > (III)

29. Arrange 2, 4, 6-trinitrophenol (I); 2, 4-dinitrophenol (II); *o*-nitrophenol (III) and *p*-nitrophenol (IV) in order of acidity:

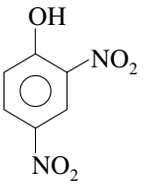
(1) I > II > III = IV (2) IV > III > II > I

(3) I > II > IV > III (4) III > II > I > IV

Sol. **[3]**

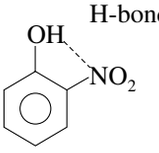


(I)

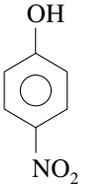


(II)

Intra-molecular H-bond



(III)



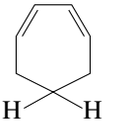
(IV)

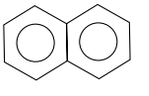
$\Rightarrow$ Removal of Proton becomes difficult, so it is less acidic than para nitrophenol

Acidic strength $\propto$ −M, −I $\propto \frac{1}{+M, +I}$

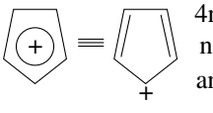
(I) > (II) > (IV) > (III)

30. Which one of the following substances is aromatic?

(1)  (2) 

(3)  (4) 

Sol. **[4]**

(1) 

4n = 4

n = 1

anti aromatic

(2) non-planar

(3) non-planar due to repulsion between adjacent H-atom

(4) 4n + 2 = 10

n = 2

EXERCISE 1

1. In the compound $CH_2=CH-CH_2-CH_2-C\equiv CH$, the ($C_2-C_3$) bond is of the type:

(1) $sp - sp^2$ (2) $sp^3 - sp^3$

(3) $sp - sp^3$ (4) $sp^2 - sp^3$

2. Which of the following series contains electrophile only?

(1) H_2O, SO_3, $\overset{\oplus}{N}O_2$ (2) NH_3, H_2O, BI_3

(3) ROH, NH_3, $\overset{\oplus}{N}O_2$ (4) $AlCl_3$, SO_3, $\overset{\oplus}{Cl}$

3. Give the correct order of increasing acidity of the following compounds.

$ClCH_2COOH$ (I) CH_3CH_2COOH (II)

$ClCH_2CH_2COOH$ (III) $(CH_3)_2CHCOOH$ (IV)

CH_3COOH (V)

(1) V < II < IV < I < III

(2) IV < II < V < III < I

(3) III < I < IV < II < V

(4) V < IV < II < I < III

4. Which of the following acids has lowest pK_a value?

(1) $CH_3-\underset{NO_2}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OH$ (2) $\underset{NO_2}{\underset{|}{CH_2}}-CH_2-\overset{O}{\overset{\|}{C}}-OH$

(3) $\underset{Cl}{\underset{|}{CH_2}}-\overset{O}{\overset{\|}{C}}-OH$ (4) $CH_3-\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-OH$

5. A nucleophile is called an ambident nucleophile if:

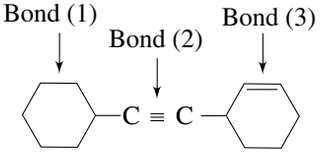
(1) It is capable of acting as nucleophile as well as an electrophile

(2) Its attacking atom has two lone pairs

(3) It has two possible electron donating sites

(4) It can act lewis acid

6. Rank the indicated bonds in each compounds in order of increasing bond strength:



(1) 1 < 2 < 3 (2) 3 < 1 < 2

(3) 1 < 3 < 2 (4) 2 < 3 < 1

7. Arrange the following groups in order of decreasing *m*-directing strength. $-\overset{+}{N}R_3$, –CN, $-NO_2$, –COOH

(1) $-\overset{+}{N}R_3 > -NO_2 > -CN > -COOH$

(2) $-COOH > -CN > -NO_2 > -\overset{+}{N}R_3$

(3) $-CN > -NO_2 > -COOH > -\overset{+}{N}R_3$

(4) $-NO_2 > -CN > -\overset{+}{N}R_3 > -COOH$

8. (I) $CH_3-O-CH=CH-CH=CH_2$

(II) $CH_3-O-\overset{\oplus}{C}H-CH=CH-\overset{\oplus}{C}H_2$

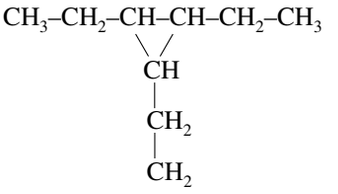
(III) $CH_3-\overset{\oplus}{O}=CH-CH=CH_2-\overset{\oplus}{C}H_2$

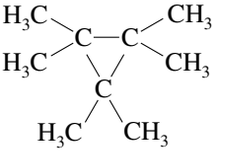
Among these three canonical structures (through more are possible) what would be their relative contribution in the hybrid:

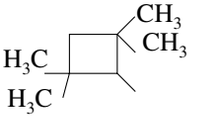
(1) I > II > III (2) III > II > I

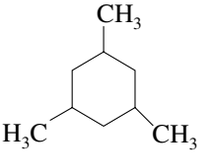
(3) I > III > II (4) III > I > II

9. An organic compound has molecular formula C_9H_{18}. Its all carbon atoms are sp^3 hybridised and its all hydrogen atoms are identical. Its structural formula can be:

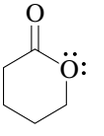
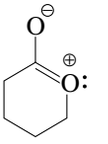
(1) 

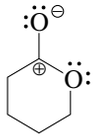
(2) 

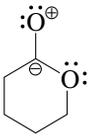
(3) 

(4) 

10. Stability order of the following resonating structure will be–

(i)  (ii) 

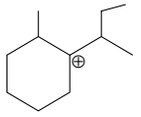
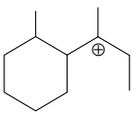
(iii) 

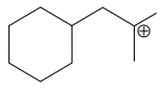
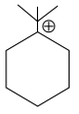
(iv) 

(1) i > ii > iii > iv (2) ii > i > iii > iv

(3) iii > ii > i > iv (4) i > iii > ii > iv

11. Which carbocation is the most stable?

(1)  (2) 

(3)  (4) 

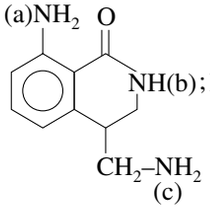
12. Compare acidic strength–

(i) $CHCl_3$ (ii) CHF_3

(iii) $CH_3–CH_3$

(1) i > ii > iii (2) ii > i > iii

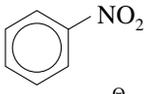
(3) iii > i > ii (4) ii > iii > i

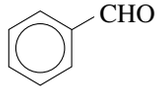
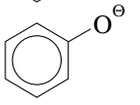
13. 

(1) a > b > c (2) b > a > c

(3) c > a > b (4) c > b > a

14. Electrophile $\overset{\oplus}{N}O_2$ attacks the following:

(I)  (II) 

(III)  (III) 

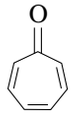
In which cases $\overset{\oplus}{N}O_2$ will attack at meta position

(1) II and IV (2) II and III

(3) II and IV (4) I only

15. Which of the structures below would be aromatic?

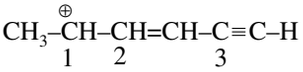
(i)  (ii) 

(iii)  (iv) 

(1) i and iv (2) i, iii and iv

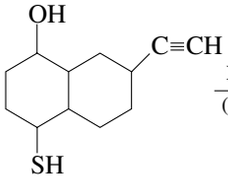
(3) iii and iv (4) ii

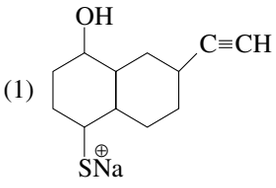
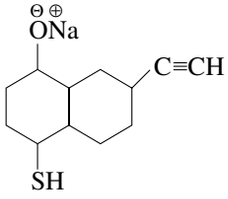
16. What is the hybridisation of C_1, C_2, C_3 carbon in the following compound?

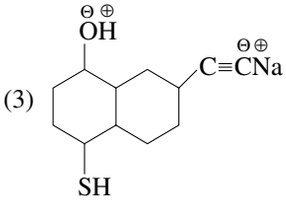
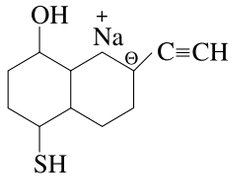


(1) sp^3, sp^3, sp^3 (2) sp^3, sp^2, sp^2

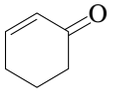
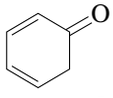
(3) sp^3, sp^2, sp (4) sp^2, sp^2, sp

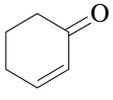
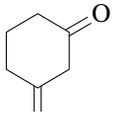
17.  (A); Product (A) is:

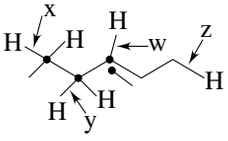
(1)  (2) 

(3)  (4) 

18. Which of the following has longest C – O bond?

(1)  (2) 

(3)  (4) 

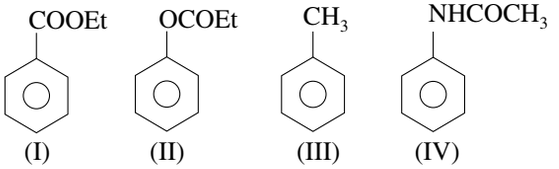
19. 

Arrange the (C–H) bonds x, y and z in decreasing order of their bond dissociation energies in homolysis

(1) y > x > z > w (2) z > x > w > y

(3) w > x > z > y (4) y > z > w > x

20. Find the correct order of electron density at benzene ring:

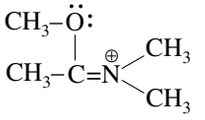
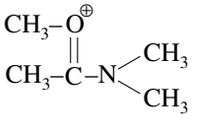


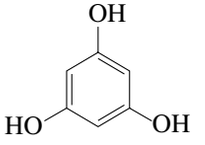
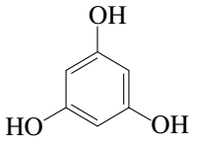
(I) (II) (III) (IV)

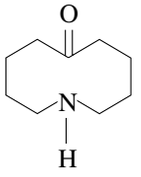
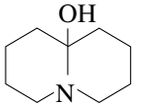
(1) IV > III > II > I (2) I > II > III > IV

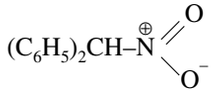
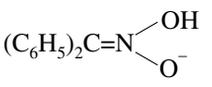
(3) IV > II > I > III (4) IV > II > III > I

21. Which of the following pairs of structure are resonance structure?

(i)  and 

(ii)  and 

(iii)  and 

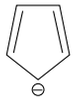
(iv)  and 

(1) (i) and (iv) (2) (ii) and (iii)

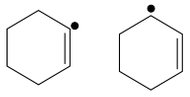
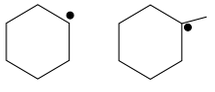
(3) (i) and (ii) (4) All of these

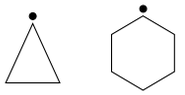
22. Which of the following anions is resonance destabilised?

(1)  (2) 

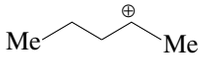
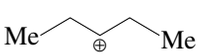
(3)  (4) 

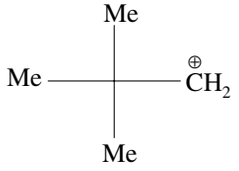
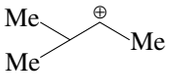
23. In which of the following pairs, 1st is more stable than 2nd?

(1)  (2) 

(3)  (4) $Ph_3C^{\bullet}$, $(CH_3)_3C^{\bullet}$

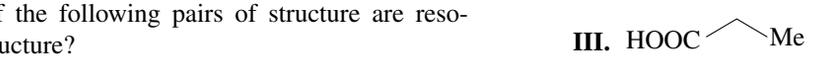
24. Which of the following carbocations is most stable?

(1)  (2) 

(3)  (4) 

25. The decreasing order of the acidic character is:

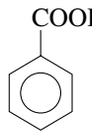
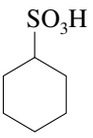
I. COOC–≡–H **II.** 

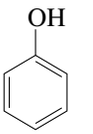
III. 

(1) I > II > III (2) III > II > I

(3) II > I > III (4) III > I > II

26. Which of the following is least acidic?

(1)  (2) 

(3)  (4) 

27. Amongst NO_2, CH_3, OCH_3, Br, CMe_3, the decreasing order of groups or atoms having negative inductive effect is:

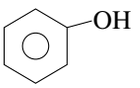
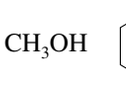
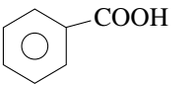
(1) $NO_2 > Br > OCH_3 > CMe_3 > CH_3$

(2) $NO_2 > OCH_3 > Br > CMe_3 > CH_3$

(3) $NO_2 > Br > OCH_3 > CH_3 > CMe_3$

(4) $Br > NO_2 > OCH_3 > CH_3 > CMe_3$

28. The correct order of the decreasing pK_a values of the compounds is:

I II III IV

(1) I > II > III > IV (2) II > I > III > IV

(3) III > IV > I > II (4) IV > III > I > II

29. The order of ease of heterolysis of following t-butyl compound is:

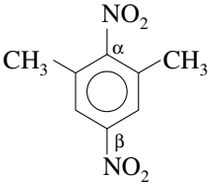
(I) $(CH_3)_3C–OH$ (II) $(CH_3)_3C–OAc$

(III) $(CH_3)_3C–Cl$

(1) I < II < III (2) III < II < I

(3) I < III < II (4) II < I < III

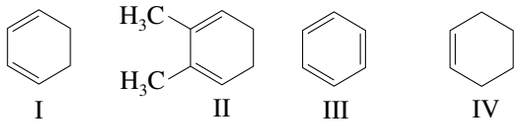
30. Compare C–N bond length α, β as indicated:



(1) α > β (2) α = β

(3) α < β (4) can't be predicted

31. The decreasing order of bond length of C=C in the following compounds is:

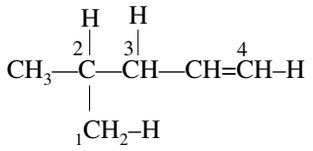


I II III IV

(1) II > I > IV > III (2) III > II > I > IV

(3) II > III > I > IV (4) IV > I > II > III

32. C_1–H, C_2–H, C_3–H and C_4–H the homolytic bond dissociation energy is in the order:



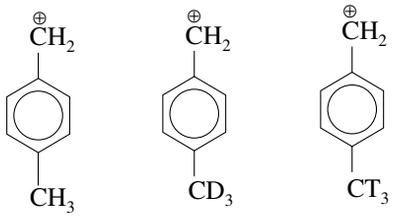
(1) C_2–H > C_3–H > C_4–H > C_1–H

(2) C_1–H > C_4–H > C_2–H > C_3–H

(3) C_2–H > C_3–H > C_1–H > C_4–H

(4) C_4–H > C_1–H > C_3–H > C_2–H

33. Arrange the following cation in increasing order of stability

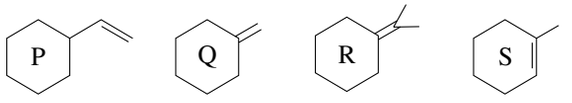


(A) (B) (C)

(1) A < B < C (2) A < C < B

(3) C < A < B (4) C < B < A

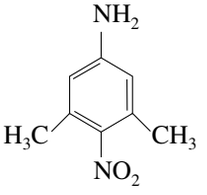
34. Arrange the following alkenes in increasing order of their enthalpy of hydrogenation (–ΔH):



(1) R < S < Q < P (2) R < S < P < Q

(3) P < Q < R < S (4) P < Q < S < R

35. Which of the following effects of —NO_2 group operates on —NH_2 group in this molecule?



(1) Only –I effect

(2) Only – M effect

(3) Both –I and –M effect

(4) Only + M effect

36. The decreasing order of –I effect of the orbitals is:

I. sp **II.** sp^2

III. sp^3

(1) I > II > III (2) III > II > I

(3) I > III > II (4) II > III > I

37. Electrophile in the case of chlorination of benzene in the presence of $FeCl_3$ is:

(1) Cl^+ (2) Cl^-

(3) Cl (4) $FeCl_3$

38. Identify the strongest nucleophile.

(1) CH_3CH_2SH (2) $CH_3COO^{\ominus}$

(3) CH_3NH_2 (4) $NC-\overset{\ominus}{C}H_2$

39. Among the following the correct order of basicity is:

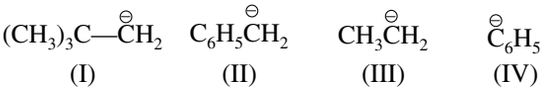
(1) $NH_2^{\ominus} > OH^{\ominus} > RO^{\ominus} > RCOO^{\ominus}$

(2) $NH_2^{\ominus} > RO^{\ominus} > OH^{\ominus} > RCOO^{\ominus}$

(3) $RCOO^{\ominus} > NH_2^{\ominus} > RO^{\ominus} > OH^{\ominus}$

(4) $RCOO^{\ominus} > RO^{\ominus} > NH_2^{\ominus} > OH^{\ominus}$

40. Identify the correct order of stability among the following carbanions

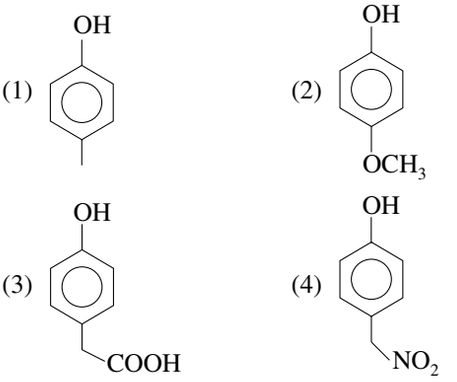


(I) (II) (III) (IV)

(1) I > III > IV > II (2) I > IV > III > II

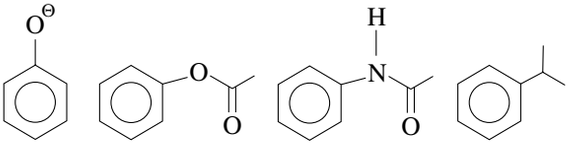
(3) II > III > IV > I (4) II > IV > III > I

41. Value of pK_a will be minimum for:



(1) (2) (3) (4)

42. The order of reactivity of the compounds

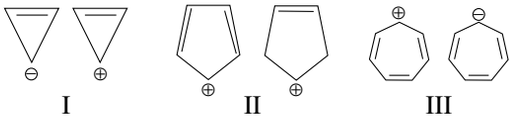


(I) (II) (III) (IV)

Towards substitution with a given electrophile is:

(1) IV > III > II > I (2) I > II > III > IV
(3) III > II > I > IV (4) I > III >II > IV

43. In which pair second ion is less stable than first?

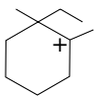
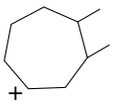


I II III

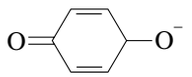
(1) (I) and (II) (2) (II) and (III)
(3) only (II) (4) only (III)

44. Which of the following carbocation will undergo favourable rearrangement?

(1)  (2) 

(3)  (4) 

45. In which of the following, all C–O bonds are not of equal length?

(1)  (2) $CH_3–COO^-$

(3) CO_3^{2-} (4) NO_2^-

46. Arrange *o*-toluic acid (I), *m*-toluic acid (II), *p*-toluic acid (III) and benzoic acid (IV) in order of decreasing acid strength.

(1) I > II > III > IV (2) I > II > IV> III
(3) III > IV> I > II (4) I > IV > II > III

47. In the given ionic reaction, designate the nucleophile and the leaving group

$CH_3–CH_2–Br + NaI \longrightarrow CH_3–CH_2–I + NaBr$

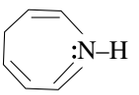
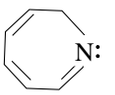
(1) $Nu^{\ominus} = Br^{\ominus}$, $L^{\ominus} = I^{\ominus}$
(2) $Nu^{\ominus} = I^{\ominus}$, $L^{\ominus} = Br^{\ominus}$
(3) $Nu^{\ominus} = I^{\ominus}$, $L^{\ominus} = \overset{\ominus}{C}H_2CH_3$
(4) $Nu^{\ominus} = \overset{\ominus}{C}H_2CH_3$, $L^{\ominus} = Br^{\ominus}$

48. The decreasing order of nucleophilicities of the following is

I. $Br^{\ominus}$ **II.** $MeO^{\ominus}$
III. $Me_2N^{\ominus}$ **IV.** $Me_3C^{\ominus}$

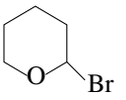
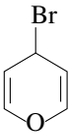
(1) I > II > III > IV (2) IV > III > II > I
(3) IV > III > I > II (4) II > I > III > IV

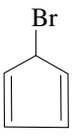
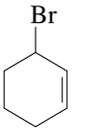
49. Which of the following is best classified as heterocyclic aromatic compound?

(1)  (2) 

(3)  (4) 

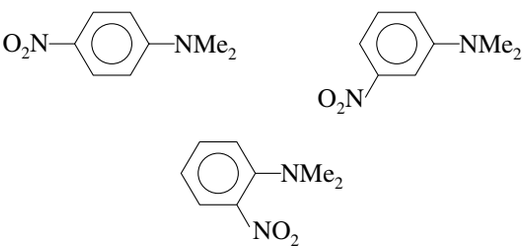
50. Among the following which is more reactive toward $AgNO_3$?

(1)  (2) 

(3)  (4) 

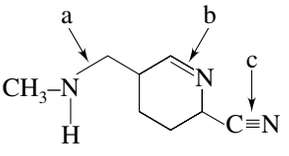
EXERCISE 2

1. The correct order of resonance energy in the following is:



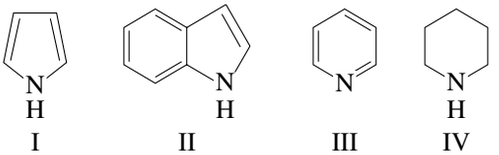
(1) II > I > III (2) I > II > III
(3) III > II > I (4) II > III > I

2. Rank the indicated bond in the given compound in order of decreasing bond strength:



(1) a > b > c (2) c > b > a
(3) b > c > a (4) c > a > b

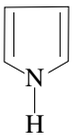
3. The correct order of basicity of the compounds is-



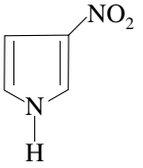
I II III IV

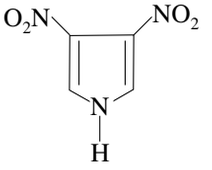
(1) IV > III > II > I (2) III > IV > I > II
(3) IV> III > I > II (4) III > IV > II > I

4. The weakest base amongst the following is:

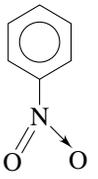
(1) 

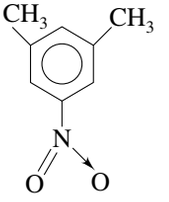
(2) 

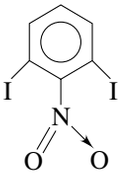
(3) 

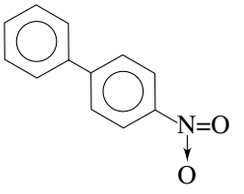
(4) 

5. In which of the following molecules, $-NO_2$ group is not coplanar with phenyl ring?

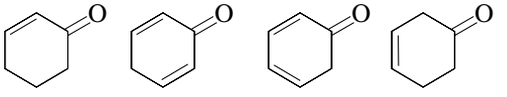
(1) 

(2) 

(3) 

(4) 

6. Among these compounds, which one has maximum resonance energy?

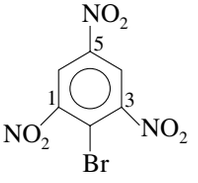


(I) (II) (III) (IV)

(1) I (2) II

(3) III (4) IV

7. Which of the following statements would be true about this compound?



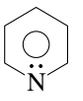
(1) All three C–N bonds are of same length

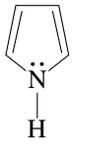
(2) C_1–N and C_3–N bonds are of same length but shorter than C_5–N bond

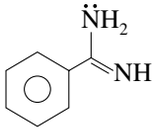
(3) C_1–N and C_3–N bonds are of same length but longer than C_5–N bond

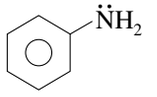
(4) C_1–N and C_3–N bonds are of different length but both are longer than C_5–N bond

8. The decreasing order of basic characters of the following is:

I. 

II. 

III. 

IV. 

(1) III > I > IV > II (2) II > I > IV > II

(3) IV > III > II > I (4) I > II > III > IV

9. The decreasing order of nucleophilicities of the following is:

I. H_2O **II.** EtOH

III. $MeCOO^{\ominus}$ **IV.** $\overset{\ominus}{O}H$

V. $EtO^{\ominus}$

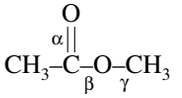
(1) I > II > III > V > IV

(2) I > II > III > IV > V

(3) IV > V > III > II > I

(4) V > IV > III > II > I

10. α, β and γ are three (C–O) bonds in methyl acetate;

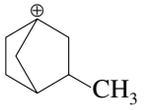


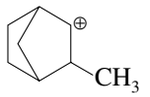
the bond lengths are in the order:

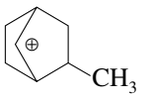
(1) α > β > γ (2) α < β < γ

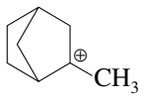
(3) α = β = γ (4) α < β = γ

11. Which of the following carbonium ion is the most stable?

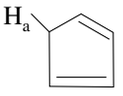
(1) 

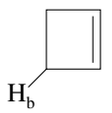
(2) 

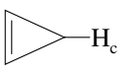
(3) 

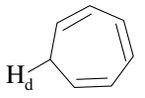
(4) 

12. Which of the following will have the lowest pK_a value?

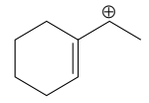
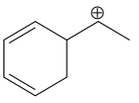
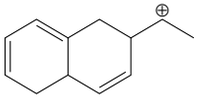
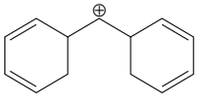
(1) 

(2) 

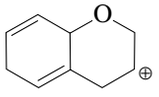
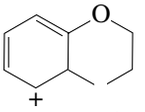
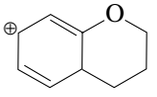
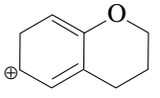
(3) 

(4) 

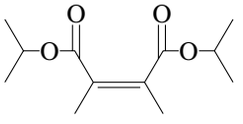
13. The most stable carbocation is:

(1) 
(2) 
(3) 
(4) 

14. Which of the following is most stable cation?

(1) 
(2) 
(3) 
(4) 

15. A synthetic cockroach repellent has following structure,



The compound contains:

(1) sp^3 and sp^2-hybridised carbon atom
(2) Only sp^2-hybridised carbon atom
(3) sp, sp^2 and sp^3-hybridised carbon atom
(4) Only sp^3-hybridised carbon atom

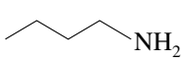
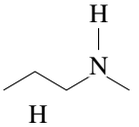
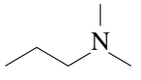
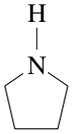
16. The correct order of increasing nucleophilicity in protic solvent is:

(1) $SH^{\ominus} > CN^{\ominus} > I^{\ominus} > OH^{\ominus} > N_3^{\ominus}$
(2) $N_3^{\ominus} > OH^{\ominus} > I^{\ominus} > CN^{\ominus} > SH^{\ominus}$
(3) $CN^{\ominus} > SH^{\ominus} > I^{\ominus} > OH^{\ominus} > N_3^{\ominus}$
(4) $OH^{\ominus} > CN^{\ominus} > SH^{\ominus} > I^{\ominus} > N_3^{\ominus}$

17. Which of the following is anti aromatic?

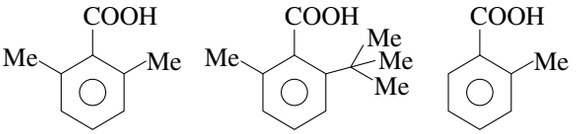
(1) Cyclopentadienyl anion
(2) Cyclopentadienyl cation
(3) Cycloheptatrienyl cation
(4) Anthracene

18. What is the increasing order of basic strength of the following compounds in aqueous solution?

(I) 
(II) 
(III) 
(IV) 

(1) I < II < III < IV
(2) I < II < IV < III
(3) III < I < II < IV
(4) III < I < IV < II

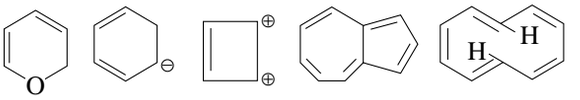
19. Arrange in increasing order of pK_b value of given substance:



(I) (II) (III)

(1) I < II < III
(2) III < I < II
(3) II < I < III
(4) II < III < I

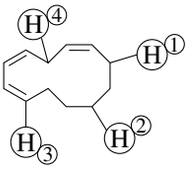
20. Which of the following compounds are aromatic?



(I) (II) (III) (IV) (V)

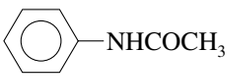
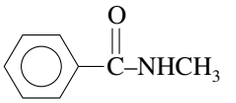
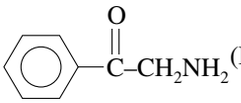
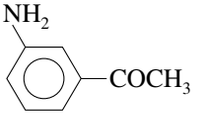
(1) III and IV
(2) I and II
(3) II, III and IV
(4) III, IV and V

21. Arrange them in increasing bond dissociation energy of C–H bond:



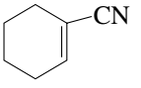
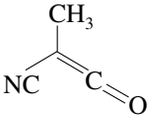
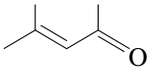
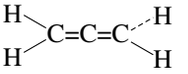
(1) 1 > 2 > 3 > 4
(2) 4 > 3 > 2 > 1
(3) 4 > 1 > 3 > 2
(4) 3 > 2 > 1 > 4

22. The correct order of basic strength of the following is:

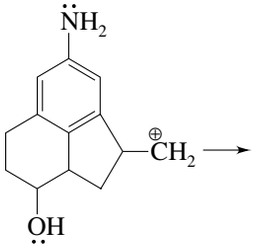
(I) 
(II) 
(III) 
(IV) 

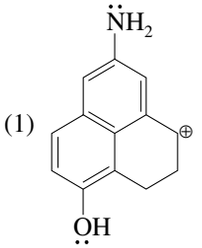
(1) I > II > III > IV
(2) IV > II > III > I
(3) III > IV > II > I
(4) III > II > IV > I

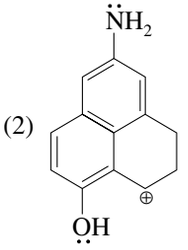
23. Which of the following molecules does not contain sp^3 hybridised carbon atoms?

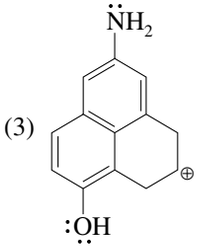
(1) 
(2) 
(3) 
(4) 

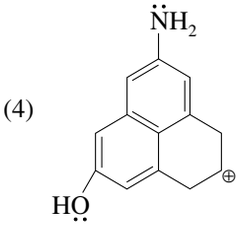
24. Following carbocation rearranges to from:



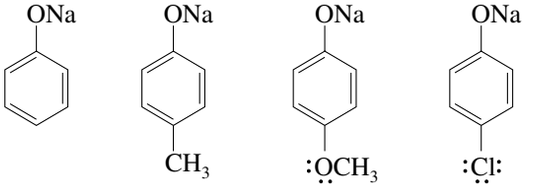
(1) 

(2) 

(3) 

(4) 

25. The correct nucleophilicity order is:

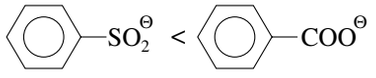


(1) (2) (3) (4)

(1) 1 > 2 > 3 > 4 (2) 3 > 2 > 1 > 4

(3) 3 > 2 > 4 > 1 (4) 2 > 1 > 3 > 4

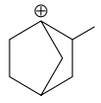
26. The correct leaving group ability has been mentioned in the option

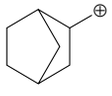
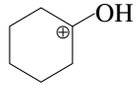
(1) 

(2) $CF_3SO_3^{\ominus} > CCl_3SO_3^{\ominus}$

(3) $I^{\ominus} < {}^{\ominus}CN$ (4) ${}^{\ominus}NH_2 > {}^{\ominus}OH$

27. Find out correct stability order in the following carbocations:

(I)  (II) 

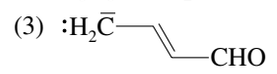
(III)  (IV) 

(1) IV > I > III > II (2) IV > III > I > II

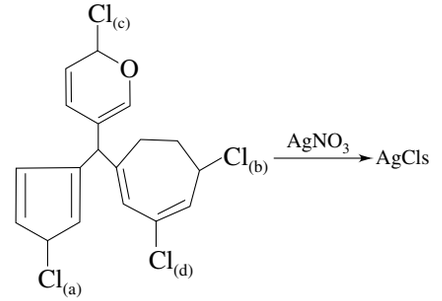
(3) I > IV > III > II (4) I > III > IV > II

28. The most unstable carbanion among the following is:

(1) $H_5C_6 - \overset{\ominus}{\ddot{C}}H_2$ (2) $\overset{\ominus}{\ddot{C}}Cl_3$

(3)  (4) $:\overline{C}_6H_5$

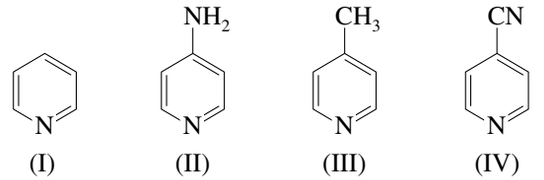
29. Which Cl will eliminate with fastest rate in the form of $Cl^{\ominus}$ to form AgCl?



(1) $Cl_{(c)}$ (2) $Cl_{(b)}$

(3) $Cl_{(a)}$ (4) $Cl_{(d)}$

30. The correct order of increasing basic nature for the following compounds is:

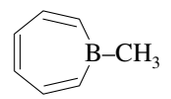


(I) (II) (III) (IV)

(1) IV < I < III < II (2) I < II < III < IV

(3) IV < III < II < I (4) II < IV < I < III

31. The compound shown is planar and all the carbon-carbon bond lengths are the same. What can you deduce about the bonding of boron from these observations?



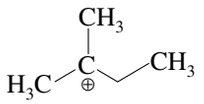
(1) The boron is sp^2-hybridised and the p-orbital contains an unshared pair of electrons

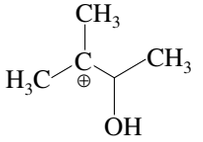
(2) The boron is sp^2-hybridised and a hybrid orbital contains an unshared pair of electrons

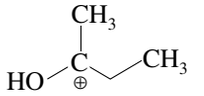
(3) The boron is sp^2-hybridised and a hybrid orbital is vacant

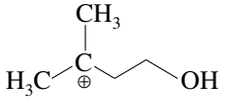
(4) The boron is sp^2-hybridised and the p-orbital is vacant

32. Which of the following cations is the most stable?

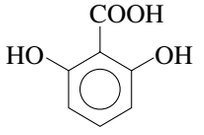
(1) 

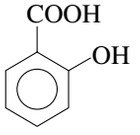
(2) 

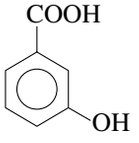
(3) 

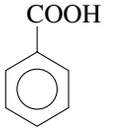
(4) 

33. The decreasing order of acidic character of the following is:

(I) 

(II) 

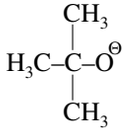
(III) 

(IV) 

(1) I > II > III > IV (2) III > IV > II > I

(3) IV > III > II > I (4) I > II > IV > III

34. Consider the following nucleophiles (A) and (B)

(A)  (B) $HO^{\ominus}$

Select correct statements about (A) and (B)

(1) A is weaker nucleophile and weaker base compared to B which is stronger nuclephile and stronger base

(2) A is stronger nucleophile and stronger base compared to B which is weaker nuclephile and weaker base

(3) A is weaker nucleophile and stronger base compared to B which is strong nuclephile and weaker base

(4) None of these

35. Which of the following is the incorrect order of bond lengths?

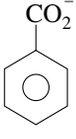
(1) C – C > C = C > C ≡ C > C ≡ N

(2) C = N > C = O > C = C > C = S

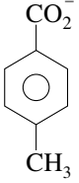
(3) C = C > C = N > C = O > C ≡ N

(4) C – C > C = C > C ≡ C > C – H

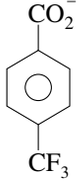
36. Arrange in increasing order of leaving group ability:



(I)



(II)



(III)

(1) II < I < III (2) I < III < II

(3) III < II < I (4) I = II = III

37. Arrange these compounds in the increasing order of their aromatic character

(A)

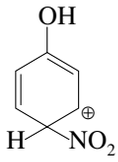
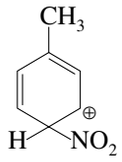
(B)

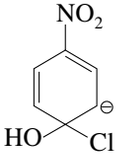
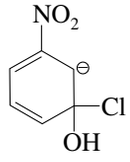
(C)

(1) C, B, A (2) A, B, C

(3) A, C, B (4) A = B = C

38. Consider the following statement:

(I)  is more stable than 

(II)  is more stable than 

(1) I and II both are correct

(2) I and reverse of II are correct

(3) II and reverse of I are correct

(4) I and II both are incorrect

39. Arrange the CH_3COO^-, $C_6H_5O^-$ and $C_6H_5SO_3^-$ anions as leaving group in the decreasing order if the pK_a values of their conjugate acids are 4.5, 10 and 2.6 respectively

(1) $C_6H_5SO_3^- > CH_3COO^- > C_6H_5O^-$

(2) $C_6H_5O^- > CH_3COO^- > C_6H_5SO_3^-$

(3) $CH_3COO^- > C_6H_5SO_3^- > C_6H_5O^-$

(4) $CH_3COO^- > C_6H_5SO_3^- > C_6H_5O^-$

40. The order of decreasing nucleophilicities of the following species is:

(1) $CH_3\overset{\ominus}{S} > CH_3\overset{\ominus}{O} > CH_3C\overset{\ominus}{O}O > CH_3OH$

(2) $CH_3C\overset{\ominus}{O}O > CH_3\overset{\ominus}{S} > CH_3\overset{\ominus}{O} > CH_3OH$

(3) $CH_3OH > CH_3\overset{\ominus}{S} > CH_3C\overset{\ominus}{O}O > CH_3\overset{\ominus}{O}$

(4) $CH_3\overset{\ominus}{O} > CH_3OH > CH_3C\overset{\ominus}{O}O > CH_3\overset{\ominus}{S}$

EXERCISE 3

One and More Than One Option Correct Type Question

1. Among the following which statement is correct?

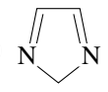
(1) 4 nitrophenol is more acidic than 3,5-dimethyl-4-nitrophenol

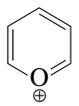
(2) Among R_2NH,  and $R-C\equiv\ddot{N}$ weakest base is $R-C\equiv\ddot{N}$

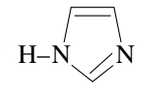
(3) Bridge head carbocation is rarely formed

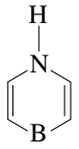
(4) p-fluorophenol is stronger acid than p-chlorophenol

2. Which of the following are aromatic?

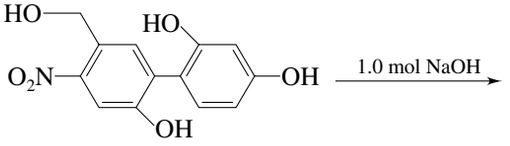
(1) 

(2) 

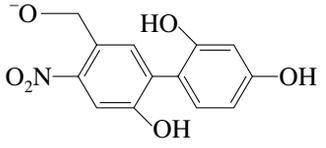
(3) 

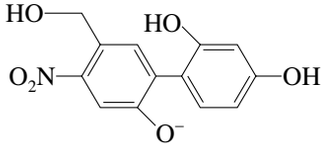
(4) 

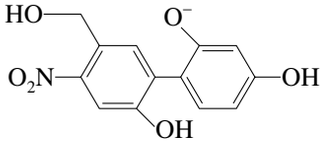
3. Predict the major product in the following reaction.

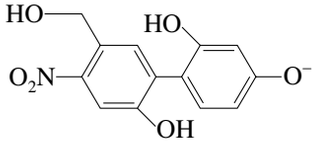


1.0 mol

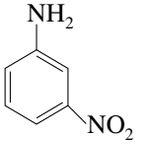
(1) 

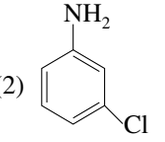
(2) 

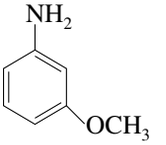
(3) 

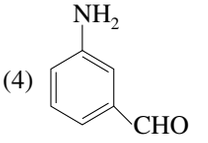
(4) 

4. Which of the following is/are more basic than its own para-isomer?

(1) 

(2) 

(3) 

(4) 

5. In which of the following the first anion is more stable than the second?

(1) $O_2N-\overset{\ominus}{C}H_2$ and $F-\overset{\ominus}{C}H_2$

(2) $\overset{\ominus}{C}F_3$ and $\overset{\ominus}{C}Cl_3$

(3) $F_3C-\overset{\ominus}{C}H_2$ and $Cl_3C-\overset{\ominus}{C}H_2$

(4) $CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H_2$ and $H_2N-\overset{\ominus}{C}H_2$

6. In the vinyl cation, the positively charged carbon is sp hybridised. Which statement about the hybridisation type of the negatively charged carbon in the vinyl carbanion is incorrect?

(1) The carbon is sp hybridised to help to stabilise the orbital with the lone pair

(2) The carbon is sp hybridised to maximise s-character in the orbital with the lone pair

(3) The carbon is sp hybridised to minimise repulsion between the bonding and non-bonding electrons

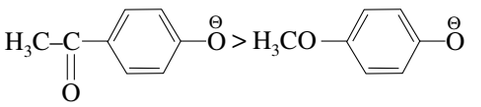
(4) The carbon is sp^2 hybridised to minimise angle strain around pi-bond

7. Which of the following is correct order of nucleophilicity in CH_3OH ?

(1) $\ddot{N}H_3 < \ddot{N}H_2 - \ddot{N}H_2$

(2) $CH_3CH_2\overset{\ominus}{O} > \overset{\ominus}{O}H > CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}$

(3) $F^{\ominus} > Cl^{\ominus} > Br^{\ominus} > I^{\ominus}$

(4) 

8. What is/are true regarding a reactive intermediate formed in a reaction?

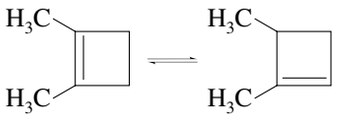
(1) It is the species present at the maxima of the activation energy diagram

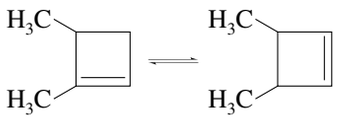
(2) It is formed for infinitesimal time only, cannot be isolated practically

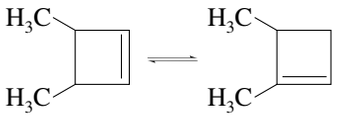
(3) The most stable reactive intermediate leads to the formation of major product

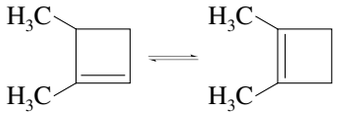
(4) It is responsible for more than one product in a reaction

9. Which of the following process is/are exothermic?

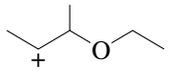
(1) 

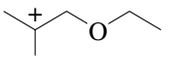
(2) 

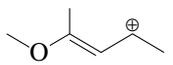
(3) 

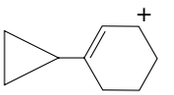
(4) 

10. Which of the following carbocation (s) undergo favourable rearrangement into more stable one?

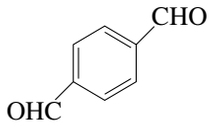
(1) 

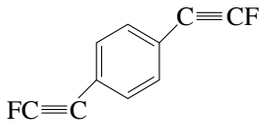
(2) 

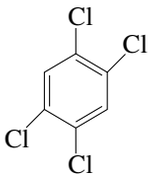
(3) 

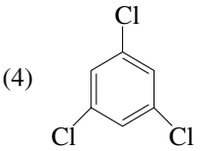
(4) 

11. Which of the following (s) is/are non-polar?

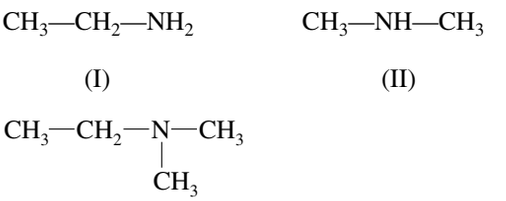
(1) 

(2) 

(3) 

(4) 

12. Consider the following amines.



(I) (II) (III)

Which of the following statements is/are correct regarding their basicity?

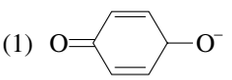
(1) In aqueous solution, the increasing basicity is I < II < III

(2) In gas phase, the basic strength follows the order I < II < III

(3) The pKa values of these amines in gas phase is in the order III < II < I

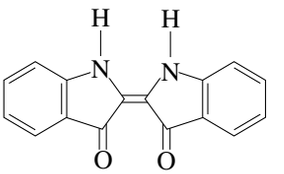
(4) In aqueous solution, II evolve maximum heat on the basis of per mol when neutralised by adding excess of HCl

13. In which of the following, all C—O bonds are of equal length?

(1)  (2) $CH_3—COO^-$

(3) HCO_3^- (4) NO_2^-

14. Consider the molecule indigotin



The correct statement (s) regarding the compound (indigotin) is/are

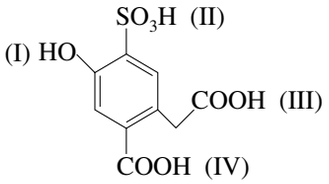
(1) In exhibit geometrical isomerism and its trans isomer is more stable

(2) It exhibit enantiomerism

(3) Its 'CiS' isomer has greater solubility in water than the trans one

(4) It is a planar molecule with very large resonance stabilisation energy

15. Which of the following statement applies correctly regarding acidity of the following acid?



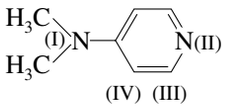
(1) One mole of acid would require 4.0 mol of NaOH for complete neutralisation

(2) Proton labelled II will be deprotonated first during neutralisation

(3) On treatment with $NaHCO_3$, its one mole would require two moles of base

(4) The acid is stronger than both benzene sulphonic acid and benzoic acid

16. Which of the following deduction regarding following base is/are true?



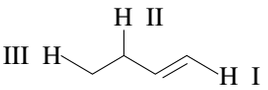
(1) Nitrogen I is protonated first during stepwise neutralisation

(2) Nitrogen II is protonated first during stepwise neutralisation

(3) Conjugate acid has a resonance structure with complete valence shells of all atoms

(4) $-OCH_3$ group at IV will increase basic strength while the same from positions III will decrease basic strength

17. The correct statement(s) concerning the labelled hydrogens in the following molecule is/are



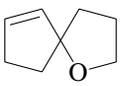
(1) II undergo easiest homolytic bond fission in a chemical reaction

(2) Amongst the labelled hydrogens, C—H II has greatest bond length

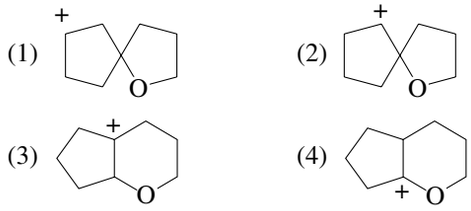
(3) Amongst the labelled hydrogens C—H I has the shortest bond length

(4) Hydrogens labelled I and II take part in hyperconjugation

18. Alkenes on electrophilic attack by H^+ forms carbocation. Which is/are the probable carbocation possible in this reaction?



$\xrightarrow{H+}$ Most stable carbocation



Assertion and Reason Type Question

(1) If both Statement-I and Statement-II are correct and Statement-II is the correct explanation for Statement-I

(2) If both Statement-I and Statement-II are correct and Statement-II is not the correct explanation for Statement-I

(3) If Statement-I is correct and Statement-II is incorrect

(4) If Statement-I is incorrect and Statement-II is correct

19. Statement-1: In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.

Statement-2: The amino group being completely protonated in strongly acidic solution, the lone pair of electrons of the nitrogen is no longer available for resonance.

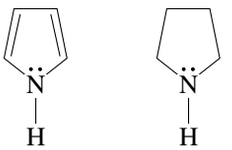
20. Statement-1: $Me-\overset{\oplus}{C}H_2$ is more stable than $MeO-CH_2^{\oplus}$

Statement-2: Me is a + I group where as MeO is a – I group

21. Statement-1: $\ddot{C}F_2$ is good electrophile than $:CCl_2$

Statement-2: Electronegativity of F is greater than electronegativity of Cl.

22. Statement-1: Pyrrolidine (II) is more basic than pyrrole (I)



(I) (II)

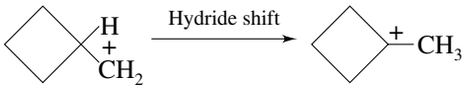
Statement-2: Protonated pyrrole has resonance stabilisation of positive charge in aromatic ring.

23. Statement-1: The difference between Ka_1, and Ka_2 for dicarboxylic acids of type

decreases as n increases

Statement-2: On increasing n the – I effect of – COOH group decreases (Ka_1, decreases) also + I effect of $-COO^-$ group decreases (Ka_2 increases)

24. **Statement-I:** Following is a favourable rearrangement of carbocation:

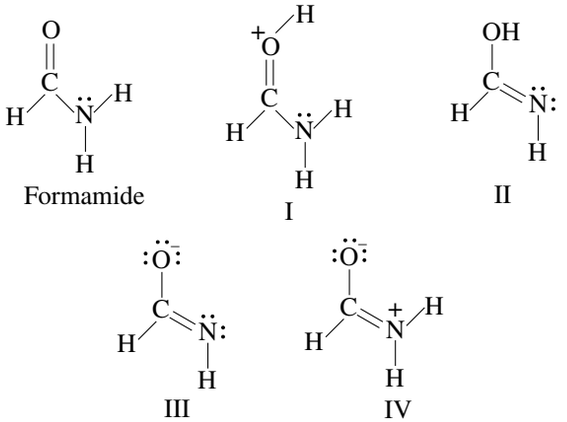


Statement-II: A tertiary alkyl carbocation is more stable than primary alkyl carbocation.

Comprehension Type Question

Comprehension (Q. 25–27)

Amide is a conjugated system, exhibit resonance, Following are formamide and structures that bear some relationship to the Lewis structure of formamide.



25. Which is a resonance contributor to formamide?

(1) Only I (2) Only II

(3) Only III (4) Only IV

26. Which represents a conjugate acid of formamide?

(1) Only I (2) Only II

(3) Only III (4) Only IV

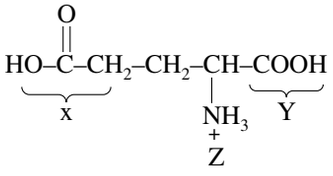
27. Which is capable of showing stereoisomerism?

(1) Only I (2) Only II

(3) Only III (4) Only IV

Comprehension (Q. 28–30)

Consider the following amino acid (protonated) to answer the next three questions.



28. the order of acidic strength of X, Y and Z is

(1) X > Y > Z (2) Z > X > Y

(3) Y > Z > X (4) Y > X > Z

29. If the amino acid shown above is treated with 1.0 mole of NaOH, the species formed is

(1) $\bar{O}CO–CH_2CH_2–\underset{\overset{+}{NH_3}}{CH}–COOH$

(2) $HOOC–CH_2CH_2–\underset{\overset{+}{NH_3}}{CH}–COO^-$

(3) $HOCO–CH_2CH_2–\underset{NH_2}{CH}–COOH$

(4) $HOOC–CH_2CH_2–\underset{NH_3}{CH}–O^-$

30. If the above amino acid is treated with excess of NaOH, what would be formed?

(1) $\bar{O}OC–CH_2CH_2–\underset{NH_2}{CH}–COO^-$

(2) $HOOC–CH_2CH_2–\underset{NH_2}{CH}–COO^-$

(3) $\bar{O}OC–CH_2CH_2–\underset{\overset{+}{NH_2}}{CH}–COO^-$

(4) $\bar{O}OC–CH_2CH_2–\underset{NH_2}{CH}–COOH$

Column Matching Type Question

31. Match the following: (More than one option in column-II may match with single option in column-I). Match the hybridisation state of below listed carbon atoms.

$CH_2=C=CH–CH_2–C\equiv C–CH_2–NH_2$

Column-I	***Column-I***
Carbon atoms	***Hybridization state***
(A) C_1	(P) sp
(B) C_2	(Q) sp^2
(C) C_5	(R) sp^3
(D) C_6	(S) dsp^2

(1) A → P; B → Q; C → R; D → S

(2) A → S; B → P; C → Q; D → R

(3) A → R; B → Q; C → P; D → S

(4) A → R; B → P; C → Q; D → P

32.

Column-I	***Column-II***
(A) $A – B \rightarrow A^+ + :B^-$	(p) Free radical
(B) $CH_3\overset{\oplus}{C}H–CH_3$	(q) Heterolytic cleavage
(C) $A – A \rightarrow \dot{A} + \dot{A}$	(r) Carbocation

(D) $CH_2N_2 \rightarrow \ddot{C}H_2 + N_2$ (s) Nucleophile

(E) $CH_3\ddot{O}H$ (t) Carbene

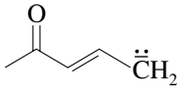
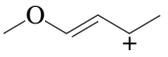
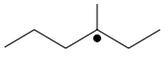
(1) A → q; B → r; C → p; D → s; E → t

(2) A → q; B → p; C → r; D → t; E → s

(3) A → r; B → q; C → p; D → t; E → s

(4) A → q; B → r; C → p; D → t; E → s

33. Column-I has listed some common reactive intermediates and column-II has listed some of the properties possessed by these intermediates. Match the quantity from column-I with the quantities from Column-II

Column-I	***Column-II***
(A) 	(p) Has more stable resonance structure
(B) 	(q) Paramagnetic
(C) 	(r) Hyperconjugation stabilises the intermediates
(D) $:CH_2$	(s) Acts as a strong Lewis acid

(1) A → q; B → p; C → q, s; D → p, r

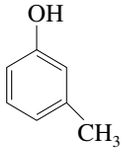
(2) A → p; B → q; C → r; D → s

(3) A → s; B → r; C → p; D → q

(4) A → p; B → p, r, s; C → q, r; D → q, s

Single Digit Integer Type Question

34. How many of the following are stronger acid than phenol?



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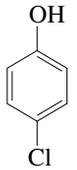

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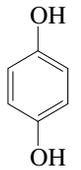

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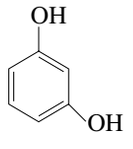

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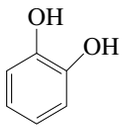

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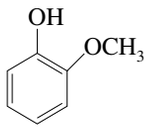
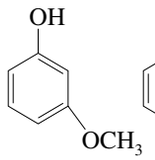


VI



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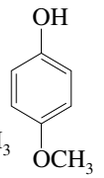
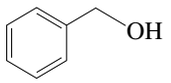
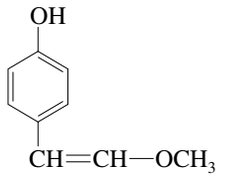


VIII

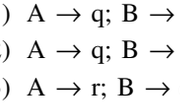


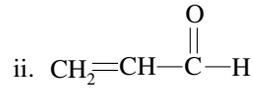
IX

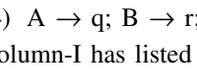


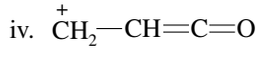
X

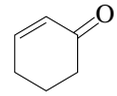
35. In how many of the following, at least one of the C—O bond is weaker than the C—O bond in acetaldehyde?

i. 

ii. 

iii. 

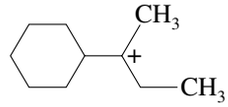
iv. 

v. 

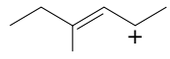
vi. CO_3^{2-}

vii. NCO^-

36. The total number of contributing structures showing hyperconjugation for the following carbocation is

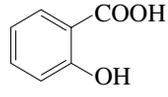


37. If the following carbocation is formed in a chemical reaction that finally bonds with bromide nucleophile, how many different bromination products are expected?

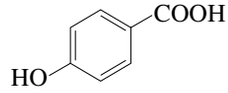


38. In carbene ($:CH_2$), what is the maximum number of valence electrons that may have same spin direction?

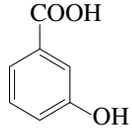
39. From the list below how many of them are stronger acid than benzoic acid



I



II



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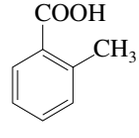

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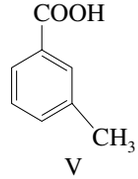
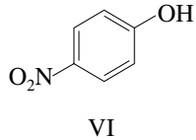
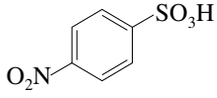


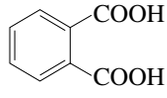
V



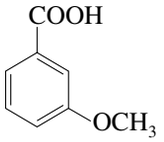
VI



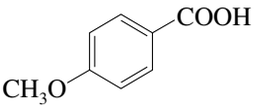
VII



VIII



IX

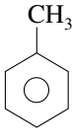


X

40. X = N Number of compound unstable at room temperature.

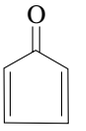
(a) 

(b) 

(c) 

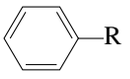
(d) 

(e) 

(f) 

EXERCISE 4

1. In the following benzyl/allyl system **[AIEEE-2002]**

$R–CH=CH_2$ or 

(R is alkyl group)

Increasing order of inductive effect is-

(1) $(CH_3)_3C– > (CH_3)_2CH– > CH_3CH_2–$

(2) $CH_3CH_2– > (CH_3)_2CH– > (CH_3)_3C–$

(3) $(CH_3)_2CH– > CH_3CH_2– > (CH_3)_3C–$

(4) $(CH_3)_3C– > CH_3CH_2– > (CH_3)_2CH–$

2. The correct order of increasing basic strength of the bases NH_3, CH_3NH_2 and $(CH_3)_2NH$ is **[AIEEE-2003]**

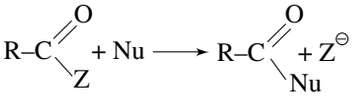
(1) $NH_3 < CH_3NH_2 < (CH_3)_2NH$

(2) $CH_3NH_2 < (CH_3)_2NH < NH_3$

(3) $CH_3NH_2 < NH_3 < (CH_3)_2NH$

(4) $(CH_3)_2NH < NH_3 < CH_3NH_2$

3. Rate of the reaction **[AIEEE-2004]**



Is fastest when Z is-

(1) Cl (2) NH_2

(3) OC_2H_5 (4) $OCOCH_3$

4. Consider the acidic nature of the carboxylic acids- **[AIEEE-2004]**

(a) PhCOOH (b) o–$NO_2C_6H_4COOH$

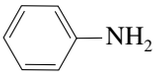
(c) p–$NO_2C_6H_4COOH$ (d) m–$NO_2C_6H_4COOH$

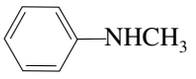
Which of the following order is correct ?

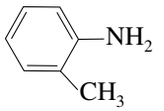
(1) a > b > c > d (2) b > d > c > a

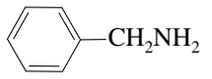
(3) b > d > a > c (4) b > c > d > a

5. Which of the following is the strongest base- **[AIEEE-2004]**

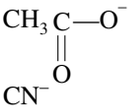
(1) 

(2) 

(3) 

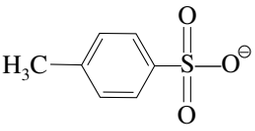
(4) 

6. The decreasing order of nucleophilicity among the nucleophiles **[AIEEE-2005]**

(a) 

(b) CH_3O^-

(c) CN^-

(d) 

(1) (d) > (c) > (b) > (a) (2) (a) > (b) > (c) > (d)

(3) (c) > (b) > (a) > (d) (4) (b) > (c) > (a) > (d)

7. Amongst the following the most basic compound is **[AIEEE-2005]**

(1) Aniline (2) benzylamine

(3) p-nitroaniline (4) acetanilide

8. The increasing order of stability of the following free radicals is– **[AIEEE-2006]**

(1) $(C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$

(2) $(C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C} < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$

(3) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H$

(4) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C}$

9. $CH_3Br + Nu^- \rightarrow CH_3 – Nu + Br^-$

The decreasing order of the rate of the above reaction with nucleophiles (Nu^-) A to D is **[AIEEE-2006]**

[Nu– = (A) PhO^-, (B) AcO^-, (C) HO^-, (D) CH_3O^-]

(1) D > C > B > A (2) A > B > C > D

(3) B > D > C > A (4) D > C > A > B

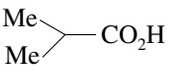
10. Among the following acids, which has the lowest pK_a value? **[AIEEE-2006]**

(1) $(CH_3)_2CH–COOH$ (2) CH_3CH_2COOH

(3) CH_3COOH (4) HCOOH

11. The correct order of increasing acid strength of the compounds- **[AIEEE-2006]**

(A) CH_3CO_2H (B) $MeOCH_2CO_2H$

(C) CF_3CO_2H (D) 

(1) B<D<A<C (2) D<A<C<B

(3) D<A<B<C (4) A<D<C<B

12. Which one of the following is the strongest base in aqueous solution? **[AIEEE-2007]**

(1) Trimethylamine (2) Aniline

(3) Dimethylamine (4) Methylamine

13. Presence of a nitro group in a benzene ring **[AIEEE-2007]**

(1) activates the ring towards electrophilic substitution

(2) renders the ring basic

(3) deactivates the ring towards nucleophilic substitution

(4) deactivates the ring towards electrophilic substitution

14. Arrange the carbanions, $(CH_3)\overset{\ominus}{C}$, $\overset{\ominus}{C}Cl_3$, $(CH_3)_2\overset{\ominus}{C}H$, $C_6H_5\overset{\ominus}{C}H_2$, in order of their decreasing stability- **[AIEEE-2009]**

(1) $(CH_3)_2\overset{\ominus}{C}H > \overset{\ominus}{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_3\overset{\ominus}{C}$

(2) $\overset{\ominus}{C}Cl_3 > C_6H_5\overset{\ominus}{C}H_2 > (CH_3)_2\overset{\ominus}{C}H > (CH_3)_3\overset{\ominus}{C}$

(3) $(CH_3)_3\overset{\ominus}{C} > (CH_3)_2\overset{\ominus}{C}H > C_6H_5\overset{\ominus}{C}H_2 > \overset{\ominus}{C}Cl_3$

(4) $C_6H_5\overset{\ominus}{C}H_2 > \overset{\ominus}{C}Cl_3 > (CH_3)_3\overset{\ominus}{C} > (CH_3)_2\overset{\ominus}{C}H$

15. The correct order of increasing basicity of the given conjugate bases (R=CH_3) is **[AIEEE-2010]**

(1) $RCOO^- > HC \equiv \bar{C} > \bar{R} < \bar{N}H_2$

(2) $\bar{R} < CH \equiv \bar{C} < RCOO^- < \bar{N}H_2$

(3) $RCOO^- < \bar{N}H_2 < CH \equiv \bar{C} < \bar{R}$

(4) $RCOO^- < CH \equiv \bar{C} < \bar{N}H_2 < \bar{R}$

16. Consider thiol anion ($RS^{\ominus}$) and alkoxy anion ($RO^{\ominus}$). Which of the following statements is correct? **[AIEEE-2011]**

(1) $RS^{\ominus}$ is less basic but more nucleophilic than $RO^{\ominus}$

(2) $RS^{\ominus}$ is more basic and more nucleophilic than $RO^{\ominus}$

(3) $RS^{\ominus}$ is more basic but less nucleophilic than $RO^{\ominus}$

(4) $RS^{\ominus}$ is less basic and less nucleophilic than $RO^{\ominus}$

17. The correct order of acid strength of the following compounds is: **[AIEEE-2011]**

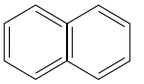
(A) Phenol (B) p-Cresol

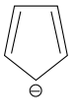
(C) m-Nitrophenol (D) p-Nitrophenol

(1) D > C > A > B (2) B > D > A > C

(3) A > B > D > C (4) C > B > A > D

18. The non aromatic compound among the following is– **[AIEEE-2011]**

(1)  (2) 

(3)  (4) 

19. Ortho-Nitrophenol is less soluble in water than p- and m-Nitrophenols because– **[AIEEE-2012]**

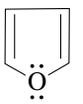
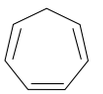
(1) o-Nitrophenol shows intramolecular H-bonding

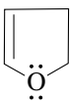
(2) o-Nitrophenol shows intermolecular H-bonding

(3) Melting point of o-Nitrophenol is lower than those of m-and p-isomers.

(4) o-Nitrophenol is more volatile in steam than those of m-and p-isomers

20. Which of the following compounds are antiaromatic **[AIEEE Online-2012]**

(I)  (II) 

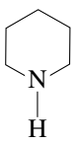
(III)  (IV) 

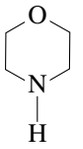
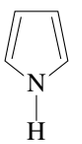
(V)  (VI) 

(1) (III) and (VI) (2) (V) and (VI)

(3) (I) and (V) (4) (I) and (IV)

21. In the following compounds: **[AIEEE Online-2012]**

(1)  (II) 

(III)  (IV) 

The order of basicity is as follows:

(1) IV > III > II > I (2) II > III > I > IV

(3) I > III > II > IV (4) III > I > II > IV

22. Dipole moment is shown by:

[AIEEE Online-2012]

(1) trans-2, 3-dichloro-2-butene

(2) 1, 2-dichlorobenzene

(3) 1, 4-dichlorobenzene

(4) trans-1, 2-dinitroethene

23. Which of the following cannot be represented by resonance structures?

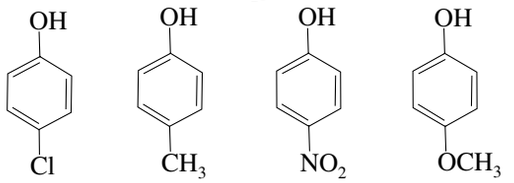
[AIEEE Online-2012]

(1) Dimethyl ether (2) Carboxylate anion

(3) Toluene (4) Nitrate anion

24. Arrange the following compounds in order of decreasing acidity:

[JEE Main online-2012]



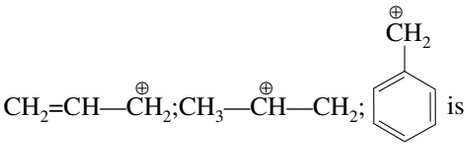
(I) (II) (III) (IV)

(1) III > I > II > IV (2) IV > III > I > II

(3) II > IV > I > III (4) I > II > III > IV

25. The order of stability of the following carbocations

[JEE Main Online-2013]



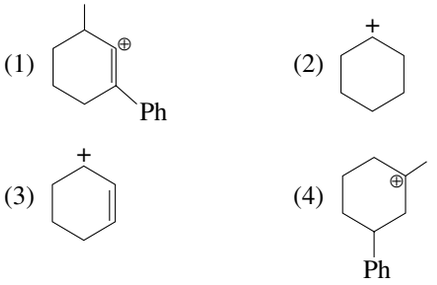
(I) (II) (III)

(1) I > II > III (2) III > I > II

(3) III > II > I (4) II > III > I

26. Which one of the following is the most stable?

[JEE Main Online-2013]



27. The order of basicity of amines in gaseous state is

[JEE Main Online-2013]

(1) 1° > 2° > 3° > NH_3 (2) 3° > 2° > NH_3 > 1°

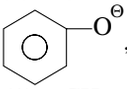
(3) 3° > 2° > 1° > NH_3 (4) NH_3 > 1° > 2° > 3°

28. In nucleophilic substitution reaction, order of halogens as incoming (attacking) nucleophile is should be-

[JEE Main Online-2013]

(1) $Br^- > I^- > Cl^-$ (2) $I^- > Br^- > Cl^-$

(3) $Cl^- > Br^- > I^-$ (4) $Cl^- > I^- < Br^-$

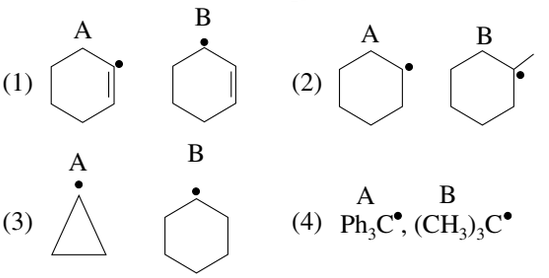
29. Which one of the following substituents at position is most effective in stabilising the phenoxide  , ion? **[JEE Main Online-2014]**

(1) $–CH_3$ (2) $–OCH_3$

(3) $–COCH_3$ (4) $–CH_2OH$

30. In which of the following pairs A is more stable than B?

[JEE main Online-2014]



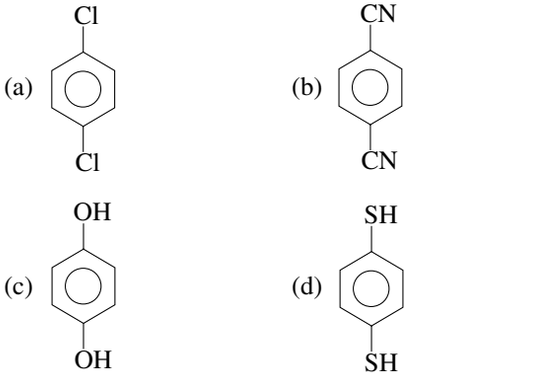
31. Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value?

[JEE Main Online-2014]

(1) CH_3NH_2 (2) $(CH_3)_3N$

(3) $C_6H_5NH_2$ (4) $(CH_3)_2NH$

32. or which of the following molecule significant $\mu \neq 0$? **[JEE Main Online-2014]**

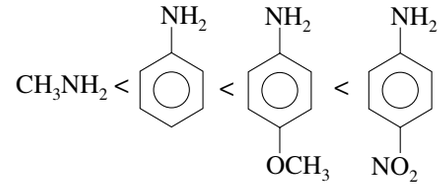


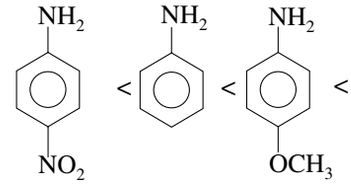
(1) a and b (2) only c

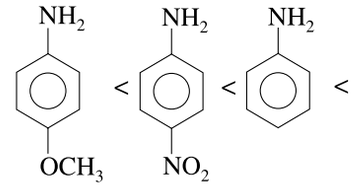
(3) c and d (4) only a

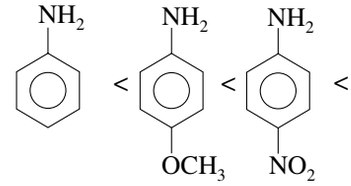
33. Arrange the following amines in the order of increasing basicity

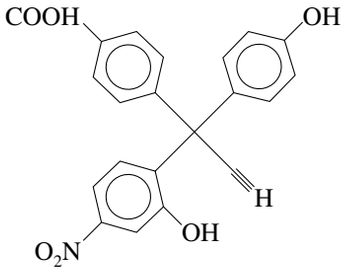
JEE Main Online-2015]

(1) $CH_3NH_2 <$  $<$ $<$

(2)  $< CH_3NH_2$

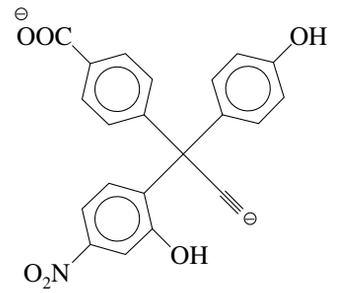
(3)  $< CH_3NH_2$

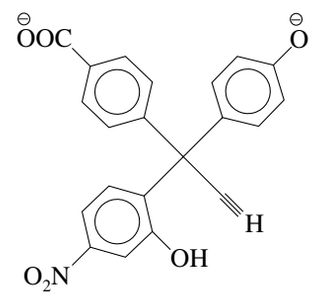
(4)  $< CH_3NH_2$

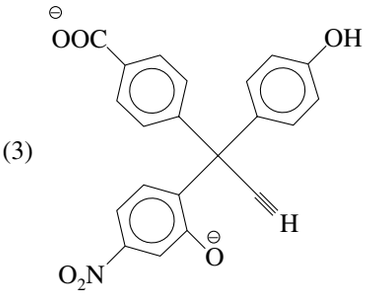
34. 

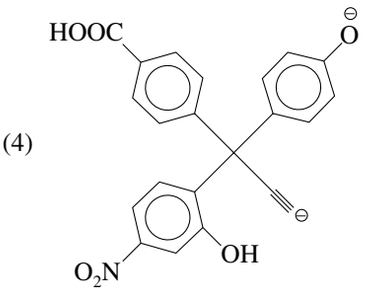
[IIT-2003]

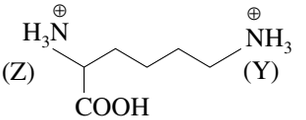
When X is made to react with 2 eq. of $NaNH_2$ the product formed will be -

(1) 

(2) 

(3) 

(4) 

35. (Z)  (Y)

(X)

Correct order of acidic strength is:

[IIT-2004]

(1) x > y > z (2) z > y > x

(3) y > z > x (4) x > z > y

36. For-1-methoxy-1, 3-butadiene, which of the following resonating structure is least stable?

[IIT-2005]

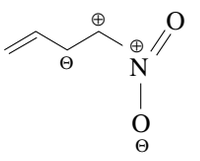
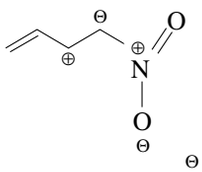
(1) $\overset{\ominus}{C}H_2–\overset{\oplus}{C}H–CH–CH=CH–O–CH_3$

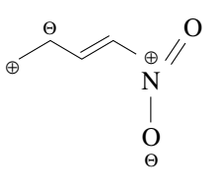
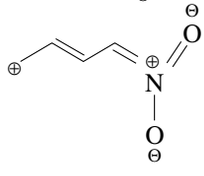
(2) $\overset{\ominus}{C}H_2–CH=CH–CH–\overset{\oplus}{O}–CH_3$

(3) $CH_2=CH–\overset{\oplus}{C}H=\overset{\ominus}{C}H–O–CH_3$

(4) $CH_2=CH–\overset{\ominus}{C}H–CH=\overset{\oplus}{O}–CH_3$

37. Among the following, the least stable resonance structure is: **[IIT-2007]**

(1)  (2) 

(3)  (4) 

38. **Statement-1**: *p*-Hydroxybenzoic acid has a lower boiling point that *o*-hydroxybenzoic

Statement-2: *o*-Hydroxybenzoic acid has intramolecular hydrogen bonding. **[IIT-2007]**

(1) If both Statement-I and Statement-II are correct and Statement-II is the correct explanation for Statement-I

(2) If both Statement-I and Statement-II are correct and Statement-II is not the correct explanation for Statement-I

(3) If Statement-I is correct and Statement-II is incorrect

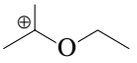
(4) If Statement-I is incorrect and Statement-II is correct

39. Hyperconjugation involves overlap of the following orbitals **[IIT-2008**

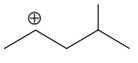
(1) $\sigma - \sigma$ (2) $\sigma - p$

(3) $p - p$ (4) $\pi - \pi$

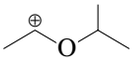
40. The correct stability order for the following species is- **[IIT-2008]**



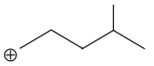
(I)



(II)



(III)

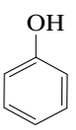


(IV)

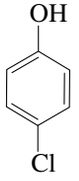
(1) II > IV > I > III (2) I > II > III > IV

(3) II > I > IV > III (4) I > III > II > IV

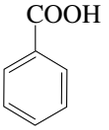
41. The correct acidity order of the following is **[IIT-2009]**



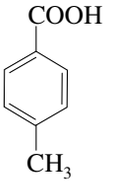
(I)



(II)



(III)

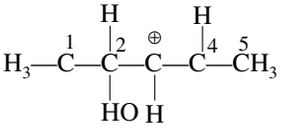


(IV)

(1) III > IV > II > I (2) IV > III > I > II

(3) III > II > I > IV (4) II > III > IV > I

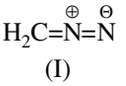
42. In the following carbocation, H/CH_3 that is most likely to migrate to the positively charged carbon is- **[IIT-2009]**



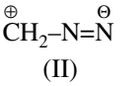
(1) CH_3 at C – 4 (2) H at C– 4

(3) CH_3 at C – 2 (4) H at C – 2

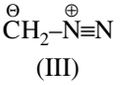
43. The correct stability order of the following resonance structures is-



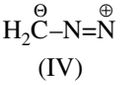
(I)



(II)



(III)



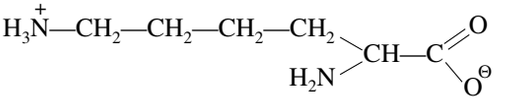
(IV)

[IIT-2009]

(1) I > II > IV > III (2) I > III > II > IV

(3) II > I > III > IV (4) III > I > IV > II

44. Out of the following the alkene that exhibits optical isomerism is

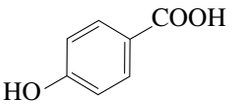


[IIT-2010]

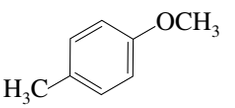
(1) 1 (2) 2

(3) 3 (4) 4

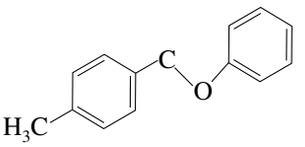
45. The compounds P, Q and S **[IIT-2010]**



(P)



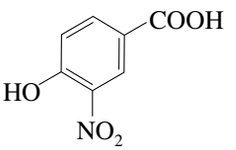
(Q)



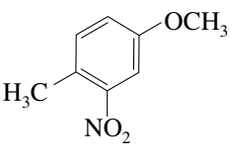
(S)

were separately subjected to nitration using HNO_3/ H_2SO_4 mixture. The major product formed in each case respectively, is

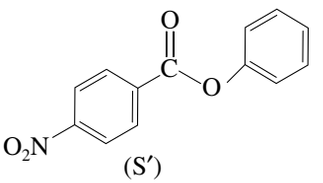
(1)



(P′)

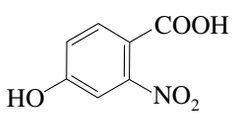


(Q′)

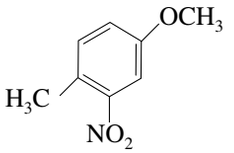


(S′)

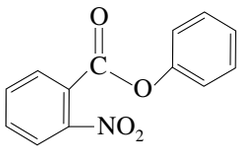
(2)



(P′)

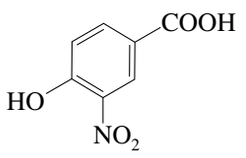


(Q′)

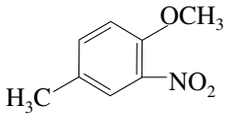


(S′)

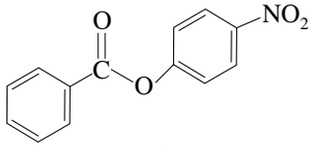
(3)



(P′)

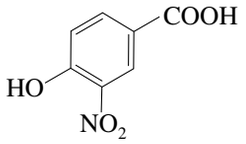


(Q′)

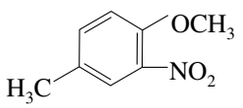


(S′)

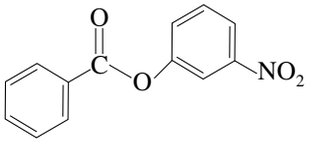
(4)



(P′)



(Q′)



(S′)

46. Among the following compounds, the most acidic is- **[IIT-2011]**

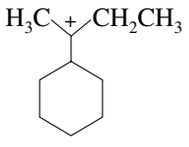
(1) p-nitrophenol

(2) p-hydroxybenzoic acid

(3) o-hydroxybenzoic acid

(4) p-toluic acid

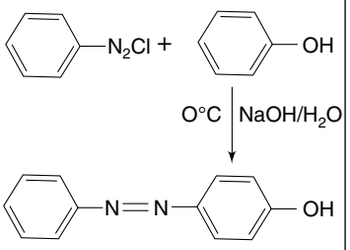
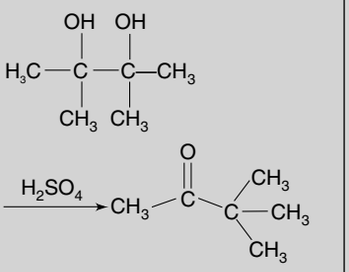
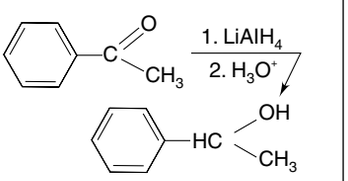
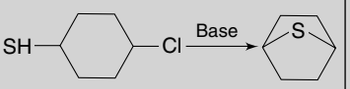
47. The total number of contributing structures showing hyperconjugation (involving C–H bonds) for the following carbocation is **[IIT-2011]**



(1) 6 (2) 4

(3) 3 (4) 2

48. Match the column reaction in Column I with appropriate options in Column II. **[ITT Adv. 2011]**

	Column I		Column II
i.		p.	Racemic mixture
ii.		q.	Addition reaction
iii.		r.	Substitution reaction
iv.		s. t.	Coupling reaction Carbocation intermediate

Codes

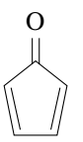
	i	ii	iii	iv
(1)	r, s	t	p, q	q
(2)	p	r, s	q, s	t
(3)	r, s	p	t	r, s
(4)	q	t	p, t	q, r

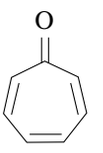
49. Which of the following molecules, in pure form, is (are) **unstable** at room temperature?

[IIT-2012]

(1) 

(2) 

(3) 

(4) 

50. In allene (C_3H_4), the type(s) of hybridisation of the carbon atoms, is (are) **[ITT Adv. 2012]**

(1) sp ad sp^3 (2) sp and sp^2

(3) only sp^3 (4) sp^2 and sp^3

51. The hyperconjugative stabilities of tert-butyl cation and 2-butene, respectively, are due to **[IIT-2013]**

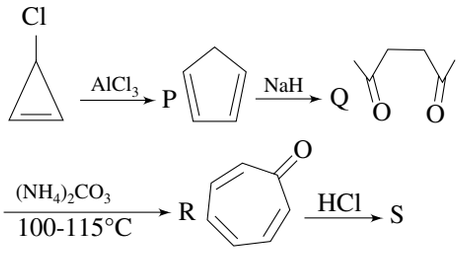
(1) $\sigma \rightarrow$ p(empty) and $\sigma \rightarrow \pi^*$ electron delocalisations

(2) $\sigma \rightarrow \sigma^*$ and $\sigma \rightarrow \pi$ electron delocalisations

(3) $\sigma \rightarrow$ p (filled) and $\sigma \rightarrow \pi$ electron delocalisations

(4) p(filled) $\rightarrow \sigma \rightarrow \pi^*$ electron delocalisations

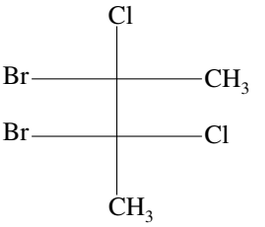
52. Among P, Q, R and S, the aromatic compound(s) is/are **[IIT Adv. 2013 (MCQ)]**



(1) P (2) Q

(3) R (4) S

53. The total number(s) of stable conformers with non-zero dipole moment for the following compound is (are) **[JEE(Adv)-2014]**



54. Hydrogen bonding plays a central role in the following phenomena: **[JEE Adv-2014 (MCQ)]**

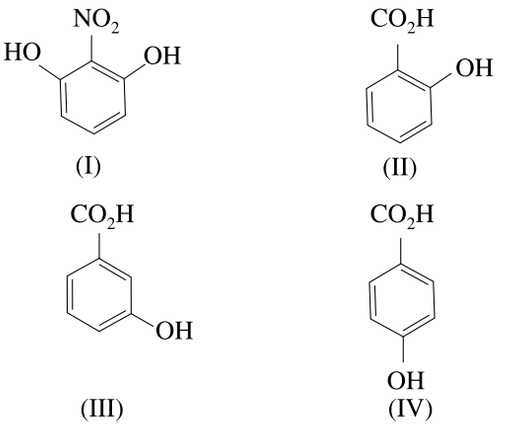
(1) Ice floats in water

(2) higher lewis basicity of primary amines than tertiary amines in aqueous solutions

(3) Formic acid is more acidic than acetic acid

(4) Dimerisation of acetic acid in benzene

55. The correct order of acidity for the following compounds is **[JEE(Adv)-2016]**



(1) I > II > III > IV (2) III > I > II > IV

(3) III > IV > II > I (4) I > III > IV > II

ANSWER KEY

EXERCISE # 1

1. (4)	2. (4)	3. (2)	4. (4)	5. (3)
6. (3)	7. (1)	8. (3)	9. (2)	10. (1)
11. (3)	12. (1)	13. (3)	14. *	15. (3)
16. (4)	17. (1)	18. (2)	19. (3)	20. (4)
21. (3)	22. (3)	23. (4)	24. (1)	25. (1)
26. (3)	27. (3)	28. (2)	29. (1)	30. (1)
31. (2)	32. (4)	33. (4)	34. (1)	35. (1)
36. (1)	37. (1)	38. (1)	39. (2)	40. (4)
41. (4)	42. (4)	43. (4)	44. (2)	45. (1)
46. (4)	47. (2)	48. (2)	49. (4)	50. (2)

EXERCISE # 2

1. (2)	2. (2)	3. (3)	4. (4)	5. (3)
6. (3)	7. (3)	8. (1)	9. (4)	10. (2)
11. (4)	12. (1)	13. (1)	14. (2)	15. (1)
16. (1)	17. (2)	18. (4)	19. (2)	20. (1)
21. (4)	22. (4)	23. (4)	24. (1)	25. (2)
26. (2)	27. (1)	28. (4)	29. (1)	30. (1)
31. (4)	32. (3)	33. (1)	34. (3)	35. (2)
36. (1)	37. (3)	38. (1)	39. (1)	40. (1)

EXERCISE # 3

1. (1,2,3)	2. (2,3,4)	3. (3)	4. (1,4)	
5. (1,3)	6. (1,2,3)	7. (1,2)	8. (2,3,4)	
9. (3,4)	10. (1,2)	11. (1,2,3,4)		
12. (2,3,4)	13. (2,3)	14. (1,3,4)	15. (1,2,4)	
16. (2,3)	17. (1,2,3)	18. (4)	19. (4)	20. (3)
21. (4)	22. (3)	23. (1)	24. (4)	25. (4)
26. (1)	27. (2)	28. (4)	29. (2)	30. (3)
31. (4)	32. (4)	33. (4)	34. (3)	35. (5)
36. (6)	37. (8)	38. (4)	39. (6)	40. (3)

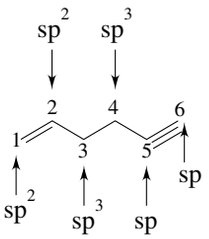
EXERCISE # 4

1. (1)	2. (1)	3. (1)	4. (4)	5. (4)
6. (4)	7. (2)	8. (4)	9. (4)	10. (4)
11. (3)	12. (3)	13. (4)	14. (2)	15. (4)
16. (1)	17. (1)	18. (4)	19. (1)	20. (2)
21. (3)	22. (2)	23. (1)	24. (1)	25. (2)
26. (3)	27. (3)	28. (2)	29. (3)	30. (4)
31. (4)	32. (4)	33. (2)	34. (3)	35. (4)
36. (3)	37. (1)	38. (4)	39. (2)	40. (4)
41. (1)	42. (4)	43. (2)	44. (2)	45. (3)
46. (3)	47. (1)	48. (1)	49. (2,3)	50. (2)
51. (1)	52. (1,2,3,4)	53. (3)	54. (1,2,4)	55. (1)

HINT AND SOLUTION

EXERCISE # 1

1. [4]



Hence, C_2 and C_3 are sp^2-and sp^3-hybridised

2. [4]

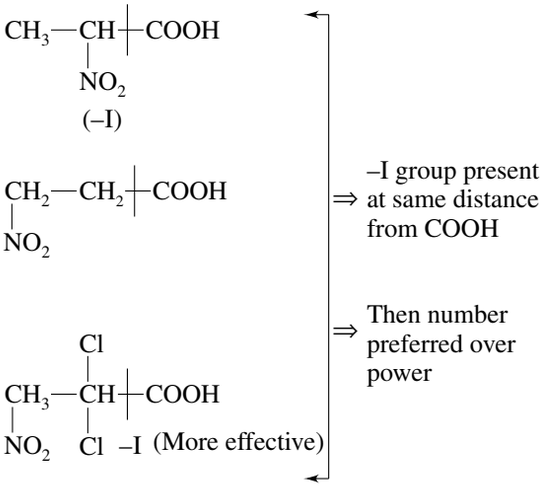
e-deficient species are electrophile

3. [2]

Acid strength $\propto$ – I $\propto \frac{1}{+I}$

Also –I power increases as the distance from source group decreases

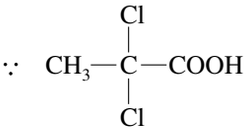
4. [4]



For – I (Preferable order)

→ Distance > Number > Power

Acidic strength $\propto$ – I Power $\propto \frac{1}{+I \text{ power}} \propto \frac{1}{PK_a}$

$\because$ 

$\Rightarrow$ Most + effective – I most Acidic least PKa

Between number and strength, number dominates in the groups having –I effect.

5. [3]

Nuclophile having two nucleophilic site (e^-–denating site) is ambident nucleophle.

6. [3]

Bond-1	Bond-2	Bond-3
sp^3-sp^3	sp-sp	sp^2-sp^2

% s $\propto$ E.N $\propto$ bond strength

(1) < (3) < (2)

7. [1]

$$-NR_3 > -NO_2 > -CN > -COOH$$

↓ De-activating power

↓ m-directing strength

8. [3]

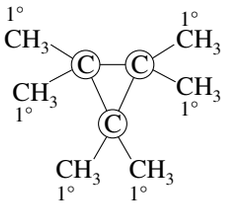
(I) Structure → non polar (most stable)

(II) Structure → Incomplete octet

(III) Structure → Complete octet

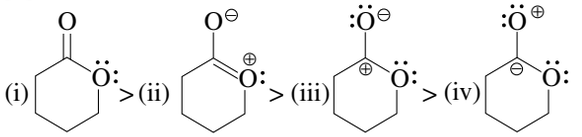
$\therefore$ (I) > (III) > (II)

9. [2]



→ All 1°C attach with 4°C so 1°H are identical

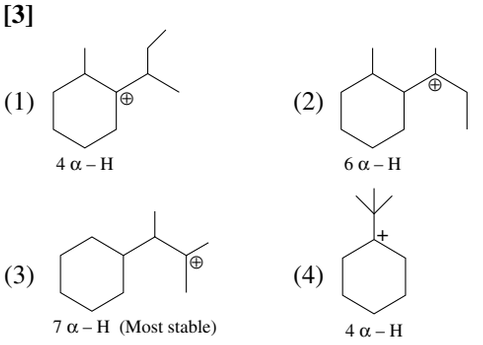
10. [1]



non polar complete octet More E.N –ve More E.N +ve

Incomplete octet

11. [3]



4 α – H 6 α – H

7 α – H (Most stable) 4 α – H

12. [1]

$CHCl_3 \longrightarrow \overset{\ominus}{C}Cl_3$ Most stable, due to pπ-dπ bonc

Most acidic

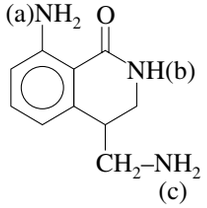
$CHF_3 \longrightarrow \overset{\ominus}{C}F_3$ EWG stabilised anion

$CH_3–CH_3 \longrightarrow CH_3\overset{\ominus}{C}H_2$

ERG, destabilised anion

Stability of anion ∝ Acid strength of conjugate

13. [3]



c > a > b

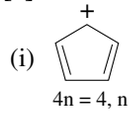
l.p localised less de-localised more de-localised

(due to cross conjugation)

14. [2]

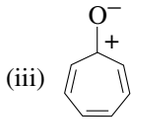
De-activating group are meta director.

15. [3]



4n = 4, n = 1
Anti aromatic

4n = 4, n = 1
Anti aromatic



4n + 2 = 6, n = 1
Aromatic

4n + 6 = 2, n = 0
Aromatic

16. [4]

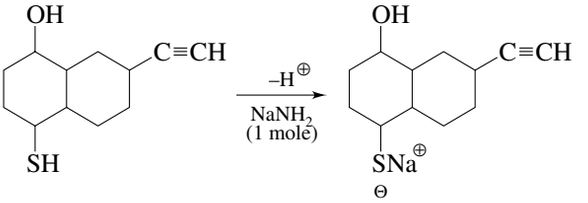
$CH_3–\overset{\oplus}{C}H–CH=CH–C\equiv C–H$

(1) (1) (3)

sp^2 sp^2 sp

17. [1]

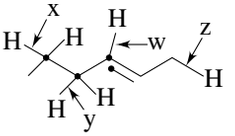
Removal of most acidic H takes place, according to size factor, Acidic strength ∝ size



18. [2]

Resonance ∝ bond length of double bond

19. [3]



$\overset{-x}{\dot{C}H_2}–CH_2–CH=CH–CH_3$ (H effect only)

$\overset{-y}{CH_3}–\dot{C}H–CH=CH–CH_3$ (R + H) effect

$\overset{-w}{CH_3–CH_2}–\dot{C}=CH–CH_3$ More EN caries radical (like +ve) unstable

$\overset{-z}{CH_3–CH_2–CH=CH–}\dot{C}H_2$ Only R effect

Bond dissociation energy (B.D.E)

$$\propto \frac{1}{\text{stability of carbon free radical}}$$

20. [4]

e-density of benzene ring ∝ E.R.G Power

Thus $–NHCOCH_3$ > –OCOEt > $–CH_3$ > COOEt

21. [3]

In reasonating structures atoms always at same position only migration of e^- takes place.

22. [3]

π . π conjugation dominant (– ve) is not in conjugation

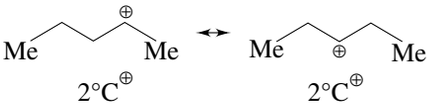
23. [4]

$Ph–\dot{C}(Ph)–Ph$ > $CH_3–\dot{C}(CH_3)–CH_3$

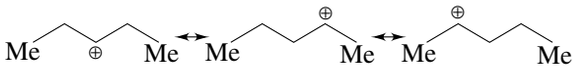
Resonance stable

24. [1]

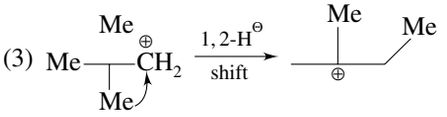
Here (1) is stable because it would not change to other stable carbocation. It can only change $2°C^{\oplus}$ to $2°C^{\oplus}$.

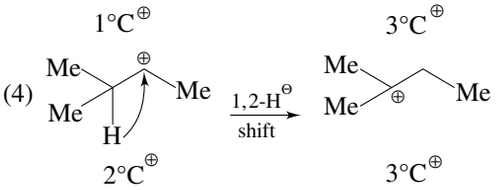


On the other hand, (2) can change to two $2°C^{\oplus}$ structures.



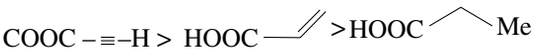
Furthermore, (3) is stabilised by 1, 2-Me shift and (2) is stabilised by 1, 2-$H^{\oplus}$ shift.





So (1) is most stable.

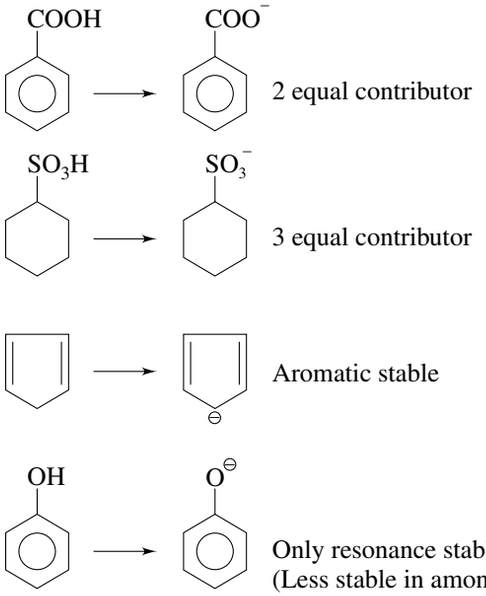
25. [1]



Acidic order: $sp > sp^2 > sp^3 (C \equiv C > C = C > C - C)$

26. [3]

Acidic strength ∝ stability of conjugate anion



27. [3]

Electron deficient molecules are electrophile

28. [2]

Acidic strength ∝ stability of anion

Thus carboxylic acid is more acidic than alcohol due to formation of equal contributor canonical form of carboxylate ion.

Further in same group

$$\text{Acidic strength} \propto -M, -I \propto \frac{1}{+M, +1}$$

$$\text{Acidic strength} \propto K_a \propto \frac{1}{pK_a}$$

Hence of pK_a is (II > I > III > IV)

29. [1]

Ease of hetrolysis ∝ Leaving ability of anion

∝ Acidic strength of conjugate acid of anion.

Leaving (anion) → $\overset{\ominus}{O}H$ $\overset{\ominus}{O}Ac$ $\overset{\ominus}{C}l$

Acidic strength order of conjugate acid → H_2O < ACOH < HCl

Hence order of case of hetralysis is (I) < (II) < (III)

30. [1]

α–NO_2 comes out of plane due to ortho effect,

So $\alpha(C - N) > \beta(C - N)$

(partial double bond character) in $\beta(C - N)$ due to resonance.

31. [2]

(i) Bond length (C=C bond) ∝ Resonance effect

(ii) Bond length (C=C bond) ∝ H-effect

C=C bond length is maximum in (III) because of resonance.

In (I) and (II) resonance is same but due to Hyperconjugation in (II) C=C bond length is higher than (I)

32. [4]

Bond dissociation energy

$$\propto \frac{1}{\text{stability of C – free radical}}$$ (refer solved example)

33. [4]

Stability of carbocation ∝ + H effect

+H power $CH_3 > CD_3 > CT_3$

34. [1]

Heat of hydrogenation ∝ reactivity

$$\text{Reactivity} \propto \frac{1}{\text{Stability of alkene}}$$ (Reoetivity)

Stability of alkene $\propto$ number of α – H(due to +H)

(P)	(Q)	(R)	(S)
1α–H	4α–H	10α–H	7α–H

35. [1]

No –M effect of $-NO_2$ work because of steric hindrance (ortho effect)

36. [1]

The more the s character, the more is the penetration effect of s orbital towards the nucleus, and hence more $\bar{e}$-withdrawing effect. So, sp(50% s) > sp^2(33% s) > sp^3(25% s).

37. [1]

$FeCl_3 + Cl_2 \longrightarrow Cl^{\oplus} + FeCl_4^{\ominus}$

38. [1]

$\rightarrow$ Nucleophilic strength predominantly depends upon size

$\rightarrow$ N.S $\propto$ Size of nucleophilic site

39. [2]

$\overset{\ominus}{N}H_2 > R-\overset{\ominus}{O} > \overset{\ominus}{O}H > R-\underset{\underset{O}{\|}}{C}-O^{\ominus}$

EN↓ BS↑ +↑ BS↑

No Conjugation B.S↑ | Conjugation B.S↓

Also $\underset{+I}{R} - O^{\ominus} > -\overset{\ominus}{O}H$

Base strength $\propto$ +I power

40. [4]

$(CH_3)_3\overset{\uparrow +I}{C}-\overset{\ominus}{C}H_2$ $C_6H_5\overset{\ominus}{C}H_2$ (Resonance stable) $CH_3-\overset{\downarrow +I}{C}H-\overset{\ominus}{C}H_2$ More EN –ve charge

(II) > (I) , (III) , (IV)

E.N.↓ E.N.↑

($\overset{\ominus}{C}$ sp^3) ($\overset{\ominus}{C}$ sp^2)

(II) > (IV) > (I) , (III)

Same EN

$\left(\text{stability of } -\overset{\ominus}{C}- \propto -I \propto \frac{1}{+I}\right)$

(II) > (IV) > (III) > (I)

41. [4]

Acid strength $\propto$ Ka $\propto \frac{1}{pKa} \propto$ – I, M $\propto \frac{1}{I, +M}$

Thus pKa $\propto$ +M, + I $\propto \frac{1}{-M, -I}$

$-M(-NO_2) > -M(-COOH)$

42. [4]

Reactivity of aromatic substance towards electrophile

(Ar.SE) $\propto$ ERG $\propto \frac{1}{EWG}$

$ERG(-O^{\ominus} > -NH-\overset{\overset{O}{\|}}{C}-CH_3 > -O-\overset{\overset{O}{\|}}{C}-CH_3 > -\underset{\underset{CH_3}{|}}{CH}-CH_3)$

(i) > (iii) > (ii) > (iv)

43. [4]

(I)  < 

Anti aromatic Aromatic

(II)  < 

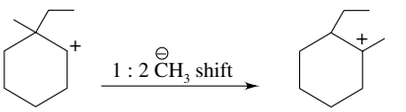
Anti aromatic non Aromatic

(III)  > 

Aromatic Anti aromatic

44. [2]

- Such rearrangement in which carbocation gets stabilised is the most favorable

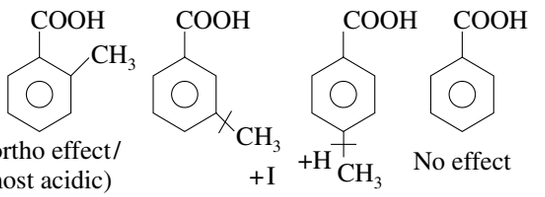


less stable more stable stable

45. [1]

In option 2, 3, 4 Equal contributed canonical form will exist hence same bond length between participating atom.

46. [4]



(ortho effect/ most acidic) (I) (II) (III) (IV)

Acid strength $\propto$ – H, – I $\propto \frac{1}{+H,\ +I}$

(I) > (IV) > (II) > (III)

47. [2]

$CH_3–CH_2\overset{Lg}{|}Br + Na\overset{Nu}{|}I \rightarrow CH_3–CH_2–I + NaBr$

48. [2]

Acidity : HBr > MeOH > Me_2NH > Me_3CH

Basicity and nucleophilicity:

$Br^{\ominus} < MeO^{\ominus} < Me_2N^{\ominus} < Me_3C^{\ominus}$

i.e., IV > III > II > I

49. [4]

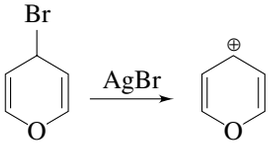
4n + 2 = 6

n = 1

aromatic

50. [2]

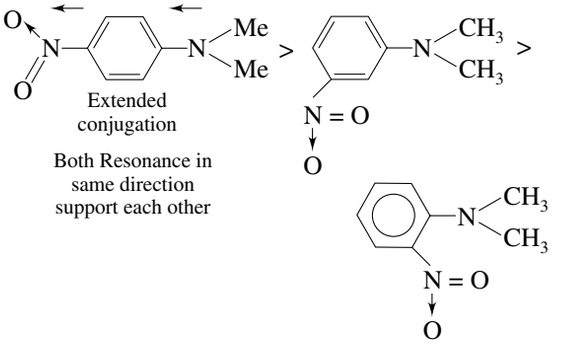
Reactivity of R–Br $\propto$ stability of $—C^{\oplus}$



Aromatic stable

EXERCISE # 2

1. [2]



Extended conjugation

Both Resonance in same direction support each other

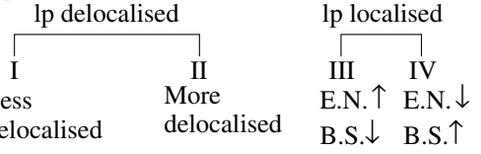
Due to SIR effect Resonance is less

2. [2]

Bond strength $\propto$ E.N. $\propto$ % of S character

c > b > a.

3. [3]

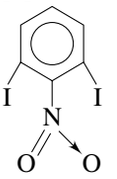


Thus order is IV > III > > I > II

4. [4]

Basic strength $\propto$ – M, –I $\propto \frac{1}{+M,\ +I}$

5. [3]



$\rightarrow$ Due to presence of 2-bulky group at the ortho position of nitro group.

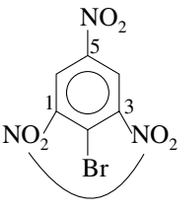
$\rightarrow$ $–NO_2$ comes out of plane, due to SIR effect (ortho effect).

6. [3]

Resonance $\propto$ Resonance energy

In (III), continuous conjugation Resonance energy

7. [3]



Out of plane (SIR Effect)

C_1—N & C_3—N out of plane due to SIR Effect

C_5—N present in resonance

Resonance $\propto \frac{1}{\text{BL of single bond}}$

Thus (C_1—N = C_3—N > C_5—N)

8. [1]

(I)

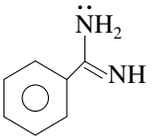
ℓp localised

more basic

(II)

ℓp delocalised also participate in aromatisation

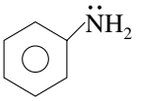
more stable, least basic



(III)

Phenyl imidine

most basic



(IV)

ℓp delocalised

less basic

9. [4]

Acidity:

$H_3O^{\oplus} > \overset{\ominus}{E}tOH_2$ >MeCOOH > H_2O > EtOH

Basicity and nucleophilicity:

$H_2O < MeOH < MeCOO^{\ominus} < \overset{\ominus}{O}H < EtO^{\ominus}$

i.e. V > IV > III > II > I

10. [2]

$\alpha \rightarrow$ (double bond) in resonance

$\beta \rightarrow$ (single bond) in resonance

$\gamma \rightarrow$ pure single bond

$\alpha < \beta < \gamma$

11. [4]

• positive charge at bridge head C cause unstability due to Bredt's rule

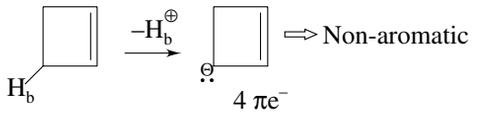
• 3° carbocation (carbonium) most stable

12. [1]

(I) 

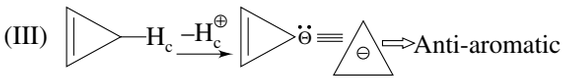
6 πe^-

In delocalisation

(II) 

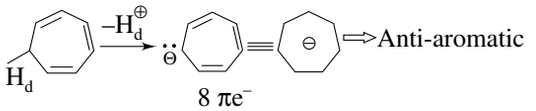
4 πe^-

In delocalisation

(III) 

4 πe^-

In delocalisation

(IV) 

8 πe^-

In delocalisation

The order of Aromatic stability is:

Aromatic > Non-aromatic > Anti-aromatic

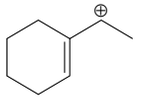
I > II > IV > III

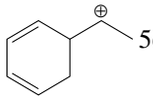
IV has more resonating structures than III, and is therefore, more stable.

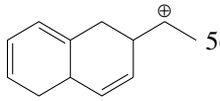
$\therefore$ H_a in I is more acidic since it will give $H^{\oplus}$ faster to become a stable aromatic anion. Thus least Pk_a value.

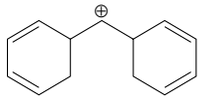
13. [1]

Due to resonance and hyperconjugation.

(1)  Resonance + 3α-H Most stable

(2)  5α-H

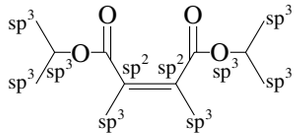
(3)  5α-H

(4)  2α-H

14. [2]

Due to higher extent of conjugation

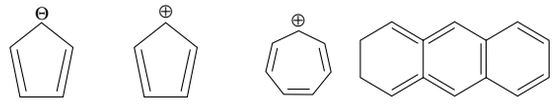
15. [1]



16. [1]

Nucleophilicity ∝ Attacking rate of anion

17. [2]



4n + 2 = 5πe	4n + 2 = 4πe	4n + 2 = 6πe	4n + 2 = 14πe
n =1	n =1	n =1	n =3
Aromatic	Anti Aromatic	Aromatic	Aromatic

18. [3]

In aqueous solution, amine basically follows the order

NH_3 < tertiary < primary < secondary

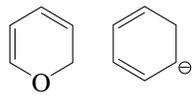
This is due to the combined effected of induction and stabilization of conjugate acid through H-bonding. Also, a cyclic amine is more basic (IV) than acyclic amine (II). If their degrees are same. Hence, the overall order is

K_b : III(3°) < I(1°) < II(2°, acyclic) < IV(2°, cyclic).

19. [2]

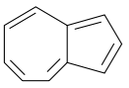
- Acidic strength ∝ ortho effect
- Ortho effect ∝ steric hindrance at ortho position

20. [1]



Partial conjugation
non-planer
non-aromatic

4n + 2 = 2πe
n = 1
Aromatic

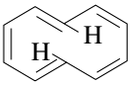


(IV)

$4n + 2 = 10\pi e$

n = 2

Aromatic



(V)

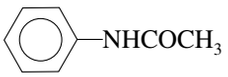
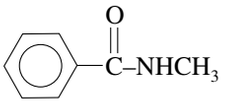
Non planer due to repulsion between adjacent H

21. [4]

Bond dissociation energy (B.D.E) $\propto \frac{1}{\text{Stability of C – free radical}}$

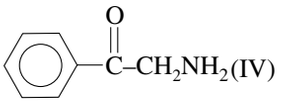
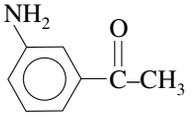
22. [4]

Rule 1 Base strength $\propto \frac{1}{\text{Delocalisation of } \ell p}$

(I)  (II) 

ℓp delocalised

In amide ℓp less delocalised

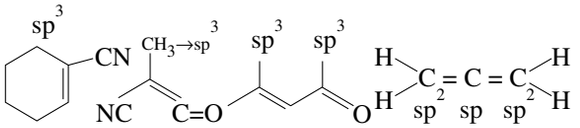
(III)  (IV) 

ℓp localised

ℓp delocalised

Rule 2 Base strength $\propto$ + M, +I $\propto \frac{1}{-M, I}$

23. [4]



24. [1]

$\rightarrow$ Ring expansion takes place

25. [2]

When nucleophilic centre is same then

Nucleophility $\propto$ basic strength $\propto$ +M, +I $\propto \frac{1}{-M, -I}$

26. [2]

27. [1]

Stability of  $\propto$ conjugation $\propto$ H-effect (α–H)

Note: positive charge at bridge head C de-stabilised carbocation due to Bredt's rule.

28. [4]

(I) Stable by resonance

(II) Stable by pπ – pπ bonding

(III) Stable by resonance

(IV) negative charge do not participate in resonance (less stable)

29. [1]

By the removal of $-Cl_{(C)}$, due formation of aromatic stable carbocation

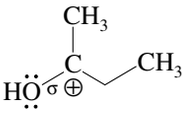
30. [1]

Base strength $\propto$ +M, +I $\propto \frac{1}{-M, -I}$

31. [4]

Theory based

32. [3]



- (positive)-ℓp conjugation
- most stable

33. [1]

(I) Acidic strength $\propto$ ortho effect

(II) Acidic strength $\propto$ –M, –I $\propto \frac{1}{+M, +I}$

34. [3]

Base strength $\propto$ +I $\propto \frac{1}{-I}$

Nucleophilic strength $\propto \frac{1}{\text{steric hindrance}}$

35. [2]

Bond length $\propto \frac{1}{\%S} \propto \frac{1}{EN}$

36. [1]

Leaving group ability $\propto$ acid strength of conjugate acid $\propto \frac{1}{\text{Base strength of (anion)}}$

37. [3]

Aromaticity $\propto$ resonance energy

38. [1]

39. [1]

Power of leaving group $\propto$ acid strength of conjugate acid $\propto \frac{1}{pK_a}$

$CH_3–COO^- \longrightarrow CH_3–COOH$ $\quad pK_a = 4.5$

$C_6H_5– \longrightarrow C_6H_5–OH$ $\quad pK_a = 10$

$C_6H_5– \longrightarrow C_6H_5–SO_3H$ $\quad pK_a = 2.6$

40. [1]

- Negative charged ions are better nucleophile
- NS $\propto$ size (dominating factor)
- NS $\propto$ base strength

EXERCISE # 3

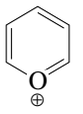
1. [1, 2, 3]

Due to H-bond and p-fluoro phenol exceptionally less acidic than p-chloro phenol

2. [2, 3, 4]

(1) 

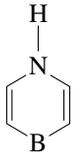
Non aromatic
non-planar

(2) 

4n + 2 = 6
n = 1
aromatic

(3) 

4n + 2 = 6
n = 1
aromatic

(4) 

4n + 2 = 6
n = 1
aromatic

3. [3]

Here, the negative charge of conjugate base is stabilized by electron withdrawing resonance effect of $-NO_2$ group.

4. [1, 4]

Both —NO_2 and —CHO exert electron withdrawing resonance effect but from ortho and para-positions so decreases basic strength, hence meta-isomer is more basic.

Both —Cl and —OCH_3 give electron donating resonance effect from ortho and para-positions, increases basic strength hence, their meta-isomer is less basic.

5. [1, 3]

(i) Stability of Carboanion $\propto$ Conjugation

(ii) Stability of Carboanion $\propto -I \propto \frac{1}{+I}$

$$H_2N\overset{\ominus}{C}H_2 < CH_3-\underset{\|}{\overset{O}{C}}-\overset{\ominus}{C}H_2$$

conjugation

$$\overset{\ominus}{C}F_3 < \overset{\ominus}{C}Cl_3$$

$p\pi-d\pi$ conjugation

(1) $O_2N\overset{\ominus}{C}H_2$ and $F-\overset{\ominus}{C}H_2$

$-I(-NO_2) > -I(-F)$

(2) $\overset{\ominus}{C}F_3$ and $\overset{\ominus}{C}Cl_3$

$p\pi-d\pi$ conjugation

(3) F_3C-CH_2 and Cl_3C-CH_2

$-I(CH_3) > -I(CCl_3)$

(4) $H_2N-\overset{\ominus}{C}H_2$ and $CH_3-\underset{\|}{\overset{O}{C}}-\overset{\ominus}{C}H_2$

conjugation

6. [1, 2, 3]

Theory based

7. [1, 2]

In same period

Nucleophilicity $\propto$ Base strength

In same group

Nucleophilicity $\propto$ Size (If Protic solvent, CH_3–OH)

So that $F^- > Cl^- > Br^- > I^-$ (incorrect)

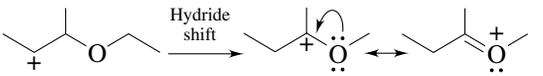
8. [2, 3, 4]

Reactive intermediates are formed for very small time, cannot be isolated practically. The most stable reactive intermediate is always formed in largest amount, hence from the major product. It is the reactive intermediates that leads to several products in a reaction

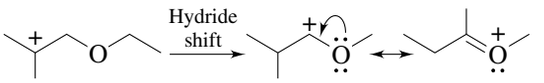
9. [3, 4]

In both option (3) and (4), less substituted, less stable alkene is being transformed into more stable alkene.

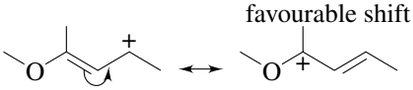
10. [1, 2]

(1) 

3°resonance
Stabilised
(more stable)

(2) 

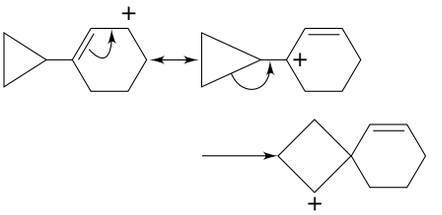
Stabilised by
Resonance
favourable shift

(3) 

I II

3° resonance
(stabilised more stable)

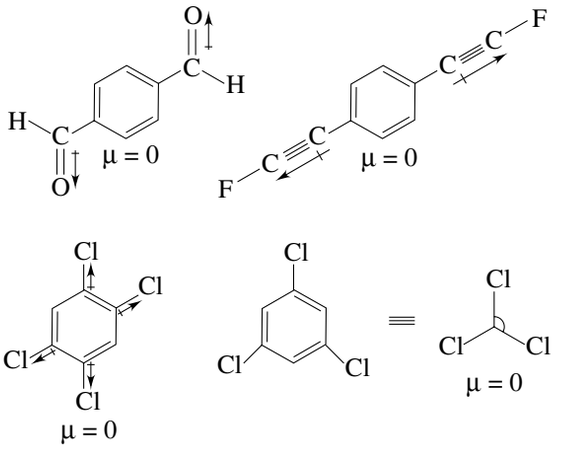
However, the above step is resonance delocalisation (I and II are canonical forms) not the required rearrangement.

(4) 

Less stable than the
Previous carbonation

Although the above ring expansion increases stability of cyclopropyl ring but decreases overall stability because of loss of resonance.

11. [1, 2, 3, 4]



12. [2, 3, 4]

Among amines, the order of basic strength in gas phase is $1° < 2° < 3°$. Therefore, the order of K_b will also be the same Since, $pK_b = -\log K_b$, the order of pK_b would be reverse of the order of K_b, i.e. pK_b $3° < 2° < 1°$.

13. [2, 4]

(2) $CH_3—\overset{\overset{O}{\|}}{C}—\overset{\ominus}{O} \longleftrightarrow CH_3—\overset{\overset{\ominus O}{|}}{C} = O^-$

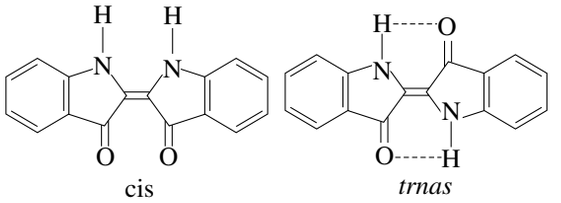
Equivalent resonance structures

(4) $\overset{\ominus}{O}—N=O \longleftrightarrow O=N—O^-$

Equivalent resonance

In option 1, 3, unequal contributor is formate other de-localisation

14. [1, 3, 4]



cis *trnas*

(Intramolecular H-bonding)

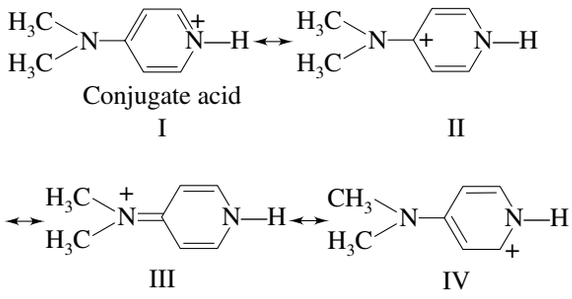
trans-isomer shown above is slightly more stable due to presence of intramolecular H-boding forming six membered ring. The molecule is planar, no enantiomerism is possible. It's *cis*-isomer has greater relative solubility in water due to free $\rangle C=O$ and $\rangle N—H$ groups capable of intermolecular H-bonding with water. Also, the molecular is planar and highly conjugated, has high resonance stabilisation energy.

15. [1, 2, 4]

All acidic groups, $—SO_3H$, —COOH and —OH would be neutralised by NaOH Sulphonic acid is most acidic, would be neutralised first, With $NaHCO_3$, $—SO_3H$ and —COOH groups would be neutralised requiring 3.0 moles of base. Electron withdrawing effect of $—SO_3H$ and —COOH increases acidity of one another.

16. [2, 3]

Nitrogen labelled-II is the most basic.



Conjugate acid

I II III IV

Both I and III have complete valence shell of all the atoms. Also, $—CH_3O$, group at position-III of original base would increase the basic strength as it would stabilise the resonance structure IV by resonance effect.

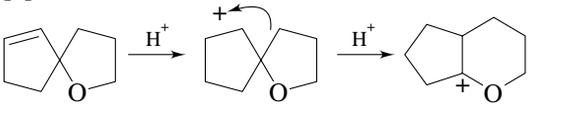
17. [1, 2, 3]

Dissociation of C—H (II) is the easiest as it produces a resonance stabilised free radical.

$CH_3—\overset{\bullet}{C}H—CH=CH_2 \longleftrightarrow CH_3—CH=CH—\overset{\bullet}{C}H_2$

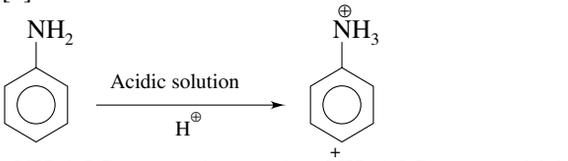
Due to hyperconjugation, bond order of C—H (II) decreases on increasing bond length. C—H (I) involves the smaller on sp^2 hybridised orbital for sigma boding, shorter bond than on C—H (II) and C—H (III) which employs bigger sp^3 hybridised orbitals for bond formation.

18. [4]



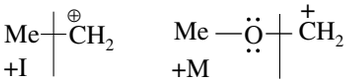
Most stability
By resonance

19. [4]



$–NH_2$(+M) group changes in $–\overset{+}{N}H_3$ (–M) group which is least reactive towards $E^{\oplus}$

20. [3]

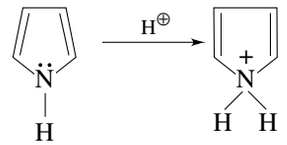


Due to resonance

21. [4]

: CCl_2 have vacant d-orbital so it is good electrophile

22. [3]



ℓp delocalised Anti aromatic

less basic

In pyrelle (I) ℓp-de localised so less basic them (II)

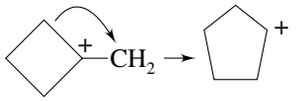
23. [1]

As distance of –I group increase from source, –I power decrease,

So that acid strength decrease.

24. [4]

It is generally true that a tertiary carbocation is more stable than primary one. However, this does not apply in the present case because it is less stable than I as II has greater angle strain. The favourable rearrangement here is ring expansion.



Primary Secondary

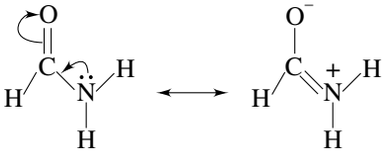
Less angle strain

25. [4]

26. [1]

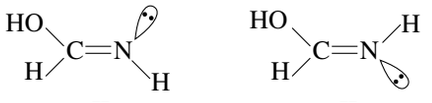
27. [2]

Sol. (25 to 27)



IV

I is obtained on protonation of formamide, hence conjugate acid. If has restricted rotation, show geometrical isomerism.



II cis II trans

28. [4]

29. [2]

30. [3]

Sol. (28 to 30)

In the given amino acid cation, –COOH α to $-\overset{+}{N}H_3$ is most acidic followed by the second –COOH group and $-\overset{+}{N}H_3$ least acidic. It is due to strong–ℓ-effect of $-\overset{+}{N}H_3$ on a-COOH

31. [4]

$$\underset{7}{\overset{sp^2}{CH_2}} = \underset{6}{\overset{sp}{C}} = \underset{5}{\overset{sp^2}{CH}} - \underset{4}{\overset{sp^3}{CH_2}} - \underset{3}{\overset{sp}{C}} \equiv \underset{2}{\overset{sp}{C}} - \underset{1}{\overset{sp^3}{CH_2}} - NH_2$$

$C_1 \longrightarrow sp^3$

$C_2 \longrightarrow sp$

$C_5 \longrightarrow sp^2$

$C_6 \longrightarrow sp$

32. [4]

(A) $\rightarrow B \longrightarrow A^+ + B^{\ominus}$

$A \rightarrow$ Heterolysis (q)

(B) $CH_3\overset{+}{C}H{-}CH_3 \rightarrow$ carbocation (r)

(C) $A - A \longrightarrow A^{\bullet} + A^{\bullet}$

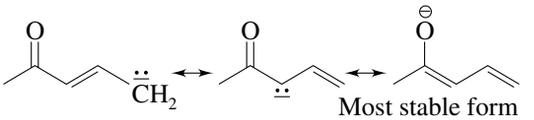
$\rightarrow$ Free radical (p)

(D) $CH_2N_2 \longrightarrow \ddot{C}H_2 + N_2$

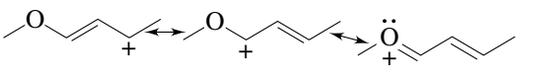
$D \longrightarrow$ carbene (t)

(E) $CH_3{-}\ddot{O}H \longrightarrow$ Nucleophile (s)

33. [4]

(i) 

Most stable form

(ii) 

Most stable form

This carbocation is also stabilised by hyperconjugation effect. Also the carbocation have deficiency of a pair of electron, act as a strong Lewis acid in chemical reaction

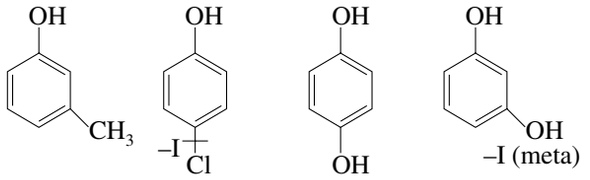
(iii) It is a free radical, therefore paramagnetic due to unpaired electron. It is also stabilised by hyperconjugation effect.

(iv) It is a carbene. It's triplet form is paramagnetic. It has deficiency of a pair of electron, acts as a strong Lewis acid during the reaction.

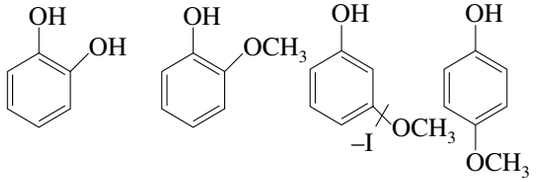
34. [3]

$$\text{Acidic strength} \propto -I, -M \propto \frac{1}{+I, +M}$$

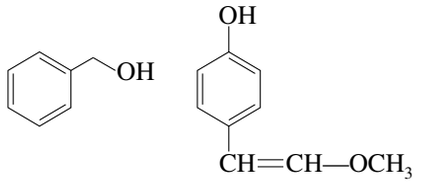
Acids stronger than phenol are : II, IV, V, VII



I II III IV



V VI VII VIII



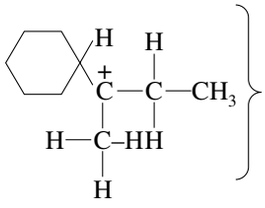
IX X

35. [5]

(i), (ii), (v), (i) and (vii) have conjugated C=O and resonance delocalisation decreases bond order of C=O less than 2, hence weaker bond than C—O bond in acetaldehyde

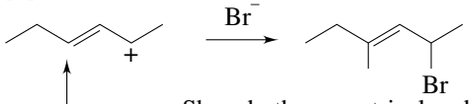
36. [6]

The given carbocation has six-H that can take part in hyperconjugation as:

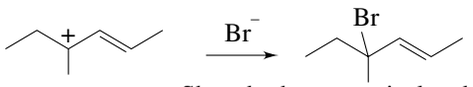


Six a-H capable of showing hyper conjugation

37. [8]



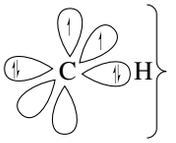
Show both geometrical and optical isomerism, total four isomers



Show both geometrical and optical isomerism, total four isomers.

38. [4]

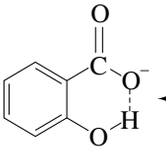
In carbene, there are a total of six valence electrons (2 bond pairs + 1 lone pair). In case of triplet carbine, there are four electrons having same spin direction.



A triplet carbene
4 electrons with up-spin and
2 electrons with down-spin

39. [6]

Acids, I, III, IV, VII, VIII and IX are all stronger than benzoic acid. I is stronger because of stabilisation of conjugate base by intramolecular H-bonding.



← Intramolecular H-bonding

III is stronger because from *meta* position, —OH exert only – I-effect, its electron donating resonance effect has no role on acidic strength.

IV is stronger acid due to loss of planarity of —COOH with phenyl ring, hence absence of electron donating resonance effect as phenyl rings on —COOH increases acidic strength.

VII is stronger because a sulphonic acid is stronger than a carboxylic acid.

VIII is stronger because electron withdrawing inductive effect of one —COOH over other increases acidic strength.

IX is stronger due to only – I-effect of methoxy group operate from *meta* position but not its electron donating resonance effect.

40. [3]

Antiaromatic substance are unstable at room temperature

EXERCISE #4

1. [1]

When R is attached with benzyl/allyl system + inductive effect occurred + I Power ∝ branching

2. [1]

As per NCERT result

In aq. solution (when R = $–CH_3$)

2° amine > 1° amine > NH_3 (basic strength)

3. [1]

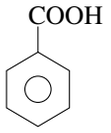
Rate of SN reaction ∝ Leaving tendency ∝ Acidic strength of conjugate acid

Since HCl is strongest acid so that $Cl^–$ is best leaving group

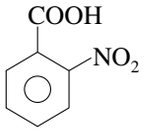
4. [4]

Acid strength $\propto$ M, –I (EWG)

$\propto \frac{1}{+M,\ +I}$ (ERG)



(a)



(b)

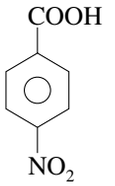
Effect → no effect

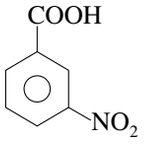
–M, –I

–I↑distance↓

Not effect → no effect

$(EWG)_1$





–M, –I

$(EWG)_2$

(c)

–I

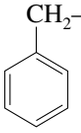
$(EWG)_3$

(d)

b > c > d > a

5. [4]

Base strength $\propto \frac{1}{\text{De. localisation of lp.}}$

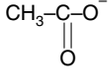
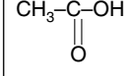
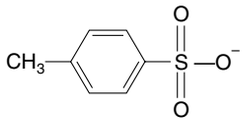
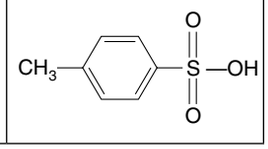


ℓp localised

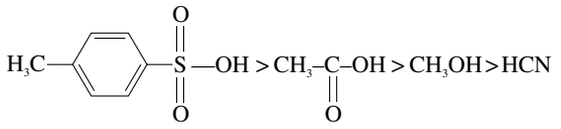
benzyl amine

6. [4]

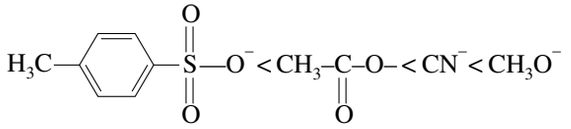
Weaker the acid, more stable is their conjugate base and greater is their nucleophilicity. Thus, nucleophilicity order of the conjugate bases is opposite to their acidic strength.

Conjugate bases	Acids
	
CH_3O^-	CH_3OH
CN^-	HCN
	

Since, alcohols and cyanides are weaker acid than sulphonic and carboxylic acids. Thus, the order of acidic strength of the given species are

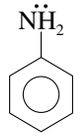


Hence, the decreasing order of nucleophilicity of the given nucleophiles is as follows



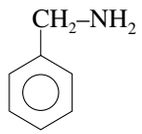
7. [2]

Base strength $\propto \frac{1}{\text{De. localisation of lp.}}$



Aniline

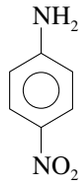
ℓp delocalised



Benzylamine

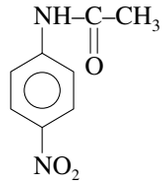
ℓp localised

most basic



p-nitroaniline

ℓp delocalised

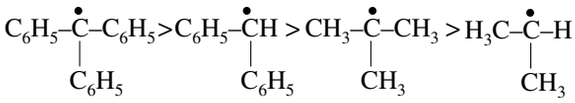


Acetanilide

ℓp delocalised

8. [4]

Free radicals stability

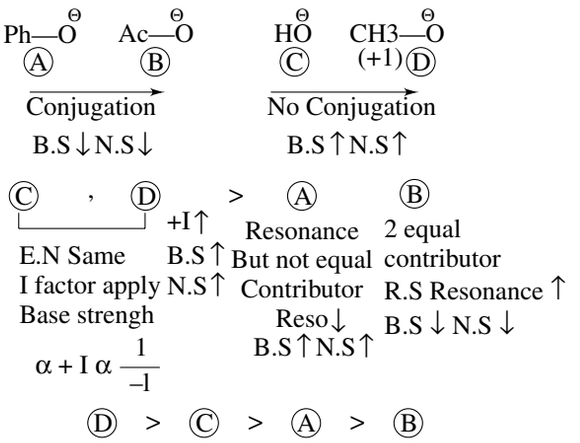


(Highly stable by delocalisation of 3 phenyl groups)

(9-hyperconjugative hydrogens and +/– effect of 3 alkyl groups)

9. [4]

When nucleophilic centre is same but category of anion is different, Then N.S α B.S

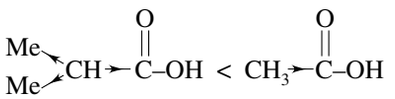


10. [4]

$pk_a = -\log K_a$, Hence, higher the value of K_a, smaller pK_a. K_a is the measure of acidic strength. It is highest for the strongest acid (d) in given case, therefore has lowest pK_a value.

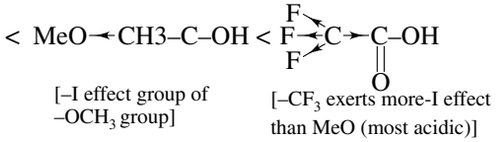
11. [3]

Acidic strength of the compound depends on the ease of release of proton –I effect exerting groups (e^- withdrawing increase the acidic strength while +I effect exerting group decreases the strength of an acid.



[2 + I effect exerting groups, increases e^- density of on O-atom, thus the release of ease of proton becomes difficult (least acidic)]

[+I effect group of $-CH_3$ group]



12. [3]

2° amine is more basic in aqueous solution CH_3–NH–CH_3

Dimethyl amine (2° amine)

13. [4]

$-NO_2$ group (e with drawing) de-crease e-density of benzene ring.

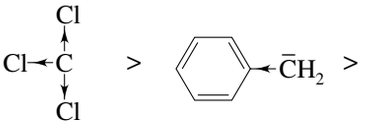
So it deactivates the benzene ring towards electrophilic substitution.

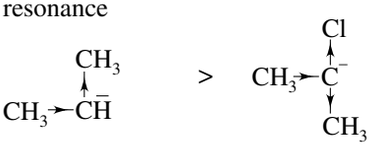
14. [2]

–/-effect (e^- withdrawing) exerting groups stabilises carbanion by the dispersal of their negative charge while +/-effect exerting (e^- releasing) groups destabilizes the carbanion by increasing electron density on them.

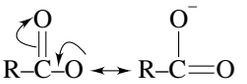
On the other hand, resonance stabilized carbanion are stable due to the involvement of their lone pair of electron with the delocalisation of π-electrons of attached phenyl group.

Thus





15. [4]



- In carboxylate ion, the negative charge is present on oxygen, is in conjugation with π bond thus it is resonance stabilised.
- $HC\equiv C^-$: Carbon is sp hybridised so its electronegativity is increased & higher relative to nitrogen.
- If negative charge atom belongs to same period
- $\overline{N}H_2$: Nitrogen is more electronegative than sp^3 hybridised C-atom. From the above discussion, it is clear that the order of the stability of conjugated bases is as

  $RCOO^- > HC \equiv \overline{C} > \overline{N}H_2 > \overline{R}$

  And higher is the stability of conjugated bases, lower will be basic character. Hence, the order of basic character is as

  $RCOO^- < HC \equiv \overline{C} - < \overline{N}H_2 < \overline{R}$

16. [1]

Nucleophilic strength $\propto$ size

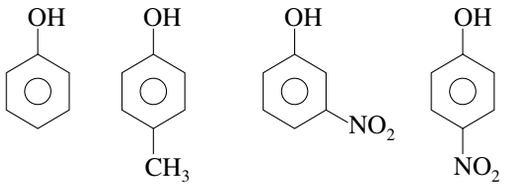
Basic strength $\propto \frac{1}{\text{size}}$

Thus $R-S^{\ominus}$ is less basic but more nuelophilic strength than $R-O^{\ominus}$

17. [1]

Acidic strength $\propto$ M, –I (EWG)

$\propto \frac{1}{+M,\ +I(ERG)}$



(A) (B) (C) (D)

No effect +H, +I (at meta position) –I –M, –I

Thus D > C > A > B

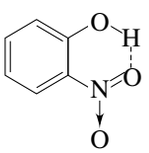
18. [4]

→ non-planar
Non aromatic

For aromatic substance molecule most be cyclic| planar conjugated and obey Huckle rule (4n + 2 = πe)

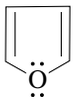
Rest other satisfied given condition so they are aromatic

19. [1]



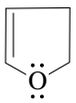
→ In tramolecular H-bond
→ Less bpt.
→ Less soluble
→ More volatile

20. [2]

(i)  planner, conjugated, 4n + 2 = 6, n = 1(aromatic)

(ii)  non-planar (non-aromatic)

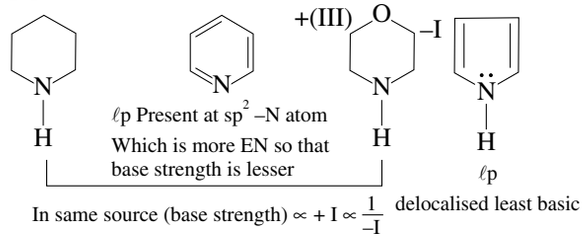
(iii)  non-planar (non-aromatic)

(iv)  non-planar (non-aromatic)

(v)  non-planar, conjugated, 4n = 4, n = 1 (Anti aromatic)

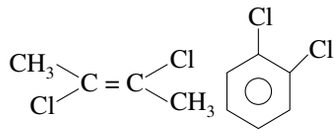
(vi)  planar, conjugated, 4n = 4, n = 1 (Anti aromatic)

21. [3]

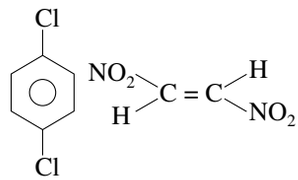


Thus I > III > II > IV

22. [2]

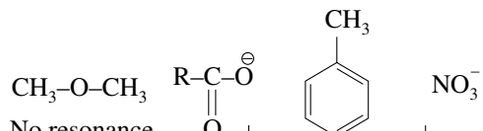


μ = 0 μ ≠ 0



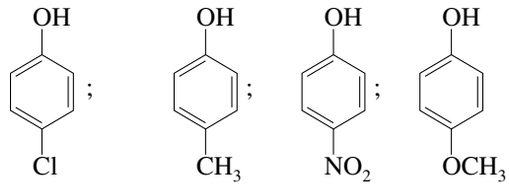
μ = 0 μ = 0

23. [1]



24. [1]

Acidic strength $\propto$ –M, –I $\propto \frac{1}{+M,\ +I}$



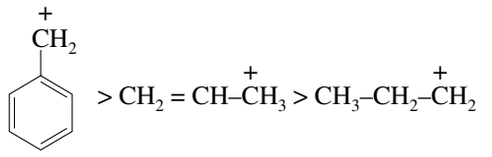
Over all +M < –I effect $(EWG)_2$ | +H, +I $(EWG)_2$ | –M, –I $(EWG)_1$ | +M > –I $(EWG)_1$

(I) (II) (III) (IV)

Thus III > I > II > IV

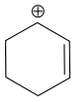
25. [2]

The order of stability of carbocation will be



(III) Benzyl carbocation (more resonance stabilised) | (I) Alyl carbocation (resonance stabilised) | (II) Propyl carbocation (stabilised by + I effect)

26. [3]



+ve charge present in conjugation with π-bond so it is most stablised.

27. [3]

Theory bosed

28. [2]

N.S. ∝ size

If solvent is not given then nucleophilic strength compared in polar solvent

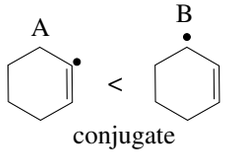
29. [3]

Stability of anion ∝ –I, –M ∝ $\frac{1}{+I,\ +M}$

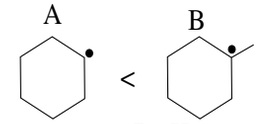
$-CH_3$	$-OCH_3$	$-\overset{\overset{O}{\|}}{C}-CH_3$	$-CH_2-OH$
+H	+M	–M	+H

30. [4]

(1) A < B (conjugate)

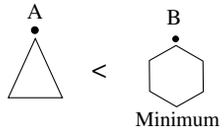


(2) A < B



4α-H 7α-H (more hyper conjugation)

(3) A < B (Minimum ring strain)



(4) A $Ph_3C^{\bullet}$ > B $(CH_3)_3C^{\bullet}$

more resonance stabilised | only hyper conjugation stabilised

31. [4]

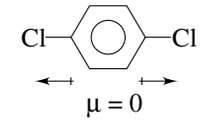
- $C_6H_5-\ddot{N}H_2$, Here ℓp de-localised so it is least basic

  As per NCERT
- In aq. solution, 2° > 1° > 3° (if R–CH_3)

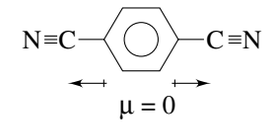
  Basic strength ↑K_b↑pK_b↓

32. [4]

In (iii) and (iv), the dipole vectors O–H and S–H are in tetrahedral plane, do not cancel, In (i) and (ii) dipole vectors cancel each other completely as:



μ = 0

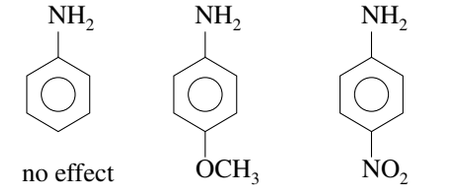


μ = 0

33. [2]

(i) in CH_3-NH_2, ℓp localised so that base strength highest

(ii) Base strength ∝ + M, + I ∝ $\frac{1}{-M,\ -I}$



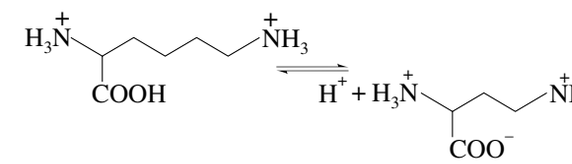
no effect | OCH_3 (+M > –I) | NO_2 (–M, –I)

34. [3]

2 moles of $NaNH_2$ would neutralise the first two more acidic groups. Here, —COOH is most acidic followed by hydroxyl group of the nitrophenol ring because —NO_2 has strong *–I* as well as –R-effect.

35. [4]

A carboxylic acid is more acidic than ammonium ion, hence X is most acidic. For 2nd most acidic group, we need Investigets the conjugate base of given ion formed after first deprotonation as:



Now in conjugate base I, COO^- is electron donating, decreases acidic strength of $-\overset{+}{N}H_3$ at α-position, hence Y is second most acidic followed by Z.

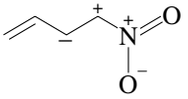
36. [3]

$CH_2=CH-\overset{\oplus}{C}H=\overset{\ominus}{C}H-O-CH_3$

Lone pair of oxygen is not the part of this mode of delocalisation.

37. [1]

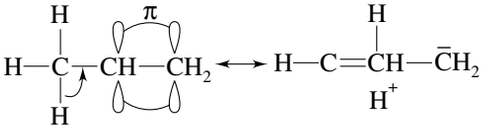
The following structure has like charge on adjacent atoms, therefore, least stable



38. [4]

Statement I is incorrect but Statement II is correct. Intramoelcular H-bonding in ortho-hydroxy benzoic acid lowers the boiling point.

39. [2]

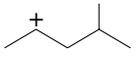


The σ-electrons of C—H bond is delocalised with p-orbitals of π-bond.

40. [4]

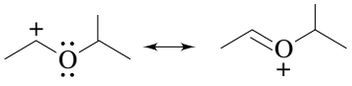
3°, has resonance stability

(I)



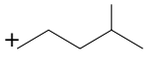
has no resonance stability but 2°

(II)



2°, has resonance stability

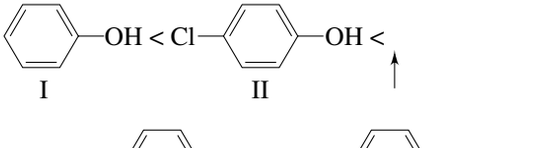
(III)



1°, has no resonance stability

(IV)

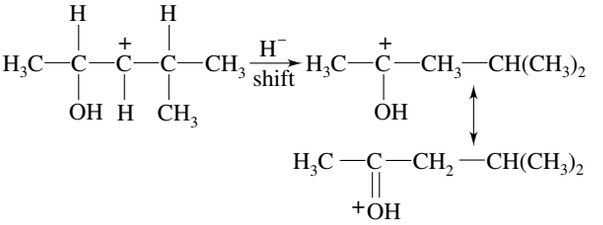
41. [1]



+ I-effect decreases acidic strength

42. [4]

H at C-2 will migrate giving resonance stabilised carbocation



43. [2]

I is most stable because it has more covalent bonds and negative charge on electronegative nitrogen, III is more stable than II and IV due to greater number of covalent bonds. Between II and IV, II is more stable since, it has negative charge on electronegative atom and positive charge on electropositive atom. Hence, overall stability order is

I > III > II > IV.

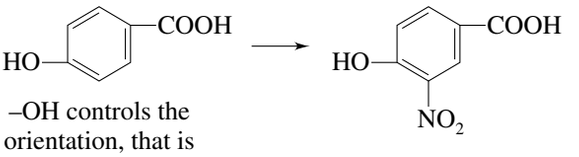
44. [2]

Lysine contains two basic groups, e.g., NH_2

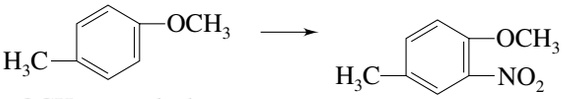
Biomolecules

Basic straight

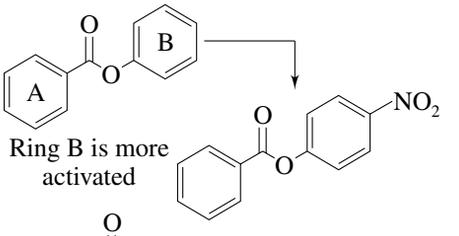
45. [3]



–OH controls the orientation, that is ortho-para directing



$-OCH_3$ controls the orientation (o/p-directing)

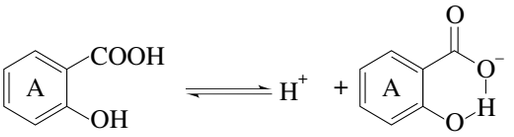


Ring B is more activated

and $-O-\overset{O}{\overset{\|}{C}}-Ph$ is (o/p-directing)

46. [3]

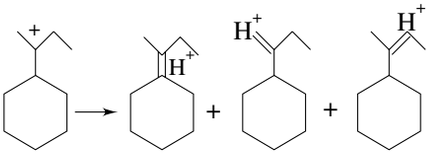
A monosubstituted benzoic acid is stronger than monosubstituted phenol as former being a carboxylic acid. Among the given substituted benzoic acid, ortho-hydroxy acid is strongest acid although —OH causes electron donation by resonance effect which tends to decrease acid strength. It is due to a very high strength of conjugate base by intramolecular H-bond which outweight the electron donating resonance effect of —OH.



The overall order of acid-strengthof given four acids is ortho-hydroxybenzoic acid (pK_a = 2.98) > Toluic acid pK_a = 4.37) > p-hydroxybenzoic acid (pK_a = 4.58) > p-nitrophenol (pK_a = 7.15)

47. [1]

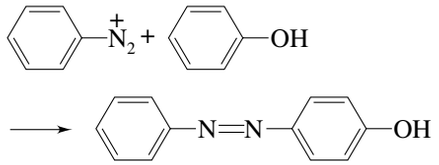
There are total 6 α-H attached to sp^2 carbon and they all can participate in hyperconjugation.



(Three structures) (Two structures)

48. [1]

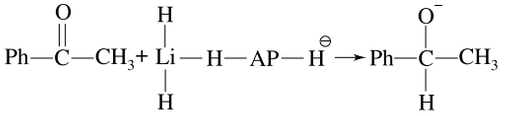
(i)



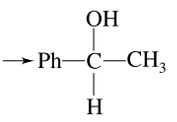
This is an example of electrophilic substitution at para position of phenol, giving a coupling product.

(ii) Pianacol-pinacolone rearrangement, occur

(iii)



Nucleophilic addition



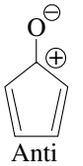
(iv) Nucleophilic addition occur at sp^2 (planar) carbon, generating a chiral centre, hence product will be a racemic mixture.

49. [2, 3]

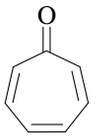
(1) Aromatic

(2) Anti aromatic

(3) Anti



(4) Aromatic



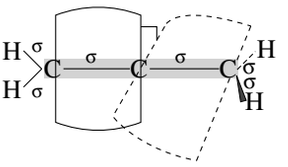
Anti aromatic substance also unstable

50. [2]

Allene is the name given to propdiene, $H_2C=C=CH_2$.

Hybridisation of an atom is determined by determining the number of hybrid orbitals at that atom which is equal to the number of sigma (s) bonds plus number of lone pairs at the concerned atom.

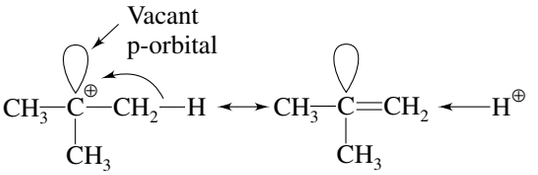
Pi(π) bonds are not formed by hybrid orbitals, therefore, not counted for hybridisation.



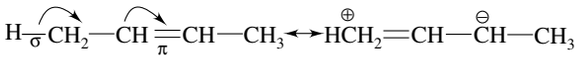
Here, the terminal carbons have only three sigma bonds associated with them, therefore, hybridisation of terminal carbons is sp^3. The central carbon has only two sigma bonds associated, hence hybridisation at central carbon is sp.

51. [1]

Spreading out charge by the overlap of an empty p-orbital with an adjacent σ bond is called hyper-conjugation. This overlap (the hyperconjugation) delocalises the positive charge on the carbocation, spreading it over a larger volume, and this stabilises the carbocation.



tertiary butyl carbocation has one vacant p-orbital hence, it is stabilised by σ-p (empty) hyperconjugation.



In 2-butene, stabilisation is due to hyperconjugation between $\sigma - \pi^*$ electron delocalisation.

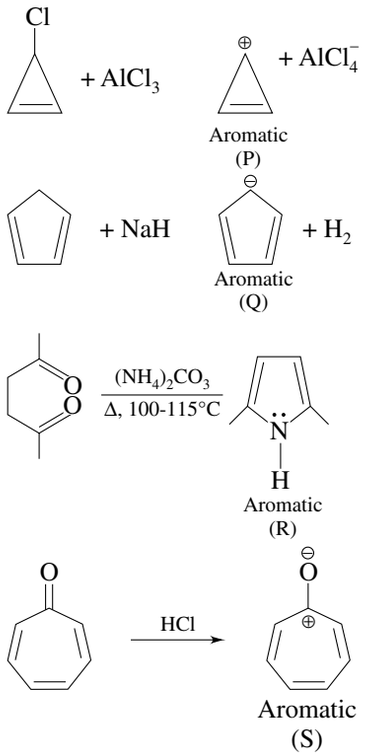
52. [1, 2, 3, 4]

A species is said to have aromatic character if

(a) ring is planar.

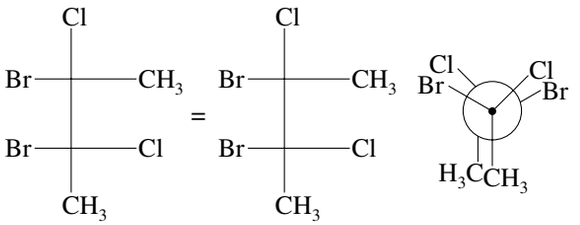
(b) there is complete delocalisation of p electrons.

(c) Huckel rule, i.e. (4n + 2) rule is followed. Where n is the number of rings (4n + 2) = π electron delocalised.

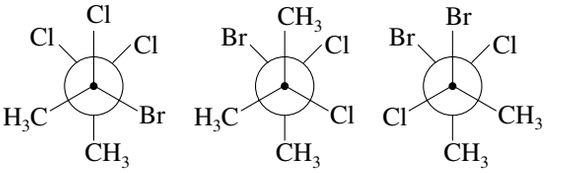


53. [3]

This problem can be solved by using concept of conformational analysis of given organic compound. To the question draw the stable conformational structures of organic compound and determine the net resultant dipole moment.



Stable conformer (with $\mu \neq 0$)



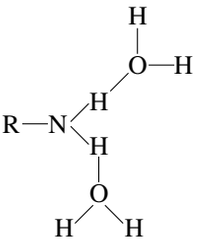
These three have non-zero dipole moment due to non-cancellation of all dipole moment created by C–Cl and C–Br bond.

54. [1, 2, 4]

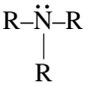
This problem can be solved by using concept of H-bonding and applications of H-bonding.

(1) Ice floats in water due to the low density of ice as compare to water which is due to open cage like structure (formed by intermolecular H-bonding).

(2) Basic strength of $RNH_2 > R_3N$. It is also explained by hydrogen bonding.

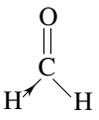


Two H-bonds are possible with water present in aqueous solution. (stabilise by solvation)

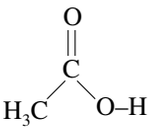


No H-bonding is possible with water present in aqueous solution. (stabilisation by salvation is very)

(3)

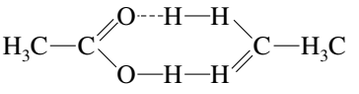


More acidic due to the presence of H. (Due to the absence of electron donating group)



Less acidic than HCOOH due to presence of CH_3 (Electron donating group)

(4) Dimerisation of acetic acid in benzene is due to intermolecular hydrogen bonding.



55. [1]

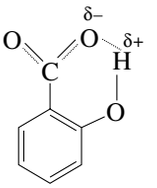
–OH group displays both kinds of effect:

An electron withdrawing acid-strengthening inductive effect from the meta-position and an electron-releasing acid weakening resonance effect from the para-position (at this position, resonance effect overweighs the inductive effect)

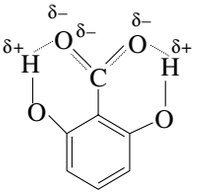
o-hydroxybenzoic acid (II) is far stronger than the corresponding meta and para isomers as the carboxylate ion it stabilised by intramolecular H-bonding

2,6-dihydroxybenzoic acid (I) forms carboxylate ion which is further stabilised by intramoleular H-bonding, Thus, correct order is

I > II > III > IV



II



I
(most stable)