GENERAL ORGANIC CHEMISTRY-II

CONTENTS

JEE(Advanced) Syllabus

Fission of covalent bond: Free radicals, electrophiles, nucleophiles, carbocations, carbonanions and tautomerism. Acidic and basic strength of organic compounds.

JEE(Main) Syllabus

Bases, Acids & Tautomerism : Inductive, Resonance and Hyperconjugation Effect, Applications of Electronic Effects, Tautomerism and Acid-base.

General Organic Chemistry-II

Applications of electronic effects:

Th1: Reaction intermediates

Reactive, shortlived, high energy, unstable species, those are formed in the course of organic reactions are called reaction intermediates.

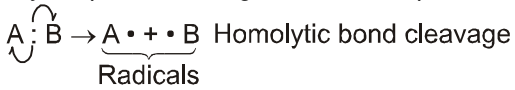
Reaction intermediates generally formed after bond breaking and before bond formation.

A covalent bond can get cleaved by:

(i) Heterolytic cleavage (ii) Homolytic cleavage.

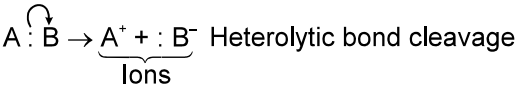
Homolytic fission of covalent bonds:

The bond may break in such a way that each fragment takes away one of the electrons of the bond. This process is called homolysis, produces fragments with unpaired electron called radicals.

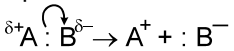


Heterolytic fission of covalent bonds:

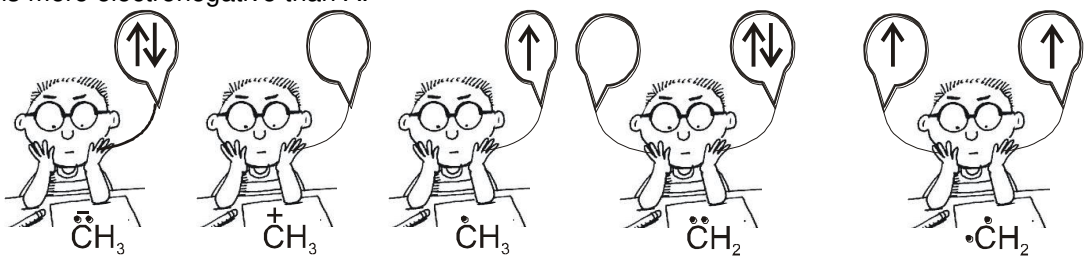
The bond breaks in such a way that one fragment takes away both electrons of the bond, leaving the other fragment with an empty orbital. This kind of cleavage called heterolysis, produces charged fragments or ions.



Heterolysis of a bond normally requires polarized bond.



Polarisation of a bond usually result from different electronegatives of the atoms joined by the bond. The greater the difference in electronegativity, the greater the polarisation. In the given instance, atom B is more electronegative than A.



Section (A) : Carbanions

D1: A carbon intermediate which contain three bond pair and a negative charge on it, is called carbanion.

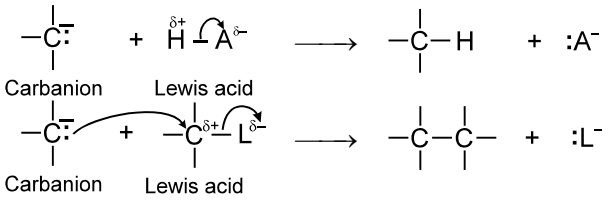
Hybridisation: Hybridisation of carbanion may be sp^3, sp^2 or sp.

Hybridisation	Example
sp^3	$\overset{\ominus}{C}H_3$, $CH_3-\overset{\ominus}{C}H_2$, $CH_3\overset{\ominus}{C}HCH_3$, $(CH_3)_3\overset{\ominus}{C}$, 
sp^2	$H_2C=\overset{\ominus}{C}H$, $CH_2=CH-\overset{\ominus}{C}H_2$, 
sp	$HC\equiv\overset{\ominus}{C}$

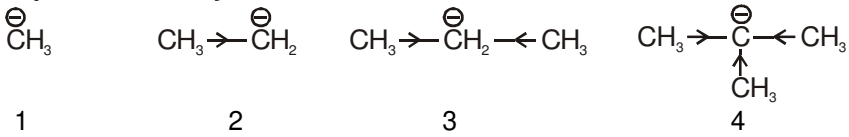
Stability of carbanion: Carbanions are stabilised by electron withdrawing effect as

(i) – I effect (ii) –M effect (iii) Delocalisation of charge

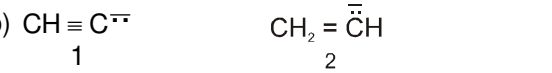
Carbanions are Lewis bases. In their reactions they seek a proton or some other positive centre to which they can donate their electron pair and thereby neutralize their negative charge.



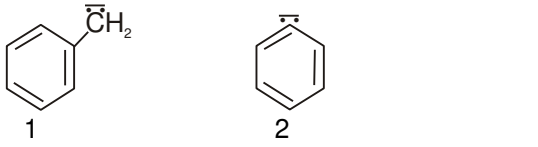
Examples of stability order:

Ex. (a)  (Stability order: 1>2>3>4)

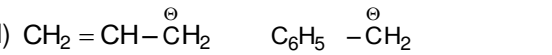
1 2 3 4

(b)  (Stability order: 1 > 2 > 3)

1 2 3

(c)  (Stability order:1 > 2 > 3)

1 2 3

(d)  (Stability order : 1 < 2 < 3)

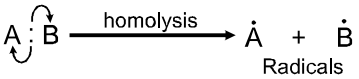
1 2 3

Rearrangement: Generally carbanions do not undergo rearrangement.

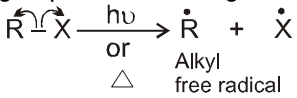
Section (B) : Carbon free radicals

D2: **Free radical:** An uncharged intermediate which has three bond pair and an unpaired electron on carbon.

Homolysis of covalent bond results into free radical intermediates possess the unpaired electrons.



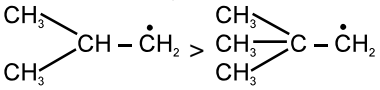
It is generated in presence of sun light, peroxides or high temperature



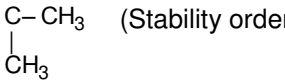
Note: (i) It is neutral species with odd e^-.
(ii) It is paramagnetic in nature due to odd e^-.
(iii) Rearrangement is not observed generally.
(iv) Carbon atom having odd electron is in sp^2 hybridised state
(v) Any reaction if it is carried out in the presence of sunlight, peroxide or high temperature it generally proceeds via free radical intermediate.

☞ **Stability of free radical:** It is stabilised by resonance, hyperconjugation and + I groups.

Ex. (a) $\dot{C}H_3 < CH_3-\dot{C}H_2 < CH_3-\dot{C}H-CH_3 < CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{\dot{C}}}}}-CH_3$ (Stability order)

(b) $CH_3-\dot{C}H_2 > CH_3-CH_2-\dot{C}H_2 >$  (Stability order)

(Due to resultant of inductive effect and hyperconjugation, both operates in same direction)

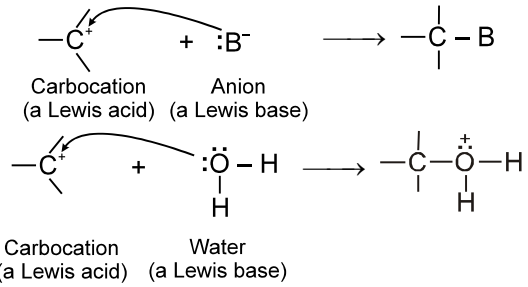
(c) $(C_6H_5)_3C^{\bullet} > (C_6H_5)_2\dot{C}H > C_6H_5-\dot{C}H_2 >$  (Stability order)

Section (C) : Carbocations

D3: A carbon intermediate which contain three bond pair & a positive charge on it is called carbocation.
Hybridisation: Carbocation may be sp^2 or sp hybridized.

Hybridisation	Example
sp^2	$\overset{\oplus}{C}H_3$, $CH_3\overset{\oplus}{C}H_2$, $CH_3\overset{\oplus}{C}HCH_3$, $(CH_3)_3\overset{\oplus}{C}$
sp	$H_2C=\overset{\oplus}{C}H$, $HC\equiv\overset{\oplus}{C}$

Carbocations are electron deficient. They have only six electrons in their *valence shell, and because of this, carbocations act as Lewis acids. Most of the carbocations are short*-lived and highly reactive, they occur as intermediates in some organic reactions. Carbocations react with Lewis bases or ions that can donate the electron pair that they need to achieve a stable octet of electrons (i.e., the electronic configuration of a noble gas):



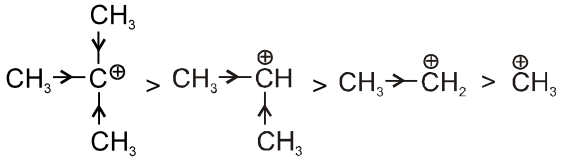
Because carbocations are electron seeking reagents, chemists call them electrophiles. All Lewis acids, including protons, are electrophiles. By accepting an electron pair, a proton achieves the valence shell configuration of helium; carbocations achieve the valence shell configuration of Neon.

Stability: Carbocations are stabilised by
(i) +M effect (ii) Delocalisation of charge (iii) Hyperconjugation (iv) +I effect

General stability order:

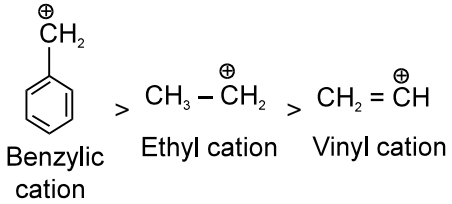
$$Ph_3\overset{\oplus}{C} > Ph_2\overset{\oplus}{C}H > Ph-\overset{\oplus}{C}H-R > CH_2=CH-\overset{\oplus}{C}H-R \gtrsim (CH_3)_3\overset{\oplus}{C} \gtrsim Ph\overset{\oplus}{C}H_2 > CH_2=CH-\overset{\oplus}{C}H_2 \gtrsim (CH_3)_2\overset{\oplus}{C}H > CH_3-\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3 > CH_2=\overset{\oplus}{C}H \simeq$$ 

Ex.



t-Butyl carbocation has +I effect of three Me–groups and also Hyperconjugation effect which makes it most stable.

Ex.



In Benzyl cation, extensive resonance is seen which stabilises $C^{\oplus}$.
In Ethyl carbocation +I and hyperconjugation of Me–group stabilizes carbocation.
In vinyl carbocation stability decreases rapidly since carbon of (CH_2) is sp^2 hybridized which is slightly more electronegative hence acts as – I group which increases (+) charge density.

Rearrangement of carbocations:

Whenever an Intermediate carbocation is formed in reaction it may rearranges.

Only those carbocation will rearrange which can produce more stable species. It can be done either by

(i) Shifting of H, alkyl, aryl, bond (1, 2 shifting)

(ii) Ring expansion (more strained ring to less strained ring)

(iii) Ring contraction

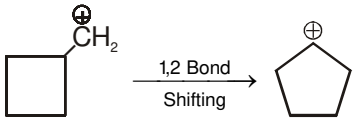
(i) Shifting of H, alkyl, aryl, (1, 2 shift)

(a) $CH_3 - \underset{CH_3}{\overset{}{CH}} - \overset{\oplus}{C}H_2 \xrightarrow[\text{Shifting}]{1,2\ H^{\ominus}} CH_3 - \underset{CH_3}{\overset{\oplus}{C}} - CH_3$

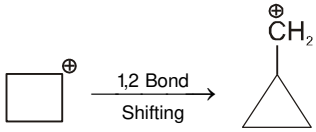
(b) $CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - \overset{\oplus}{C}H_2 \xrightarrow[\text{Shifting}]{1,2\ Me^{\ominus}} CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - CH_2 - CH_3$

(c) $Ph - \underset{Ph}{\overset{Ph}{C}} - \overset{\oplus}{C}H_2 \xrightarrow[\text{Shifting}]{1,2\ Ph^{\ominus}} Ph - \underset{}{\overset{Ph}{C}} - CH_2 - Ph$

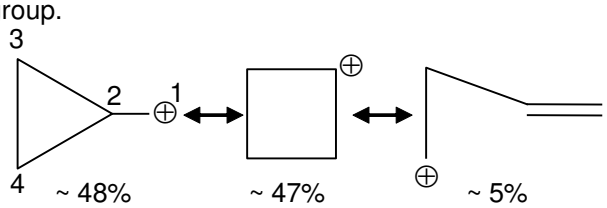
(ii) Ring expansion:



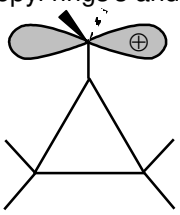
(iii) Ring contraction:



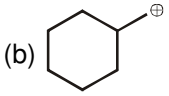
Note: **Cyclopropylmethyl cation:** In solvolysis of simple primary cylcopropylmethyl systems the rate is enhanced because of the participation by the σ-bonds of the rings. The ion that forms initially is an unarranged cyclopropylmethyl cation that is symmetrically stabilized, that is, both the 2, 3 and 2, 4σ-bonds help stabilize the positive charge. Cyclopropyl group stabilizes on adjacent positive charge even better than a phenyl group.

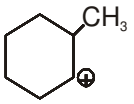
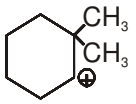
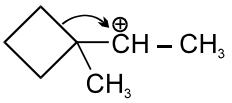


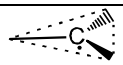
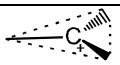
This special stability, which increases with each additional cyclopropyl group, is a result of conjugation between the bend orbitals of the cyclopropyl rings's and the vacant P-orbital of cationic carbon.



Q. Rearrange (if applicable) the following carbocations into more stable form:

(a) $CH_3 - CH_2 - \overset{\oplus}{C}H_2$ (b)  (c) $CH_3 - \underset{CH_3}{\overset{CH_3}{\overset{\oplus}{C}}} - CH - CH_3$

(d)  (e)  (f) 

	Carbon free radical	Carbocation	Carbanion
			
Shape	trigonal planar	trigonal planar	Pyramidal
Hybridisation	sp^2	sp^2	sp^3
No. of electrons in outermost shell	7	6	8

D4: Carbenes (Divalent Carbon intermediates) :

There is a group of intermediates in which carbon forms only two bonds. These neutral divalent carbon species are called carbenes. Most carbenes are highly unstable that are capable of only fleeting existence. Soon after carbenes are formed, they usually react with another molecules.

Methods of preparation of carbene :

$CHCl_3 + HO^{\ominus} \xrightarrow{-HCl} :CCl_2$ $\qquad$ $CH_2I_2 + Zn \xrightarrow[\Delta]{-ZnI_2} :CH_2$

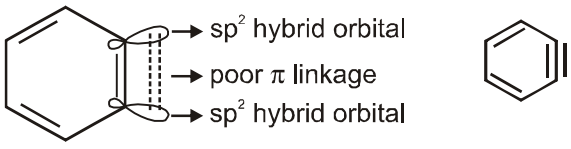
$CH_2N_2 \xrightarrow{h\nu \text{ or } \Delta} N_2\uparrow + :CH_2$ $\qquad$ $CH_2 = C = O \xrightarrow{\Delta} :CH_2 + CO\uparrow$

Types of carbene	**Singlet** 	**Triplet** $-\dot{\underset{\cdot}{C}}-$
Shape	Bent	Linear
Hybridisation	sp^2	sp
Nature of reaction	stereospecific	None
State	Excited state	Ground state
Magnetic	Diamagnetic	Paramagnetic
Nature	Paired electrons	Diradical

D5: Nitrenes: The nitrogen analog of carbenes are nitrenes. They are very much reactive since in them octet of N is incomplete. In nitrenes only one valencies of N are satisfied.

$R - \ddot{N}$ $\qquad$ $H - \ddot{N}$

D6: Benzyne : The benzene ring has one extra C–C π bond in benzyne



Clearly, we can see that the newly formed π bond cannot enter in resonance with other π orbitals of ring. Since it is in perpendicular plane.

It is also important to note that hybridisation of each carbon involved in 'Benzynic bond' is sp^2 since the overlap between these sp^2 hybrid orbitals is not so much effective.

Section (D) : Basic strength

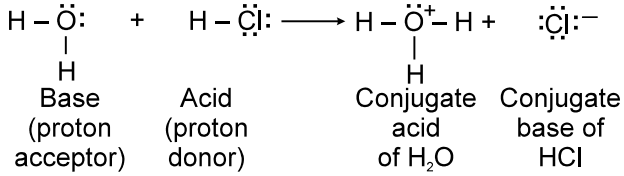
Th2. Bases

D7: **(a) Arhenius base:** Base is a substance that can donate (or loose) OH^- ions in H_2O.

D8: **(b) The Bronsted Lowry definition of acids and bases:**

An acid is a substance that can donate (or loose) a proton, and a base is a substance that can accept a proton.

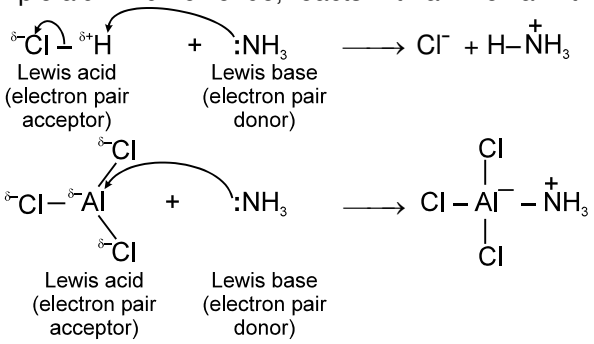
Let us consider, an example of this concept, the reaction that occurs when gaseous hydrogen chloride dissolves in water :



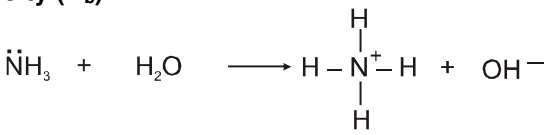
D9: **(c) The Lewis definition of acids and bases:**

Lewis proposed that acids are electron pair acceptors and bases are electron pair donors.

For example aluminiumchloride, reacts with ammonia in the same way that a proton donor does.



(d) Basicity (K_b):



$$K_b = \frac{[NH_4^+]\ [OH^-]}{[NH_3]}$$

$$pK_b = -\log K_b$$

Basicity order in periodic table:

(1) Basic strength decreases down the group,

(2) Basic strength decreases along the period because electron neagativity increases, so electron donor tendency decreases.

1.1 Aliphatic bases:

(1) On the basis of +I effect basic strength of amines should be $3^º > 2^º > 1^º > NH_3$

But this order is applicable only when the amines are in gaseous state or in case of non-polar aprotic solvent.

(2) Basic strength of nitrogeneous compound depends upon the hybridised state of nitrogen

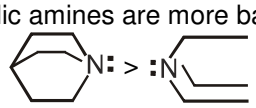
$$R{-}CH_2{-}CH_2{-}NH_2 > R{-}CH_2{-}CH{=}NH > R{-}CH{=}CH{-}NH_2 > R{-}C{\equiv}N$$

sp^3 (localised) sp^2 (localised) sp^2 (delocalised) sp

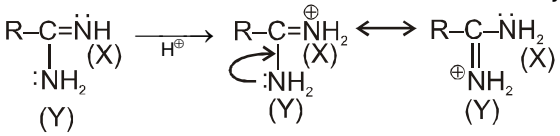
(3) More electronegative atom (–I group) will decrease the basic strength

$$CH_3{-}CH_2{-}CH_2{-}NH_2 > CH_2{=}CH{-}CH_2{-}NH_2 > H{-}C{\equiv}C{-}CH_2{-}NH_2$$

(4) Cyclic amines are more basic than acyclic amines of same nature



(5) Amidines are more basic in nature because their conjugate acid are more stable due to resonance.

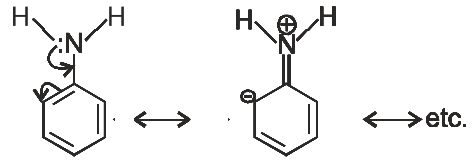


Nitrogen (X) is more basic than nitrogen (Y).

Th3. Basic strength of aromatic amines and substituted anilines:

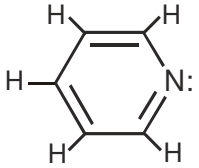
(a) Aniline:

Lone pair of aniline lies in conjugation with a multiple bond, it resides in '2p' atomic orbital, so that it can get resonance stabilisation and hence, basic strength decreases. So, Aniline is a weaker base than NH_3.

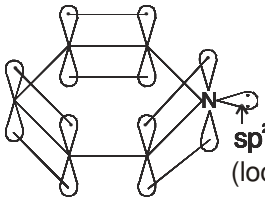


(b) Pyridine (C_5H_5N) : 6-π electrons, aromatic

S.F. :



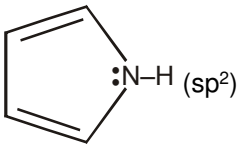
A.O. Diagram:



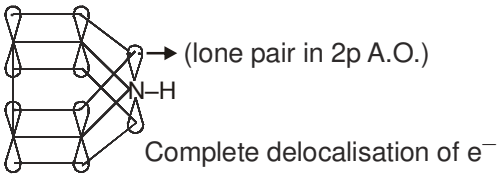
Lone pair of N in pyridine is localised so it is more basic than aniline.

(c) Pyrrole (C_4H_5N:) : 6-π electrons, aromatic

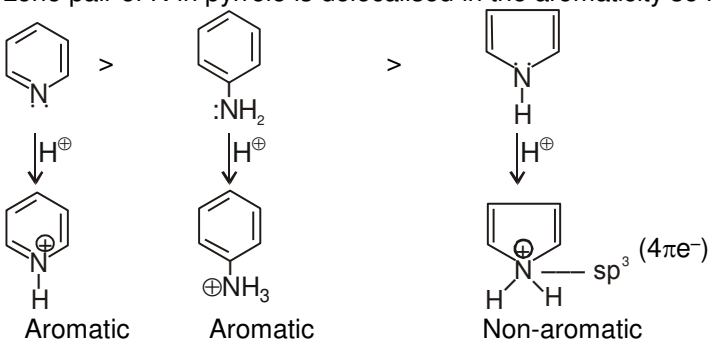
S.F. :



A.O. Diagram:



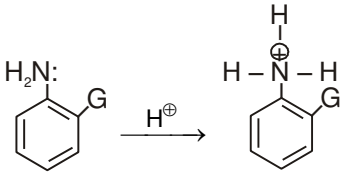
Lone pair of N in pyrrole is delocalised in the aromaticity so it is very less basic than aniline.



(d) Ortho substituted anilines :

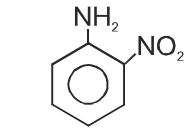
Electron releasing groups (ERG) +M, HC, +I increases the K_b and
Electron withdrawing groups (EWG) –m, –I decreases the K_b

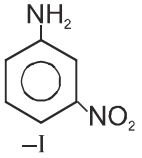
Steric effect of ortho-substituent in aniline (ortho effect) :

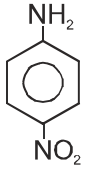


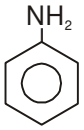
(i) Ortho-substituted anilines are mostly weaker bases than aniline itself.
(ii) Ortho-substituent causes steric hinderance to solvation in the product (conjugate acid i.e. cation).
(iii) The small groups like $-NH_2$ or $-OH$ do not experience (SIR) due to small size.

Ex. (a) G = (–M, –I); NO_2


(–I –M,ortho effect)

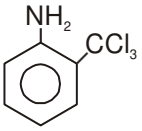

–I

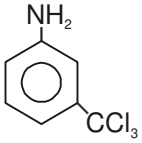

(–I–M)

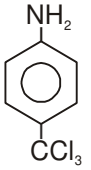


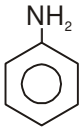
(Aniline > m > p > o).

(b) G = (–I); CCl_3





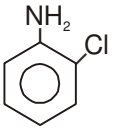


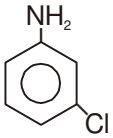


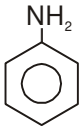
(Aniline > p > m > o).

Only (–I) decides the order.

(c) G = (–I > + m); Cl



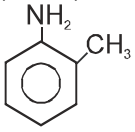


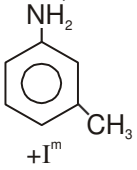


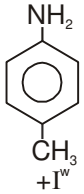
(Aniline > p > m > o)

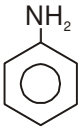
Only (–I) decides the order.

(d) G = (+I, HC); If R = $-CH_3$ (Toluidines)


Ortho effect,
+I
HC

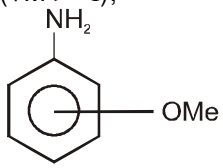

$+I^m$


$+I^w$
HC → more dominating



p > m > aniline > o

(e) G = (+M > –I);



K_b order : p > Aniline > o > m

General basicity order :

$$R_3\overset{\ominus}{C} > R_2\overset{\ominus}{C}H > R-\overset{\ominus}{C}H_2 > \overset{\ominus}{C}H_3 > \overset{\ominus}{P}h > Ph\overset{\ominus}{C}H_2 > \overset{\ominus}{N}H_2 > Ph_2\overset{\ominus}{C}H > Ph_3\overset{\ominus}{C} > \overset{\ominus}{H} > R-C\equiv\overset{\ominus}{C} > R\overset{\ominus}{C}\underset{\underset{O}{\|}}{C}H_2$$


$\approx R-\overset{\ominus}{O} \gtrsim \overset{\ominus}{O}H \gtrsim CH_3\overset{\ominus}{O} > CO_3^{2-} > Ph\overset{\ominus}{O} > R\overset{\ominus}{S} > RCO\overset{\ominus}{O} > O\overset{\ominus}{C}N > H_2O > \overset{\ominus}{Cl}$

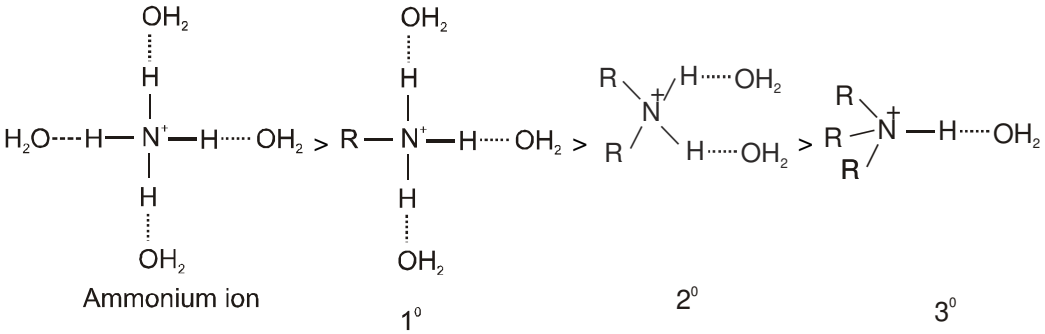
Th4. Solvent effect in bases :

The trend is not regular in the aqueous state as evident by their pKb values given in Table.

Name of amine	pK_b	Name of amine	pK_b
Methanamine	3.38	N,N-Diethylethanamine	3.25
N-Metheylmethanamine	3.27	Phenylmethanamine	4.70
N, N-Dimethylmethanamine	4.22	Aniline	9.38
Ethanamine	3..29	N-Methylaniline	9.30
N-Ethylethanamine	3.00	N,N-Dimethylaniline	8.92

Table : pK_b Values of Amines in Aqueous Phase (Ref. NCERT)

In the aqueous phase, the substituted ammonium cations get stabilised not only by electron releasing effect of the alkyl group (+I) but also by solvation with water molecules. The greater the size of the ion (Alkyl groups are hydrophobic and inhibits H bonding and solvation.), lesser will be the solvation and the less stabilised is the ion. The order of solvation of ions are as follows:



Ammonium ion 1^0 2^0 3^0

Greater is the stability of the substituted ammonium cation, stronger should be the corresponding amine as a base.

On the basis of above two sequences, we can say that the basic strength of amines is the combined effect of inductive effect, steric hindrance and solvation.

$R_2NH > RNH_2 > R_3N > NH_3$ (if $R = CH_3$) ..... (1)

$R_2NH > R_3NH > RNH_2 > NH_3$ (if $R = C_2H_5$) .....(2)

Th5. Reactions of bases :

(i) **Nature of aqueous solution:** Amines combine with water to form alkyl ammonium hydroxides. This gives hydroxide ions in solution, thus the aqueous solution of amines is basic in nature.

$RNH_2 + HOH \rightleftharpoons R\overset{+}{N}H_3OH^- \rightleftharpoons [RNH_3]^+ + OH^-$

1º Amine

$R_2NH + HOH \rightleftharpoons R_2\overset{+}{N}H_2OH^- \rightleftharpoons [R_2NH_2]^+ + OH^-$

2º Amine

The aqueous solution of amines behave like NH_4OH and gives the precipitate of ferric hydroxide with ferric chloride.

$3RNH_3OH + FeCl_3 \longrightarrow Fe(OH)_3 + 3RNH_3Cl$

Brown ppt.

(ii) **Aliphatic and aromatic amines form salt because of their basic nature:**

$RNH_2 + H_2O \longrightarrow R\overset{+}{N}H_3\,\overset{-}{O}H$

Alkylammoniumhydroxide

$RNH_2 + HCl \longrightarrow R\overset{+}{N}H_3\,\overset{-}{C}l$

Alkylammoniumchloride

$RNH_2 + H_2SO_4 \longrightarrow (R\overset{+}{N}H_3)_2\,SO_4^{-2}$

Similarly we get

$C_6H_5NH_2 + H_2O \longrightarrow C_6H_5\overset{+}{N}H_3\,\overset{-}{O}H$

Aniliniumhydroxide

$C_6H_5NH_2 + HCl \longrightarrow C_6H_5\overset{+}{N}H_3\,\overset{-}{C}l$ or $C_6H_5NH_2 : HCl$

Aniliniumchloride Anilinehydrochloride

Salts of amines are ionic compounds and hence water soluble.

Section (E) : Acidic strength

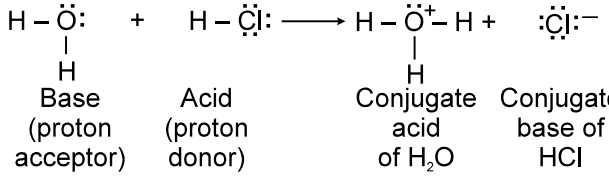
Th6. Acids

D10: **(a) Arhenius acid:** An acid is a substance that can donate (or loose) a proton in H_2O.

D11: **(b) The Bronsted Lowry definition of acids and bases:**

An acid is a substance that can donate (or loose) a proton, and a base is a substance that can accept a proton.

Let us consider, an example of this concept, the reaction that occurs when gaseous hydrogen chloride dissolves in water :

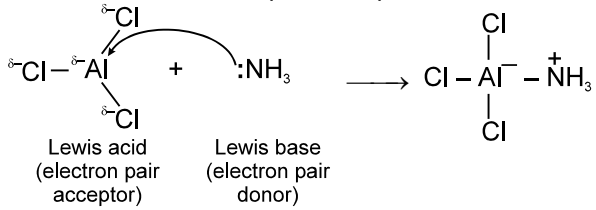


Hydrogen chloride, a very strong acid, transfers its proton to water. Water acts as a base and accepts the proton. The products that result from this reaction are a hydronium ion (H_3O^+) and a chloride ion (Cl^-).

The molecule or ion that forms when an acid loses its proton is called the conjugate base of that acid. (The chloride ion is the conjugate base of HCl). The molecule or ion that is formed when a base accepts a proton is called the conjugate acid of that base.

D12: **(c) The Lewis definition of acids and bases**

Lewis proposed that acids are electron pair acceptors and bases are electron pair donors.



(d) Acid dissociation constant (K_a) :

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

$$K_{eq} = \frac{[RCOO^-]\ [H_3O^+]}{[RCOOH]\ [H_2O]}$$

$$K_a = \frac{[RCOO^-]\ [H_3O^+]}{[RCOOH]}$$

$$pK_a = -\log K_a$$

6.1 Relative acidity of hydrocarbons :

Being most electronegative the sp hybridised carbon atom of ethyne polarizes its C–H bond to the greatest extent causing its H to be most positive therefore ethyne is most acidic hydrocarbon.

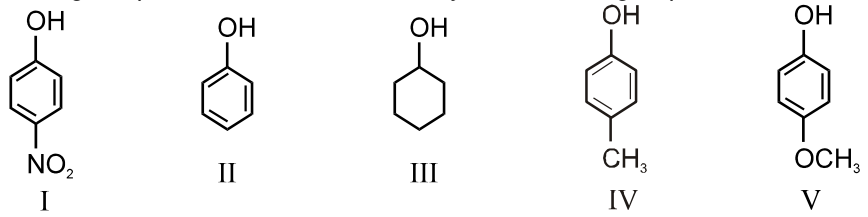
$HC \equiv CH > H_2C = CH_2 > H_3C - CH_3$

6.2 Acidity of phenols :

The phenoxide ion is more stabilised by resonance than the unionised phenol.

Groups which are –I, –m increases acidic character of phenol because effectively dispersing the negative charge of phenoxide ion. Alternatively + I and + m groups decreases acid strength.

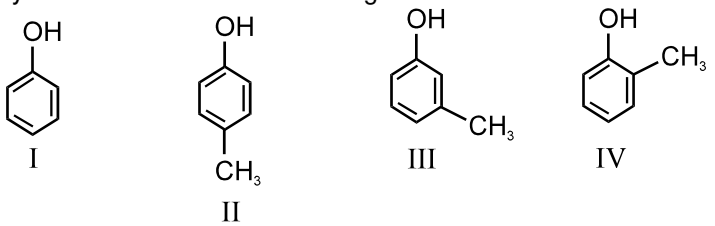
Ex. (a)



Ans. Acid strength order : I > II > IV > V > III

Sol. Step-1. III will be least acidic as it has no dispersion of negative charge (No delocalisation of negative charge).
Step-2. Since –I, –m group will increase acid strength, Nitrophenol will be most acidic followed by phenol,
Step-3. Amongst cresol and methoxyphenol, methoxyphenol has +M effect of $-OCH_3$ which increases e^- density hence decrease acidic strength

Ex. (b)

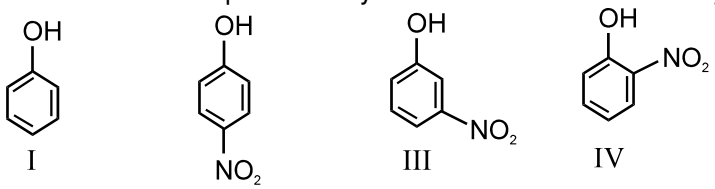


I II III IV

Ans. Acid strengh order: I > III > II > IV

Sol. Step-1: Notice that CH_3 have +I effect so all methylphenols (cresols) are less acidic than phenol (I).
Step-2: Now amongst cresols p- and o-CH_3 are increasing the e^- density due to their hyper conjugation but ortho isomer has viable +I effect also, which will help in destabilising phenoxide ion therefore o- is least acidic. Since at meta position only +I works it as least e^- density amongst the cresol.

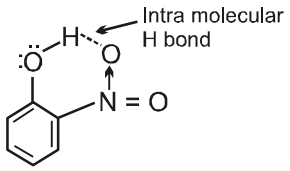
Ex. (c)



I II III IV

Ans. Acid strength order: II > IV > III > I

Sol. Step-1 : In nitrophenols –I effect of NO_2 will help to increase acidic strength hence phenol is least acidic amongst all nitrophenols
Step-2 : Only –I effect is applicable in meta nitrophenol it will be number three. Now –o, –p have both –I and –m effect of NO_2 group over OH and in this particular case para isomer is more acidic than ortho since



H is trapped by NO_2 group.

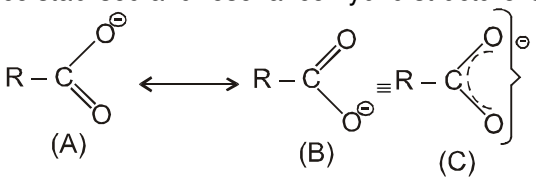
Table : pK_a values of some phenols and Ethanol. **(Ref. NCERT)**

Compound	Formula	pKa	Compound	Formula	pKa
o-Nitrophenol	o–O_2N–C_6H_4–OH	7.2	o-Cresol	o-CH_3–C_6H_4–OH	10.2
m-Nitrophenol	m–O_2N–C_6H_4–OH	8.3	m-Cresol	m-$CH_3C_6H_4$–OH	10.1
p-Nitrophenol	p-O_2N–C_6H_4–OH	7.1	p-Cresol	p-CH_3–C_6H_4–OH	10.2
Phenol	C_6H_5–OH	10	Ethanol	C_2H_5OH	15.9

From the above data, you will note that phenol is million times more acidic than ethanol.

6.3 Acidity of carboxylic acids :

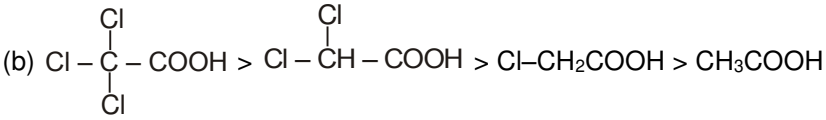
Conjugate base of carboxylic acid exists as two equivalent cannonical structures (A) and (B). This ion is resonance stablised and resonance hybrid structure is (C).



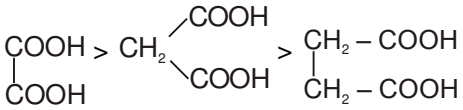
(A) (B) (C)

Electron withdrawing group (–M, –I effect) increases acidic nature.
Electron releasing group (+M, +I effect) decreases acidic nature.

Ex. (a) $F–CH_2–COOH > Cl–CH_2COOH > Br–CH_2COOH > I–CH_2COOH$

(b) 

(c) $HCOOH > CH_3COOH > CH_3–CH_2–COOH$

(d) 

The effect of the following groups in increasing acidicty order is **[Ref. NCERT]**

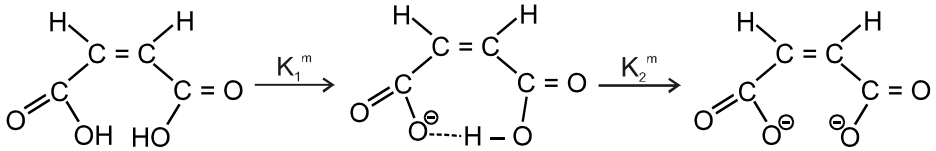
$Ph < I < Br < Cl < F < CN < NO_2 < CF_3$

Thus, the following acids are arranged in order of decreasing acidity (based on pK_a values) :

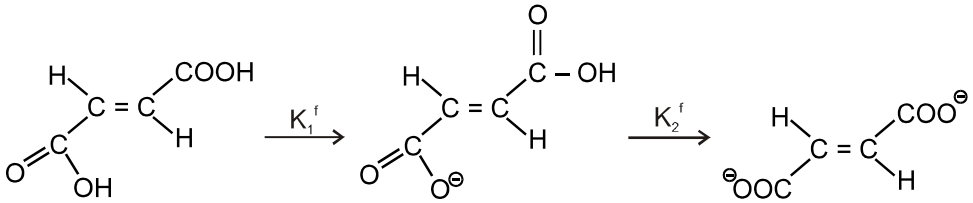
$CF_3COOH > CCl_3COOH > CHCl_2COOH > NO_2CH_2COOH > NC–CH_2COOH > FCH_2COOH > ClCH_2COOH > BrCH_2COOH > HCOOH > ClCH_2CH_2COOH > C_6H_5COOH > C_6H_5CH_2COOH > CH_3COOH > CH_3CH_2COOH$

6.4 Comparison between two geometrical isomers :

Maleic acid :



Fumaric acid :



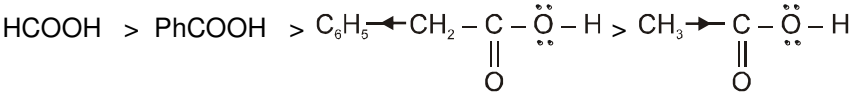
Now $K_1^m > K_1^f$

Since the conjugate base is stabilised by intramolecular H bonding.

But $K_2^f > K_2^m$ Since in maleate ion, after donation of $H^{\oplus}$ two $–COO^{\ominus}$ groups faces each other and makes system unstable. In fumarate ion this repulsion is minimised.

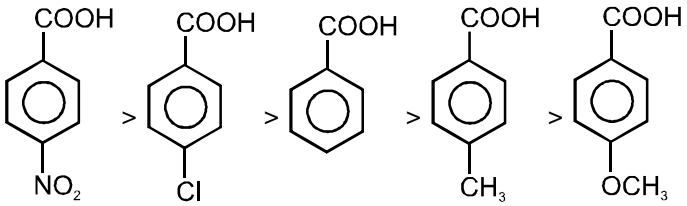
6.5 Acidic strength of substituted benzoic acids :

Formic acid is more acidic than benzoic acid while phenyl acetic acid is more acidic than acetic acid.

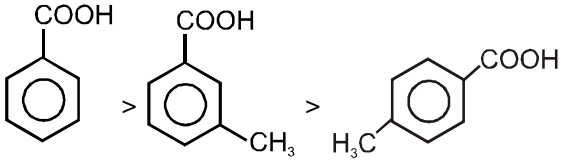


Electron withdrawing group attached to benzene ring will increase the acidic strength while electron releasing group decreases acidic strength.

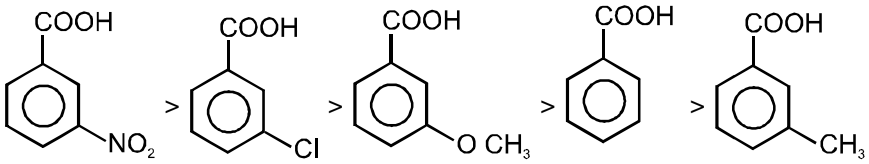
If electron donating group present at para position than it is always less acidic than benzoic acid.



Also it is less acidic then meta substituted benzoic acid.



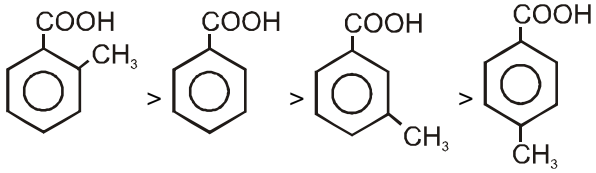
On the other hand if e^- withdrawing group is present at meta position then it is more acidic than benzoic acid.



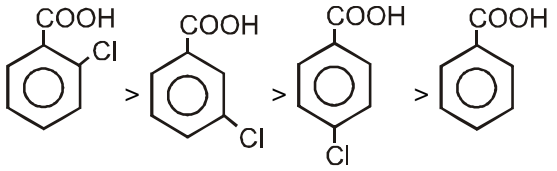
Th7. Ortho effect :

D13. It is common observation that generally ortho substituted benzoic acids are more acidic as compared to their isomers and benzoic acids itself. This is called ortho effect (which is combined effect of steric hindrance, crowding & electronic effect) in benzoic acid. However exceptions are seen.

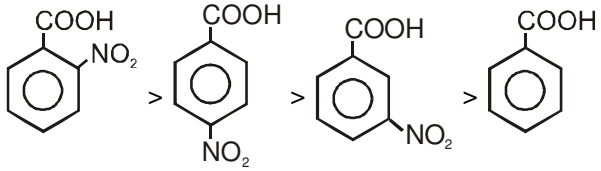
Ex. (a)



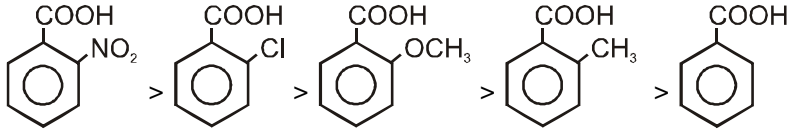
(b)



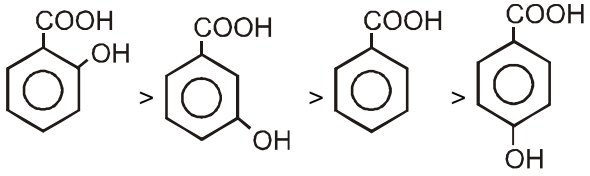
(c)



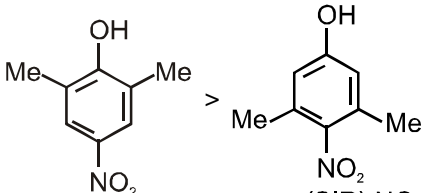
(d)



(e)



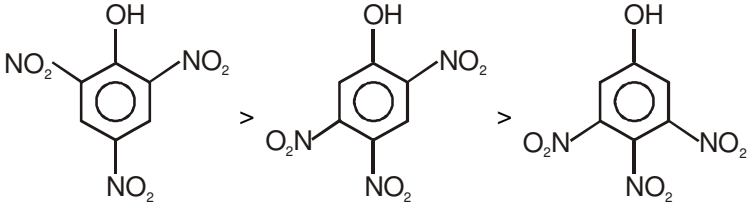
(f)



(–m)

(SIR) NO_2 not in plane, so NO_2group does not exerts –m with benzene nucleus

(g)



(picric acid)

Section (F) : Feasible reactions of acids and bases

Th8. Reaction of acid with salt:

(1) NaX + HY ⟶ NaY + HX

Salt of Weak acid Strong Acid

Remark: A stronger acid displaces the weaker acid from weak acid metal salt. The weaker acid is released out as a gas or liquid or precipitates out as a solid. The weaker acid cannot displace the stronger acid from the salt.

1. $2\,NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl$
2. $Na_2SO_4 + 2HCl \longrightarrow$ No reaction
3. $CH_3COONa + CH_3SO_3H \longrightarrow CH_3COOH + CH_3SO_3Na$ (feasible)
4. $CH_3COONa + PhOH \longrightarrow PhONa + CH_3COOH$ (not feasible)

Section (G) : Tautomerism

Th9. Tautomerism

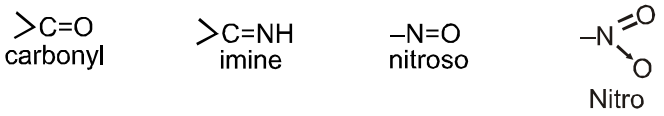
D14: Definition :

Tautomerism is a phenomenon by which a single compound exists in two or more readily interconvertible structures that differ in the relative positions of at least one atomic nucleus, generally hydrogen.

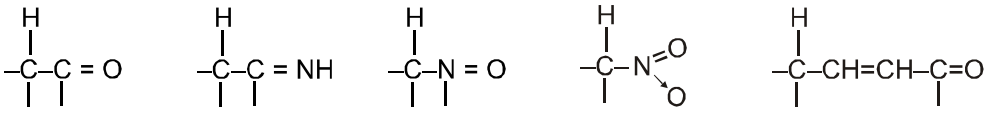
These two isomers remain in dynamic equilibrium and can be isolated also give different lab test.

Conditions :

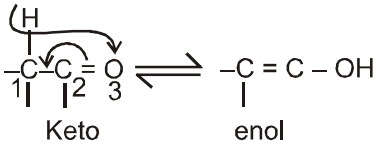
1. Usually present in the following functional groups



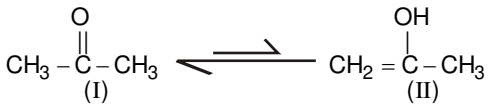
2. Basic need for its existence is attachment of these groups with the sp^3 hybridised C-atom having atleast one hydrogen atom as –

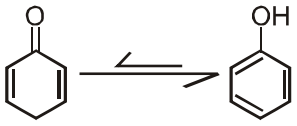


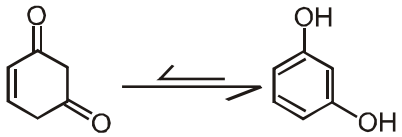
To get tautomer of above structures α-hydrogen atom is shifting to more electronegative atom attached to double bond (i.e. hydrogen atom from 1st atom to 3rd atom) and double bond is developed between 1,2-atom from 2,3-atom. This can be represented as:

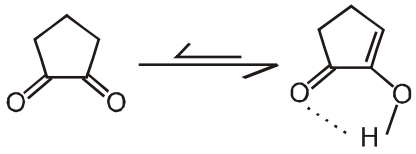


These two forms (remain in equilibrium) are called tautomers of each other. The interconvertibility of tautomers is a chemical reaction which involves making and breaking of bonds.

Ex. (a) 

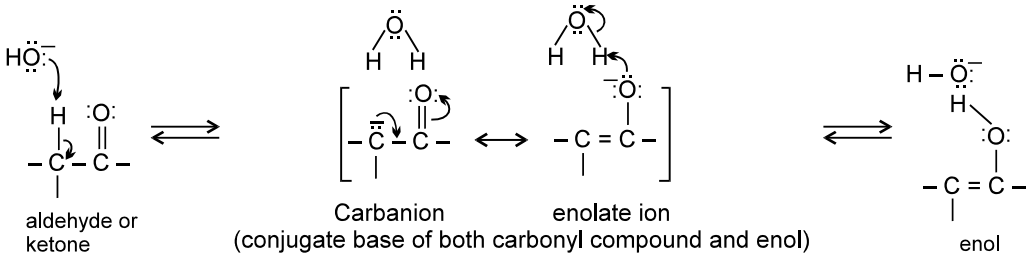
(b) 

(c) 

(d) 

Th10. Keto-enol tautomerisation :

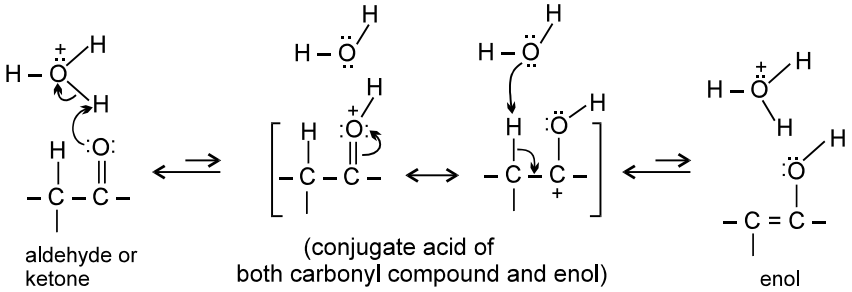
10.1 (A) Base-catalyzed enolization :



Protonation of the carbanion by water on the α-carbon gives back the carbonyl compound. Protonation on oxygen gives the enol. Notice that the enolate ion is the conjugate base of both the carbonyl compound and the enol.

(B) Acid-catalyzed enolization :

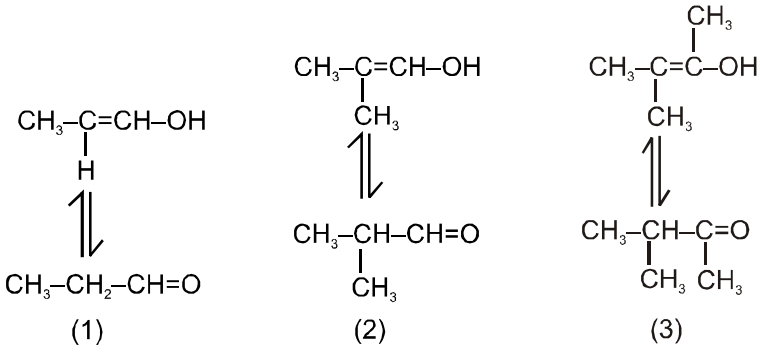
Involves the conjugate acid of the carbonyl compound. Recall that this ion has carbocation characteristics. Loss of the proton from oxygen gives back the starting carbonyl compound; loss of the proton from the α-carbon gives the enol. Notice that an enol and its carbonyl isomer have the same conjugate acid.



10.2 % Enol content in the carbonyl compounds :

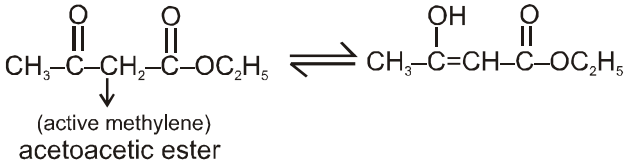
(a) For monocarbonyl % Enol is very less

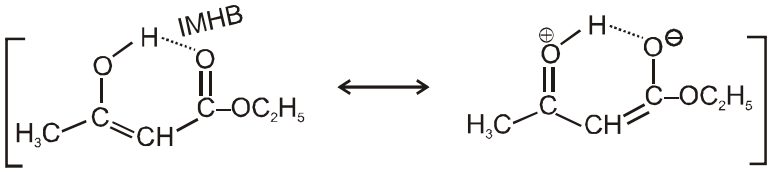
(b) Enol content increases with increase in the stability of enol by resonance, hyperconjugation, hydrogen bonding etc.



Decreasing order of enol content for above carbonyl compounds is : 3 > 2 > 1.

(c) For a carbonyl compound having active methylene group percentage of enol content will be more because enolic form has intramolecular H-bonding and also it will be stabilised by resonance.





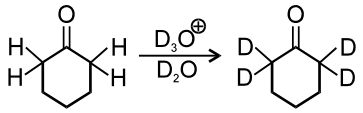
(d) If active methylene group is more acidic then enol content will be more.

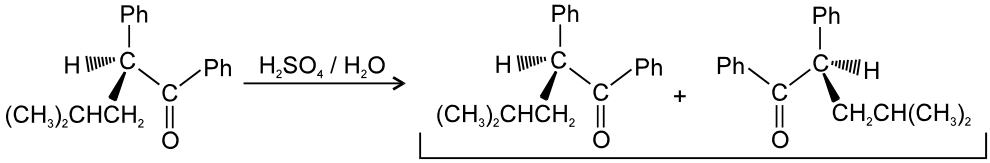
For example in acetyl acetone ($CH_3–\overset{O}{\overset{\|}{C}}–CH_2–\overset{O}{\overset{\|}{C}}–CH_3$) enolic content is 75–76% while it is 7–8% in acetoacetic ester because ester group shows less electron withdrawing nature than keto group.

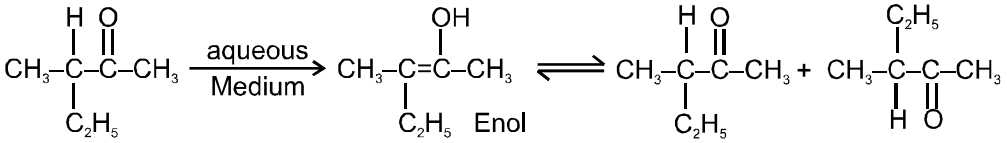
(e) Percentage of enol content is more in non-polar media while % of keto form is more in polar media.

Th11. Racemisation and D-exchange :

Exchange of α-hydrogen from deuterium as well as racemization at the α-carbon are catalyzed not only by bases but also by acids due to the phenomenon of tautomerisation.

1.  (D-exchange)

2. 

3. 

Optical acitive — Optical inacitive — (dℓ mixture)

Th12. Other examples of tautomers *(not to be done in class only for the reference of students)*

(a) Imine-Enamine system :

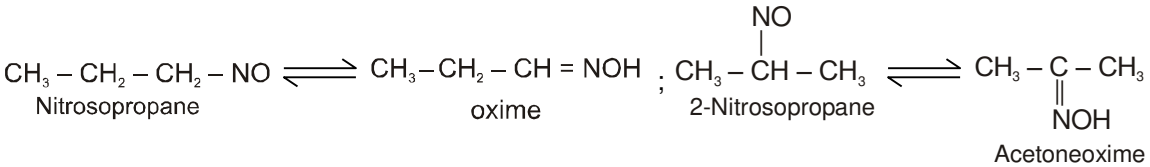
$$R_2CH – CR = NR \rightleftharpoons R_2C = CR – NH – R$$

Imine — Enamine

Among these two tautomers, enamines are stable only when there is no hydrogen on the nitrogen, otherwise the imine form predominates.

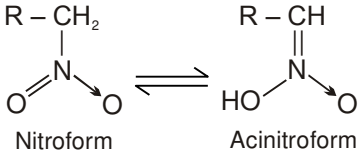
(b) Nitroso-oxime system:

Like primary and secondary nitro compounds, primary and secondary nitroso compounds also exhibit tautomerism with their more stable isonitroso or oxime form.



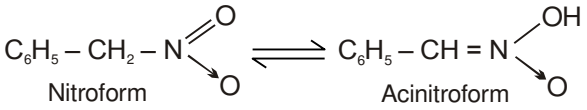
(c) Nitro-Acinitro system:

The acidic nature of the nitro compounds gives rise to the belief that the nitro compounds exist in two forms, a more stable or normal nitro form and the less stable acinitro form.



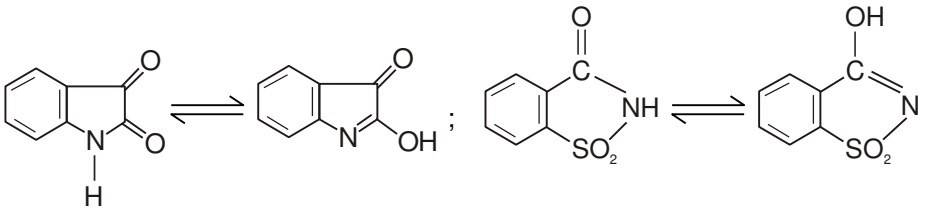
Nitroform Acinitroform

The stability of the nitro form is more as compared to the acinitro form because it is stabilised by resonance.



Nitroform Acinitroform

(d) Lactam-Lactim system :



CHECK LIST

	Definitions (D)	
D1 :	Carbanion	☐
D2 :	Free radicals	☐
D3 :	Carbocation	☐
D4 :	Carbenes (Divalent carbon intermediates)	☐
D5 :	Nitrenes	☐
D6 :	Benzyne	☐
D7 :	Arhenius base	☐
D8 :	Bronsted base	☐
D9 :	Lewis definition of acids and bases	☐
D10 :	Arhenius acid	☐
D11 :	Bronsted acid	☐
D12 :	Lewis definition of acids and bases	☐
D13 :	Ortho effect	☐
D14 :	Tautomerism	☐

	Theories (Th)	
Th1 :	Reaction intermediates	☐
Th2 :	Bases	☐
Th3 :	Basic strength of aromatic amines and substituted anilines	☐
Th4 :	Solvent effect in bases	☐
Th5 :	Reactions of bases	☐
Th6 :	Acids	☐
Th7 :	Ortho effect	☐
Th8 :	Reactions of acids with salts	☐
Th9 :	Tautomerism	☐
Th10 :	Keto-enol tautomerisation	☐
Th11 :	Racemisation and D-exchange	☐
Th12 :	Other examples of tautomers	☐

Exercise-1

Marked questions are recommended for Revision.

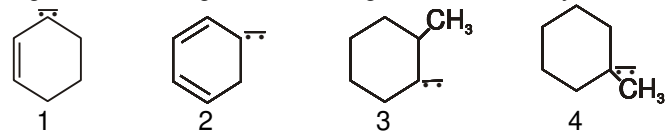
PART - I : SUBJECTIVE QUESTIONS

Section (A) : Carbanions

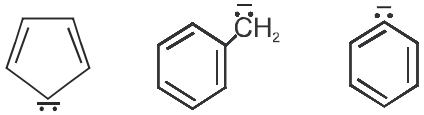
A-1. Arrange the following in decreasing order of stability.

(a)	$\overset{\ominus}{C}H_2-NO_2$, 1	$\overset{\ominus}{C}H_2-CHO$ 2	$CH\equiv\overset{\ominus}{C}$ 3
(b)	$CH_3-CH_2-CH_2-\overset{\ominus}{C}H_2$ 1	$CH_3-\overset{\ominus}{C}H-CH_2CH_3$ 2	$(CH_3)_2\overset{\ominus}{C}-CH_2CH_3$ 3

A-2. Arrange the following in decreasing order of stability

(a) 

1 2 3 4

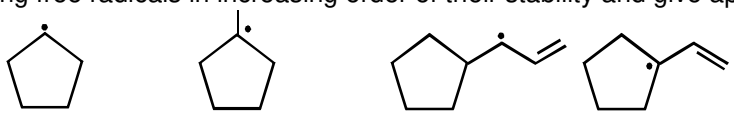
(b) 

1 2 3

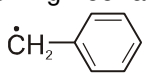
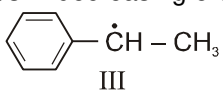
(c) $\overline{\underline{C}}Cl_3$ $\overline{\underline{C}}F_3$
1 2

Section (B) : Carbon free radicals

B-1. Rank the following free radicals in increasing order of their stability and give appropriate reasons.

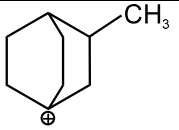
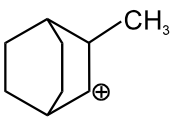
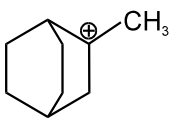
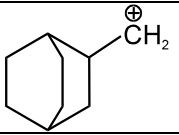

(I) (II) (III) (IV)

B-2. Arrange the following free radicals in decreasing order of stability :

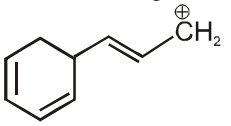
$CH_3-\dot{C}H_2$ I  II  III $\dot{C}H_3$ IV

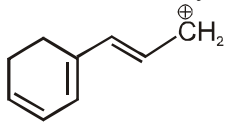
Section (C) : Carbocations

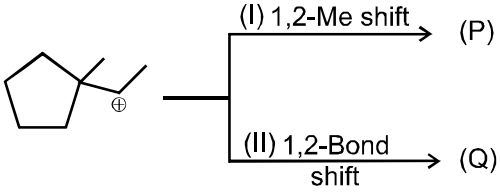
C-1. Arrange the following carbocations in decreasing order of their stability :

	(I)	(II)	(III)	(IV)
(P)	$CH_3-CH_2-\overset{\oplus}{C}H_2$	$CH_3-CH(F)-\overset{\oplus}{C}H_2$	$CH_3-CH(Br)-\overset{\oplus}{C}H_2$	$CH_3-CH(Cl)-\overset{\oplus}{C}H_2$
(Q)	$CH_3-\overset{\oplus}{C}H-C_2H_5$	$(CH_3)_2\overset{\oplus}{C}-CH_3$	$Ph-\overset{\oplus}{C}(CH_3)-C_2H_5$	$Ph-\overset{\oplus}{C}(Ph)-C_2H_5$
(R)				

C-2. Which of the following carbocation is more stable and why ?


(I)


(II)

C-3. 

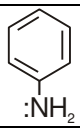
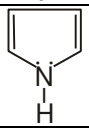
Draw the structures of P and Q.

Section (D) : Basic strength

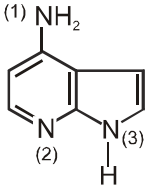
D-1. Compare the basic strength of the following compounds:

$C_2H_5O^-$ **(I)** $C_2H_5^-$ **(II)** $C_2H_5NH^-$ **(III)** NH_2^- **(IV)** F^- **(V)**

D-2. Compare the basic strength of the following compounds :

(a)	$PhNH_2$	Ph_2NH	Ph_3N
(b)			
(c)	$CH_3–\underset{\displaystyle Ph}{\underset{\vert}{CH}}–NH_2$	$CH_3–CH_2–\underset{\displaystyle Ph}{\underset{\vert}{\ddot{N}H}}$	$Ph–CH_2–CH_2–NH_2$

D-3. Which of the following group is most basic in the given compounds :

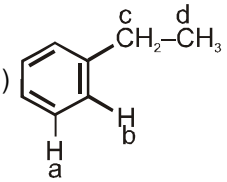


D-4. Which of the following is a stronger base ? Give reason to justify your answer.

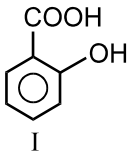
$CH_2 = CH – \ddot{N}H_2$ (I) $\qquad$ $CH_2 = \ddot{N} – CH_3$ (II)

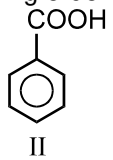
Section (E) : Acidic strength

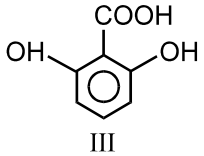
E-1. Which 'H' atom is most acidic in the following compounds.

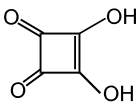
(I) $\overset{a}{CH_3}–\overset{b}{CH}=\overset{c}{CH_2}$ $\qquad$ (II) $\overset{a}{CH_3}–\overset{\displaystyle O}{\overset{\Vert}{C}}–\overset{b}{CH_2}–\overset{\displaystyle O}{\overset{\Vert}{C}}–\overset{c}{H}$ $\qquad$ (III) 

E-2. Arrange the following in decreasing order of acidity


I


II


III

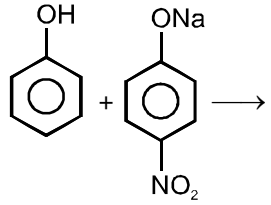
E-3. The given compound X =  is a strong acid. Justify this statement.

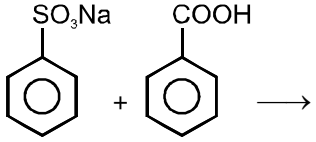
Section (F) : Feasible reactions of acids and bases

F-1. Which of the follwing reactions is/are feasible ?

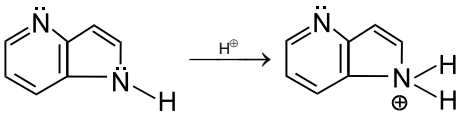
(a) $CH_3COOH + HCOONa \longrightarrow$

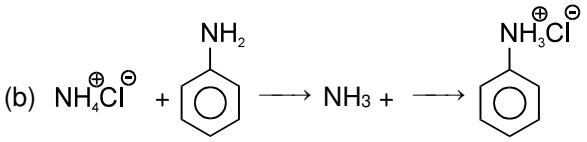
(b) $HC\equiv C-Na + H_2O \longrightarrow$

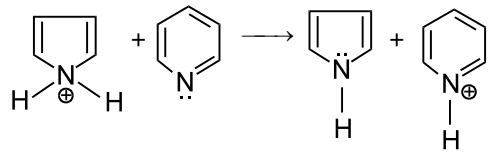
(c) 

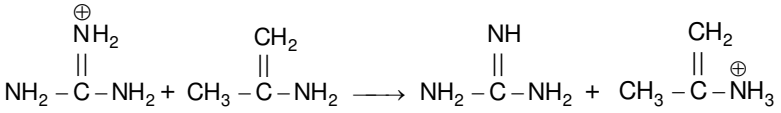
(d) 

F-2. Which of the following reaction is feasible?

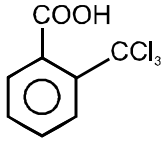
(a) 

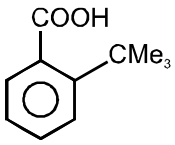
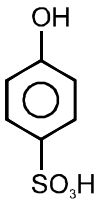
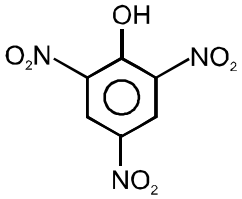
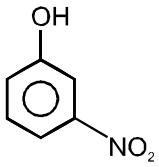
(b) 

(c) 

(d) 

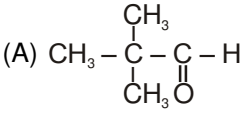
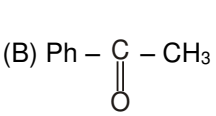
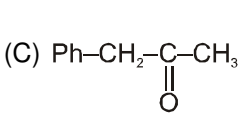
F-3. Which of the following acids (given below) react with $NaHCO_3$ and liberate $CO_2(g)$?

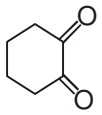
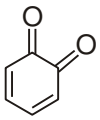
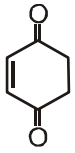
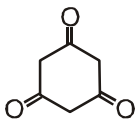
CCl_3-COOH CH_3-CH_2-OH  HCl

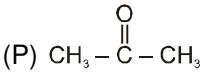
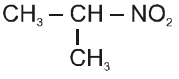
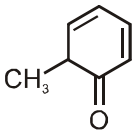
Section (G) : Tautomerism

G-1. Which of the following compounds can exhibit tautomerism ?

(A)  (B)  (C)  (D) 

(E)  (F)  (G)  (H) 

G-2. Write the tautomers of the following compounds :

(P)  (Q) $CH_3-CH=NH$ (R)  (S) 

G-3. Monocarbonyl compounds have very small percentage enol form at equilibrium. Explain.

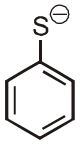
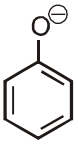
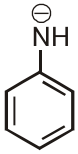
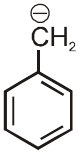
PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Carbanions

A-1. Which of the following is the least stable carbanion?

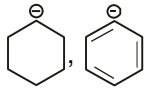
(A) $HC \equiv \overline{C}$ (B) $(C_6H_5)_3\overline{C}$ (C) $(CH_3)_3\overline{C}$ (D) $\overline{C}H_3$

A-2. The most stable anion is :

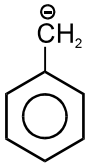
(A)  (B)  (C)  (D) 

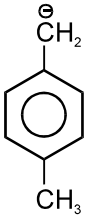
A-3. In which of the following pairs of carbanion the first one is more stable than second.

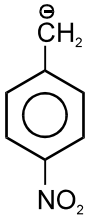
(A) $\overset{\ominus}{C}F_3$, $\overset{\ominus}{C}Cl_3$ (B) $HC \equiv \overset{\ominus}{C}$, $H_2C = \overset{\ominus}{C}H$

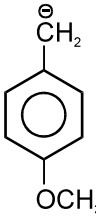
(C)  (D) $(CH_3)_3\overset{\ominus}{C}$, $H_3C - \overset{\ominus}{C}H_2$

A-4. Arrange the following carbanions in decreasing order of stability :


I

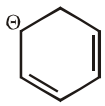
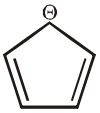
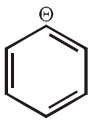
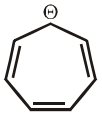

II


III

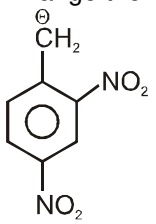

IV

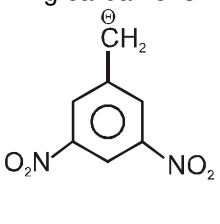
(A) III > I > IV > II (B) III > II > I > IV (C) I > III > II > IV (D) III > I > II > IV

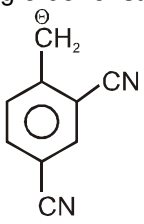
A-5. The most stable anion is :

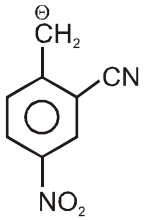
(A)  (B)  (C)  (D) 

A-6. Arrange the following carbanions in increasing order of stability :


I


II


III


IV

(A) III > IV > I > II (B) I > III > IV > II (C) I > II > III > IV (D) I > IV > III > II

Section (B) : Carbon free radicals

B-1. Among the following, the paramagnetic species is :

(A) Free radical (B) Carbocation (C) Carbanion (D) All the three

B-2. The stability of given free radicals in decreasing order is :

(i) $CH_3-\dot{C}H_2$ (ii) $CH_3-\dot{C}H-CH_3$ (iii) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle \dot{C}}{|}}-CH_3$ (iv) $\dot{C}H_3$

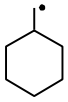
(A) iii > iv > i > ii (B) i > ii > iii > iv (C) iii > ii > iv > i (D) iii > ii > i > iv

B-3. Which of the following is the correct order of stability of free radicals ?

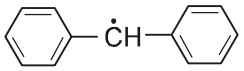
(A) benzyl > allyl > 2º > 1º (B) allyl > benzyl > 2º > 1º

(C) allyl > 2º > 1º >benzyl (D) benzyl > 2º > 1º > allyl

B-4. Most stable radical among the following is :

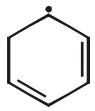
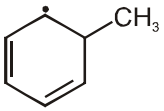
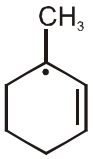
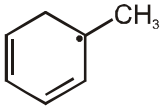
(A)  (B)  (C)  (D) 

B-5. Arrange the following radicals in decreasing order of their stability.

(I) $\dot{C}H_3$ (II) $CH_3-\dot{C}H_2$ (III)  (IV) 

(A) IV > I > III > II (B) IV > III > II > I (C) I > II > III > IV (D) IV > III > I > II

B-6. Least stable radical among the following is :

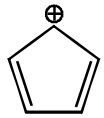
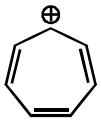
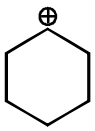
(A)  (B)  (C)  (D) 

Section (C) : Carbocations

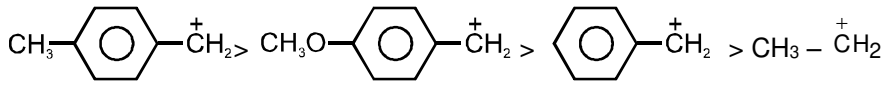
C-1. The most unstable carbocation is :

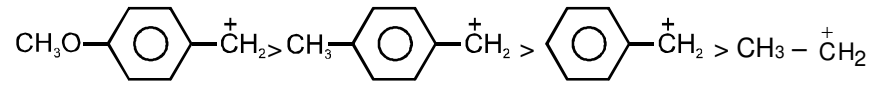
(A) $CH_3\overset{\oplus}{C}H_2$ (B) $Cl-CH_2-\overset{\oplus}{C}H_2$ (C) $\overset{\oplus}{C}H_2-CHO$ (D) $\overset{\oplus}{C}H_2-O-CH_3$

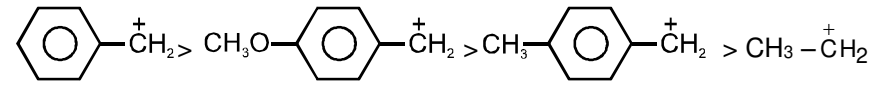
C-2. The most stable carbocation is :

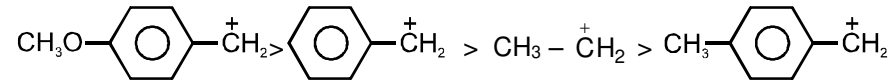
(A)  (B)  (C)  (D) 

C-3. Which of the following shows the correct order of decreasing stability ?

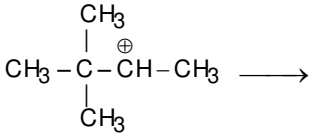
(A) 

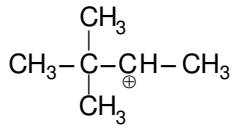
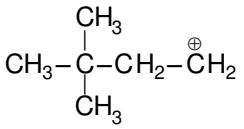
(B) 

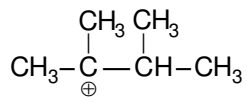
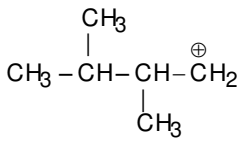
(C) 

(D) 

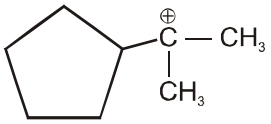
C-4. Which of the following is the rearranged more stable carbocation of the given species ?

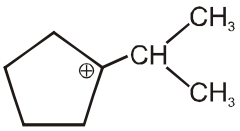
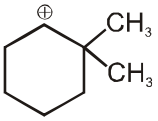
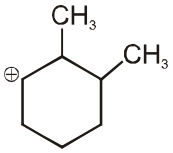
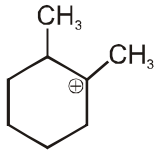


(A)  (B) 

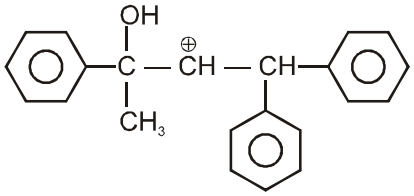
(C)  (D) 

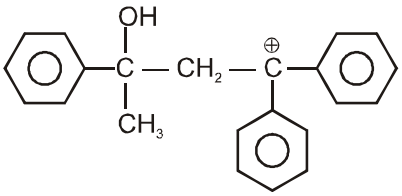
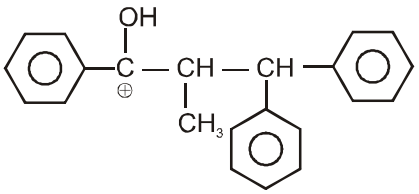
C-5. Most stable rearranged form of given carbocations is :

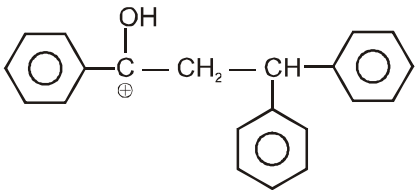
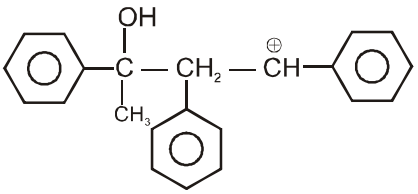


(A)  (B)  (C)  (D) 

C-6. Which of the following in the rearranged more stable carbocation of the given species?



(A)  (B) 

(C)  (D) 

Section (D) : Basic strength

D-1. The correct basic strength order of following anions is :

(A) $CH_3\overset{\ominus}{C}H_2 > \overset{\ominus}{N}H_2 > CH_2=\overset{\ominus}{C}H > CH\equiv\overset{\ominus}{C} > \overset{\ominus}{O}H > \overset{\ominus}{F}$

(B) $\overset{\ominus}{N}H_2 > CH_3\overset{\ominus}{C}H_2 > CH_2=\overset{\ominus}{C}H > CH\equiv\overset{\ominus}{C} > \overset{\ominus}{F} > \overset{\ominus}{O}H$

(C) $CH_3\overset{\ominus}{C}H_2 > CH_2=\overset{\ominus}{C}H > \overset{\ominus}{N}H_2 > CH\equiv\overset{\ominus}{C} > \overset{\ominus}{O}H > \overset{\ominus}{F}$

(D) $\overset{\ominus}{F} > \overset{\ominus}{O}H > CH\equiv\overset{\ominus}{C} > CH_2=\overset{\ominus}{C}H > \overset{\ominus}{N}H_2 > CH_3\overset{\ominus}{C}H_2$

D-2. Which of the following shows the correct order of decreasing basicity in gas phase ?

(A) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$ (B) $(CH_3)_2NH > (CH_3)_3N > CH_3NH_2 > NH_3$

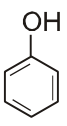
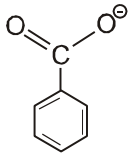
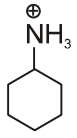
(C) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$ (D) $(CH_3)_2NH > CH_3NH_2 > NH_3 > (CH_3)_3N$

D-3. Find the order of basic strength. (If R = Me) ?

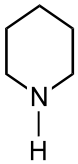
(I) $R_4N^+OH^-$ (II) R_3N (III) R_2NH (IV) RNH_2

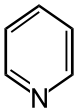
(A) I > III > IV > II (B) IV > III > I > II (C) II > IV > III > I (D) II > IV > I > III

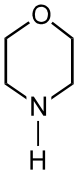
D-4. Which of the following cannot be a base?

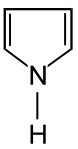
(A)  (B) $CH_3-\overset{\overset{O}{\|}}{C}-NH_2$ (C)  (D) 

D-5. Select the basic strength order of following molecules ?


(I) Piperidine

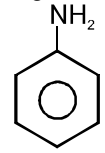

(II) Pyridine

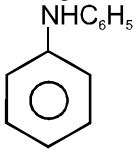

(III) Morpholine

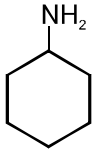

(IV) Pyrrole

(A) (IV) > (I) > (III) > (IV)
(B) (III) > (I) > (IV) > (II)
(C) (II) > (I) > (III) > (IV)
(D) (I) > (III) > (II) > (IV)

D-6. Arrange the following in increasing order of pKa value ?

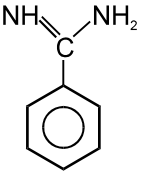
(I) 

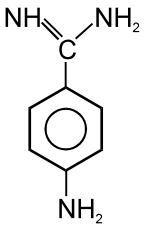
(II) 

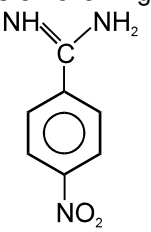
(III) 

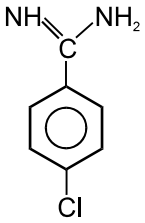
(A) II < I < III
(B) III < I < II
(C) III < II < I
(D) II < III < I

D-7. Select the decreasing order of relative basic strengths of following species :

(I) 

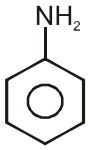
(II) 

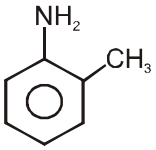
(III) 

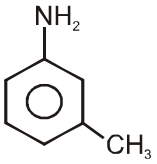
(IV) 

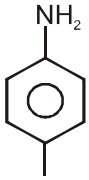
(A) II > IV > I > III
(B) III > I > IV > II
(C) III > IV > I > II
(D) II > I > IV > III

D-8. Select the basic strength order of following molecule :


(I)


(II)


(III)


(IV)

(A) II > III > IV > I
(B) II > IV > III > I
(C) IV > II > III > I
(D) IV > III > I > II

Section (E) : Acidic strength

E-1. Among the following compounds, the strongest acid is :
(A) HC ≡ CH
(B) C_6H_6
(C) C_2H_6
(D) CH_3OH

E-2. Which of the following is not correct decreasing K_a order.
(A) $CH_4 > NH_3 > H_2O > HF$
(B) $CH_3–OH > CH_3–NH_2 > CH_3–F > CH_3–CH_3$
(C) HI > HBr > HCl > HF
(D) $PhOH > H_2O > C_2H_5OH > CH_3–C\equiv CH$

E-3. Which of the following acid has the smallest dissociation constant ?
(A) $CH_3–\underset{\displaystyle NO_2}{\underset{|}{CH}}–COOH$
(B) $O_2N–CH_2–CH_2–COOH$
(C) $Cl–CH_2–CH_2–COOH$
(D) $NC–CH_2–CH_2–COOH$

E-4. Find the strongest acid among the following compounds is :
(A) $HOOC–(CH_2)_2–COOH$
(B) $H_3N^{\oplus}–(CH_2)_2–COOH$
(C) $F–(CH_2)_2–COOH$
(D) $CH_3–(CH_2)_2–COOH$

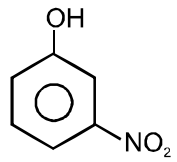
E-5. Which of the following option shows the correct order of decreasing acidity :
(A) $PhCO_2H > PhSO_3H > PhCH_2OH > PhOH$
(B) $PhSO_3H > PhOH > PhCH_2OH > PhCO_2H$
(C) $PhCO_2H > PhOH > PhCH_2OH > PhSO_3H$
(D) $PhSO_3H > PhCO_2H > PhOH > PhCH_2OH$

E-6. Arrange increasing order of acidic strength of following dibasic acids :

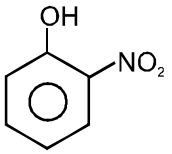
(I) oxalic acid, (II) succinic acid, (III) malonic acid, (IV) adipic acid

(A) III < II < I < IV (B) II < III > I > IV (C) I > III > II > IV (D) II > I > III < IV

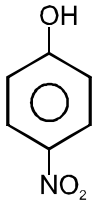
E-7.



I



II

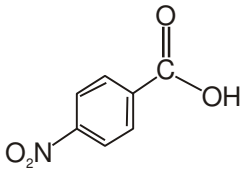


III

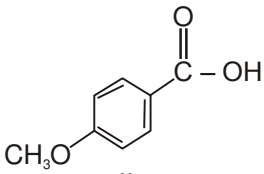
Arrange above phenol in increasing order of pK_a value :

(A) I < II < III (B) III < I < II (C) III < II < I (D) I < III < II

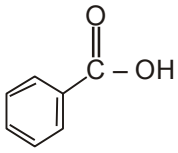
E-8. Order of K_a of following acids is :



I



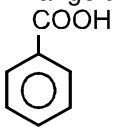
II



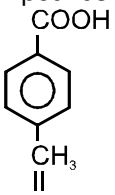
III

(A) I > II > III (B) II > I > III (C) I > III > II (D) III > I > II

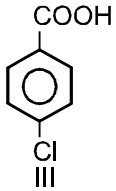
E-9. Arrange the following compounds in increasing order of their acidic strength.



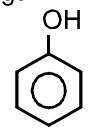
I



II



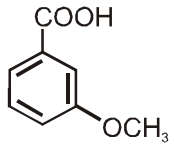
III

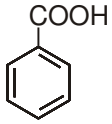


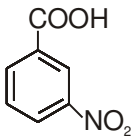
IV

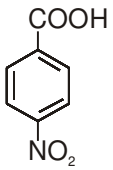
(A) IV < II < I < III (B) I < II < III < IV (C) IV < II < III < I (D) I < III < II < IV

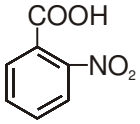
E-10. Find the order of K_a of following compounds :

(I) 

(II) 

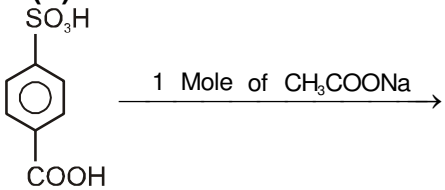
(III) 

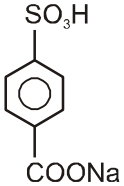
(IV) 

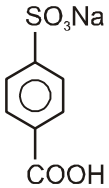
(V) 

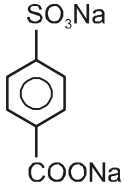
(A) I < II < III < IV < V (B) IV < I < III < II < V (C) III < II < I < IV < V (D) II < I < III < IV < V

Section (F) : Feasible reactions of acids and bases

F-1.  ; The products will be :

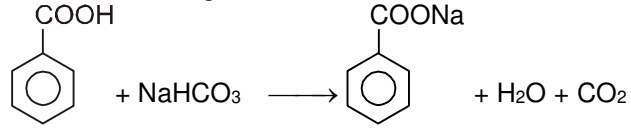
(A)  + CH_3COOH

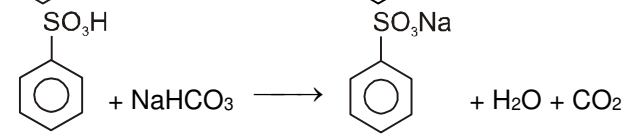
(B)  + CH_3COOH

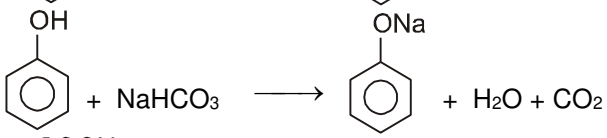
(C)  + CH_3COOH

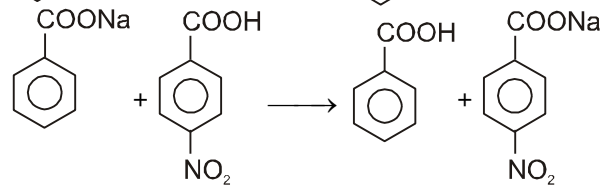
(D) Reaction is not feasible

F-2. Which of the following reactions is not feasible ?

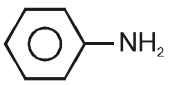
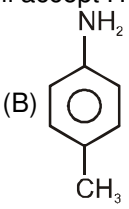
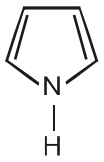
(A) 

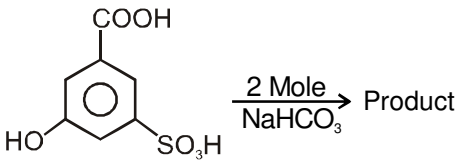
(B) 

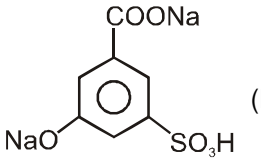
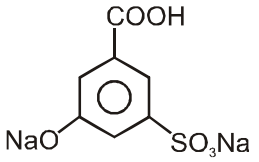
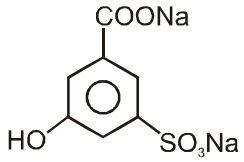
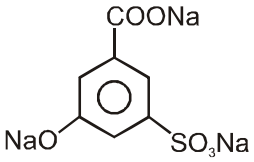
(C) 

(D) 

F-3. Which of the following will accept H^+ from NH_4^+ ion.

(A)  (B)  (C)  (D) $CH_3–CH_2–NH_2$

F-4. 

(A)  (B)  (C)  (D) 

Section (G) : Tautomerism

G-1. Keto-enol tautomerism does not observe in :

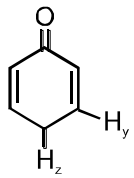
(A) $C_6H_5-\overset{\overset{O}{\|}}{C}-H$ (B) $C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3$

(C) $C_6H_5-\overset{\overset{O}{\|}}{C}-CH(CH_3)_2$ (D) $C_6H_5-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

G-2. The enolic form of acetone contains :

(A) 9 σ bonds, 1 π bond and 2 lone pairs (B) 8 σ bond, 2 π bond and 2 lone pairs

(C) 10 σ bond, 1 π bond and 1 lone pair (D) 9 σ bond, 2 π bond and 1 lone pair

G-3. Molecule  can be enolised by which hydrogen ?

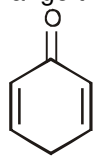
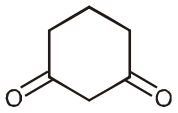
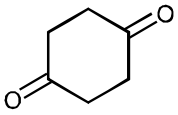
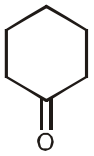
(A) y–H (B) z–H (C) both (D) None of these

G-4. Which among the following compound will give maximum enol content in solution :

(A) $C_6H_5-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$ (B) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

(C) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3$ (D) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-COOC_2H_5$

G-5. Arrange the following in decreasing order of percentage enol content.

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

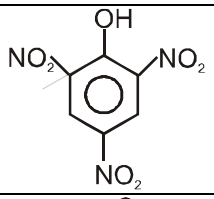
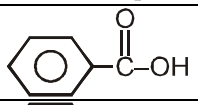
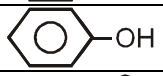
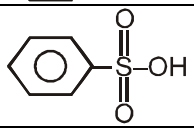
(A) I > II > III > IV (B) II > I > III > IV (C) II > III > I > IV (D) III > II > IV > I

PART - III : MATCH THE COLUMN

1. Match the column :

	Column-I (Keto)		**Column-II (% enol)**
(A)	$CH_3-CH=O$	(x)	95 %
(B)	$Ph-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-Ph$	(y)	76 %
(C)	$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OEt$	(z)	0.0001 %
(D)	$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$	(w)	7.2 %

2. Match the column :

	Column-I		**Column-II**
(A)	$NaHCO_3$ will react with	(p)	
(B)	Na will react with	(q)	
(C)	NaOH will react with	(r)	
(D)	$NaNH_2$ will react with	(s)	

Exercise-2

Marked questions are recommended for Revision.

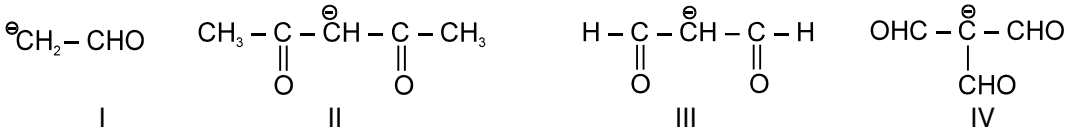
PART - I : ONLY ONE OPTION CORRECT TYPE

1. Arrange the following carbanions in decreasing order of stability :

$^{\ominus}CH_2-Cl$ (I) $^{\ominus}CH_2-CN$ (II) $^{\ominus}CH_2-NO_2$ (III) $^{\ominus}CH_2-CH_3$ (IV)

(A) III > II > IV > I (B) III > II > I > IV (C) III > I > II > IV (D) II > III > I > IV

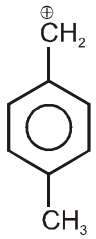
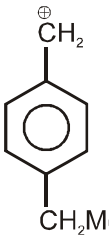
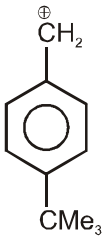
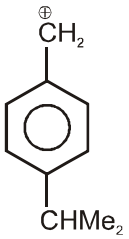
2. Correct decreasing stability order of following carbanions :



I II III IV

(A) III > IV > II > I (B) IV > II > III > I (C) IV > III > II > I (D) III > II > I > IV

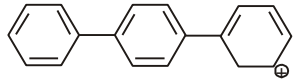
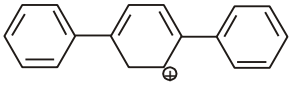
3. Select the most stable intermediates :

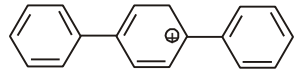
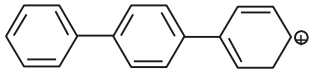
(A)  (B)  (C)  (D) 

4. Which of the following is most stable carbocation?

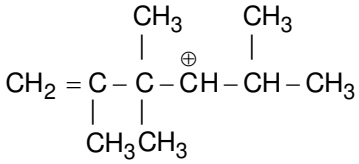
(A) $CH_3\overset{\oplus}{C}H_2$ (B) $CH_3\overset{\oplus}{C}=O$ (C) $CH_3-\overset{\oplus}{C}=NH$ (D) $CH_2=\overset{\oplus}{C}H$

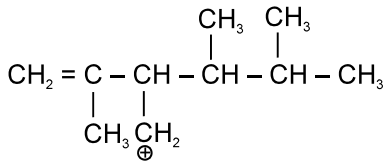
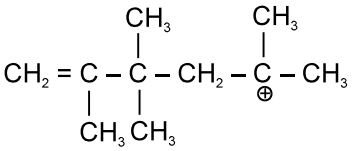
5. The most stable carbocation is :

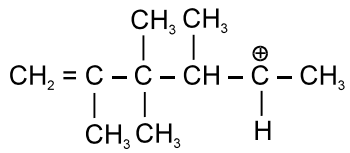
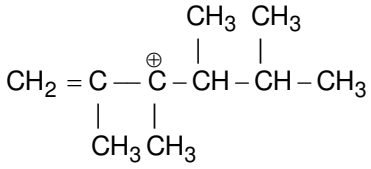
(A)  (B) 

(C)  (D) 

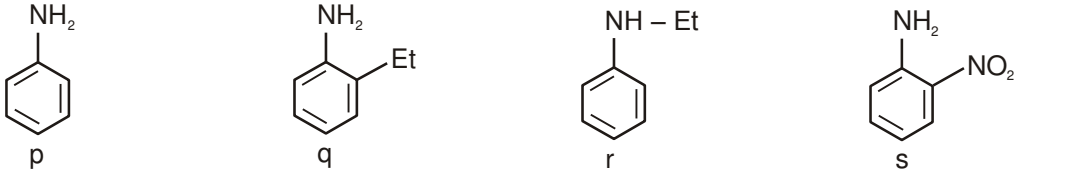
6. The following carbocation rearranges to



(A)  (B) 

(C)  (D) 

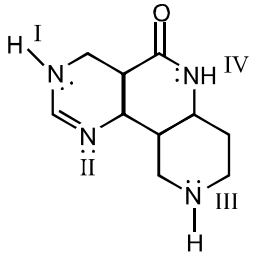
7. Correct basic strength order is :



p q r s

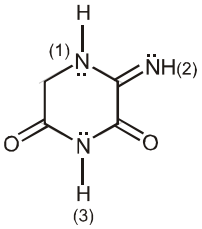
(A) r > q > p > s (B) r > p > q > s (C) q > r > p > s (D) r > q > s > p

8. The order of basic strength of the given basic nitrogen atoms is :



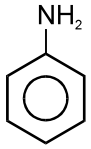
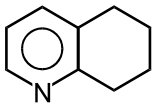
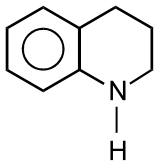
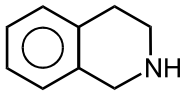
(A) III > II > I > IV (B) III > I > II > IV (C) I > III > II > IV (D) II > III > I > IV

9. In the labelled N-atoms which is correct basic strength order :

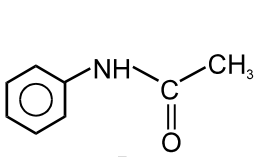


(A) 2 > 1 > 3 (B) 3 > 1 > 2 (C) 2 > 3 > 1 (D) All are equally basic

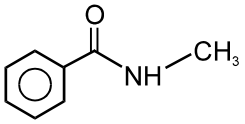
10. Choose the strongest base among the following :

(A)  (B)  (C)  (D) 

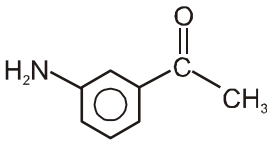
11. Select the basic strength order of following molecules ?



I



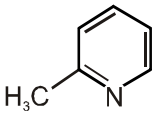
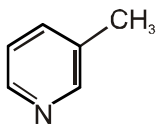
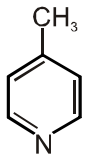
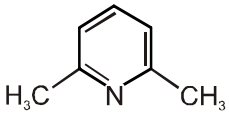
II



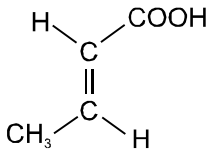
III

(A) III > II > I (B) II > III > I (C) I > III > II (D) III > I > II

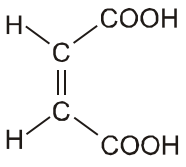
12. Which is the weakest base among the followings ?

(A)  (B)  (C)  (D) 

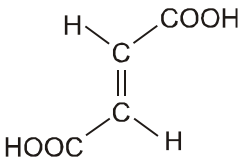
13. Write the order of K_{a_1} values of following acids :



(I)



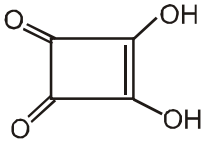
(II)

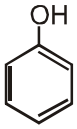


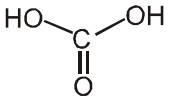
(III)

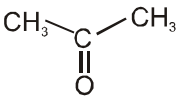
(A) II > III > I (B) I > III > II (C) III > II > I (D) II > I > III

14. The acid strength order is :


I

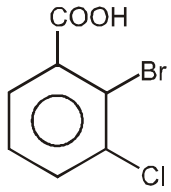

II

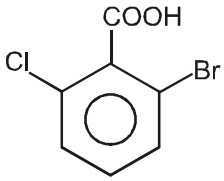

III

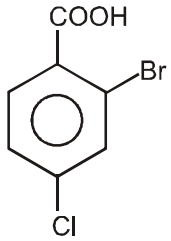

IV

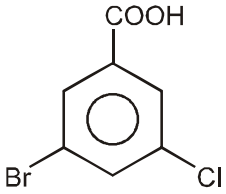
(A) I > IV > II > III (B) III > I > II > IV (C) II > III > I > IV (D) I > III > II > IV

15. (X) ($C_6H_3ClBrCOOH$) are a dihalosubstituted benzoic acids. The strongest acid among all isomers is -

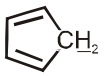
(A) 

(B) 

(C) 

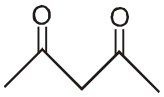
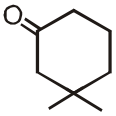
(D) 

16. The order of acidity of the H-atoms underlined in the following compounds is in the order :

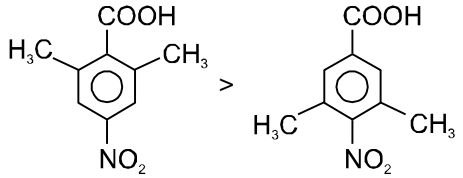
(I) Ph-$C\underline{H_2}$-CH_3 (II) Ph–CH=CH–$C\underline{H_3}$ (III) Ph-CH=$C\underline{H_2}$ (IV) 

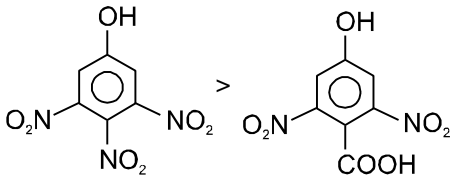
(A) IV>II>I>III (B) II>IV>III>I (C) III>IV>I>II (D) I>III>II>IV

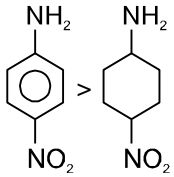
17. Most acidic hydrogen is present in :

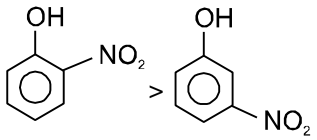
(A)  (B)  (C) $(CH_3CO)_3CH$ (D) $(CH_3)_3COH$

18. The correct orders are :

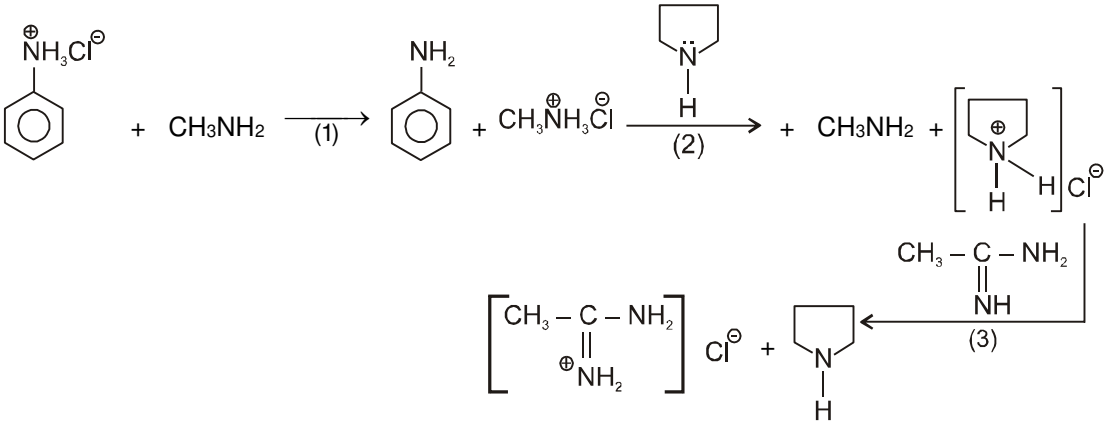
(A)  Acid strength

(B)  Acid strength

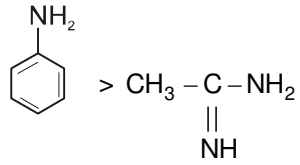
(C)  Basic strength

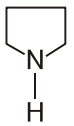
(D)  Boiling point

19. Observe the following sequence of reactions :

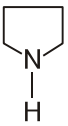


Select the correct option regarding the relative basic strength (K_b) :

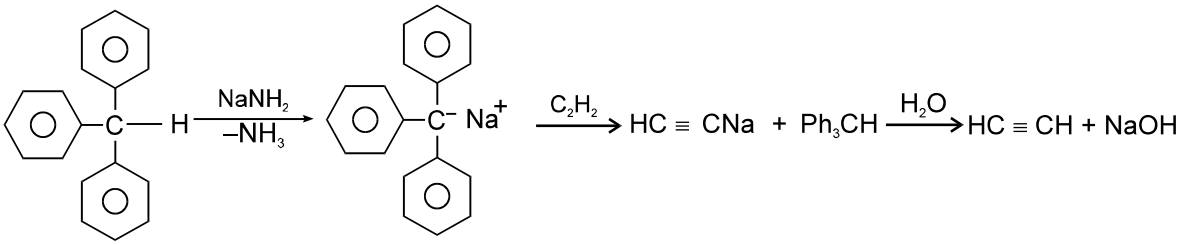
(A)  > $CH_3-\underset{\underset{NH}{||}}{C}-NH_2$

(B)  > $CH_3-\underset{\underset{NH}{||}}{C}-NH_2$

(C) $CH_3-\underset{\underset{NH}{||}}{C}-NH_2 > CH_3NH_2$

(D) $CH_3NH_2 >$ 

20. Order of K_a which can be predicted by following reaction is :



(A) $NH_3 > Ph_3CH > C_2H_2 > H_2O$ (B) $H_2O > HC{\equiv}CH > Ph_3CH > NH_3$

(C) $HC{\equiv}CH > H_2O > Ph_3CH > NH_3$ (D) $Ph_3CH > HC{\equiv}CH > H_2O > NH_3$

21. The gases produced in the following reactions are respectively

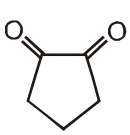
I : $CH_3NH_2 + NH_4Br \longrightarrow$

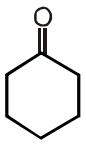
II : $CH_3SO_3H + NaHCO_3 \longrightarrow$

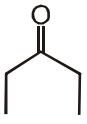
III : $CH_3-\underset{\underset{O}{||}}{C}-NH_2 + NaH \longrightarrow$

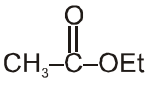
(A) NH_3, NH_3, CO_2 (B) NH_3, SO_2, H_2 (C) NH_3, SO_2, NH_3 (D) NH_3, CO_2, H_2

22. Decreasing order of enol content of the following compounds in liquid phase


(1)


(2)

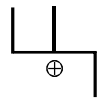
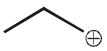
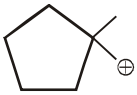
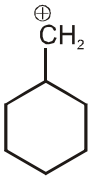
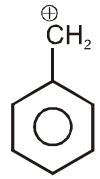
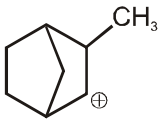
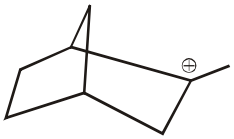
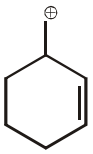
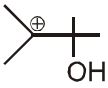
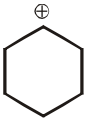
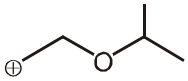

(3)


(4)

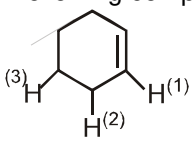
(A) 2 > 1 > 3 > 4 (B) 1 > 2 > 3 > 4 (C) 4 > 3 > 2 > 1 (D) 3 > 1 > 2 > 4

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

1. How many of the following carbocation can undergo rearrangement :

(a) 
(b) 
(c) 
(d) 
(e) 
(f) 
(g) 
(h) 
(i) 
(j) 
(k) 

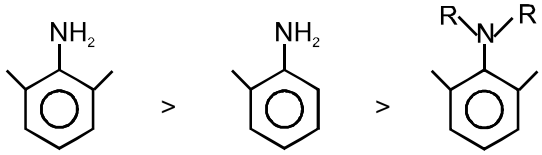
2. Consider following compound, which H-atom deprotonated first ?

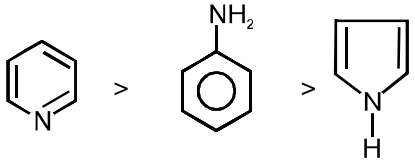


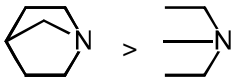
3. How many of the following are correct orders for Basic Strength :

S_1 : $CH_3–\underset{\displaystyle CH_3}{\overset{|}{N}}H$ > $CH_3–NH_2$ > $CH_3–\underset{\displaystyle CH_3}{\overset{|}{N}}–CH_3$

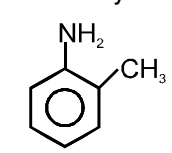
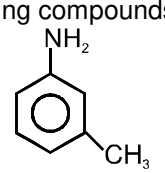
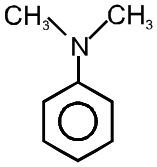
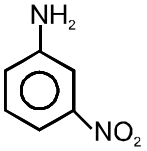
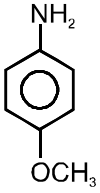
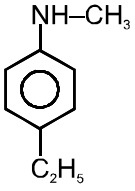
S_2 : $C_2H_5–\underset{\displaystyle C_2H_5}{\overset{|}{N}}H$ > $C_2H_5–\underset{\displaystyle C_2H_5}{\overset{|}{N}}H–C_2H_5$ > $C_2H_5–NH_2$

S_3 : 

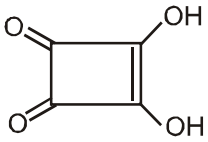
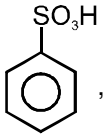
S_4 : 

S_5 :  > > $C_2H_5–NH_2$

4. How many following compounds are more basic than aniline.



$CH_3–CH_2= NH$





5. How many of the following compounds give CO_2 on reaction with $NaHCO_3$.


, HCl,

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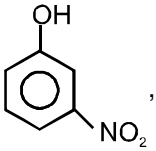
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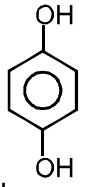
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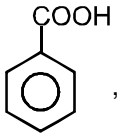
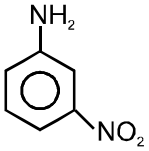
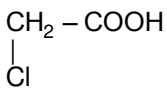
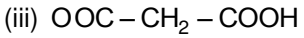
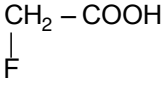
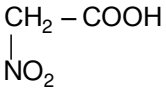
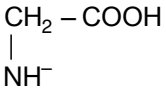
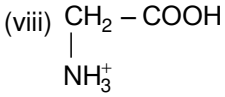
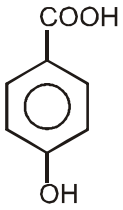
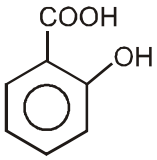

, HCOOH, C_2H_5–OH, CH_3COOH,


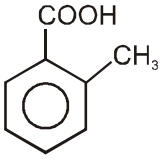
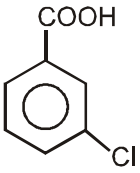
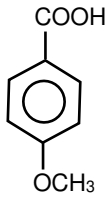
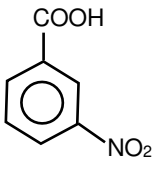
6. How many of the following are more acidic than HCOOH.

(i) 
(ii) CH_3–COOH
(iii) 
(iv) NC–CH_2–COOH

(v) 
(vi) 
(vii) 
(viii) 

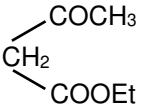
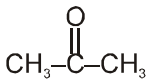
7. How many of the following compound have less pKa than benzoic acid :

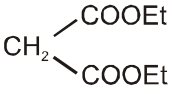
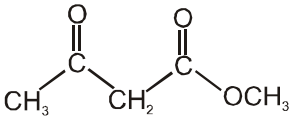
(i) HCOOH
(ii) CH_3COOH
(iii) 
(iv) 

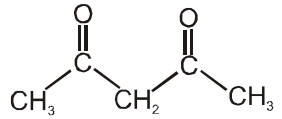
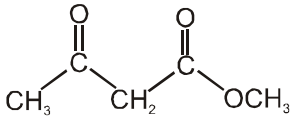
(v) 
(vi) 
(vii) 
(viii) 

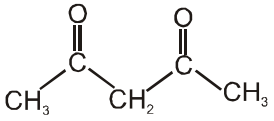
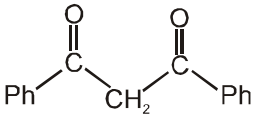
8. 90 g of acetic acid react with excess of $NaHCO_3$ then what volume of CO_2 will produce at S.T.P. Write your answer in terms of nearest integer.

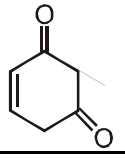
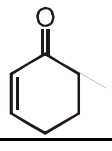
9. In how many of the following pairs first will have higher enol content than second.

(i) 
&


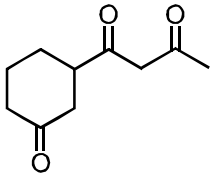
(ii) 
&


(iii) 
&


(iv) 
&


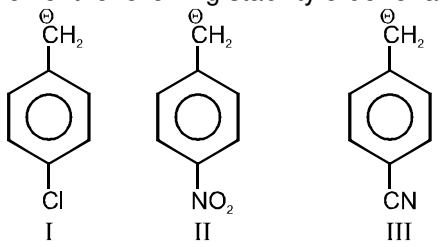
(v) 
&


10. Consider the following compound and write number of enolizable H-atom

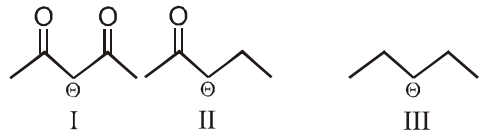


PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. Which of the following stability order of anions is/are correct :

(A)  II > III > I

(B) $\overset{\ominus}{C}H_2-C(=O)-H$ (I) $\quad \overset{\ominus}{C}H_2-C(=O)-OCH_3$ (II) $\quad \overset{\ominus}{C}H_2-CH_3$ (III) I > II > III

(C)  I > II > III

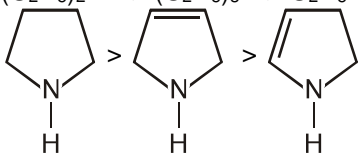
(D) $\overset{\ominus}{C}H_3$ (I) > $\overset{\ominus}{C}D_3$ (II) I > II

2. Which of the following is/are correct for basic strength :

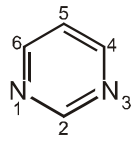
(A) $(CH_3)_2NH > (CH_3)_3N > CH_3NH_2 > NH_3$

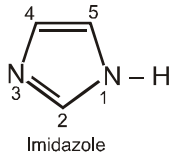
(B) $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

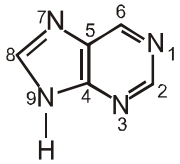
(C) $PhNH_2 > Ph_2NH > Ph_3N$

(D) 

3.


Pyrimidine


Imidazole


Purine

Among the following which statement(s) is/are correct :

(A) Both N of pyrimidine are same basic strength

(B) In imidazole protonation take places on N-3.

(C) In purine only one lone pair of N is delocalised.

(D) Pyrimidine, imidazole and purine all are aromatic.

4. Consider the following compounds

$O_2N-CH_2-C(=O)-OH$ (I) $\quad F-CH_2-C(=O)-OH$ (II) $\quad Ph-CH_2-C(=O)-OH$ (III) $\quad CH_3-CH_2-C(=O)-OH$ (IV)

Which statement is/are correct :

(A) I > II > III > IV (Acidic strength order)

(B) I is most acidic because of –M effect of $-NO_2$ group

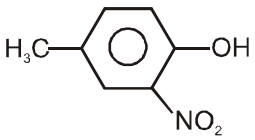
(C) I is most acidic because of –I effect of $-NO_2$ group

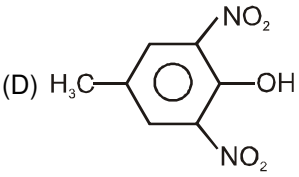
(D) IV is least acidic because of +I Effect.

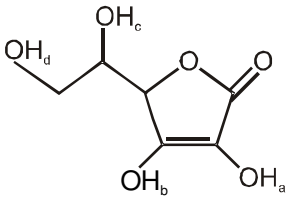
5. Carbolic acid is less acidic than :

(A) CH_3COOH

(B) 

(C) 

(D) 

6. 

Observe the compound and choose correct statement :

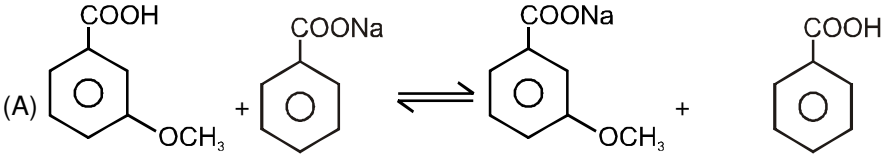
(A) It has carboxylic acid group

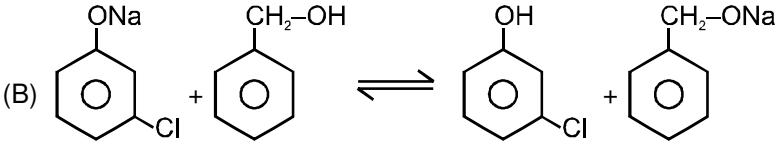
(B) It is Ascorbic acid

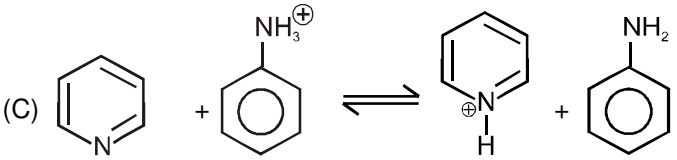
(C) H_b is most acidic Hydrogen atom

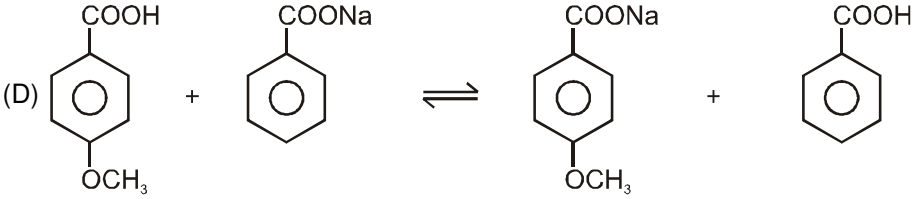
(D) H_a is least acidic Hydrogen atom

7. Which of the following reactions favour backward direction?

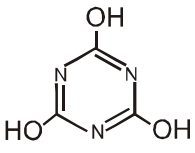
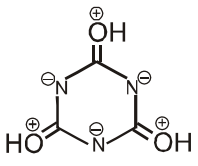
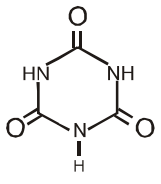
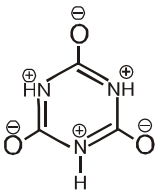
(A) 

(B) 

(C) 

(D) 

8. The **correct** statement(s) concerning the structures P, Q, R & S is/are

(P)  **(Q)**  **(R)**  **(S)** 

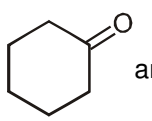
(A) Q & S are not resonating structures

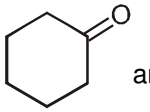
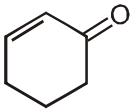
(B) R & S are resonating structures

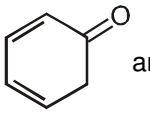
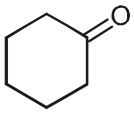
(C) P & R are tautomers

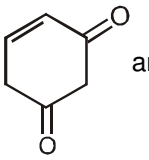
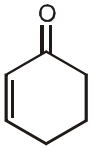
(D) P & Q are resonating structures

9. Among the given pairs, in which pair second compound has less enol content :

(A)  and 

(B)  and 

(C)  and 

(D)  and 

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension # 1

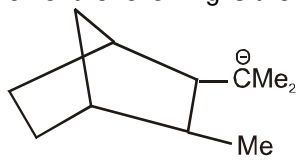
Reaction intermediates: Reaction intermediates are short lived species and are highly reactive. They are formed by heterolytic and homolytic bond fission. There are various types of reaction intermediates in which the most important are carbocation, carbanion and free radical.

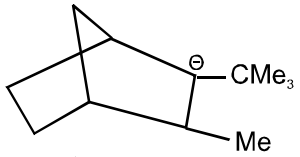
Carbocation is an organic species in which carbon have positive charge and six electrons in its outermost shell. The stability of carbocation can be increased by positive inductive effect, hyperconjugation and delocalisation. If α-atom with respect to carbocation has one or more lone pair of electrons then lone pair of electron strongly stabilises the carbocation due to octet completion.

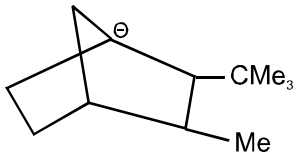
Species in which carbon have negative charge is called carbanion. Carbanion carries three bond pairs and one lone pair. The stability of carbanion can be increased by negative inductive effect, negative mesomeric effect and delocalisation.

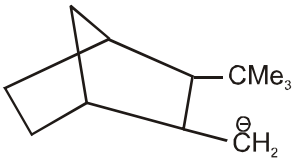
Free radical is a species which have seven electrons in its outermost shell. The stability of free radical can be increased by hyperconjugation and delocalisation.

1. Which of the following is the most stable carbanion intermediate ?

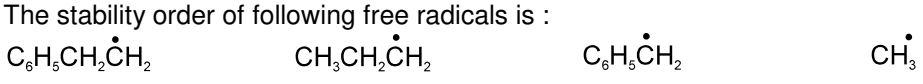
(A) 

(B) 

(C) 

(D) 

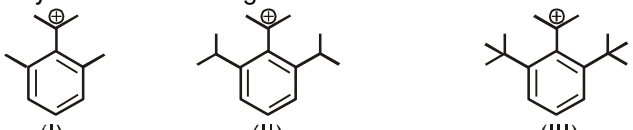
2. The stability order of following free radicals is :



I II III IV

(A) I > II > III > IV (B) II > III > I > IV (C) I > III > II > IV (D) III > II > I > IV

3. The stability order of following carbocations is



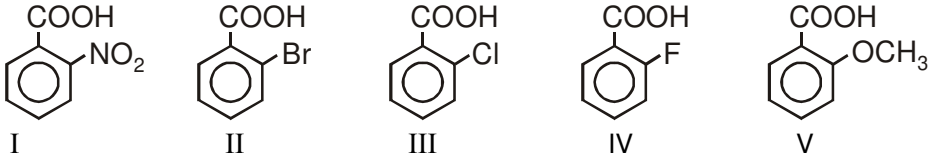
(I) (II) (III)

(A) I > II > III (B) II > I > III (C) III > I > II (D) II > III > I

Comprehension # 2

Ortho effect is a special type of effect that is shown by o-substituents. This ortho-effect operates at the benzoic acids irrespective of the polar type. Nearly all o-substituted benzoic acid are stronger than benzoic acid. Benzoic acid is a resonance stabilised and so the carboxyl group is coplanar with the ring. An o-substituent tends to prevent this coplanarity.

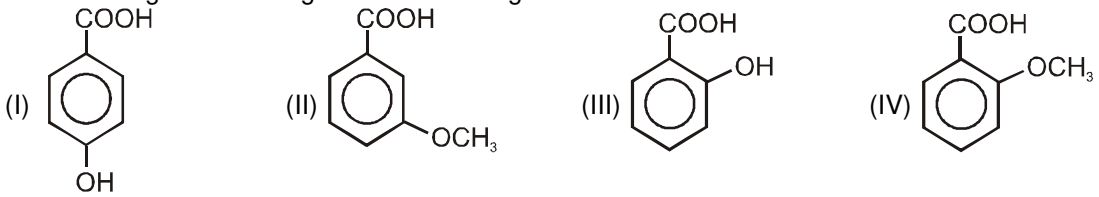
4. What is the order of K_a of following compounds ?



I II III IV V

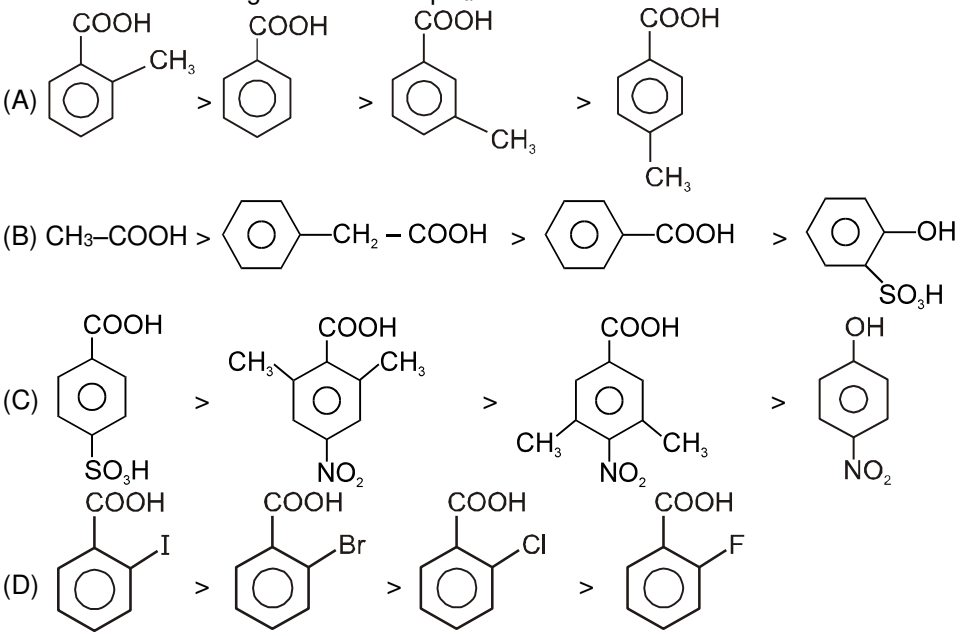
(A) I > II > III > IV > V (B) II > I > III > IV > V (C) V > IV > III > I > II (D) III > II > I > V > IV

5. Which among the following will be the strongest acid ?



(A) I (B) II (C) III (D) IV

6. Which of the following is/are correct pK_a order ?



Comprehension # 3

The lone pair of amines makes them basic. They react with acids to form acid-base salts. Amines are more basic than alcohols, ethers and water. When an amine is dissolved in water, an equilibrium is established, where water acts as an acid and transfer a proton to the amine. The basic strength of an amine can be measured by basicity constant K_b.

Arylamines are less basic than alkylamines because the lone pair of nitrogen is delocalised with the aromatic ring and are less available for donation.

Substituted arylamines can be either more basic or less basic than aniline, depending on the substitutent. ERG substituents, such as $–CH_3$, $–NH_2$ and $–OCH_3$ increases the basicity and EWG substituents, such as –Cl, $–NO_2$ and –CN decreases basicity. While sp^2-hybridized nitrogen atom in pyridine is less basic than the sp^3-hybridized nitrogen in an alkylamine.

7. Select the correct order of K_b.

(A) CH_3NH_2 > NaOH

(B) Pyridine > $CH_3–\ddot{N}H–CH_3$

(C) p-Methyl aniline > p-Chloroaniline > p-Amino acetophenone

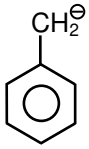
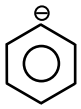
(D) p-Bromoaniline > p-Nitroaniline > p-Amino benzaldehyde

8. pK_b order of the following compound is :

(I) NH_2OH (II) NH_2NH_2 (III) NH_3 (IV) H_2O

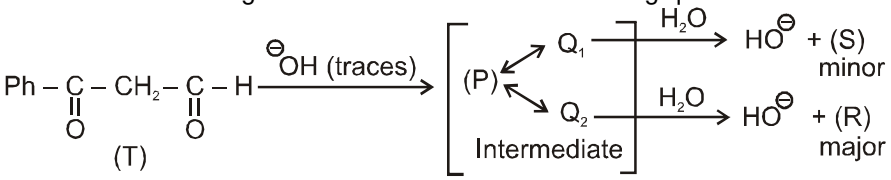
(A) IV > I > II > III (B) III > II > I > IV (C) I > IV > II > III (D) III > I > II > IV

9. The most basic carbanion is :

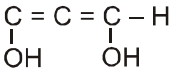
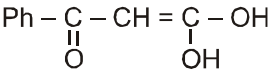
(A)  (B) $CH\equiv C^{\ominus}$ (C)  (D) 

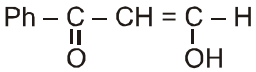
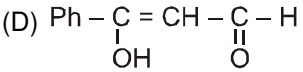
Comprehension # 4

Observe the following reaction and answer the following questions :

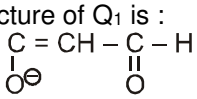
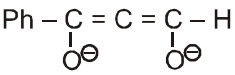


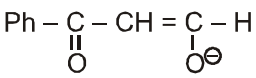
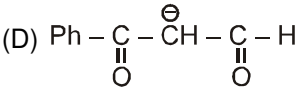
10. The product 'R' is **:**

(A)  (B) 

(C)  (D) 

11. The structure of Q_1 is :

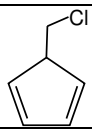
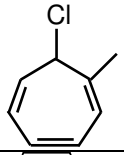
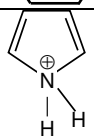
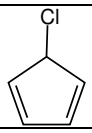
(A)  (B) 

(C)  (D) 

Comprehension # 5

Answer 12, 13 and 14 by appropriately matching the information given in the three columns of the following table.

Column-1, 2 & 3 containing starting material, reaction condition & electronic effect / intermediate respectively.

Column-1		Column-2		Column-3	
(I)		(i)	$SbCl_5$ or $AlCl_{3(Anhy.)}$	(P)	Rearrangement
(II)		(ii)	Na	(Q)	Resonance
(III)		(iii)	H^+	(R)	Hyperconjugation
(IV)		(iv)	NaOH	(S)	Carbocation intermediate

12. Which combination will give hydrogen gas ?

(A) (III) (iii) (P) (B) (II) (ii) (R) (C) (IV) (ii) (Q) (D) (I) (iii) (P)

13. In which product formation is not possible ?
(A) (I) (ii) (Q) (B) (II) (i) (R) (C) (III) (ii) (Q) (D) (IV) (i) (S)

14. In which amongs the following aromatic product will not form ?
(A) (I) (i) (P) (B) (II) (i) (Q) (C) (III) (iv) (Q) (D) (IV) (ii) (Q)

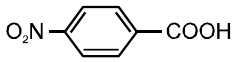
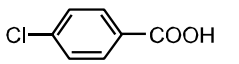
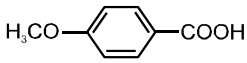
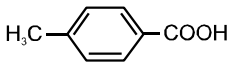
Exercise-3

*** Marked Questions may have more than one correct option.**

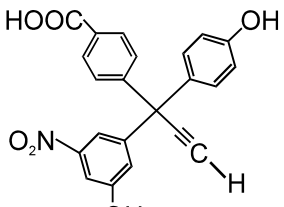
PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

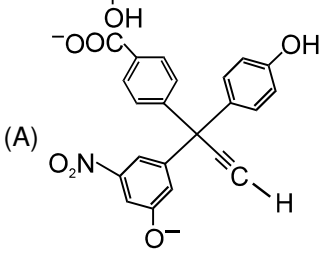
1. Which of the following acid has the lowest value of acid dissociation constant : **[JEE-02(S), 3/90]**
(A) $CH_3CHFCOOH$ (B) FCH_2CH_2COOH (C) $BrCH_2CH_2COOH$ (D) $CH_3CHBrCOOH$

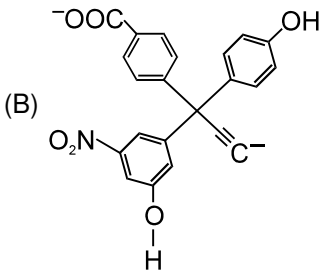
2. Match the K_a values : **[JEE-03(M), 2/60]**

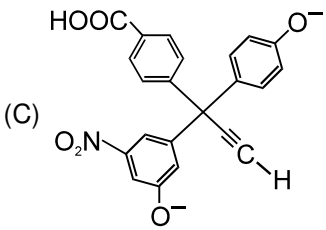
	Compounds		**K_a**
(a)	Benzoic acid	(i)	3.3×10^{-5}
(b)		(ii)	6.3×10^{-5}
(d)		(iii)	30.6×10^{-5}
(e)		(iv)	6.4×10^{-5}
(f)		(v)	4.2×10^{-5}

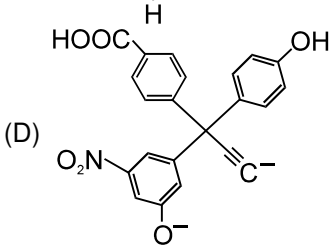
3. Compound A of molecular formula $C_9H_7O_2Cl$ exists in keto form and predominantly in enolic form 'B'. On oxidation with $KMnO_4$'A' gives m-Chlorobenzoic acid. Identify 'A' and 'B'. **[JEE(M)-03]**

4.  $\xrightarrow{2 \text{ moles } NaNH_2}$ A. The product A will be - **[JEE-03(S), 3/84]**

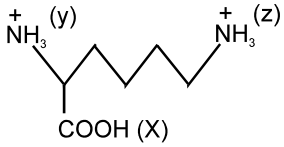
(A) 

(B) 

(C) 

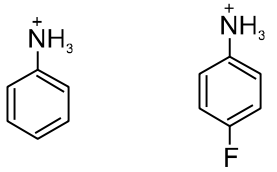
(D) 

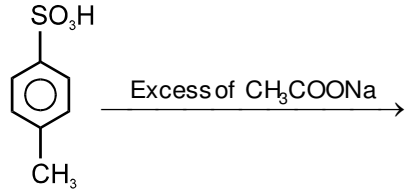
5. What is the acidity order of x, y & z ? **[JEE-04(S), 3/84]**



(A) x > y > z (B) x > z > y (C) y > z > x (D) z > y > x

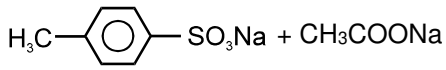
6. Which one of the following two compounds is the stronger acid? Explain why? **[JEE 2004, 4/60]**

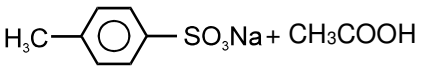


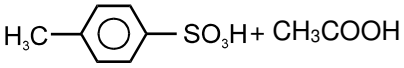
7. 

[JEE-05(S), 3/84]

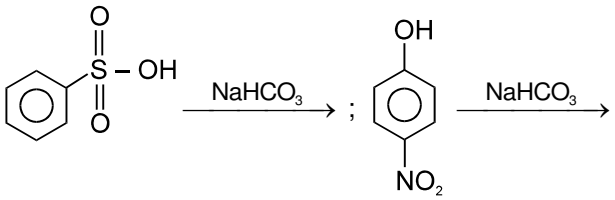
The products will be :

(A) 

(B) 

(C) 

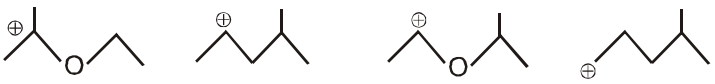
(D) 

8. 

Benzenesulphonic acid and para nitrophenol react with $NaHCO_3$ separately. The gases produced are respectively. **[JEE-06, 3/184]**

(A) SO_2, CO_2 (B) SO_2, CO (C) SO_2, NO_2 (D) CO_2, CO_2

9. The correct stability order for the following species is : **[JEE-08, 3/163]**

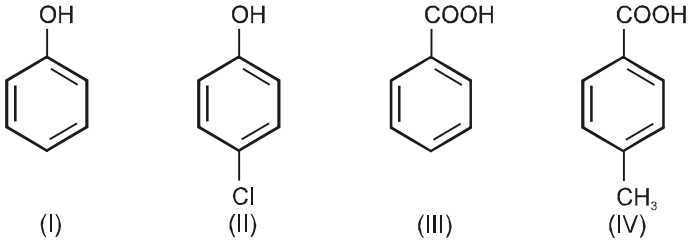


(I) (II) (III) (IV)

(A) (II) > (IV) > (I) > (III) (B) (I) > (II) > (III) > (IV)

(C) (II) > (I) > (IV) > (III) (D) (I) > (III) > (II) > (IV)

10. The correct acidity order of the following is : **[JEE-09, 3/160]**

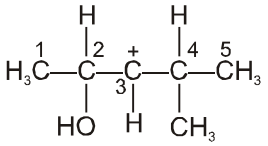


(I) (II) (III) (IV)

(A) (III) > (IV) > (II) > (I) (B) (IV) > (III) > (I) > (II)

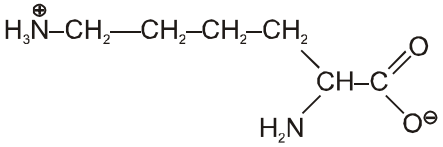
(C) (III) > (II) > (I) > (IV) (D) (II) > (III) > (IV) > (I)

11. In the following carbocation; H/CH_3 that is most likely to migrate to the positively charged carbon is **[JEE-09, 3/160]**



(A) CH_3 at C-4 (B) H at C-4 (C) CH_3 at C-2 (D) H at C-2

12. The total number of basic groups in the following form of lysine is : **[JEE-10, 3/163]**

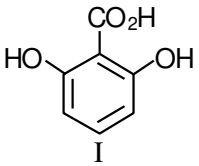


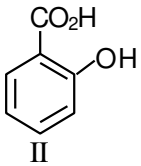
13. Among the following compounds, the most acidic is : **[JEE-11, 3/180]**
(A) p-nitrophenol (B) p-hydroxybenzoic acid
(C) o-hydroxybenzoic acid (D) p-toluic acid

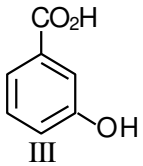
14. The carboxyl functional group (– COOH) is present in **[JEE-12,3/136]**
(A) picric acid (B) barbituric acid
(C) ascorbic acid (D) aspirin

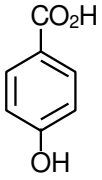
15. The compound that does **NOT** liberate CO_2, on treatment with aqueous sodium bicarbonate solution, is: **[JEE(Advanced) 2013, 2/120]**
(A) Benzoic acid (B) Benzenesulphonic acid
(C) Salicylic acid (D) Carbolic acid (Phenol)

16. The correct order of acidity for the following compounds is **[JEE(Advanced) 2016, 3/124]**


I

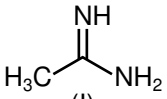

II

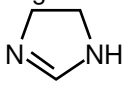

III

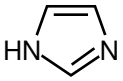

IV

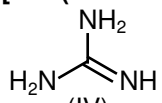
(A) I > II > III > IV (B) III > I > II > IV (C) III > IV > II > I (D) I > III > IV > II

17. The order of basicity among the following compounds is **[JEE(Advanced) 2017, 3/122]**


(I)


(II)


(III)

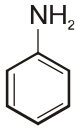

(IV)

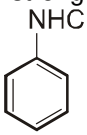
(A) II > I > IV > III (B) I > IV > III > II (C) IV > II > III > I (D) IV > I > II > III

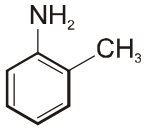
PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

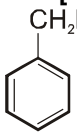
1. The correct order of increasing basic nature for the bases NH_3, CH_3NH_2 and $(CH_3)_2NH$ is: **[AIEEE-2003, 3/225]**
(1) $CH_3NH_2 < NH_3 < (CH_3)_2NH$ (2) $(CH_3)_2NH < NH_3 < CH_3NH_2$
(3) $NH_3 < CH_3NH_2 < (CH_3)_2NH$ (4) $CH_3NH_2 < (CH_3)_2NH < NH_3$

2. Which of the following is the strongest base? **[AIEEE-2004, 3/225]**

(1) 

(2) 

(3) 

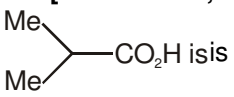
(4) 

3. Consider the acidity of the carboxylic acids : **[AIEEE-2004, 3/225]**
(i) PhCOOH (ii) o-$NO_2C_6H_4COOH$ (iii) p-$NO_2C_6H_4COOH$ (iv) m-$NO_2C_6H_4COOH$
(1) i > ii > iii > iv (2) ii > iii > iv > i (3) iii > ii > iv > i (4) ii > iv > iii > i

4. Among the following acid which has the lowest pK_a value ? **[AIEEE-2005, 3/225]**
(1) CH_3CH_2COOH (2) $(CH_3)_2CH–COOH$ (3) HCOOH (4) CH_3COOH

5. Amongst the following the most basic compound is **[AIEEE-2005, 3/225]**
(1) p-Nitroaniline (2) Acetanilide (3) Aniline (4) Benzylamine

6. The increasing order of stability of the following free radicals is : **[AIEEE-2006, 3/165]**
(1) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C}$
(2) $(C_6H_5)_2\dot{C} < (C_6H_5)_2\dot{C}H < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$
(3) $(C_6H_5)_2H\dot{C} < (C_6H_5)_3\dot{C}H < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$
(4) $(CH_3)_2H\dot{C} < (CH_3)_3\dot{C} < (C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H$

7. The correct order of increasing acid strength of the compounds. **[AIEEE-2006, 3/165]**
(a) CH_3CO_2H (b) $MeOCH_2CO_2H$ (c) CF_3CO_2H (d)  is
(1) b < d < a < c (2) d < a < c < b (3) d < a < b < c (4) a < d < c < b

8. Which one of the following is the strongest base in aqueous solution? **[AIEEE-2007, 3/120]**
(1) Dimethylamine (2) Methylamine (3) Trimethylamine (4) Aniline

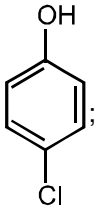
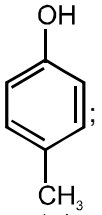
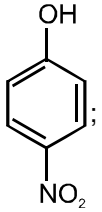
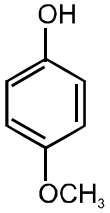
9. Arrange the carbanions, $(CH_3)_3\overline{C}$, $\overline{C}Cl_3$, $(CH_3)_2\overline{C}H$, $C_6H_5\overline{C}H_2$ in order of their decreasing stability: **[AIEEE-2009, 4/144]**
(1) $(CH_3)_2\overline{C}H > \overline{C}Cl_3 > C_6H_5\overline{C}H_2 > (CH_3)_3\overline{C}$
(2) $\overline{C}Cl_3 > C_6H_5\overline{C}H_2 > (CH_3)_2\overline{C}H > (CH_3)_3\overline{C}$
(3) $(CH_3)_3\overline{C} > (CH_3)_2\overline{C}H > C_6H_5\overline{C}H_2 > \overline{C}Cl_3$
(4) $C_6H_5\overline{C}H_2 > \overline{C}Cl_3 > (CH_3)_3\overline{C} > (CH_3)_2\overline{C}H$

10. The correct order of increasing basicity of the given conjugate bases (R = CH_3) is: **[AIEEE-2010, 4/144]**
(1) $RCO\overline{O} < HC \equiv \overline{C} < \overline{R} < \overline{N}H_2$ (2) $\overline{R} < HC \equiv \overline{C} < RCO\overline{O} < \overline{N}H_2$
(3) $RCO\overline{O} < \overline{N}H_2 < HC \equiv \overline{C} < \overline{R}$ (4) $RCO\overline{O} < HC \equiv \overline{C} < \overline{N}H_2 < \overline{R}$

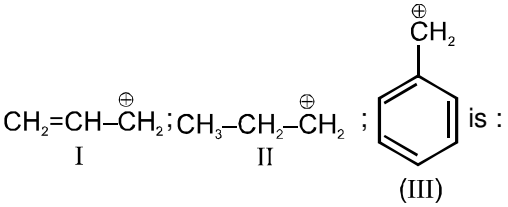
11. The strongest acid amongst the following compounds is : **[AIEEE-2011, 4/120]**
(1) CH_3COOH (2) HCOOH
(3) $CH_3CH_2CH(Cl)CO_2H$ (4) $ClCH_2CH_2CH_2COOH$

12. Identify the compound that exhibits tautomerism. **[AIEEE-2011, 4/120]**
(1) 2-Butene (2) Lactic acid (3) 2-Pentanone (4) Phenol

13. The correct order of acid strength of the following compounds: **[AIEEE-2011, 4/120]**
(A) Phenol (B) p-Cresol (C) m-Nitrophenol (D) p-Nitrophenol
is :
(1) D > C > A > B (2) B > D > A > C (3) A > B > D > C (4) C > B > A > D

14. Arrange the following compounds in order of decreasing acidity : **[JEE(Main)-2013, 4/120]**

(I)

(II)

(III)

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

15. The order of stability of the following carbocations : **[JEE(Main)-2013, 4/120]**

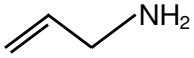


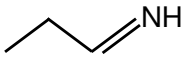
(1) III > II > I (2) II > III > I (3) I > II > III (4) III > I > II

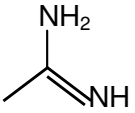
16. Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value? **[JEE(Main)-2014, 4/120]**

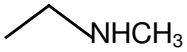
(1) $(CH_3)_2NH$ (2) CH_3NH_2 (3) $(CH_3)_3N$ (4) $C_6H_5NH_2$

17. The increasing order of basicity of the following compounds is : **[JEE(Main)-2018, 4/120]**

(a) 

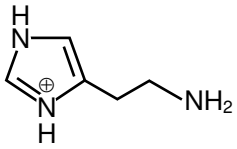
(b) 

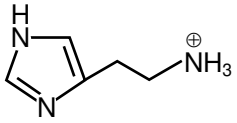
(c) 

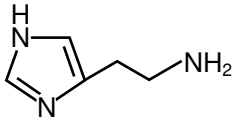
(d) 

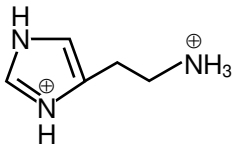
(1) (b) < (a) < (d) < (c) (2) (d) < (b) < (a) < (c)
(3) (a) < (b) < (c) < (d) (4) (b) < (a) < (c) < (d)

18. The predominant form of histamine present in human blood is (pK_a, Histidine = 6.0) **[JEE(Main)-2018, 4/120]**

(1) 

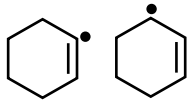
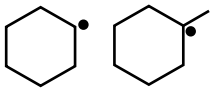
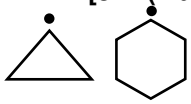
(2) 

(3) 

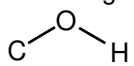
(4) 

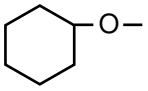
JEE(MAIN) ONLINE PROBLEMS

1. In which of the following pairs A is more stable than B ? **[JEE(Main) 2014 Online (09-04-14), 4/120]**

(1)  (2)  (3)  (4) $Ph_3C^{\bullet}$, $(CH_3)C^{\bullet}$

2. Which one of the following statements is **not** correct ? **[JEE(Main) 2014 Online (11-04-14), 4/120]**

(1) Alcohols are weaker acids than water.
(2) Acid strength of alcohols decreases in the following order $RCH_2OH > R_2CHOH > R_3COH$.
(3) Carbon-oxygen bond length in methanol, CH_3OH is shorter than that of C–O bond length in phenol.
(4) The bond angle  in methanol is 108.9º.

3. Which one of the following substituents at para-position is most effective in stabilizing the phenoixde  , ion? **[JEE(Main) 2014 Online (19-04-14), 4/120]**

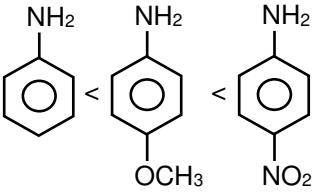
(1) $–CH_3$ (2) $–OCH_3$ (3) $–COCH_3$ (4) $–CH_2OH$

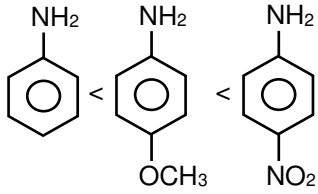
4. Which one of the following compounds will not be soluble in sodium bicarbonate ? **[JEE(Main) 2014 Online (19-04-14), 4/120]**

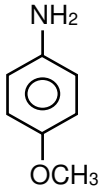
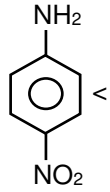
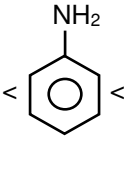
(1) 2,4,6-Trinitrophenol (2) Benzoic acid
(3) o-Nitrophenol (4) Benzene sulphonic acid

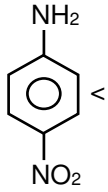
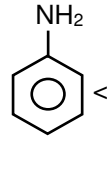
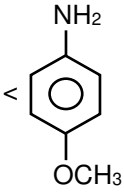
5. Arrange the following amines in the order of increasing basicity :

[JEE(Main) 2015 Online (10-04-15), 4/120]

(1) CH_3NH_2 <  < <

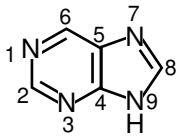
(2)  < < < CH_3NH_2

(3)  <  <  < CH_3NH_2

(4)  <  <  < CH_3NH_2

6. The "N" which does not contribute to the basicity for the compound is :

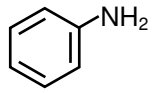
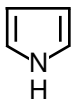
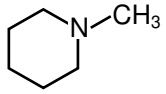
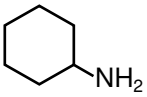
[JEE(Main) 2016 Online (10-04-16), 4/120]



(1) N 7 (2) N 1 (3) N 9 (4) N 3

7. Among the following compounds, the increasing order of their basic strength is :

[JEE(Main) 2017 Online (09-04-17), 4/120]

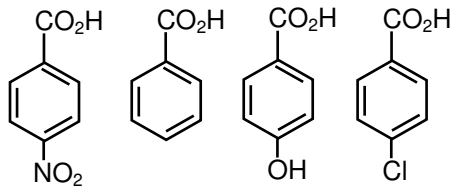
(I)  (II)  (III)  (IV) 

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

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

8. The increasing order of the acidity of the following carboxylic acids is :

[JEE(Main) 2018 Online (15-04-18), 4/120]



I II III IV

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

9. Which amongst the following is the strongest acid ? **[JEE(Main) 2019 Online (09-01-19), 4/120]**

(1) $CHBr_3$ (2) $CHCl_3$ (3) CHI_3 (4) $CH(CN)_3$

10. The correct decreasing order for acid strength is : **[JEE(Main) 2019 Online (09-01-19), 4/120]**

(1) $CNCH_2COOH > O_2NCH_2COOH > FCH_2COOH > ClCH_2COOH$

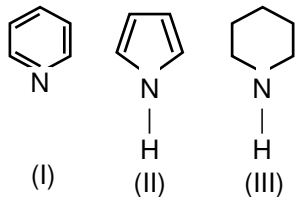
(2) $FCH_2COOH > NCCH_2COOH > NO_2CH_2COOH > ClCH_2COOH$

(3) $NO_2CH_2COOH > NCCH_2COOH > FCH_2COOH > ClCH_2COOH$

(4) $NO_2CH_2COOH > FCH_2COOH > CNCH_2COOH > ClCH_2COOH$

11. Arrange the following amines in the decreasing order of basicity :

[JEE(Main) 2019 Online (09-01-19), 4/120]



(I) (II) (III)

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

12. The increasing basicity order of the following compounds is:

[JEE(Main) 2019 Online (09-01-19), 4/120]

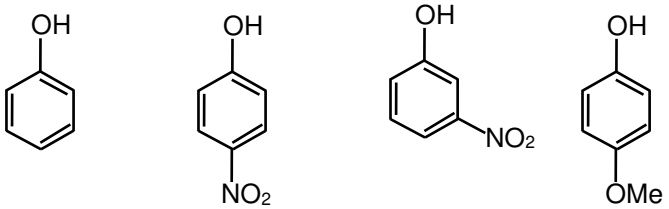
(A) $CH_3CH_2NH_2$ (B) $CH_3CH_2\underset{\displaystyle CH_2CH_3}{\underset{|}{N}}H$ (C) $H_3C-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_3$ (D) $Ph-\underset{\displaystyle CH_3}{\underset{|}{N}}-H$

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

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

13. The increasing order of the pK_a values of the following compounds is :

[JEE(Main) 2019 Online (10-01-19), 4/120]

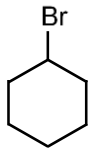
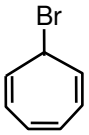
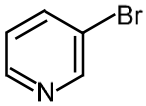
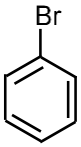


A B C D

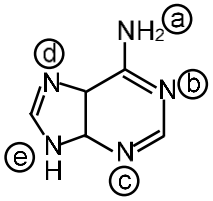
(1) C < B < A < D (2) B < C < D < A (3) B < C < A < D (4) D < A < C < B

14. Which of the following compounds will produce a precipitate with $AgNO_3$?

[JEE(Main) 2019 Online (11-01-19), 4/120]

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

15. In the following compound the favourable site/s for protonation is /are :



[JEE(Main) 2019 Online (11-01-19), 4/120]

(1) (a) and (e) (2) (a) and (d) (3) (b), (c) and (d) (4) (a)

16. The correct order of acid strength of compounds CH≡CH, $CH_3-C\equiv CH$ and $CH_2=CH_2$ is as follows :

[JEE(Main) 2019 Online (12-01-19), 4/120]

(1) $CH_3-C\equiv CH > CH\equiv CH > CH_2=CH_2$ (2) $CH_3-C\equiv CH > CH_2=CH_2 > HC\equiv CH$

(3) $HC\equiv CH > CH_3-C\equiv CH > CH_2=CH_2$ (4) $CH\equiv CH > CH_2=CH_2 > CH_3-C\equiv CH$

Answers

EXERCISE - 1

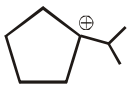
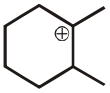
PART - I

A-1. (a) 1 > 2 > 3 ; (b) 1 > 2 > 3 **A-2.** (a) 2 > 1 > 3 > 4 ; (b) 1 > 2 > 3 ; (c) 1 > 2

B-1. Stability order : I < II < III < IV
IV is most stable being 3º and delocalised but III is 2º and delocalised.

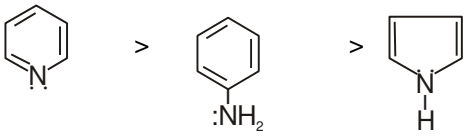
B-2. III > II > I > IV **C-1.** (P) I > III > IV > II ; (Q) IV > III > II > I ; (R) III > II > IV > I

C-2. (II) is more stable carbocation due to extented conjugation

C-3. (P) =  ; (Q) = 

D-1. II > III > IV > I > V

D-2. (a) $PhNH_2$ > Ph_2NH > Ph_3N

(b) 

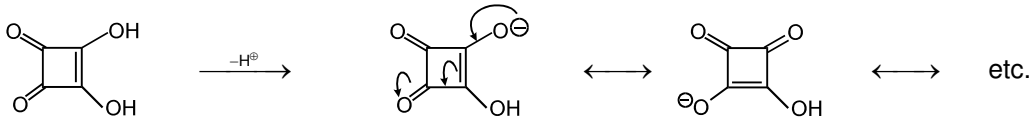
(c) $Ph–CH_2–CH_2–NH_2$ > $CH_3–\underset{\underset{Ph}{|}}{CH}–NH_2$ > $CH_3–CH_2–\underset{\underset{Ph}{|}}{\ddot{N}H}$

D-3. 2

D-4. I is less basic than II because, in compound (I) the lone pair of electrons is involved in resonance but not in II.

E-1. I - a, II - b, III - c, (acidic strength $\propto$ stability of conjugate base)

E-2. III > I > II (acidic strength $\propto$ stability of conjugate base) In III conjugate base is highly stabilised by intra molecular H-bonding.

E-3.  etc.

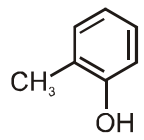
Its conjugate base (anion) is resonance stabilised like $RCOO^{\ominus}$ anion of carboxylic acid.

F-1. (a) Not feasible (b) Feasible (c) Not feasible (d) Not feasible

F-2. (c) Strong base accept H^+ ions so this reaction is feasible.

F-3. (i, iii, iv, v, vi, vii)

G-1. B, C, E, G, H can show tautomerism.

G-2. (P) $CH_3-\underset{\underset{OH}{|}}{C}=CH_2$ (Q) $CH_2=CH–NH_2$ (R) $CH_3-C(CH_3)=N(\rightarrow O)-OH$ (S) 

G-3. In Monocarbonyl Keto form is more stable due to greater strength of the carbon-oxygen double bond as compared to the carbon carbon double bond.

PART - II

A-1.	(C)	**A-2.**	(A)	**A-3.**	(B)	**A-4.**	(D)	**A-5.**	(B)
A-6.	(D)	**B-1.**	(A)	**B-2.**	(D)	**B-3.**	(A)	**B-4.**	(C)
B-5.	(B)	**B-6.**	(C)	**C-1.**	(C)	**C-2.**	(B)	**C-3.**	(B)
C-4.	(C)	**C-5.**	(D)	**C-6.**	(B)	**D-1.**	(C)	**D-2.**	(A)
D-3.	(A)	**D-4.**	(D)	**D-5.**	(D)	**D-6.**	(A)	**D-7.**	(D)
D-8.	(D)	**E-1.**	(D)	**E-2.**	(A)	**E-3.**	(C)	**E-4.**	(B)
E-5.	(D)	**E-6.**	(C)	**E-7.**	(C)	**E-8.**	(C)	**E-9.**	(A)
E-10.	(D)	**F-1.**	(B)	**F-2.**	(C)	**F-3.**	(D)	**F-4.**	(C)
G-1.	(A)	**G-2.**	(A)	**G-3.**	(B)	**G-4.**	(A)	**G-5.**	(A)

PART - III

1. (A - z) ; (B - x) ; (C - w) ; (D - y)

2. (A - p,q,s) ; (B - p,q,r,s) ; (C - p,q,r,s) ; (D - p,q,r,s)

EXERCISE - 2

PART - I

1.	(B)	**2.**	(C)	**3.**	(A)	**4.**	(C)	**5.**	(A)
6.	(D)	**7.**	(B)	**8.**	(D)	**9.**	(A)	**10.**	(D)
11.	(A)	**12.**	(D)	**13.**	(A)	**14.**	(D)	**15.**	(B)
16.	(A)	**17.**	(C)	**18.**	(A)	**19.**	(C)	**20.**	(B)
21.	(D)	**22.**	(B)						

PART - II

1.	7	**2.**	2	**3.**	4 (S_1, S_2, S_4, S_5)	**4.**	5 (ii, iii, iv, vi, vii)
5.	6 (i, ii, iii, vi, vii, ix)			**6.**	5 (i, iv, v, vi, viii)	**7.**	5 (i, iv, v, vi, viii)
8.	34	**9.**	3	**10.**	10		

PART - III

1.	(ABCD)	**2.**	(BCD)	**3.**	(ABCD)	**4.**	(ACD)	**5.**	(ACD)
6.	(BC)	**7.**	(BD)	**8.**	(ABCD)	**9.**	(ACD)		

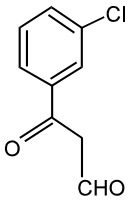
PART - IV

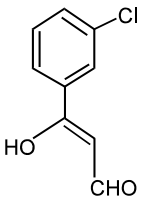
1.	(D)	**2.**	(D)	**3.**	(A)	**4.**	(A)	**5.**	(C)
6.	(B)	**7.**	(C)	**8.**	(A)	**9.**	(D)	**10.**	(D)
11.	(C)	**12.**	(C)	**13.**	(D)	**14.**	(A)		

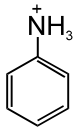
EXERCISE - 3

PART - I

1. (C) **2.** (a) – (ii) ; (b) – (iii) ; (c) – (iv) ; (d) – (i) ; (e) – (v)

3. A. 

; B. 

4. (A) **5.** (A) **6.** 

7. (B) **8.** (D) **9.** (D) **10.** (A) **11.** (D)

12. 2 **13.** (C) **14.** (D) **15.** (D) **16.** (A)

17. (D)

PART - II

JEE(MAIN) OFFLINE PROBLEMS

1. (3) **2.** (4) **3.** (2) **4.** (3) **5.** (4)

6. (1) **7.** (3) **8.** (1) **9.** (2) **10.** (4)

11. (3) **12.** (3) **13.** (1) **14.** (3) **15.** (4)

16. (1) **17.** (1) **18.** (2)

JEE(MAIN) ONLINE PROBLEMS

1. (4) **2.** (3) **3.** (3) **4.** (3) **5.** (4)

6. (3) **7.** (4) **8.** (4) **9.** (4) **10.** (3)

11. (2) **12.** (4) **13.** (3) **14.** (2) **15.** (3)

16. (3)

Additional Problems for Self Practice (APSP)

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Resonance students.

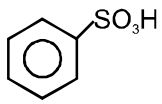
PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

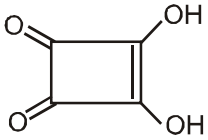
Max. Marks : 120 **Max. Time : 1 Hr.**

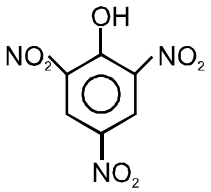
Important Instructions :

1. The test is of **1 hour** duration.
2. The Test Booklet consists of **30** questions. The maximum marks are **120.**
3. Each question is allotted **4 (four)** marks for correct response.
4. Candidates will be awarded marks as stated above in Instructions No. 3 for correct response of each question. ¼ **(one fourth)** marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
5. There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted accordingly as per instructions 4 above.

1. Which of the following would produce effervesence with sodium bicarbonate ?

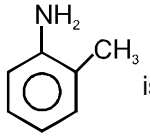
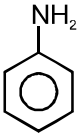
(1) 

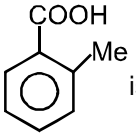
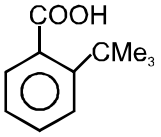
(2) 

(3) 

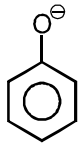
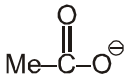
(4) All of these

2. Select correct statement from the following :

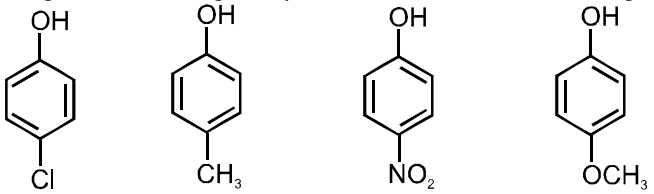
(1)  is more basic than 

(2)  is more acidic than 

(3) HC≡CH is more acidic than NH_3

(4)  is more stable than 

3. Arrange the following compounds in order of decreasing acidity.



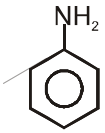
(i) (ii) (iii) (iv)

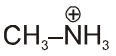
(1) (i) > (ii) > (iii) > (iv)
(2) (iii) > (i) > (ii) > (iv)
(3) (iv) > (iii) > (i) > (ii)
(4) (ii) > (iv) > (i) > (iii)

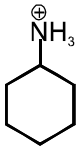
4. The order of decreasing basicity in the four halide ions is :

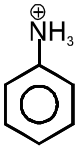
(1) $I^- > Br^- > Cl^- > F^-$ (2) $Cl^- > Br^- > I^- > F^-$ (3) $F^- > Cl^- > Br^- > I^-$ (4) $Cl^- > F^- > Br^- > I^-$

5. Correct order of acidic strength :


(i)

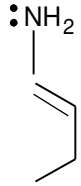

(ii)

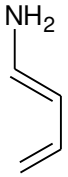

(iii)

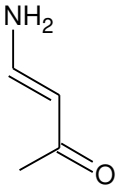

(iv)

(1) (iv) > (i) > (ii) > (iii) (2) (iv) > (iii) > (ii) > (i) (3) (iv) > (ii) > (iii) > (i) (4) (ii) > (iv) > (i) > (iii)

6. Which of the following is **incorrect** about the given molecules

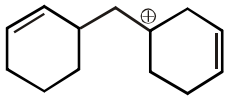
(a) 

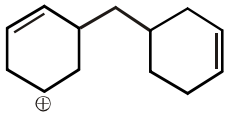
(b) 

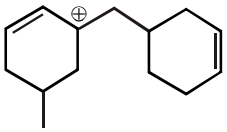
(c) 

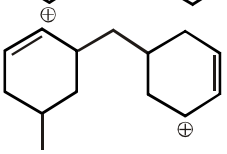
(1) The correct order of basic strength (K_b) is : a > b > c
(2) The correct order of C–N bond length is : a > b > c
(3) The correct C=C bond length order is : a > b > c
(4) The correct pK_b order is : c > b > a

7. Which of the following is the most stablized carbocation ?

(1) 

(2) 

(3) 

(4) 

8. Which one among the following is the least basic:

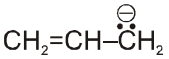
(1) $\overset{\ominus}{C}H_3$ (2) $\overset{\ominus}{N}H_2$ (3) $\overset{\ominus}{O}H$ (4) $\overset{\ominus}{F}$

9. Which is most basic in aqueous solution ?

(1) CH_3NH_2 (2) $(CH_3)_2NH$ (3) $(CH_3)_3N$ (4) $Ph–NH_2$

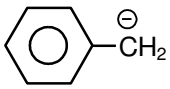
10. Stability order of given anions is :

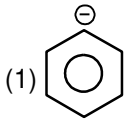

(I)

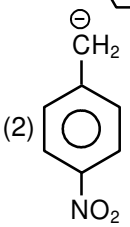

(II)

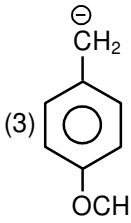

(III)

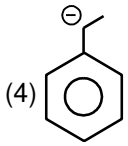
(1) I > III > II (2) I > II > III (3) III > II > I (4) III > I > II

11. Which is less basic than benzyl  carbanion?

(1) 

(2) 

(3) 

(4) 

12. The correct order of decreasing acid strength of trichloroacetic acid (A), trifluoroacetic acid (B), acetic acid (C) and formic acid (D) is :

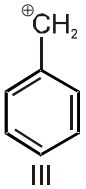
(1) B > A > D > C (2) B > D > C > A (3) A > B > C > D (4) A > C > B > D

13. Base strength is in the order of

(i) $CH_3\overset{-}{C}H_2$ (ii) $H_2C=\overset{\ominus}{C}H$ and (iii) $H-C\equiv C^{\ominus}$

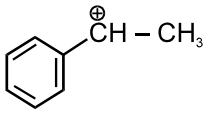
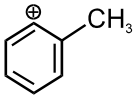
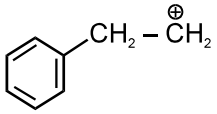
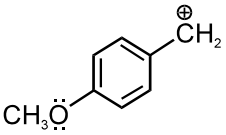
(1) (ii) > (i) > (iii) (2) (iii) > (iii) > (i) (3) (i) > (iii) > (ii) (4) (i) > (ii) > (iii)

14. The order of stability of following carbocation :

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

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

15. The most stable carbocation is :

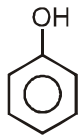
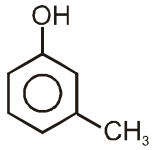
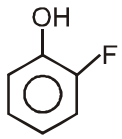
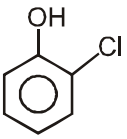
(1)  (2)  (3)  (4) 

16. Pyridine is less basic than triethylamine because :

(1) Pyridine has aromatic character (2) Nitrogen in pyridine is sp^2 hybridised

(3) Pyridine is a cyclic system (4) In pyridine, lone pair of nitrogen is delocalised

17. Which of the following phenol has lowest pK_a ?

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

18. Which is most basic among the followings ?

(1) Ph-NH_2 (2) NH_3 (3) CH_3–NH_2 (4) C_2H_5–CN

19. **Assertion :** The pK_a of acetic acid is lower than that of phenol.

Reason : Phenoxide ion is more resonance stabilised.

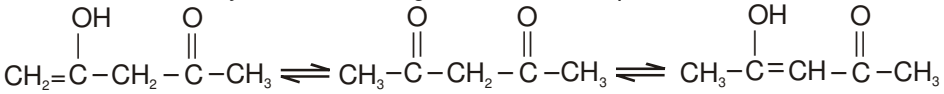
(1) If both assertion and reason are true and reason is a correct explanation of assertion.

(2) If both assertion and reason are true but reason is not a correct explanation of assertion.

(3) If assertion is true but reason is false.

(4) If assertion and reason both are false.

20. The order of stability of the following tautomeric compounds is :



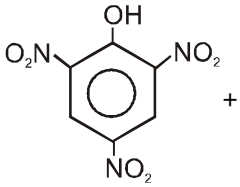
(I) (II) (III)

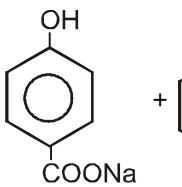
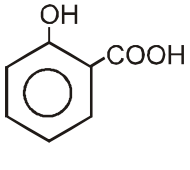
(1) III > II > I (2) II > I > III (3) II > III > I (4) I > II > III

21. The feasible reaction is :

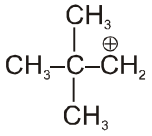
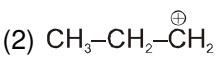
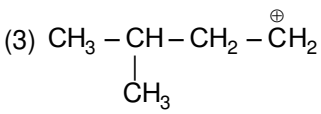
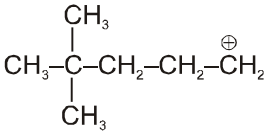
(1) $CH_3COOH + NaCl \longrightarrow$

(2) $C_6H_5COOH + KBr \longrightarrow$

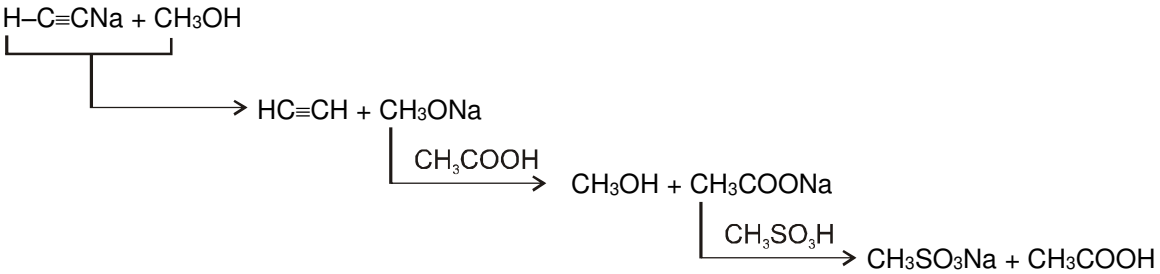
(3)  $+ KHSO_4 \longrightarrow$

(4)  $+$  $\longrightarrow$

22. In which of following carbocation rearrangement take place with change carbon skeleton :

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

23. Observe the following reaction sequence.

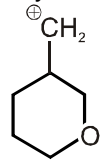
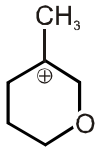
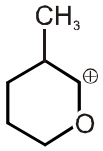
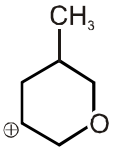


Which is correct acidic strength order :

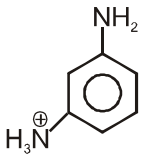
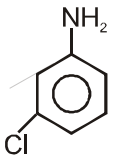
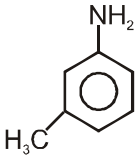
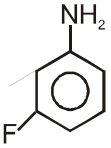
(1) HC ≡ CH > CH_3COOH > CH_3SO_3H (2) CH_3SO_3H > CH_3COOH > HC ≡ CH

(3) CH_3SO_3H > HC ≡ CH > CH_3COOH (4) CH_3COOH > CH_3SO_3H > HC ≡ CH

24. Identify the most stable carbocation among the following :

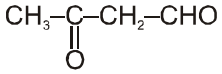
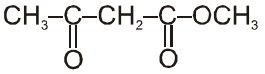
(1)  (2)  (3)  (4) 

25. Select the most basic compound.

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

26. Among the following compounds having highest enol content.

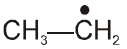
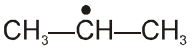
(1) CH_3COOCH_3 (2) CH_3COCH_3

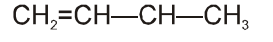
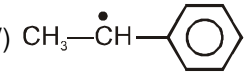
(3)  (4) 

27. Which is more basic than hydroxide (OH^-) ion?

(1) $CH_3–NH_2$ (2) $CH_3–CH_2–O^-$ (3) F^- (4) $Ph–NH_2$

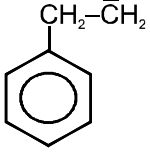
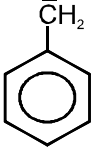
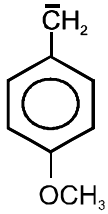
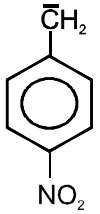
28. Give the stability order of following radicals :

(I)  (II) 

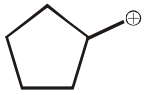
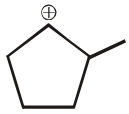
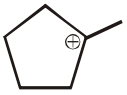
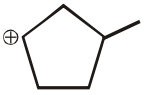
(III)  (IV) 

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

29. The most stable carbanion among the following is

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

30. Which of the following is the most stable carbocation.

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

Practice Test-1 (IIT-JEE (Main Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

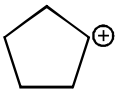
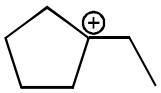
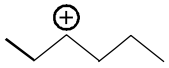
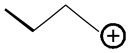
Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22	23	24	25	26	27	28	29	30
Ans.										

PART- II : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE–I

1. Which of the following is the strongest acid ? **[NSEC-2000]**
(A) 3,5-dinitrophenol (B) 2,4-dinitrophenol (C) phenol (D) 2,4,6-trinitrophenol

2. Identify the correct statement regarding effect of Cl atom bonded to the carbon atom adjacent to a carbocation carbon ? **[NSEC-2000]**
(A) It has no effect on the stability of the carbocation
(B) It destabilizes the carbocation
(C) It stabilizes the carbocation
(D) Cannot predict its effect on the carbocation from the given information.

3. Which of the following is the strongest base ? **[NSEC-2000]**
(A) $HC\equiv C^-$ (B) $CH_2 = CH^-$ (C) $CH_3CH_2^-$ (D) NH_2^-

4. Select the most stable carbocation from amongst the following. **[NSEC-2000]**
(A)  (B)  (C)  (D) 

5. Which of the following orders is true regarding the acidic nature of phenol ? **[NSEC-2001]**
(A) phenol > o-cresol < o-nitrophenol (B) phenol < o-cresol < o-nitrophenol
(C) phenol > o-cresol > o-nitrophenol (D) phenol < o-cresol > o-nitrophenol

6. Which of the following order is expected to be correct ? **[NSEC-2001]**
(A) $pK_a(ClCH_2COOH) > pK_a(CH_3COOH) < pK_a(CH_3CH_2COOH)$
(B) $pK_a(ClCH_2COOH) < pK_a(CH_3COOH) < pK_a(CH_3CH_2COOH)$
(C) $pK_a(ClCH_2COOH) > pK_a(CH_3COOH) > pK_a(CH_3CH_2COOH)$
(D) $pK_a(ClCH_2COOH) < pK_a(CH_3COOH) > pK_a(CH_3CH_2COOH)$

7. Arrange the following in the order of increasing stability : **[NSEC-2002]**
PhC^+H_2, Ph_3C^+, Me^+, Ph_2C^+H
(A) $Me^+ < PhC^+H_2 < Ph_2C^+H < Ph_3C^+$ (B) $PhC^+H_2 < Me^+ < Ph_3C^+ < Ph_2C^+H$
(C) $PhC^+H_2 < Ph_3C^+ < Me^+ < Ph_2C^+H$ (D) $PhC^+H_2 < Ph_2C^+H < Ph_3C^+ < Me^+$

8. Which of the following compounds is the most acidic ? **[NSEC-2002]**
(A) HCO_2H (B) CH_3CO_2H (C) $CH_3CH_2CO_2H$ (D) CCl_3CO_2H

9. Out of the four pK_a values 3.75, 9.89, 15.54 and 19.30, the highest pK_a value corresponds to **[NSEC-2003]**
(A) acetone (B) formic acid (C) phenol (D) methanol.

10. 

a b c d

The correct order of acidic character in the above compounds is **[NSEC-2003]**

(A) a > b > c > d (B) c > a > d > b (C) b > c > a > d (D) a > c > b > d.

11. The weakest base among the following is **[NSEC-2004]**

(A) $C_6H_5SO_3^-$ (B) $C_2H_5O^-$ (C) $C_6H_5O^-$ (D) $CH_3–CH=CH–CH_2–O^-$

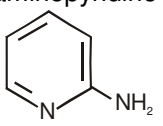
12. $\underset{(i)}{CH_3COOH}$ $\underset{(ii)}{HCOOH}$ $\underset{(iii)}{CH_2ClCOOH}$ $\underset{(iv)}{PhCOOH}$

The order of acidity in the given series of compounds is **[NSEC-2004]**

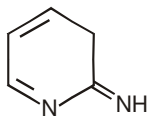
(A) (iv) < (ii) < (i) < (iii) (B) (i) < (ii) < (iii) < (iv)

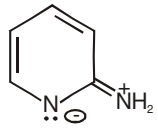
(C) (i) < (ii) < (iv) < (iii) (D) (i) < (iv) < (ii) < (iii)

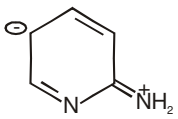
13. The proper tautomeric structure for 2-aminopyridine (X) is **[NSEC-2004]**

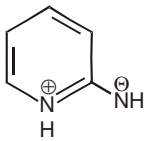


(X)

(A) 

(B) 

(C) 

(D) 

14. The correct order of acidity for the following compound is **[NSEC-2005]**

(1) Benzoic acid > phenol > p-nitrobenzoic acid > m-nitrobenzoic acid.

(2) phenol > p-nitrobenzoic acid > m-nitrobenzoic acid > benzoic acid.

(3) p-nitrobenzoic acid > m-nitrobenzoic acid > benzoic acid > phenol.

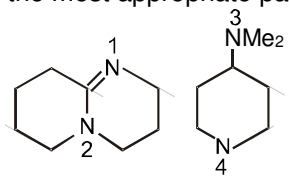
(4) m-nitrobenzoic acid > p-nitrobenzoic acid > benzoic acid > phenol.

15. Identify the group in which the order of basicity is not correct ? **[NSEC-2005]**

(A) $OH^- > H_2O > H_3O^+$ (B) $S^{2-} > HS^- > H_2S$

(C) $NH_3 > OH^- > H_2O$ (D) $Cl^- > Br > I^-$

16. Choose the most appropriate pair of nitrogens that gets protonated in the following structures.



(A) 1 and 3 (B) 2 and 4 (C) 1 and 4 (D) 2 and 3.

17. As the base changes from RNH_2 to R_2NH, to R_3N the basicity **[NSEC-2006]**

(A) $R_2NH > R_3N > RNH_2$ (B) $RNH_2 > R_3N > R_2NH$

(C) $RNH_2 > R_2NH > R_3N$ (D) $R_3N > RNH_2 > R_2NH$.

18. The most acidic of the following substances is **[NSEC-2006]**

(A) aniline (B) p-nitrophenol (C) phenol (D) acetaldehyde.

19. The observed order of carbocation stability is **[NSEC-2006]**

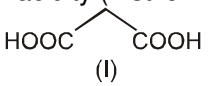
(A) $CH_3^+ > CH_3CH_2^+ > (CH_3)_2 CH^+ > (CH_3)_3C^+$

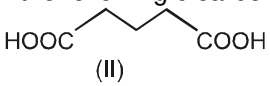
(B) $CH_3CH_2^+ > CH_3^+ > (CH_3)_2CH^+ > (CH_3)_3C^+$

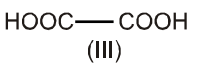
(C) $(CH_3)_2CH^+ > CH_3^+ > CH_3CH_2^+ < (CH_3)_3C^+$

(D) $(CH_3)_3C^+ > (CH_3)_2CH^+ > CH_3CH_2^+ > CH_3^+$.

20. Indicate the correct of acidity (first ionization) in the following dicarboxylic acids : **[NSEC-2007]**


(I)


(II)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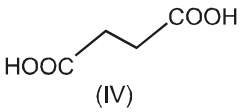

(IV)

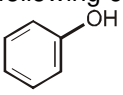
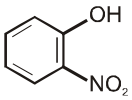
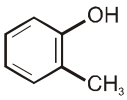
(A) I > II > III > IV (B) II > IV > I > III (C) III > I > IV > II (D) IV > II > I > III

21. The carbocation $(CH_3)_3C^+$ is stabilized primarily by : **[NSEC-2007]**
(A) hyperconjugation (B) tautomerism (C) resonance (D) conjugation

22. The correct order of acidity of the C-H proton is – **[NSEC-2007]**
(A) acetylene > ethylene > ethane (B) ethylene > ethylene > ethane
(C) ethane > ethylene > acetylene (D) acetylene > ethane >.ethylene

23. Salicylic acid is a stronger acid than p-hydroxybenzoic acid due to **[NSEC-2008]**
(A) Steric hindracne (B) Hydrogen bonding
(C) Mesomeric effect (D) Solvation energy

24. Which one of the following compounds can be deprotonated by OH fastest ? **[NSEC-2008]**
(A) HCOOH, $pK_a = 3.8$ (B) H_2S, $pK_a = 7.0$
(C) Toluene, $pK_a = 41$ (D) CH_3NH_2, $pK_a = 40$

25. The most acidic among the following compound is : **[NSEC-2009]**
(A) $Cl–CH_2–CH_2–OH$ (B)  (C)  (D) 

26. Keto and enol forms of a compound are related to each other as **[NSEC-2010]**
(A) Resonance structures (B) Conformations
(C) Configurational isomers (D) Constitutional isomers

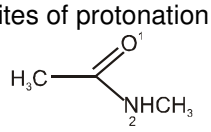
27. The correct order of acidity of the following compounds is : **[NSEC-2010]**
(I) CH_3COOH (II) $ClCH_2COOH$ (III) O_2NCH_2COOH (IV) $HOCH_2COOH$
(A) IV > II > III > I (B) I > IV > II > III (C) II > III > I > IV (D) III > II > IV > I

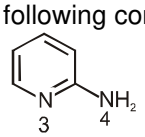
28. The order of acidities of the H-atoms underlined in the following compounds is in the order – **[NSEC-2011]**
(I) $Ph–C\underline{H}_2–CH_3$ (II) $Ph–C\equiv C\underline{H}$ (III) $Ph–CH=C\underline{H}_2$ (IV) 
(A) IV>II>I>III (B) II>IV>III>I (C) III>IV>I>II (D) I>III>II>IV

29. An electron releasing group will not stabilize which of the following groups ? **[NSEC-2012]**
(A) Carbocation (B) Carbanion (C) free radical (D) none of these

30. The most stable free radical which can be isolated is **[NSEC-2012]**
(A) Trityl radical (B) Diphenyl methyl radical
(C) 2,4,6-Tri-ter-butylphenoxy radical (D) tert-butyl radical

31. The preferred sites of protonation in the following compounds are **[NSEC-2012]**


I


II

(A) 1 and 3 (B) 2 and 4 (C) 1 and 4 (D) 2 and 3

32. Acetone and propen-2-ol are **[NSEC-2013]**

(A) enantiomers (B) keto-enol tautomers
(C) diastereoisomers (D) meso compounds

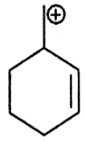
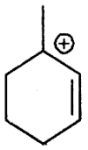
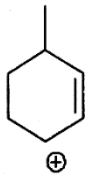
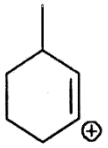
33. Which of the following does not have an active methylene group ? **[NSEC-2013]**

(A) $CH_3CH_2NO_2$ (B) $CH_3COCH_2COCH_3$
(C) $PhCOCH_2CN$ (D) $CH_3CH_2NH_2$

34. Which of the following phenols is most soluble in aqueous sodium bicarbonate ? **[NSEC-2013]**

(A) 2,4-dihydroxyacetophenone (B) p-cyanophenol
(C) 3,4-dicyanophenol (D) 2,4,6-tricyanophenol

35. The most stable carbocation is **[NSEC-2014]**

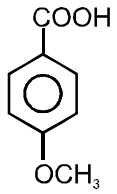
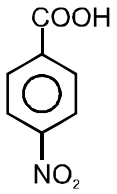
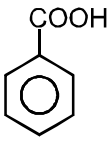
(A)  (B)  (C)  (D) 

36. The order of basicity is **[NSEC-2014]**

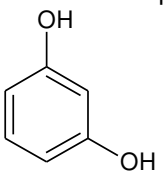
$(I)\ Ph-CONH_2$ $(II)\ Ph-NH_2$ $(III)\ Ph-CH_2-NH_2$ $(IV)\ p-OCH_3Ph-NH_2$

(A) $II > IV > I > III$ (B) $III > II > IV > I$ (C) $III > IV > II > I$ (D) I>II>IV>III

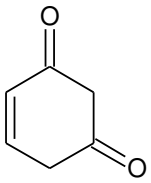
37. The pKa values of the acids A to D are found to be 4.19, 3.41, 4.46 and 4.76. The acid having pKa of 3.41 is **[NSEC-2014]**

(A)  (B) CH_3COOH (C)  (D) 

38. At normal temperature, X and Y are **[NSEC-2014]**



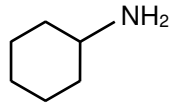
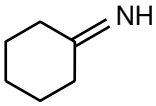
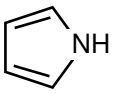
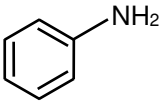
X



Y

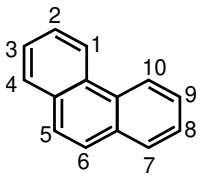
(A) resonance structures (B) tautomers
(C) functional isomers (D) positional isomers

39. The order of basicity of the following compounds is **[NSEC-2015]**

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

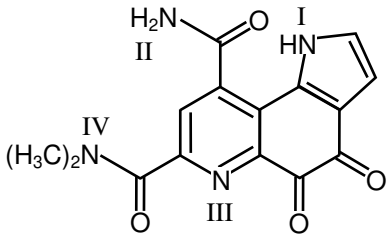
(A) I > II > IV > III (B) IV > II > I > II (C) III > II > I > IV (D) I > II > III > IV

40. In the case of dibromo derivatives of the following compound, the derivative having highest energy has the bromo substituents in positions **[NSEC-2016]**



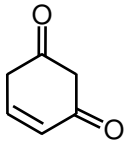
(A) 1, 2 (B) 2, 3 (C) 4, 5 (D) 1, 10

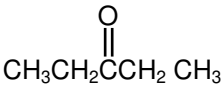
41. The most basic nitrogen in the following compound is **[NSEC-2017]**



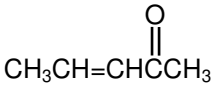
(A) I (B) II (C) III (D) IV

42. The order of enol content in the following molecules is **[NSEC-2017]**

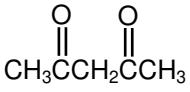

(a)



(b)



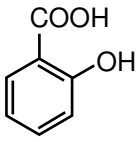
(c)



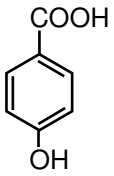
(d)

(A) a > d > c > b (B) a > c > d > b (C) a > c > b > d (D) a > b > c > d

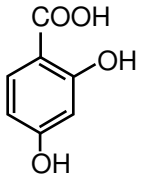
43. The order of pK_a values of the following acids is **[NSEC-2018]**



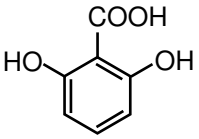
(I)



(II)



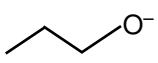
(III)



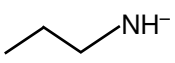
(IV)

(A) IV > I > III > II (B) III > IV > I > II (C) II > I > III > IV (D) II > III > I > IV

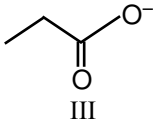
44. The correct order of basicity of the following species is **[NSEC-2018]**



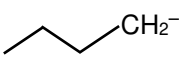
I



II



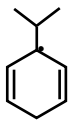
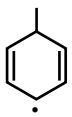
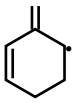
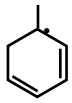
III



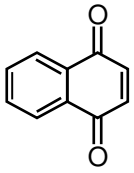
IV

(A) III < IV < II < I (B) III < I < II < IV (C) III < II < I < IV (D) IV < I < II < III

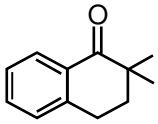
45. The most stable radical among the following is **[NSEC-2018]**

(A)  (B)  (C)  (D) 

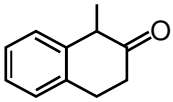
46. The molecules that can exhibit tautomerism are **[NSEC-2018]**



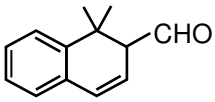
(I)



(II)



(III)



(IV)

(A) I, IV (B) II, III (C) III, IV (D) I, II

PART - III : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time : 1 Hr. **Max. Marks : 60**

Important Instructions :

A. General :

1. The test is of 1 hour duration.
2. The Test Booklet consists of 20 questions. The maximum marks are 60.

B. Question Paper Format :

3. Each part consists of five sections.
4. Section-1 contains 8 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
5. Section-2 contains 6 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
6. Section-3 contains 3 questions. The answer to each of the questions is a single-digit integer, ranging from 0 to 9 (both inclusive).
7. Section-4 contains 1 paragraphs each describing theory, experiment and data etc. 2 questions relate to paragraph. Each question pertaining to a partcular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
8. Section-5 contains 1 multiple choice questions. Question has two lists (list-1 : P, Q, R and S; List-2 : 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.

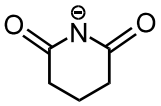
C. Marking Scheme :

9. For each question in Section 1, 4 and 5 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (–1) mark will be awarded.
10. For each question in Section 2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be answered for incorrect answer in this section.
11. For each question in Section 3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.

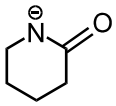
SECTION-1 : (Only One option correct Type)

This section contains 8 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.

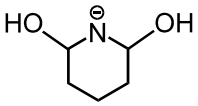
1. The stability order of the following anions :



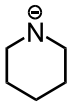
I



II



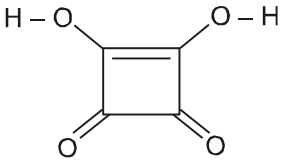
III



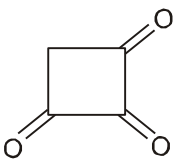
IV

(A) IV > III > II > I (B) I > II > III > IV (C) I > II > IV > III (D) I > III > II > IV

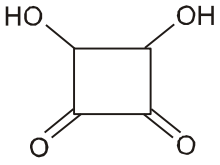
2. The correct pK_a order of the following acids is :



I



II



III

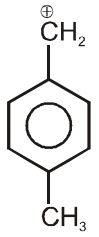
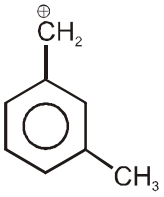
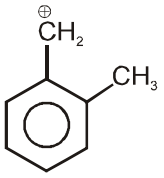
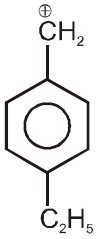
(A) I > II > III (B) I > III > II (C) III > II > I (D) III > I > II

3. The preferred sites of protonation in the following compounds are

(I) $Ph–CH_2–\overset{1}{\underset{}{C}}(=\overset{2}{NH})–NH_2$ (II) $Ph–CH_2–\overset{3}{\underset{}{C}}(=\overset{4}{O})–NH_2$

(A) 1 and 3 (B) 2 and 4 (C) 1 and 4 (D) 2 and 3

4. Which of the following carbocation is most stable :

(A)  (B)  (C)  (D) 

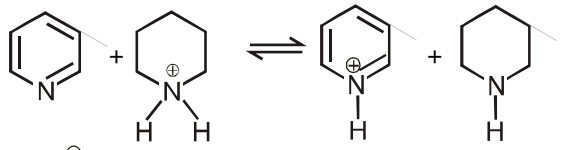
5. In which pairs first compound is stronger acid than the second ?

(A) Adipic acid, succinic acid (B) Fumaric acid, maleic acid

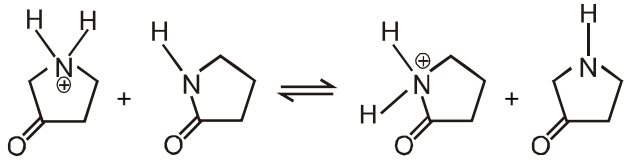
(C) Pthalic acid, terepthalic acid (D) Benzoic acid, Picric acid

6. Among the following reaction which favours forward reaction ?

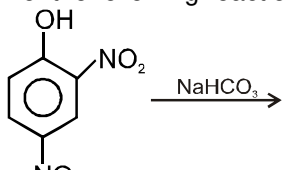
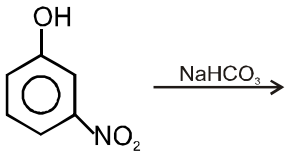
(A) $EtOH + PhO^{\ominus} \rightleftharpoons EtO^{\ominus} + PhOH$

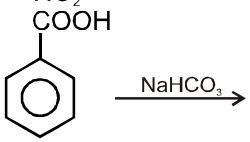
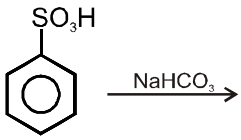
(B) 

(C) $CH_3–\overset{\ominus}{C}H_2 + CH_3–NH_2 \rightleftharpoons CH_3–CH_3 + CH_3\overset{\ominus}{N}H$

(D) 

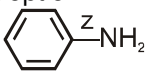
7. Which of the following reactions is/are feasible :

(i)  (ii) 

(iii)  (iv) 

(A) (i) & (ii) (B) (ii) , (iii) & (iv) (C) (i) , (ii) & (iv) (D) (i) , (iii) & (iv)

8. Compare the bond lengths and select the correct option :

$CH_3—CH_2\overset{x}{—}NH_2$ $CH_3—CH=CH\overset{y}{—}NH_2$ 

(A) x = y = z (B) x > y > z (C) x < y < z (D) x > y = z

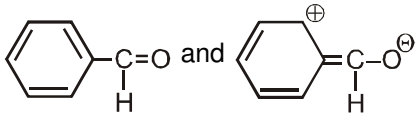
Section-2 : (One or More than one options correct Type)

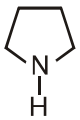
This section contains 6 multipole choice questions. Each questions has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.

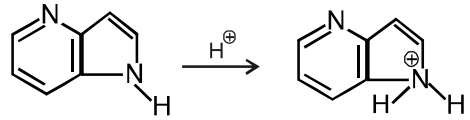
9. Which of the following compounds will show tautomerism ?
(A) 2,2- Dimethylpropanal
(B) 2,2-Dimethyl-1 nitropropane
(C) Acetyl Acetone
(D) Benzophenone

10. Which of the following is **correct** regarding stability of the following pair of species?
(A) $CH_2=\overset{+}{N}=\overset{-}{N}$ > $\overset{-}{C}H_2-\overset{+}{N}\equiv N$
(B) $CH_2=CH-\overset{+}{C}H-\overset{-}{O}$ > $\overset{-}{C}H_2-CH=CH-\overset{+}{O}$
(C) $CH_3-\overset{O}{\overset{\|}{C}}-\overset{-}{O}$ > $CH_3-CH_2-\overset{-}{O}$
(D) Pent-2-ene > 2-methylbut-2-ene

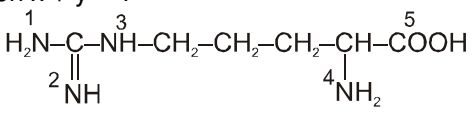
11. Which of the following is/are correct statement/statements ?
(A) Guanidine $\left[NH_2-\underset{\underset{NH}{\|}}{C}-NH_2\right]$ is more basic than pyridine because conjugate acid of guanidine has three equal contributing resonating structure.
(B) Diethylamine is stronger base than triethylamine in aqueous medium.
(C) Ortho-methyl aniline is weaker base than para-methyl aniline.
(D) 2,4,6-Trinitro-N,N-dimethyl aniline is stronger base than 2,4,6-Trinitro aniline.

12. The tautomeric pairs are
(A) $Me_2C=NOH$ and $Me_2CH-N=O$
(B) $CH_2=CH-NHCH_3$ and $CH_3-CH=N-CH_3$
(C)  and
(D) $CH_2=CH-\underset{\underset{OH}{|}}{CH}-CH_3$ and $CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$

13. In which compounds (II) is more basic than (I)
(A) $(C_2H_5)_3N$ & 
(I) (II)
(B) $H_2N-\overset{\underset{O}{\|}}{C}-NH_2$ & $H_2N-\overset{\underset{NH}{\|}}{C}-NH_2$
(I) (II)
(C) $C_2H_5-NH-C_2H_5$ & 
(I) (II)
(D) CH_3NH_2 & $(CH_3)_2NH$
(I) (II)

14. Which of the following reactions is/are not feasible :
(A) $CH_3COONa + HCOOH \longrightarrow CH_3COOH + HCOONa$
(B) $CH_3COONa + Ph-OH \longrightarrow CH_3COOH + PhONa$
(C) $NH_2-\overset{\underset{CH_2}{\|}}{C}-NH_2 + NH_2-\overset{\underset{\overset{\oplus}{N}H_2}{\|}}{C}-NH_2 \longrightarrow NH_2-\overset{\underset{CH_2}{\|}}{C}-\overset{\oplus}{N}H_2 + NH_2-\overset{\underset{NH}{\|}}{C}-NH_2$
(D) 

Section-3: (One Integer Value Correct Type.)
This section contains 3 questions. Each question, when worked out will result in one integer from 0 to 9 (both inclusive)

15. In the given molecule the sites undergoes deprotonation and protonation most readily respectively are x & y then x + y = ?


16. How many of the following compounds will accept $H^{\oplus}$ from ammonium ion.
Pyridine, Aniline, Pyrrole, Triphenyl amine,
Benzyl amine, Methyl amine, Di-methyl amine, Tri-methyl amine

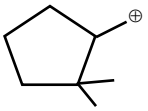
17. How many of the following compounds react with $NaHCO_3$ and liberate $CO_2(g)$
1. Salicylic acid 2. Pthalic acid 3. Picric acid 4. Resorcinol
5. Carbolic acid 6. Aspirin 7. Anisol 8. Tarteric acid

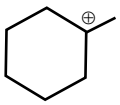
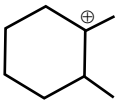
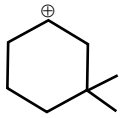
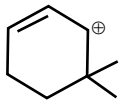
SECTION-4 : Comprehension Type (Only one option correction)

This section contains 1 paragraphs, each describing theory, experiments, data etc. 2 questions relate to the paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D)

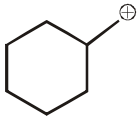
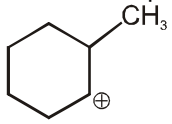
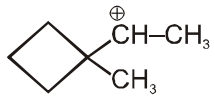
Paragraph for Questions 18 to 19

Whenever an intermediate carbocation is formed in reaction it may rearranges.
Only those carbocation will rearrange which can produce more stable species. It can be done either by:
(i) Shifting of H, alkyl, aryl, bond (1, 2-shifting)
(ii) Ring expansion
(iii) Ring contraction

18. Most stable rearranged carbocation of  is :

(A)  (B)  (C)  (D) 

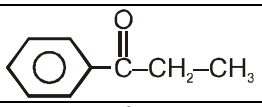
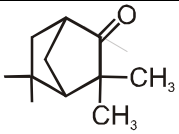
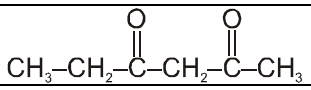
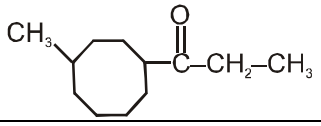
19. In which of the following carbocation rearrangement will not take place?

(A)  (B)  (C)  (D) 

SECTION-5 : Matching List Type (Only One options correct)

This section contains 1 questions, each having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (A), (B), (C) and (D) out of which one is correct

20. Match each List-I with List-II and select the correct answer using the code given below the lists.

	Column-I		Column-II
P		**1**	Zero enolizable H-atom
Q		**2**	7-enolizable H-atom
R		**3**	2-enolizable H-atom
S		**4**	3-enolizable H-atom

Code :

	P	Q	R	S		P	Q	R	S
(A)	3	1	2	4	(B)	1	2	4	3
(C)	2	1	3	4	(D)	3	2	1	4

Practice Test-2 ((IIT-JEE (ADVANCED Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

Que.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Ans.										
Que.	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
Ans.										

APSP Answers

PART - I

1.	(4)	**2.**	(3)	**3.**	(2)	**4.**	(3)	**5.**	(3)
6.	(3)	**7.**	(3)	**8.**	(4)	**9.**	(2)	**10.**	(1)
11.	(2)	**12.**	(1)	**13.**	(4)	**14.**	(3)	**15.**	(4)
16.	(2)	**17.**	(4)	**18.**	(3)	**19.**	(3)	**20.**	(1)
21.	(4)	**22.**	(1)	**23.**	(2)	**24.**	(3)	**25.**	(3)
26.	(3)	**27.**	(2)	**28.**	(2)	**29.**	(4)	**30.**	(3)

PART- II

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

PART- III

1.	(B)	**2.**	(C)	**3.**	(A)	**4.**	(C)	**5.**	(C)
6.	(C)	**7.**	(D)	**8.**	(B)	**9.**	(BC)	**10.**	(ABC)
11.	(ABCD)	**12.**	(AB)	**13.**	(ABCD)	**14.**	(BCD)	**15.**	7
16.	4 (v, vi, vii, viii)	**17.**	5 (1,2,3,6,8)	**18.**	(B)	**19.**	(B)	**20.**	(A)

APSP Solutions

PART - I

1. All acids which are stronger than carbonic acid will produces effervesence with sodium bicarbonate.

2. Self explanatory.

3. Electron withdrawing group increase acidic strength and electron relasing group decrease acidic strength.

5. An acid with weaker conjugate base is stronger.

6. The polarity of N–H bond will be maximum on the N-atom which is most electron deficient.

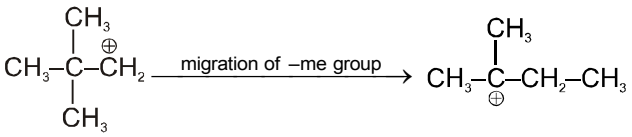
8. Lone pair electrons present on more electronegative atom is less basic.

9. Secondary amine is most basic in aqueous solution among aliphatic amines.

12. CF_3–COOH > CCl_3–COOH > HCOOH > CH_3COOH (K_a order)

20. Acetyl acetone is liquid and exist mainly as III due to intramolecular H-bonding and the correct answer is III > II > I.
However in aquous medium, the correct answer is II > III > I.

21. Salicylic acid is more acidic than p-hydroxy benzoic acid.

22. 

1º-carbocation 3º-carbocation (more stable)

29. –NO_2 group, being strong electron-withdrawing, disperses the –ve charge, hence stabilizes the concerned carbanion.

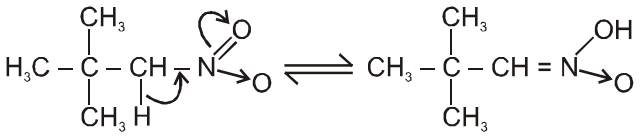
30. Stability of alkyl carbocation 3º > 2º > 1º.

PART - III

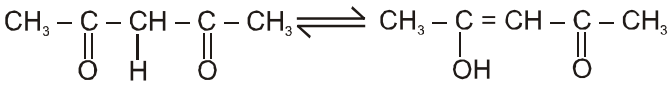
2. On the basis of stability of conjugate base due to electronic effects.

3. Protonation at site 1 and 3 is supported by resonance stabilization.

5. (C) Phthalic acid is stronger acid due to intramolecular hydrogen bonding.

9. (B) 

2,2-dimethyl-1-nitropropane

(C) 

Acetylacetone

11. All statements are correct.

12. (A,B) Nitroso $\rightleftharpoons$ oxime (Tautomer)

Imine $\rightleftharpoons$ enamine (Tautomer).

15. 5 is deprotanated since it is most acidic acid, 2 is protonated since it is most basic (guanidinic N).

x = 5, y =2 so x + y = 7

18.