ALLEN CAREER INSTITUTE KOTA (RAJASTHAN)

REACTION MECHANISM - I

NEET SYLLABUS

Electronic displacements in a covalent bond : inductive effect, electromeric effect, resonance and hyper conjugation. Homolytic and heterolytic fission of a covalent bond : free radicals, carbocations, carbanions; electrophiles and nucleophiles.

OBJECTIVES

After studying this unit, we will be able to :

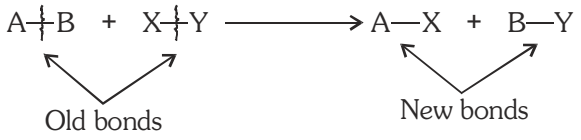
- *understand the concept of organic reaction mechanism;*
- *explain the influence of electronic displacements on structure and reactivity of organic compounds;*

"When learning is purposeful, creativity blossome. When creativity blossoms; thinking emanates. When thinking emanates, knowledge is fully lit. When knowledge is lit, economy flourishes."

A.P.J. Abdul Kalam

REACTION MECHANISM : PART-I

❑ **Reaction :** Breaking of old bond and formation of new bond is known as chemical reaction



A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as reaction mechanism. Reactants are of two types substrate and reagent.

Substrate is that reactant which supplies carbon to the new bond and the other reactant is called reagent. If both reactants supply carbon to the new bond then choice is arbitrary and in that case the molecule on which attention is focused is called substrate.

3.0 CONCEPTS TO UNDERSTAND REACTION MECHANISM :

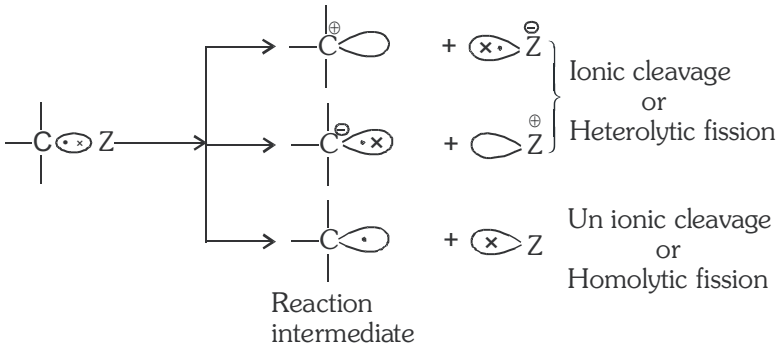
(1) Bond cleavage (2) Attacking reagent (3) Reaction intermediate (4) Electronic effect

3.1 TYPE OF BOND CLEAVAGE :

(a) Heterolytical cleavage/fission : Cleavage in which unequal distribution of electrons takes place during the bond cleavage is known as heterolytical cleavage. Due to unequal distribution of electrons, ions are formed. That's why it is also known as ionic cleavage or heterolytical cleavage.

(b) Homolytical cleavage/fission : Cleavage in which equal distribution of e^-s takes place during the chemical reaction, is known as homolytical cleavage.

Due to equal distribution of electrons, without charge unpaired electron containing species are formed, which are known as free radicals and cleavage is known as unionic cleavage/homolytical fission.



3.2 TYPES OF ATTACKING REAGENTS

These are of two types :

(a) Electrophilic reagent or electrophiles:

Electrophilic (electro + philic)
(electron + loving)

The reagent which attacks on the negative part of the molecule or having attraction for electrons are called electrophiles.

Electrophiles may be positively charged or neutral.

(i) Positively charged electrophiles :

$\overset{\oplus}{H}$, $\overset{\oplus}{SO_3H}$, $\overset{\oplus}{NO}$, $\overset{\oplus}{NO_2}$, $\overset{\oplus}{X}$, $\overset{\oplus}{R}$, $R-\overset{\oplus}{\underset{\underset{O}{\|}}{C}}$, $C_6H_5-\overset{\oplus}{N_2}$

(ii) Neutral electrophiles :- central atom e^- deficient

(a) All Lewis acids as :
BF_3, $AlCl_3$, SO_3, $ZnCl_2$, $BeCl_2$, $FeCl_3$, $SnCl_2$, CO_2, $SnCl_4$.

(b) Free radicals, carbenes and nitrenes act as electrophiles.

(b) Nucleophilic reagent or nucleophiles

Which attacks on the positive site of the substrate or loves nucleus or having attraction towards nucleus.

Nucleophilic (Nucleo + philes)
↓
(Nucleus + loving)

Nucleophiles may be negatively charged ions or posses a lone pair of electron or πe^-.

(i) Negatively charged nucleophiles.

$\overset{\ominus}{H}, \overset{\ominus}{O}H, \overset{\ominus}{O}R, \overset{\ominus}{C}N, \overset{\ominus}{X}, \overset{\ominus}{R}, R-CO\overset{\ominus}{O}, \overset{\ominus}{N}H_2, \overset{\ominus}{S}H$

(ii) All Lewis base which contains lone pairs or πe^-

$H_2\ddot{O}, R-\ddot{O}H, R-\ddot{O}-R, \ddot{N}H_3, R-\ddot{N}H_2, R_3\ddot{N}, CH_2=CH_2, CH\equiv CH.$

(iii) $\overset{*}{R}-Mg-X, LiAl\overset{*}{H}_4, NaB\overset{*}{H}_4$

The star (*) indicates the atom which donates electrons to the substrate.

Ambident nucleophile :- Nucleophiles which have two sites of electron rich centre or in which two or more atoms bear a lone pair of electrons.

Examples :- $K^{\oplus\ominus}O—N=O, \ddot{N}H_2-\ddot{O}H, \overset{\oplus}{N}a\overset{\ominus}{C}\equiv\ddot{N}$

3.3 REACTION INTERMEDIATE

❑ **Carbocation :**

Cation in which positive charge is present on carbon atom is called carbocation.

- ◆ Due to electron deficiency it acts as an electrophile and always attack on electron richer site.
- ◆ It is incomplete octet species because it has six electron in outer most shell.
- ◆ All electrons are paired.

❑ **Carbanions :** Anion in which negative charge is present on carbon atom is called carbanion.

- ◆ It has eight electron in outermost shell so it is complete octet species.
- ◆ It is an electron richer species because it has extra electron.
- ◆ Due to presence of non bonding electrons it acts as a nucleophile.

❑ **Free Radical :**

- ◆ Electrically neutral species in which unpaired electron is present on carbon atom is known as carbon free radical.
- ◆ It has seven electron or odd electron in outermost shell of unpaired electron containing carbon.
- ◆ It is electron deficient species due to incomplete octet.

❑ **Carbenes (CH_2:) :**

Carbenes are neutral carbon species in which the carbon atom is bonded to two monovalent atoms or groups and carries two nonbonded electrons.

- It behaves as an electrophile.
- It is neutral.
- 6 e^- in outermost shell.
- 4 e^- are bonded and two are nonbonded e^-.

❑ **Nitrenes (–$\ddot{N}$:)**

Nitrenes are neutral nitrogen species in which the nitrogen is bonded to one monovalent atom or group and carries four non-bonded electrons.

- It is monovalent radical.
- It is neutral.
- 6 e^- in outermost shell.
- Two are bonded and four are nonbonded electrons.

BEGINNER'S BOX-1

1. Which of the following is ambident nucleophile :-

(1) NH_2OH (2) $NCO^{\ominus}$ (3) $NO_2^{\ominus}$ (4) All of these

2. CH_3CH_2–Cl undergoes homolytic fission to produce :-

(1) $CH_3\dot{C}H_2$ and $\dot{Cl}$ (2) $CH_3\dot{C}H_2$ and $Cl^{\ominus}$

(3) $CH_3\overset{\oplus}{C}H_2$ and $Cl^{\ominus}$ (4) $CH_3\overset{\ominus}{C}H_2$ and $Cl^{\oplus}$

3. Which of the following intermediate has complete octet :-

(1) Carbocation (2) Carbanion (3) Free radical (4) Carbene

3.4 ELECTRONIC EFFECTS :

There are four effects which affect the chemical reaction due to transfer of electron

(1) Inductive effect (2) Mesomeric effect

(3) Hyperconjugation (4) Electromeric effect

3.4.1 INDUCTIVE EFFECT (I-EFFECT) :

- Polarity induced in non polar σ bond due presence of adjacent polar bond is known as inductive effect.

GOLDEN KEY POINTS

- In I-effect there is partial displacement of $e^{\ominus}$.
- After 3 or 4 C-atom I-effect is considered to be zero.
- Inductive effect decreases on increasing distance.

So **Magnitude of I effect** $\propto \frac{1}{\text{distance}}$

- I-effect of hydrogen is considered as zero.

–I groups :

$-\overset{\oplus}{O}R_2 > -\overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3 > -N\begin{matrix}O\\ \diagup\!\!\diagdown\\ O\end{matrix} > -\overset{sp}{C}\equiv N > -\overset{sp^2}{\underset{\underset{O}{\|}}{C}}-OH$

$-X > -OH > -OR > -C\equiv CH > -NH_2 > Ph > -CH=CH_2 > H(I \approx O)$

+I groups :

$-\overset{\ominus}{N}H > -\overset{\ominus}{O} > -COO^{\ominus} > -\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 > -\underset{\underset{CH_3}{|}}{CH}-CH_3 > -CH_2-CH_3 > -CT_3$

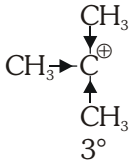
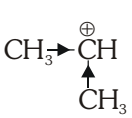
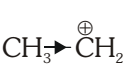
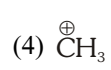
$-CD_3 > -CH_3 > T > D > H(I \approx O)$

APPLICATION OF I-EFFECT

(1) Stability of carbocation :

$$\text{Energy} \propto \text{charge} \propto \frac{1}{\text{stability}}$$

$$\text{Stability of carbocation} \propto \frac{+\text{I effect}}{-\text{I effect}}$$

Example : Stability order : (1)  > (2)  > (3)  > (4) 

3° 2° 1°

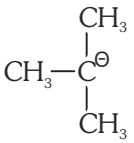
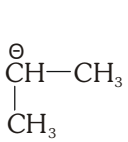
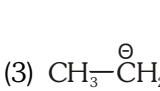
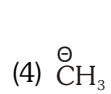
Reason : More no. of +I group.

more stable carbocation.

so stability order 1 > 2 > 3 > 4.

(2) Stability of carbanion :

$$\text{Stability of Carbanion} \propto \frac{-\text{I effect}}{+\text{I effect}}$$

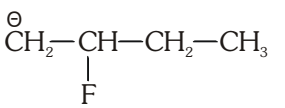
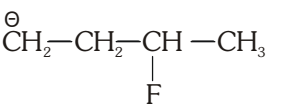
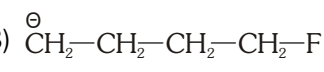
Example: (1)  (2)  (3)  (4) 

3° 2° 1°

More No. of +I group.

Less stable carbanion.

So stability order 4 > 3 > 2 > 1

Example : (1)  (2)  (3) 

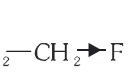
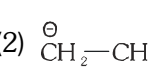
Minimum distance of –F.

Maximum –I of –F.

Minimum negative charge.

Maximum stable.

So stability order 1 > 2 > 3

Example (1)  (2)  (3)

Maximum –I of F.

Negative charge will be minimum.

Maximum stable.

So stability order 1 > 2 > 3

BEGINNER'S BOX-2

1. Most stable carbocation is :

(1) $CH_3-\overset{\oplus}{C}H_2$ (2) $Br-CH_2-\overset{\oplus}{C}H_2$

(3) $Cl-CH_2-\overset{\oplus}{C}H_2$ (4) $F-CH_2-\overset{\oplus}{C}H_2$

2. Most stable carbanion is :

(1) $\overset{\ominus}{C}H_2-CH_2-NO_2$ (2) $\overset{\ominus}{C}H_2-CH_2-CN$

(3) $\overset{\ominus}{C}H_2-CH_2-COOH$ (4) $\overset{\ominus}{C}H_2-CH_2-CH_2-CH_2-F$

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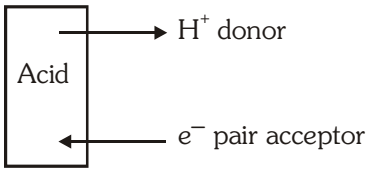
(3) Acidic and basic strength :

◆ **Acidic strength :**



Acidic strength ∝ Stability of conjugate base (anion) ∝ $\frac{\text{–I effect}}{\text{+I effect}}$

Example :

(i) $CH_3-CH_2-COOH \xrightarrow{-H^{\oplus}} CH_3-CH_2-COO^{\ominus}$ < $Cl-CH_2-COOH \xrightarrow{-H^{\oplus}} Cl-CH_2-COO^{\ominus}$ < $F-CH_2-COOH \xrightarrow{-H^{\oplus}} F-CH_2-COO^{\ominus}$

+I of $-CH_3$
anion is less stable

Maximum –I of –F
Maximum stable anion
Corresponding acid is maximum acidic.

(ii) CCl_3-COOH > CBr_3-COOH > CI_3-COOH
maximum –I of Cl
so maximum acidic.

(iii) $CH_3-CH_2-\underset{\underset{F}{|}}{CH}-COOH$ > $CH_3-\underset{\underset{F}{|}}{CH}-CH_2-COOH$ > $\underset{\underset{F}{|}}{CH_2}-CH_2-CH_2-COOH$

minimum distance of F from –COOH
maximum –I of F.
So maximum acidic.

(iv) $CH_2(NO_2)-COOH$ > $CH_2(H)-COOH$ > $CH_2(CH_3)-COOH$

$-I$ of NO_2 $+I$ of $-CH_3$

maximum acidic

(v) $HCOOH$ > CH_3-COOH > CH_3-CH_2-COOH

maximum +I

minimum acidic

(vi) $COOH-COOH$ > $CH_2(COOH)_2$ > $CH_2(CH_2-COOH)_2$

minimum distance of –COOH from other

maximum –I of –COOH on other

maximum acidic

(vii) $CH_4 \xrightarrow{-H^{\oplus}} \overset{\ominus}{C}H_3$ < $NH_3 \xrightarrow{-H^{\oplus}} \overset{\ominus}{N}H_2$ < $H_2O \xrightarrow{-H^{\oplus}} \overset{\ominus}{O}H$ < $HF \xrightarrow{-H^{\oplus}} \overset{\ominus}{F}$

Negative charge on maximum E.N.

Maximum stable anion

So corresponding acid is most acidic

(viii) $CH\equiv CH \xrightarrow{-H^{\oplus}} CH\equiv\overset{\ominus}{C}$ > $CH_3-C\equiv CH \xrightarrow{-H^{\oplus}} CH_3-C\equiv\overset{\ominus}{C}$ > $NH_3 \xrightarrow{-H^{\oplus}} \overset{\ominus}{N}H_2$ > $CH_3-NH_2 \xrightarrow{-H^{\oplus}} CH_3-\overset{\ominus}{N}H$

negative charge on more EN atom and no +I

$+I$ of $-CH_3$

$+I$ of $-CH_3$

anion is maximum stable

so corresponding acid is most acidic

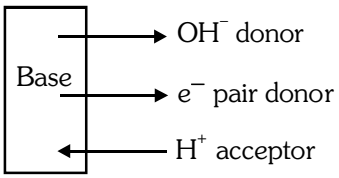
(ix). $CH_3SH \xrightarrow{-H^{\oplus}} CH_3\overset{\ominus}{S}$ > $CH_3-OH \xrightarrow{-H^{\oplus}} CH_3-\overset{\ominus}{O}$

negative charge on big size atom

more stable anion

so corresponding acid is more acidic

◆ **Basic strength :**



$$\textbf{Basic strength} \propto \textbf{+I effect} \propto \frac{\textbf{1}}{\textbf{–I effect}}$$

Ex.: (1) CH_3NH_2 (2) $C_2H_5NH_2$ (3) $C_3H_7NH_2$ (4) $C_4H_9NH_2$

Ans. 4 > 3 > 2 > 1

Maximum +I

so maximum basic

BEGINNER'S BOX-3

1. Which of the following is most acidic :

(1) $Cl_3C—COOH$ (2) $Cl_2CH—COOH$ (3) $ClCH_2—COOH$ (4) CH_3COOH

2. Which of the following is most acidic :

(1) $\overset{F}{\underset{|}{CH_2}} — COOH$ (2) $\overset{Cl}{\underset{|}{CH_2}} — COOH$

(3) $\overset{Br}{\underset{|}{CH_2}} — COOH$ (4) $\overset{I}{\underset{|}{CH_2}} — COOH$

3. Which is most basic among the following :

(1) $CH_3CH_2–NH_2$ (2) $Cl–CH_2CH_2NH_2$

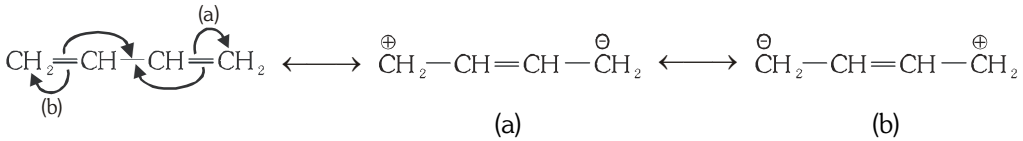
(3) $O_2N–CH_2CH_2–NH_2$ (4) $^-O–CH_2CH_2–NH_2$

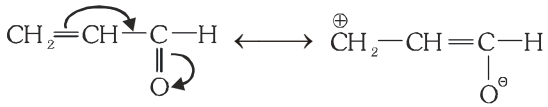
3.4.2 RESONANCE OR MESOMERIC EFFECT

Delocalization of π e^- is called as resonance or complete transfer of πe^- from one shell to another shell is called as **Resonance**.

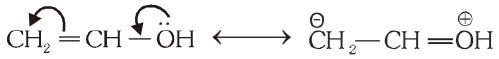
Conditions For Resonance

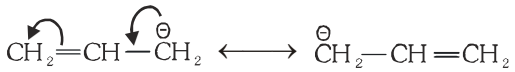
(1) If there are two π bonds in conjugation then e^- of one π bond are transferred towards another π bond.

Ex. (i) 

(ii) 

(2) If there is lone pair or a negative charge and π bond are in conjugation then lone pair of e^- or negative charge are transferred towards π bond.

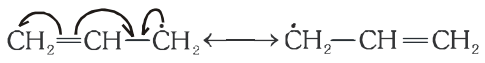
Ex. (i) 

(ii) 

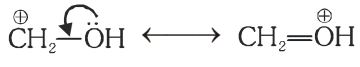
(3) If there is positive charge (vacant orbital) and π bond are in conjugation then e^- of π bond are transferred towards positive charge.

Ex. 

(4) If there is free e^- and π bond are in conjugation.

Ex. 

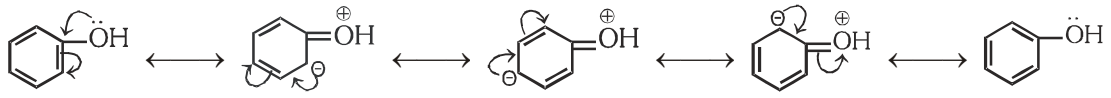
(5) If there is lone pair or negative charge and positive charge (vacant orbital) are in conjugation then e^- of lone pair or negative charge are transferred towards positive charge.

Ex. 

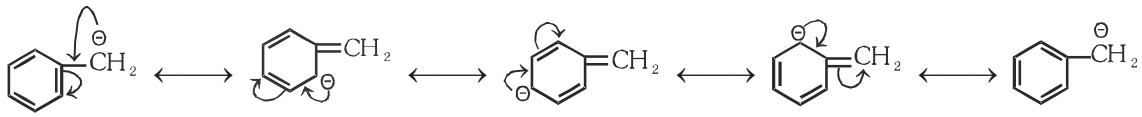
GOLDEN KEY POINTS

- In resonance only e^- are delocalised not atoms.
- The number of e^- or number of unpaired or paired e^- in all resonating structures should be same.
- It is permanent effect.
- All the resonating or canonical structures must follow the Lewis structures.

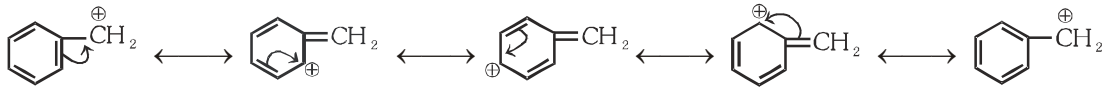
Draw resonating structures :

1. 

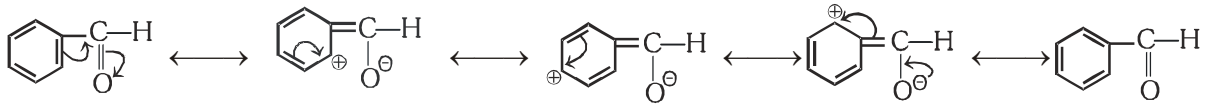
5-Resonating structures

2. 

5-Resonating structures

3. 

5-Resonating structures

4. 

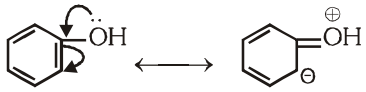
5-Resonating structures

M-effect : Delocalisation of electron in conjugated system (due to presence of EWG or EDG) is known as 'M' effect.

(1) +M effect :- Group that donates the electron pair to conjugated system is known as +M effect exerting groups and the phenomena is known as +M effect.

+M group : Lone pair containing group like

e.g. $-\ddot{N}H_2$, $-\ddot{O}H$, $-\ddot{O}R$, $-\ddot{N}R_2$, $-\ddot{S}H$, $-\ddot{N}HR$, $-\ddot{X}:$, $-\ddot{N}HCOCH_3$

eg. 

–OH group lone pair donor

So + M of –OH group

(2) –M effect :- Group, that withdraws electron pair from the conjugated system, is known as –M effect exerting groups and the phenomena is known as –M effect.

–M group : —CHO, —COOH, —COOR, —COR, $—NO_2$, —CN, —COX, $—CONH_2$, $—SO_3H$

eg. 

–CHO group withdrawing e^-.

So –CHO is –M group

APPLICATIONS OF RESONANCE EFFECT :

(1) Stability of carbocation.

Ex. Give stability order for :-

(i) $CH_2=CH-\overset{\oplus}{C}H_2$ > $CH_3\rightarrow CH_2-\overset{\oplus}{C}H_2$ > $CH_2=CH\leftarrow CH-\overset{\oplus}{C}H_2$

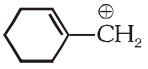
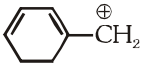
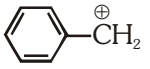
stabilized by resonance (SBR) | +I of Alkyl group | –I of Alkenyl group

(ii) $CH_3-\overset{\oplus}{\underset{\displaystyle CH_3}{\underset{|}{C}}}-CH=CH_2$ > $CH_3-\overset{\oplus}{C}H-CH=CH_2$ > $\overset{\oplus}{C}H_2-CH=CH_2$

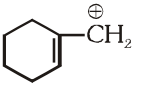
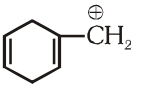
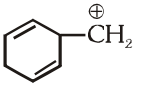
SBR and +I of two $-CH_3$ | SBR and +I of one $-CH_3$ | SBR only

(iii) $(C_6H_5)_3\overset{\oplus}{C}$ > $(C_6H_5)_2\overset{\oplus}{C}H$ > $C_6H_5\overset{\oplus}{C}H_2$ > $CH_2=CH-\overset{\oplus}{C}H_2$ > $(CH_3)_3\overset{\oplus}{C}$ > $(CH_3)_2\overset{\oplus}{C}H$ >

$CH_3-\overset{\oplus}{C}H_2$ > $\overset{\oplus}{C}H_3$ > $CH_2=\overset{\oplus}{C}H$ > $CH\equiv\overset{\oplus}{C}$

(iv)  <  < 

maximum resonance

(v)  >  > 

SBR and + I | SBR and – I | No. reso.

(vi)  >  > 

more resonance | less resonance | localized ⊕ charge

(vii) $\overset{\oplus}{C}H_2-\underset{\displaystyle O}{\underset{\|}{C}}-H$ < $\overset{\oplus}{C}H_2-CH_2-\underset{\displaystyle O}{\underset{\|}{C}}-H$

No reso. more –I of —CHO so less stable | No reso. less –I of —CHO

(2) Stability of carbanion :

Ex. Give stability order of :

(i) I. $CH_2=CH-\overset{\ominus}{C}H_2$ II. $CH_2=\overset{\ominus}{C}H$ III. $CH_3-\overset{\ominus}{C}H_2$

SBR | negative on more EN

stability order I > II > III

(ii) $(C_6H_5)_3\overset{\ominus}{C}$ > $(C_6H_5)_2\overset{\ominus}{C}H$ > $C_6H_5\overset{\ominus}{C}H_2$ > $CH_2=CH-\overset{\ominus}{C}H_2$ > $\overset{\ominus}{C}H_3$ > $CH_3-\overset{\ominus}{C}H_2$ > $(CH_3)_2\overset{\ominus}{C}H$ > $(CH_3)_3\overset{\ominus}{C}$

(iii) I.  II.  III. 

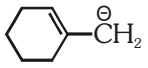
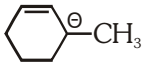
resonance stable more resonance stable localized Θ charge

stability order II > I > III

(iv) $\overset{\ominus}{C}H_2—NO_2$ $\overset{\ominus}{C}H_2—CH_2—NO_2$ $CH_3—\overset{\ominus}{C}H—NO_2$

SBR no. reso SBR but +I of CH_3

stability order I > III > II

(v) I.  II.  III. 

SBR and +I SBR SBR and more +I

stability order II > I > III

(3) Stability of free radicals.

Ex. Give stability order for :

(i) I. $CH_2=CH-\dot{C}H_2$ II. $CH_2=\dot{C}H$ III. $CH_2=CH-\dot{C}H-CH=CH_2$

less resonance no resonance more resonance

stability order III > I > II

(ii) $(C_6H_5)_3\dot{C} > (C_6H_5)_2\dot{C}H > (C_6H_5)\dot{C}H_2 > CH_2=CH-\dot{C}H_2 > (CH_3)_3\dot{C} > (CH_3)_2\dot{C}H >$

$CH_3\dot{C}H_2 > \dot{C}H_3$

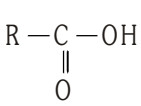
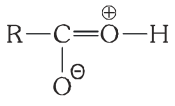
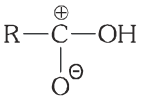
(4) Stability of resonating structures (R.S) Rules :

(i) Complete octet R.S. is more stable than incomplete octet.

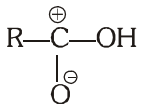
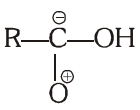
(ii) Nonpolar R.S. is more stable than polar resonating structures.

(iii) For charged R.S. negtive charge on more EN and positive charge on less EN is more stable.

Ex. Arrange the following for stability order.

(i)  >  > 

complete octet, nonpolar complete octet, polar incomplete octet

(ii)  > 

less EN atom with incomplete octet more EN atom with incomplete octet

(iii) $R-\overset{\oplus}{C}=O$ < $R-C\equiv\overset{\oplus}{O}$

incomplete octet complete octet

(iv) $CH_2=CH-\overset{\ominus}{O}$ > $\overset{\ominus}{C}H_2-CH=O$

(negative charge on more EN) (negative charge on less EN)

(5) Aromaticity (Huckel's rule) : Cyclic, planar and completely conjugated system with $(4n+2)\pi$ electrons (where n = 0, 1, 2, 3, ...) is known as aromatic compounds, these compound gains extra stability which is known as aromaticity.

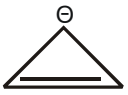
Note : [4n + 2] π electrons. (Odd number of π electron pairs) means

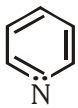
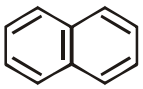
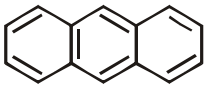
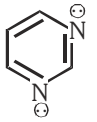
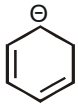
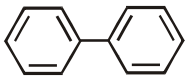
If n = 0 2π electrons or 1 pair

n = 1 6π electrons or 3 pairs

n = 2 10π electrons or 5 pairs

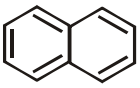
n = 3 14π electrons or 7 pairs

S.No	Compound	Cyclic	Plannar	Cyclic Resonance	Huckel Rule (4n+2) πe^-	Aromatic Yes/No
1.		✔	✔	✔	$2\pi e^-$	Yes
2.		✔	✔	✔	$4\pi e^-$	No
3.		✔	✔	✔	$4\pi e^-$	No
4.		✔	✔	✔	$6\pi e^-$	Yes
5.		✔	✔	✔	$6\pi e^-$	Yes
6.		✔	✘	✘	$4\pi e^-$	No
7.		✔	✔	✔	$6\pi e^-$	Yes
8.		✔	✔	✔	$6\pi e^-$	Yes

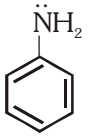
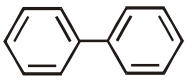
9.		✔	✔	✔	$6\pi e^-$	Yes
10.		✔	✔	✔	$6\pi e^-$	Yes
11.		✔	✔	✔	$6\pi e^-$	Yes
12.		✔	✔	✔	$10\pi e^-$	Yes
13.		✔	✔	✔	$14\pi e^-$	Yes
14.		✔	✔	✔	$6\pi e^-$	Yes
15.		✔	✘	✘	$6\pi e^-$	No
16.		✔	✔	✔	$6\pi e^-$ + $6\pi e^-$	Yes

BEGINNER'S BOX-4

1. Which of the following is nonaromatic

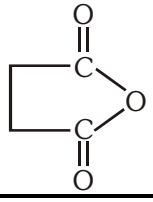
(1)  (2)  (3)  (4) 

2. Which of the following compounds are aromatic in nature

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

(1) Only a (2) a and b (3) a,b,d (4) all of these

3. Which of the following is not aromatic compound

(1)  (2)  (3)  (4) All of these

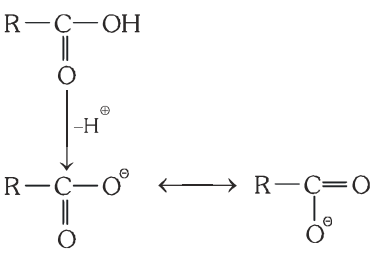
(6) Acidic and Basic strength :

(a) Acidic strength : $\left(\text{Acidic strength} \propto \text{stability of conjugate base (anion)} \propto \frac{-M,-I}{+M+I}\right)$

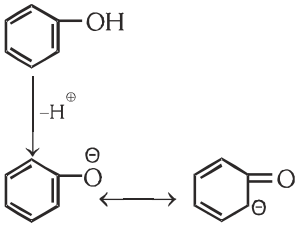
Illustrations

Illustration 1. Carboxylic acids are more acidic than phenols, why ?

Solution.



2, equal R.S. more stable anion so corresponding acid is more acidic. Here, carboxylate ion is more stable than phenoxide ion.

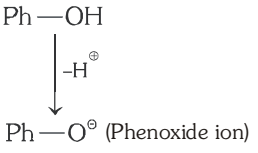


5, unequal R.S. less stable anion since –ve charge is being shared by oxygen is less electronegative carbon.

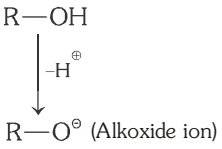
Note : The molecule having equivalent R.S. has more stability than the molecule having non equivalent R.S.

Illustration 2. Phenol is more acidic than alcohols why ?

Solution.



anion stable by resonance
So, corresponding acid is more acidic.



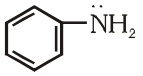
no resonance.
less stable anion

(b) Basic strength order :- Tendency to donate the electron pair by an atom or group is known as its basic strength. Compounds in which electron pair is delocalised will be less basic while, Those in which electron pair is localised will be more basic.

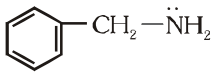
$$\left(\text{Basic strength} \propto H^{\oplus} \text{ accepting tendancy} \propto \text{l.p. donating tendency} \propto \frac{+M,+I}{-M-I}\right)$$

Ex. Give basic strength order :

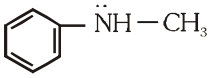
(i)



I
l.P. is stabilized by resonance
basic order —

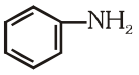


II
no reso. of l.p. so maximum basic
II > III > I



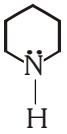
III
l.p. is stabilized by resonance and +I of CH_3

(ii)

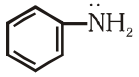


I
SBR
basic order —

II
localized l.p. on more EN
III > II > I

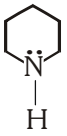
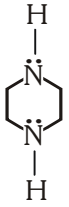


III
localized l.p. on less EN

(iii)  < 

more resonance of l.p.
so less basic

less resonance of l.p.
so more basic

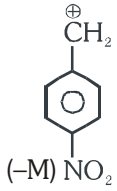
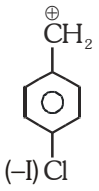
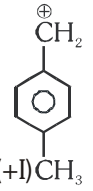
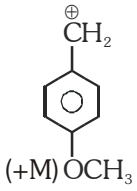
(iv)    

I	II	III	IV
l.p. on more EN so minimum basic	more –I of oxygen	+I	less – I of nitrogen

So, basic order III > IV > II > I

Illustrations

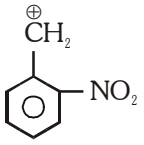
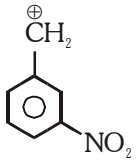
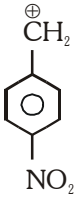
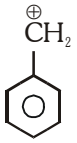
Illustration 3. Give stability order of :

(i)    

I II III IV

charge ↑ charge ↑ charge ↓ charge ↓

So stability order IV > III > II > I

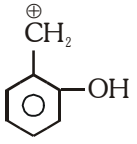
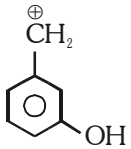
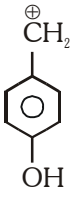
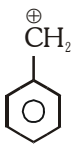
(ii)    

I II III IV

$-M_O = -M_P$ and $-M_m = 0$

but $-I_O > -I_m > -I_P$, –M and –I increases positive charge.

stability order is IV > II > III > I

(iii)    

I II III IV

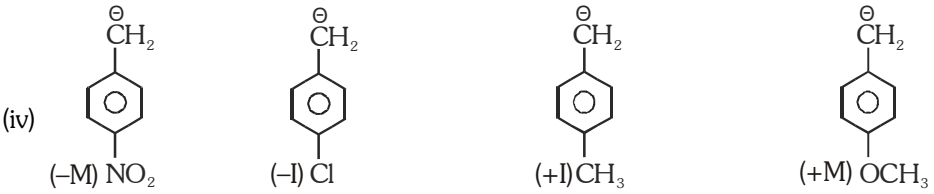
–OH group shows +M effect

$+ M_O = + M_P$ and $+ M_m = 0$ but $-I_O > -I_m > -I_P$ and + M >> – I

So +M stabilize the carbocation by decreasing positive charge

Stability order III > I > IV > II

(iv)

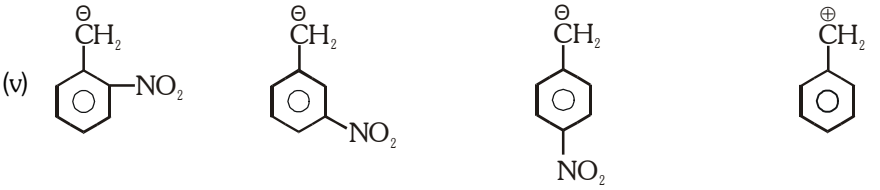


I (–M) NO_2 | II (–I) Cl | III (+I) CH_3 | IV (+M) OCH_3

charge ↓ | charge ↓ | charge ↑ | charge ↑

stability order I > II > III > IV

(v)



I	II	III	IV
–M and more –I	M = 0 only –I	–M and less –I	
charge is minimum			
So stability order	I > III > II > IV		

Illustration 4. Give acidic strength order for :

(i)

I	II	III	IV
–M	–I	+I	+M

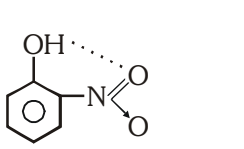
So acidic order is I > II > III > IV

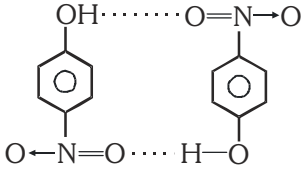
(ii)

I	II	III	IV
–M and more –I	M = 0 only –I	–M and less –I	

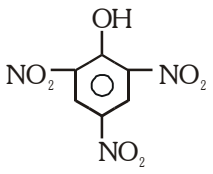
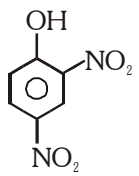
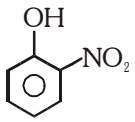
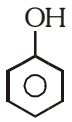
Acidic order should be I > III > II > IV but correct order is III > I > II > IV

Reason : Due to intramolecular H-bonding in ortho nitrophenol, it is less acidic than para nitrophenol.



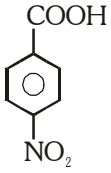
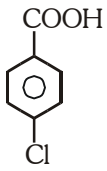
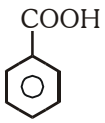
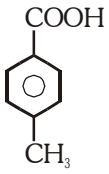
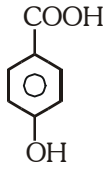


• intramolecular H-bonding	intermolecular H-bonding
• less association	more association
• less B.P.	more B.P.
• more volatile	less volatile
• less acidic	more acidic
• less soluble in water.	more soluble in water.

(iii)    

I II III IV

maximum –M and
maximum –I effect
so maximum acidic
Acidic order I > II > III > IV

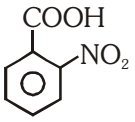
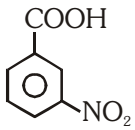
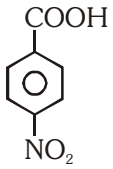
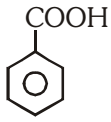
(iv)     

I II III IV V
–M –I +I +M

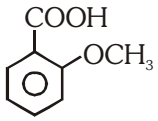
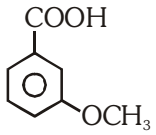
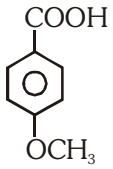
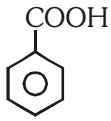
acidic order is I > II > III > IV > V

(v) H—COOH CH_3COOH C_6H_5—COOH
I II III

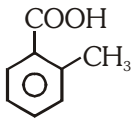
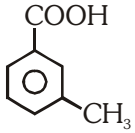
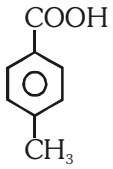
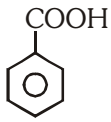
Acidic order is I > III > II

(vi)    

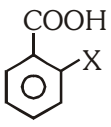
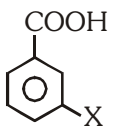
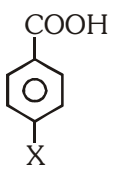
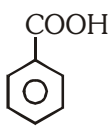
ortho effect only –I –I and –M
Acidic order is ⇒ o > p > m > benzoic acid

(vii)    

ortho effect only –I –I and +M
Acidic order is ⇒ o > m > benzoic acid > p

(viii)    

ortho effect only +I +I and +H
Acidic order is ⇒ o > benzoic acid > m > p

(xi)    

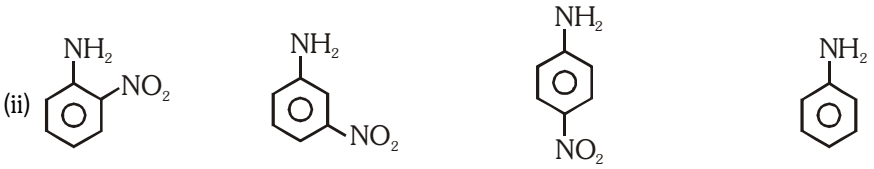
ortho effect –I (more) –I (less)
Acidic order is ⇒ o > m > p > benzoic acid

Illustration 5. Give basic strength order for :

(i) 

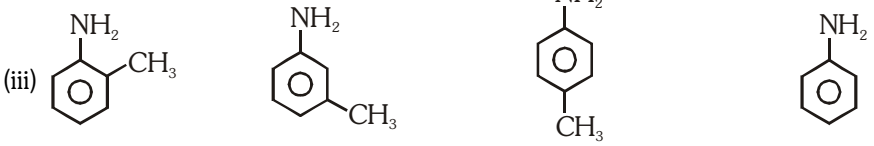
I –M | II –I | III +H | IV +M

Basic strength order IV > III > II > I

(ii) 

SIP | only –I | –M and –I

Basic strength order is ⇒ aniline > m > p > o

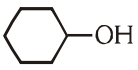
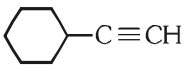
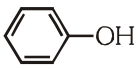
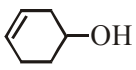
(iii) 

SIP | only +I | +H and +I

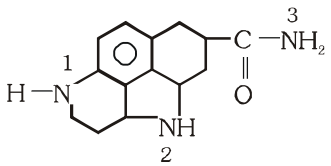
Basic strength order is ⇒ p > m > aniline > o

BEGINNER'S BOX-5

1. Most acidic among the following is :

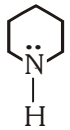
(1)  (2)  (3)  (4) 

2. Which nitrogen is most basic :-



(1) 1 (2) 2 (3) 3 (4) All are equally basic

3. Which is strongest base ?

(1) pyrole (2) Aniline (3) Pyridine (4) 

4. Which is weakest base :

(1) $C_6H_5—CH_2—NH_2$ (2) $C_6H_5—CH_2—NH—CH_3$

(3) $O_2N—CH_2—NH_2$ (4) $CH_3—NH—CHO$

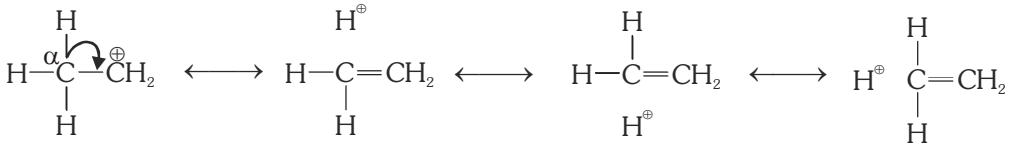
3.4.3 HYPERCONJUGATION EFFECT (H-EFFECT)

Complete transfer of e^- of C–H σ bond towards π bond or positive charge or free electron is called as H-effect (permanent effect). It is also called as No bond resonance (given by Nathen and Baker).

❑ **CONDITIONS OF H-EFFECT :**

1. If there is C–H σ bond and positive charge are in conjugation

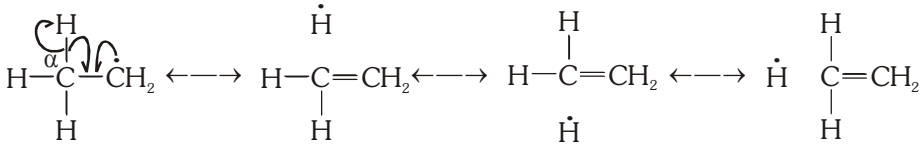
Carbon which is attached to positively charged carbon is called as α –C and H which is attached to α –C is called as α – H. So if number of α – H are more, then there will be more number of hyperconjugating structures, so more stable will be the carbocation.



all are called as hyperconjugating structures or canonical structures.

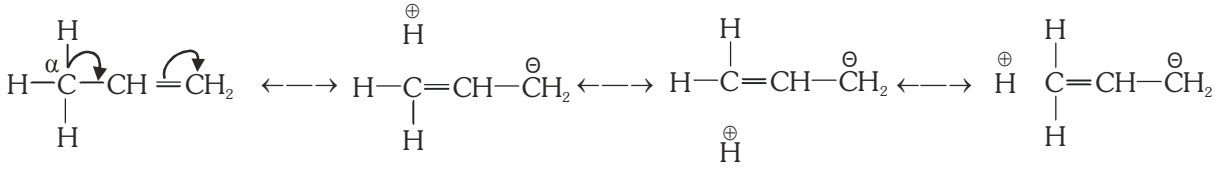
2. If there is C–H σ bond and free e^- are in conjugation then there will be H-effect.

Carbon, which is attached to C having unpaired e^-, is called as α–C and H which are attached to α-C are called as α-H.

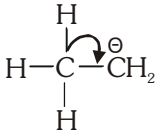


3. If there is C–H σ bond and π bond are in conjugation then there will be H-effect.

sp^3 carbon which is attached to double bonded C is called as α–C and H attached to α–C is called as α–H.



Note : If there is C—H σ bond and negative charge in conjugation then there will be no H-effect.



(No H - effect)

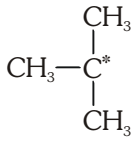
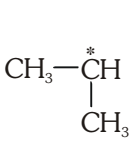
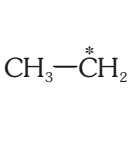
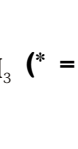
no shifting of C—H σ bond, because anion is having complete octet. ($8e^-$)

❑ **APPLICATION OF H-EFFECT**

❑ **Stability of carbocation / Free Radical /Alkene**

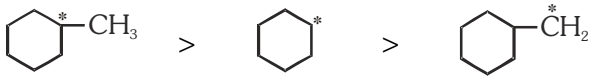
◆ Stability ∝ No. of canonical structures ∝ No. of α H.

Example : Give stability order for :-

(i)  >  >  >  **(* = +/·)**

9 α-H — 6 α-H — 3 α-H — Zero α-H

Maximum stable

(ii)  (* = +/•)

7 α-H 4 α-H 1 α-H

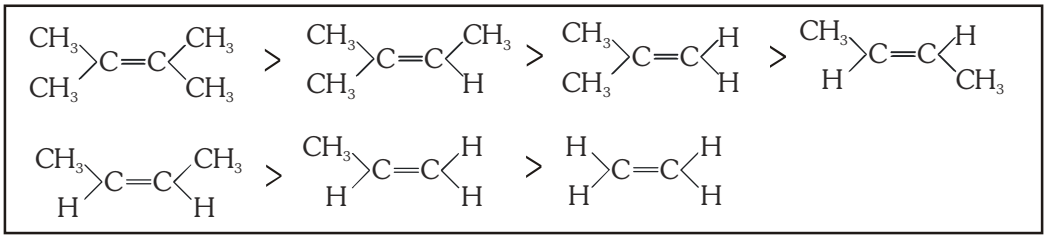
Maximum stable

(iii) $CH_3—CH=CH_2$ > $CH_2=CH_2$

3 α-H Zero α-H

more stable

(iv) Stability order of alkenes will be



GOLDEN KEY POINTS

❑ **Heat of hydrogenation :**

$R—CH=CH_2 + H_2 \longrightarrow R—CH_2—CH_3 + \Delta H$ (Heat of hydrogenation)

Heat evolved when any unsaturated hydrocarbon is hydrogenated is called heat of hydrogenation (ΔH)

(If alkene is more reactive towards hydrogen then it will evolve more ΔH)

So, $\text{Heat of hydrogenation} \propto \frac{1}{\text{stability of alkene}} \propto \frac{1}{\text{number of } \alpha - H}$

BEGINNER'S BOX-6

1. Which of the following alkene is most stable (R = CH_3).

(1) $R_2C=CR_2$ (2) $R—CH=CR_2$ (3) $R—CH=CH—R$ (4) $R—CH=CH_2$

2. Which of the following has minimum heat of hydrogenation.

(1) ethene (2) Propene (3) cis-2-butene (4) trans-2-butene

3. Which of the following is most stable.

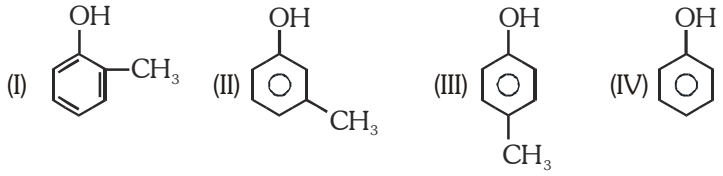
(1) Conjugated alkadiene ($CH_2=CH—CH=CH_2$)

(2) Isolated alkadiene ($CH_2=CH—CH_2—CH=CH_2$)

(3) Cumulated alkadiene ($CH_2=C=CH_2$)

(4) All are equal.

4. What is the order of acidic strangth of given molecules



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

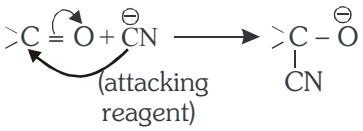
(3) IV > II > III > I (4) I > II > IV > III

3.4.4 ELECTROMERIC EFFECT : (E Effect)

Complete transfer of a shared pair of π-electrons from one atom to another atom in presence of attacking reagent, is known as 'E' effect.

(i) **Positive Eelctromeric Effect (+ E effect) :** In this effect the π -electrons of the multiple bond are transferred to that atom to which the reagent gets attached. For example :

(ii) **Negative Electromeric Effect (-E effect) :** In this effect the π- electrons of the multiple bond are transferred to that atom, to which the attacking reagent does not get attached. For example.



Shifting of π electrons :

(i) $CH_2=CH_2 \xrightarrow{\text{reagent}} \overset{\oplus}{C}H_2-\overset{\ominus}{C}H_2$

(ii) $CH_3-CH=CH_2 \xrightarrow{\text{reagent}} CH_3-\overset{\oplus}{C}H-\overset{\ominus}{C}H_2$

+I

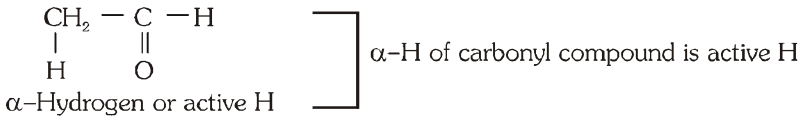
(iii) $CH_3-\overset{(a)}{C}\equiv\overset{(b)}{C}-CH_3 \xrightarrow{\text{reagent}} CH_3-\overset{\oplus}{\underset{(a)}{C}}=\overset{\ominus}{C}-CH_3$ or $CH_3-\overset{\ominus}{\underset{(b)}{C}}=\overset{\oplus}{C}-CH_3$

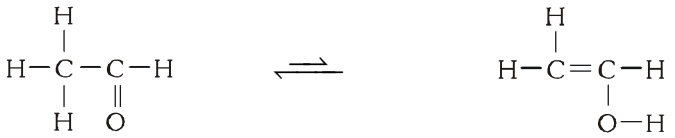
(iv) $CCl_3-CH=CH_2 \xrightarrow{\text{reagent}} CCl_3-\overset{\ominus}{C}H-\overset{\oplus}{C}H_2$

–I

3.5 TAUTOMERISM OR DESMOTROPISM

- Tautomers have same molecular formula but different structural formula due to migration of active hydrogen from one polyvalent atom to another polyvalent atom. This pnenomena is known as tautomerism.
- Desmotropism means bond turning. [Desmos = Bond ; Tropos = Turn]



Ex. 

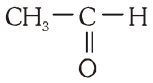
Ex. 

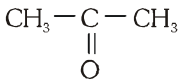
Note : **(1)** Tautomers exist in dynamic equilibrium.

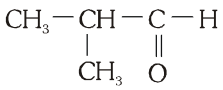
(2) By shifting of H–atom, π bond also changes its position.

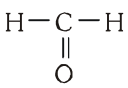
(I) Condition for Tautomerism :

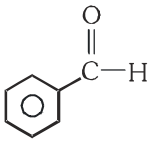
(a) For carbonyl compounds :- Carbonyl compounds having at least one active-H (α–H) show tautomerism

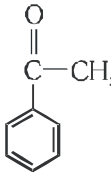
(i)  3 α H, shows tautomerism.

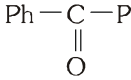
(ii)  6 α H, shows tautomerism

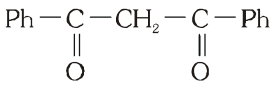
(iii)  1 α H, shows tautomerism

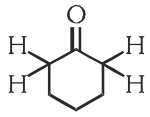
(iv)  No α H, No tautomerism

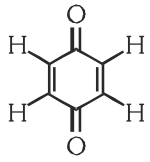
(v)  No α H, No Tautomerism

(vi)  (Acetophenone) 3 α H, shows tautomerism (Acetophenone)

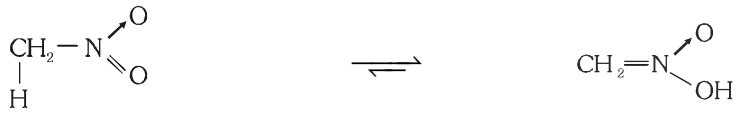
(vii)  (Benzophenone) No α H, No tautomerism (Benzophenone)

(viii)  2 α H, shows tautomerism

(ix)  4 α H, shows tautomerism

(x)  α–H, attached sp^2 carbon does not initiate in tautomerism

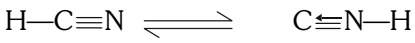
(b) For nitro compounds : Nitro compounds having at least one active-H (α – H) show tautomerism



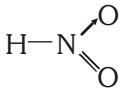
Nitro form Acinitro form

(acidic form so soluble in base)

(c) H—C≡N and H—N ⇌ C are tautomers [also Functional isomers] while R—C≡N and R—N⇌C are only Functional isomers.

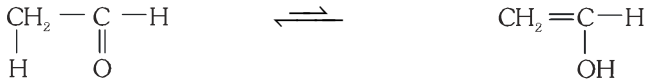


Active H

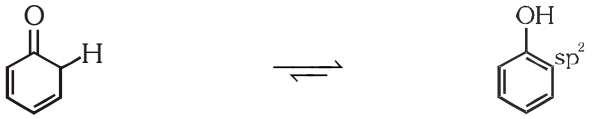
(d)  and H—O—N=O are tautomers.

Note : Nitro compounds with at least one α–H are soluble in NaOH.

(II) Enol Content :

1. 

"keto" (≈ 99%) "enol" (≈ 1%)

2. 

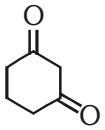
"keto" (≈ 1%) "enol" (stable by resonance and aromatic nature) (≈ 99%)

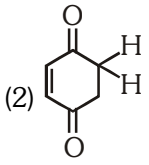
GOLDEN KEY POINTS

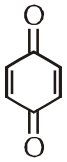
- More active the H, more will be its participation in tautomerism.
- Stability of enol form depends on (i) Resonance and (ii) H – Bond (iii) Aromaticity.

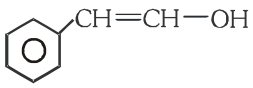
BEGINNER'S BOX-7

1. Which of the following does not show keto enol tautomerism.

(1) 

(2) 

(3) 

(4) 

2. Which of the following is not soluble in NaOH.

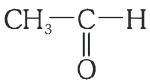
(1) $CH_3CH_2—NO_2$

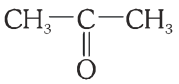
(2) $(CH_3)_2CH—NO_2$

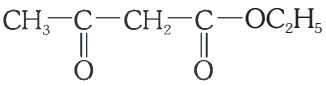
(3) $(CH_3)_3C—NO_2$

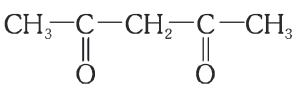
(4) $Ph—CH_2—NO_2$

3. Which of the following has highest enol content.

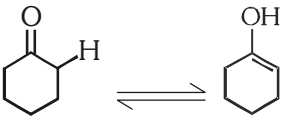
(1) 

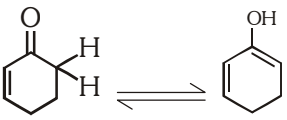
(2) 

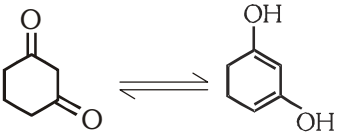
(3) 

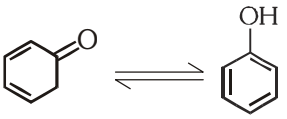
(4) 

4. In which of the following reaction most stable enol is present.

(1) 

(2) 

(3) 

(4) 

ANSWER KEY

BEGINNER'S BOX-1	**Que.**	1	2	3	
	Ans.	**4**	**1**	**2**	
BEGINNER'S BOX-2	**Que.**	1	2		
	Ans.	**1**	**1**		
BEGINNER'S BOX-3	**Que.**	1	2	3	
	Ans.	**1**	**1**	**4**	
BEGINNER'S BOX-4	**Que.**	1	2	3	
	Ans.	**4**	**4**	**3**	
BEGINNER'S BOX-5	**Que.**	1	2	3	4
	Ans.	**3**	**2**	**4**	**4**
BEGINNER'S BOX-6	**Que.**	1	2	3	4
	Ans.	**1**	**4**	**1**	**3**
BEGINNER'S BOX-7	**Que.**	1	2	3	4
	Ans.	**3**	**3**	**4**	**4**

EXERCISE-I (Conceptual Questions) Build Up Your Understanding

ATTACKING REAGENT

1. Which of the following species is an electrophile
(1) RNH_2 (2) SO_3
(3) $NO_3^{\ominus}$ (4) ROH

2. Which of the following acts as a nucleophile?
(1) $\overset{\oplus}{N}O_2$ (2) $:CCl_2$
(3) $\overset{\ominus}{N}H_2$ (4) $^{\bullet}CH_3$

REACTION INTERMEDIATES

3. Which of the following contains only three pair of electrons :
(1) Carbanion (2) Carbocation
(3) Carbon free radical (4) None

4. Carbanion is a :-
(1) Base (2) Nucleophile
(3) Both the above (4) None

I-EFFECT

5. $\overset{\ominus}{C}H_3$ is less stable than :-
(1) $CH_3—\overset{\ominus}{C}H_2$ (2) $CH_3—\overset{\ominus}{C}H—CH_3$
(3) $\overset{\ominus}{C}H_2—NO_2$ (4) $CH_3—\overset{\ominus}{C}H—C_2H_5$

6. Decreasing order of –I effect of the triad [$–NO_2$, $–\overset{\oplus}{N}H_3$, –CN] is :-
(1) $–\overset{\oplus}{N}H_3 > –NO_2 > –CN$
(2) $–\overset{\oplus}{N}H_3 > –CN > NO_2$
(3) $–CN > –NO_2 > –\overset{\oplus}{N}H_3$
(4) $–NO_2 > –CN > –\overset{\oplus}{N}H_3$

7. Most stable carbanion is :-
(1) $HC\equiv\overset{\ominus}{C}$ (2) $H_2C=\overset{\ominus}{C}H$
(3) $CH_3–\underset{CH_3}{\overset{CH_3}{C}}—\overset{\ominus}{C}H_2$ (4) $CH_3–\underset{CH_3}{C}=\overset{\ominus}{C}H$

8. The correct order of stability of given carbanions will be :-

$CH_3–\overset{\ominus}{C}H_2$ (I) $\quad CH_2=\overset{\ominus}{C}H$ (II) $\quad HC\equiv\overset{\ominus}{C}$ (III)

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

9. Which is most basic among the following :-
(1) CH_3NH_2
(2) $CH_3CH_2NH_2$
(3) NH_3
(4) $(CH_3)_2CHNH_2$

10. Which of the following has maximum pK_a :-
(1) CH_2FCOOH
(2) $CH_2ClCOOH$
(3) CH_3COOH
(4) HCOOH

11. Which of the following is most acidic
(1) Methoxy acetic acid
(2) Acetic acid
(3) Chloro acetic acid
(4) Trifluoroacetic acid

12. Which of the following show + I-effect :-
(1) – OH (2) $–OCH_3$ (3) $–CH_3$ (4) – Cl

13. Among the following the most highly ionised in water is:
(1) $CH_3CH_2CHClCOOH$
(2) $CH_3CH_2CCl_2COOH$
(3) $CH_3CHClCH_2COOH$
(4) $CH_2ClCH_2CH_2COOH$

14. The strongest acid amongst the following compounds is ?
(1) $CH_3CH_2CH(Cl)CO_2H$
(2) $ClCH_2CH_2CH_2COOH$
(3) CH_3COOH
(4) HCOOH

15. Which of the following acids is stronger than acetic acid :-
(1) Propanoic acid (2) HCOOH
(3) Butyric acid (4) $(CH_3)_2CHCOOH$

16. Which of the following acids have the lowest pK_a value :-

(1) $CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-COOH$

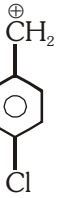
(2) $Cl-CH_2-CH_2-COOH$

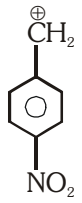
(3) CCl_3COOH

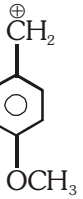
(4) $CHCl_2COOH$

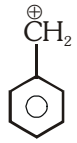
R- OR M-EFFECT

17. Most stable carbocation is :-

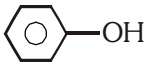
(1) 

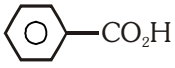
(2) 

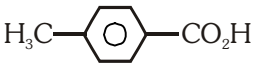
(3) 

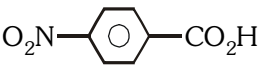
(4) 

18. Most acidic compound is :-

(1) 

(2) 

(3) 

(4) 

19. Which resonating structure of vinyl chloride is least stable :-

(1) $CH_2=CH-\ddot{\underset{\cdot\cdot}{Cl}}:$

(2) $\overset{\ominus}{C}H_2-CH=\overset{\oplus}{Cl}$

(3) $\overset{\ominus}{C}H_2-\overset{\oplus}{C}H-Cl$

(4) All have equal stability

20. The stabilization due to resonance is maximum in

(1) 

(2) 

(3) 

(4) 

21. In which of the following compounds carbon–chlorine bond distance is minimum :-

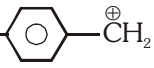
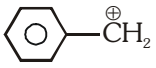
(1) CH_3-Cl

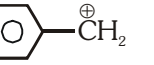
(2) $C_6H_5-CH_2-Cl$

(3) $CH_2=CH-Cl$

(4) $CH_2=CH-CH_2-Cl$

22. Consider the following carbocations

(a)  (b) 

(c)  (d) $CH_3-\overset{\oplus}{C}H_2$

The relative stabilities of these carbocations are such that :-

(1) d < b < c < a

(2) b < d < c < a

(3) d < b < a < c

(4) b < d < a < c

23. Among the following, the strongest base is :-

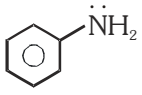
(1) $C_6H_5NH_2$

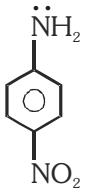
(2) p–NO_2–$C_6H_4NH_2$

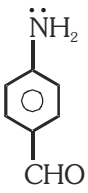
(3) m–NO_2–$C_6H_4NH_2$

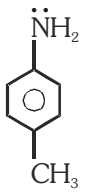
(4) $C_6H_5CH_2NH_2$

24. Arrange in decreasing order of basic strength :

(I) 

(II) 

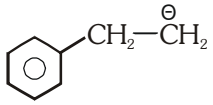
(III) 

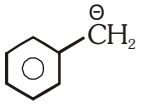
(IV) 

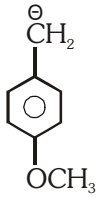
(1) I > II > III > IV (2) II > III > I > IV

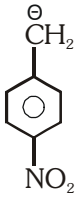
(3) IV > I > III > II (4) IV > I > II > III

25. The most stable carbanion among the following is

(1) 

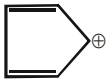
(2) 

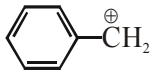
(3) 

(4) 

26. Which of the following is most stable carbocation:-

(1) 

(2) 

(3) 

(4) $CH_2=CH-\overset{\oplus}{C}H_2$

27. The oxygen atom in phenol –

(1) exhibits only inductive effect

(2) exhibits only resonance effect

(3) has more dominating resonance effect than inductive effect

(4) has more dominating inductive effect than resonance effect

28. Which is incorrect stability order :-

(1) $CH_2 = CH - \overset{\oplus}{C}H_2 \;>\; CH_3 - \overset{\oplus}{C}H - CH_3$

(2) $CH_2 = \overset{\oplus}{C}H \;<\; CH_3 - \overset{\oplus}{C}H_2$

(3) $CH_3 - CH_2 - \overset{\ominus}{C}H_2 \;>\; CH_3 - \overset{\ominus}{C}H - CH_3$

(4) $CH_3 - \overset{\oplus}{C}H_2 \;>\; CH_3O - \overset{\oplus}{C}H_2$

29. Mesomeric effect is due to :-

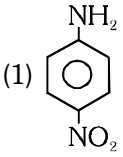
(1) Delocalization of σ $e\bar{s}$

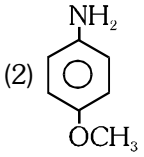
(2) Delocalization of π $e\bar{s}$

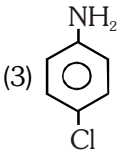
(3) Migration of H – atom

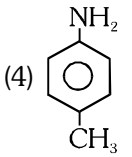
(4) Migration of proton

30. Which of the following is least basic :–

(1) 

(2) 

(3) 

(4) 

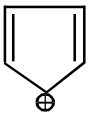
31. Among the following the pKa is minimum for :–

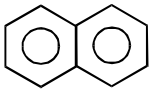
(1) C_6H_5OH (2) HCOOH

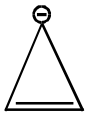
(3) C_2H_5OH (4) $CH_3C\equiv CH$

32. Among the following the aromatic compound is –

(1) 

(2) 

(3) 

(4) 

33. Which is aromatic compound among the following

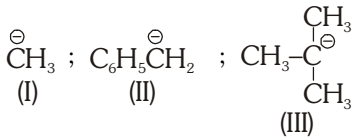
(1) 

(2) 

(3) 

(4) All the above

34. Select the correct option for stability of following carbanions :

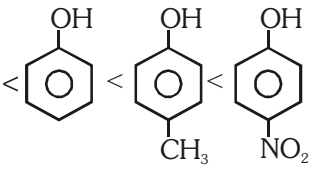


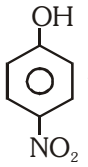
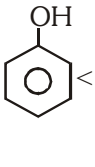
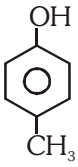
(I) (II) (III)

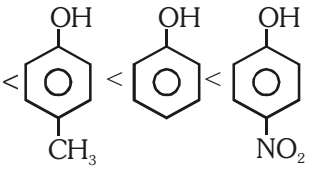
(1) I > II > III (2) II > I > III

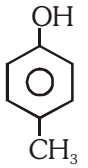
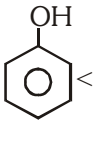
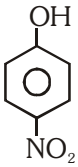
(3) III > II > I (4) II > III > I

35. Correct increasing order of acidity of the following phenols is :-

(1) $C_2H_5OH <$  $<$ $<$

(2)  $<$  $<$  $< C_2H_5OH$

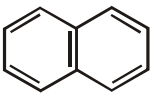
(3) $C_2H_5OH <$  $<$ $<$

(4)  $<$  $<$  $< C_2H_5OH$

36. The non aromatic compound among the following is :-

(1) 

(2) 

(3) 

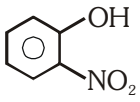
(4) 

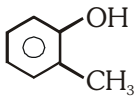
37. The correct order of acidic strength of the following compounds is :-

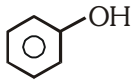
A. Phenol B. p-Cresol
C. m-Nitrophenol D. p- Nitrophenol

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

38. Which one of the following compounds is most acidic:-

(1) 

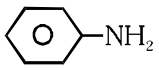
(2) 

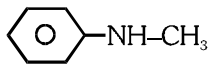
(3) 

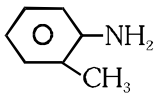
(4) $ClCH_2CH_2OH$

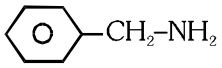
39. Which of the following is most acidic :-
(1) phenol
(2) benzyl alcohol
(3) m-chloro phenol
(4) cyclohexanol

40. Which of the following is the strongest base :-

(1) 

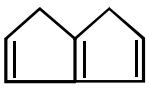
(2) 

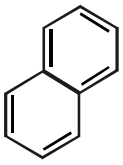
(3) 

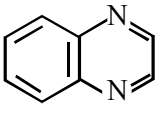
(4) 

41. The dipole moment of vinyl chloride is lower than that of methyl chloride. This is due to :-
(1) Resonance effect
(2) Inductive effect
(3) Electromeric effect
(4) Hyperconjugation

42. Which is Aromatic compound :-

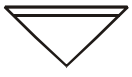
(1) 

(2) 

(3) 

(4) 2 and 3 both

43. Which of the following is the most acidic compound :-
(1) $CH_2 = CH_2$ (2) $HC \equiv CH$

(3) 

(4) 

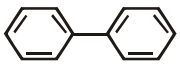
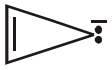
44. Among the following the strongest acid is :-
(1) CH_3COOH
(2) C_6H_5COOH
(3) m–$CH_3OC_6H_4COOH$
(4) p–$CH_3OC_6H_4COOH$

45. The least reactive chlorine is present in –
(1) Methyl chloride
(2) Allyl chloride
(3) Ethyl chloride
(4) Vinyl chloride

46. Which one of the following resonating structures of 1–methoxy–1,3–butadiene is least stable :–
(1) $\overset{\ominus}{C}H_2$–CH=CH–CH=$\overset{\oplus}{O}$–CH_3
(2) CH_2=CH–$\overset{\ominus}{C}$H–CH=$\overset{\oplus}{O}$–CH_3
(3) $\overset{\ominus}{C}H_2$–$\overset{\oplus}{C}$H–CH=CH–O–CH_3
(4) CH_2=CH–CH=CH–O–CH_3

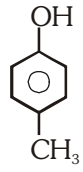
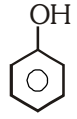
47. Four structures are given in options (a) to (d). Examine them and select the aromatic strucutures.

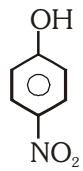
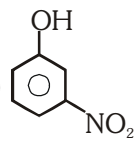
(a)  (b) 

(c)  (d) 

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

48. Order of acidic strength of the following compound will be :

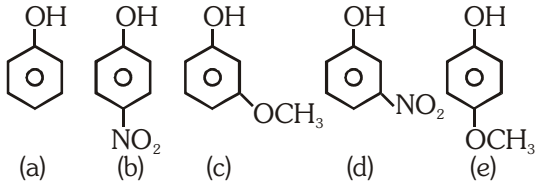
(A)  (B) 

(C)  (D) 

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

49. Phenol is less acidic than
(1) Ethanol (2) o-Nitrophenol
(3) o-Methylphenol (4) o-Methoxyphenol

50. Mark the correct order of decreasing acid strength of the following compounds.


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

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

HYPERCONJUGATION

51. Which of the following compounds exhibits hyperconjugation :
(1) Phenol (2) Ethyne
(3) Ethanol (4) Propene

52. Which of the following is least stable :–
(1) CH_3–$\overset{\oplus}{C}$H–CH_3
(2) CH_3–CH_2–$\overset{\oplus}{C}H_2$
(3) CH_3–$\overset{\oplus}{\underset{CH_3}{C}}$–$CH_3$
(4) CH_3–$\underset{CH_3}{\overset{CH_3}{C}}$–$\overset{\oplus}{C}$H–$C_6H_5$

53. Which of the following is most stable alkene :-
(1) $H_2C=CH_2$
(2) $CH_3CH=CH_2$
(3) $H_5C_2CH=CH_2$
(4) $(CH_3)_2CHCH=CH_2$

54. The correct order of increasing stability of the given alkenes is

(1) 1 – pentene > cis –2– pentene > trans – 2–pentene > 2 – methyl – 2 – butene

(2) 1 – pentene > trans –2– pentene > cis –2– pentene > 2 – methyl – 2 – butene

(3) 1 – pentene < cis –2– pentene < trans – 2–pentene < 2 – methyl – 2 – butene

(4) 1 – pentene < trans – 2–pentene < cis –2– pentene < 2 – methyl – 2 – butene

TAUTOMERISM

55. Tautomerism is due to :-

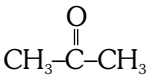
(1) Delocalization of sigma electrons

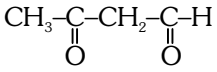
(2) Delocalization of pi electrons

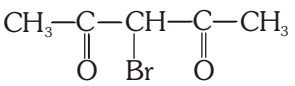
(3) Migration of active–H–atom

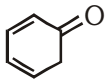
(4) None is correct

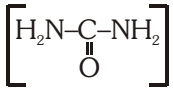
56. Which of the following will lead to maximum enolisation :–

(1) 

(2) 

(3) 

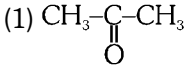
(4) 

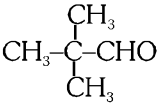
57. Urea  molecule exhibits (isomerism):-

(1) Chain (2) Position

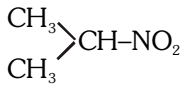
(3) Geometrical (4) Tautomerism

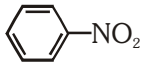
58. Tautomerism is not observed in :–

(1)  (2) Ph–CH=CH–OH

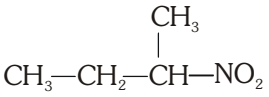
(3) $CH_3–NO_2$ (4) 

59. Which of the following is not soluble in NaOH solution :

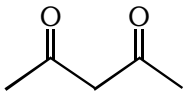
(1) 

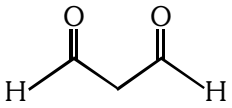
(2) 

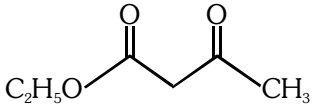
(3) $CH_3CH_2–NO_2$

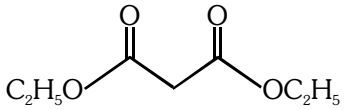
(4) 

60. Which of the following has highest enol content.

(1) 

(2) 

(3) 

(4) 

EXERCISE-I (Conceptual Questions) ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	**2**	**3**	**2**	**3**	**3**	**1**	**1**	**2**	**4**	**3**	**4**	**3**	**2**	**1**	**2**
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	**3**	**3**	**4**	**3**	**4**	**3**	**1**	**4**	**3**	**4**	**1**	**3**	**4**	**2**	**1**
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	**2**	**3**	**4**	**2**	**3**	**1**	**2**	**1**	**3**	**4**	**1**	**4**	**4**	**3**	**4**
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	**3**	**4**	**1**	**2**	**4**	**4**	**2**	**2**	**3**	**3**	**4**	**4**	**4**	**2**	**2**

EXERCISE-II (Previous Year Questions)

AIPMT/NEET & AIIMS (2006-2018)

AIPMT 2006

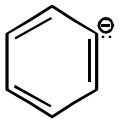
1. Which of the following is more basic than aniline
(1) Diphenyl amine (2) Triphenyl amine
(3) p-nitro aniline (4) Benzyl amine

AIPMT 2007

2. Which of the following presents the correct order of the acidity in the given compounds :
(1) $FCH_2COOH > CH_3COOH > BrCH_2COOH > ClCH_2COOH$
(2) $BrCH_2COOH > ClCH_2COOH > FCH_2COOH > CH_3COOH$
(3) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$
(4) $CH_3COOH > BrCH_2COOH > ClCH_2COOH > FCH_2COOH$

AIPMT 2008

3. The stability of carbanions in the following:-

(a) $RC\equiv\overset{\ominus}{C}$ (b) 

(c) $R_2C=\overset{\ominus}{C}H$ (d) $R_3C-\overset{\ominus}{C}H_2$

is in the order of:-
(1) (d) > (b) > (c) >(a) (2) (a) >(c) >(b) >(d)
(3) (a) > (b) > (c) > (d) (4) (b) > (c) > (d) >(a)

4. Basic strength of:-

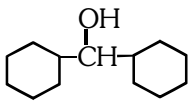
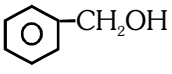
(a) $H_3C-\overset{\ominus}{C}H_2$ (b) $H_2C=\overset{\ominus}{C}H$ and

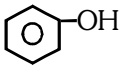
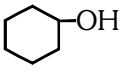
(c) $HC\equiv\overset{\ominus}{C}$

is in the order of:-
(1) (a) > (c)> (b) (2) (a) > (b) > (c)
(3) (b)> (a) > (c) (4) (c) > (b) > (a)

AIPMT 2010

5. Which one of the following compounds has the most acidic nature ?

(1)  (2) 

(3)  (4) 

6. Given are cyclohexanol (I), acetic acid (II), 2, 4, 6-trinitrophenol (III) and phenol (IV). In these the order of decreasing acidic character will be :-
(1) III > IV > II > I
(2) III > II > IV > I
(3) II > III > I > IV
(4) II > III > IV > I

AIPMT Mains-2010

7. Among the following four compounds :-
(a) phenol (b) methyl phenol
(c) metanitrophenol (d) paranitrophenol,
The acidity order is :
(1) c > d > a > b (2) c > d > c > b
(3) b > a > c > d (4) d > c > a > b

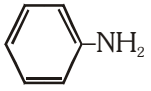
8. Which of the following species is not electrophilic in nature :-
(1) BH_3 (2) $\overset{\oplus}{H_3O}$
(3) $\overset{\oplus}{N}O_2$ (4) $\overset{\oplus}{C}l$

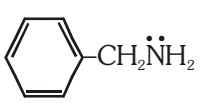
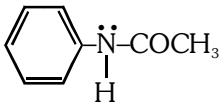
AIIMS 2010

9. The correct order of pka is
(I) CH_3COOH
(II) CH_3CH_2COOH
(III) $C_6H_5\ CH_2\ COOH$
(IV) $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-COOH$
(1) IV > III > II > I
(2) III > IV > II > I
(3) IV > II > III > I
(4) II > I > III > IV

AIPMT Mains-2011

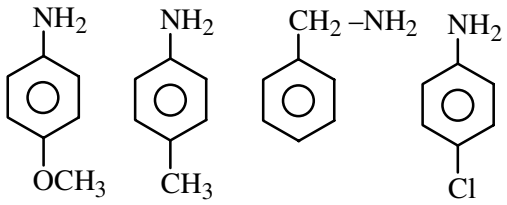
10. Which of the following compounds is most basic ?

(1)  (2)

(3)  (4) 

AIIMS 2011

11.



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

The correct decreasing order of pK_b is:–

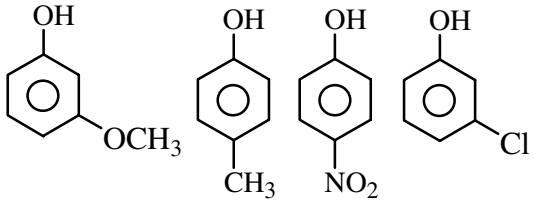
(1) I > II > III > IV

(2) III > IV > II > I

(3) II > III > IV > I

(4) IV > II > I > III

12.



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

The correct decreasing order of pK_a is:–

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

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

AIPMT Pre.-2012

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

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

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

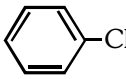
AIIMS 2012

14. Pk_a increases in benzoic acid, substituent "x" bonded at para position then "x" is :-

(1) –COOH (2) $-NO_2$

(3) –CN (4) $-OCH_3$

NEET-UG 2013

15. The radical,  is aromatic because it has :-

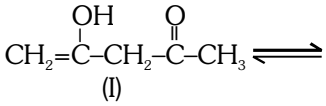
(1) 6p–orbitals and 7 unpaired electrons

(2) 6p–orbitals and 6 unpaired electrons

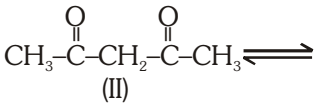
(3) 7p–orbitals and 6 unpaired electrons

(4) 7p–orbitals and 7 unpaired electrons

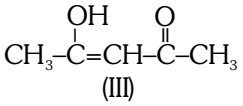
16. The order of stability of the following tautomeric compounds is :-



(I)



(II)



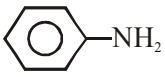
(III)

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

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

AIIMS 2014

17. Correct decreasing order of pK_b value of following compounds:-

(I)  (II) $CH_3-\ddot{N}H_2$

(III) $CH_3-\ddot{N}H-CH_3$ (IV) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle \ddot{}}{\underset{|}{N}}}-CH_3$

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

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

18. Decreasing order of stability of following carbocations is :-

(A) $m\text{-}CH_3O-C_6H_4-CH_2^+$ (B) $p\text{-}CH_3O-C_6H_4-CH_2^+$

(C) $C_6H_5-CH_2^+$ (D) $p\text{-}NO_2-C_6H_4-CH_2^+$

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

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

19. Decreasing order of basic strength is :-

(I) CH_3NH_2 (II) $C_6H_5CH_2NH_2$

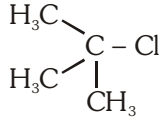
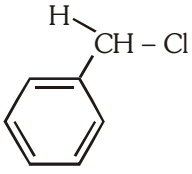
(III) $p\text{-}CH_3O-C_6H_4-NH_2$ (IV) $m\text{-}CH_3O-C_6H_4-NH_2$

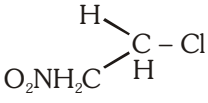
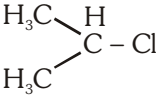
(1) I > II > III > IV (2) II > IV > I > III

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

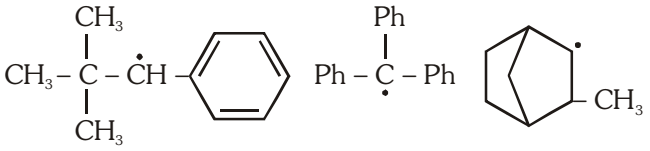
AIPMT 2015

20. In which of the following compounds, C–Cl bond ionisation shall give most stable carbonium ion?

(1)  (2) 

(3)  (4) 

21. Consider the following compounds

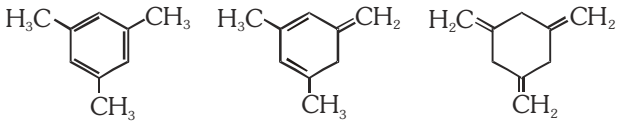


(I) (II) (III)

Hyperconjugation occurs In :-

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

22. Given :-



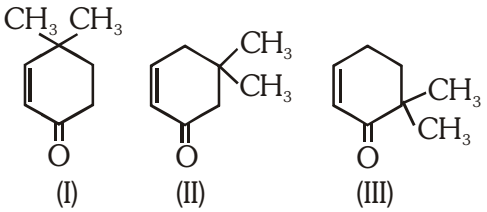
(I) (II) (III)

The enthalpy of the hydrogenation of these compounds will be in the order as :-

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

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

23. Which of the given compounds can exhibit tautomerism?

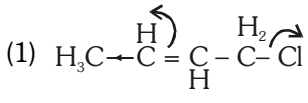


(I) (II) (III)

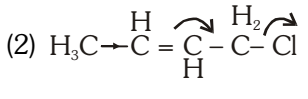
(1) I and III (2) II and III

(3) I, II and III (4) I and II

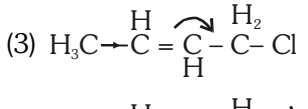
24. Which of the following is the most **correct** electron displacement for a nucleophilic reaction to take place?



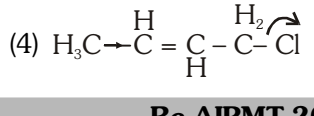
(1)



(2)



(3)



(4)

Re-AIPMT 2015

25. Which of the following statements is not correct for a nucleophile ?

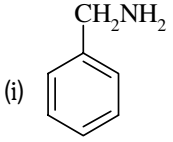
(1) Nucleophiles attack low e^- density sites

(2) Nucleophiles are not electron seeking

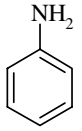
(3) Nucleophile is a Lewis acid

(4) Ammonia is a nucleophile

26. Correct order of K_b is

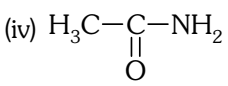


(i)



(ii)

(iii) $CH_3CH_2–NH_2$



(iv)

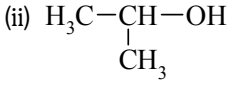
(1) iv > iii > ii > i (2) iii > i > ii > iv

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

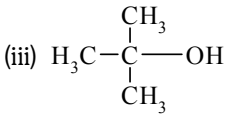
AIIMS 2015

27. Correct order of pK_a is

(i) $CH_3–CH_2–OH$



(ii)

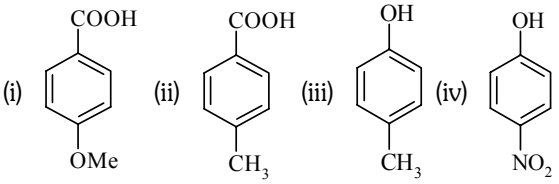


(iii)

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

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

28. Correct order of acidic strength is



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

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

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

NEET-I 2016

29. The correct statement regarding a carbonyl compound with a hydrogen atom on its alpha carbon,is :-

(1) a carbonyl compound with a hydrogen atom on its alpha-carbon never equilibrates with its corresponding enol.

(2) a carbonyl compound with a hydrgen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as aldehyde-ketone equilibration.

(3) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as carbonylation.

(4) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as keto-enol tautomerism.

30. The **correct** statement regarding the basicity of arylamines is :-

(1) Arylamines are generally less basic than alkylamines because the nitrogen lone-pair electrons are delocalized by interaction with the aromatic ring π electron system.

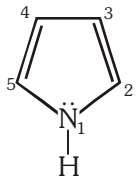
(2) Arylamines are generally more basic than alkylamines because the nitrogen lone-pair electrons are not delocalized by interaction with the aromatic ring π electron system.

(3) Arylamines are generally more basic than alkylamines because of aryl group.

(4) Arylamines are generally more basic than alkylamines, because the nitrongen atom in arylamines is sp-hybridized.

NEET-II 2016

31. In pyrrole



The electron density is maximum on :-

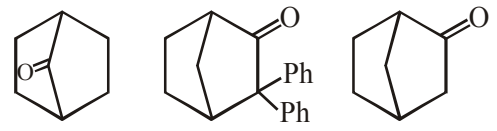
(1) 2 and 4

(2) 2 and 5

(3) 2 and 3

(4) 3 and 4

32. Which among the given molecules can exhibit tautomerism ?



I II III

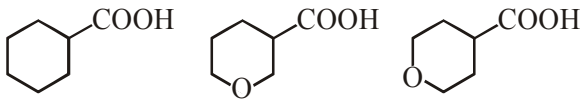
(1) Both I and II

(2) Both II and III

(3) III only

(4) Both I and III

33. The **correct** order of strengths of the carboxylic acids



I II III

is

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

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

NEET(UG) 2017

34. Which one is the correct order of acidity ?

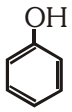
(1) $CH \equiv CH > CH_3 - C \equiv CH > CH_2 = CH_2 > CH_3 - CH_3$

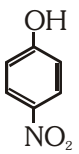
(2) $CH \equiv CH > CH_2 = CH_2 > CH_3 - C \equiv CH > CH_3 - CH_3$

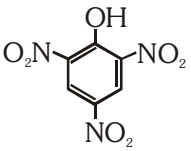
(3) $CH_3 - CH_3 > CH_2 = CH_2 > CH_3 - C \equiv CH > CH \equiv CH$

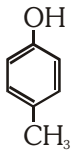
(4) $CH_2 = CH_2 > CH_3 - CH = CH_2 > CH_3 - C \equiv CH > CH \equiv CH$

35. Which one is the most acidic compound ?

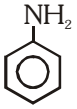
(1) 

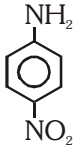
(2) 

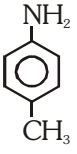
(3) 

(4) 

36. The **correct** increasing order of basic strength for the following compounds is :

(I) 

(II) 

(III) 

(1) III < I < II

(2) III < II < I

(3) II < I < III

(4) II < III < I

37. The **correct** statement regarding electrophile is :-

(1) Electrophile is a negatively charged species and can form a bond by accepting a pair of electrons from another electrophile

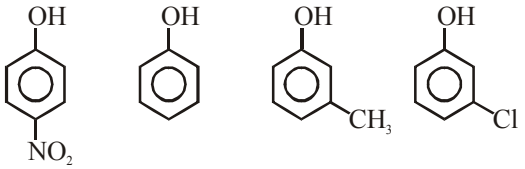
(2) Electrophiles are generally neutral species and can form a bond by accepting a pair of electrons from a nucleophile

(3) Electrophile can be either neutral or positively charged species and can form a bond by accepting a pair of electrons from a nucleophile

(4) Electrophile is a negatively charged species and can form a bond by accepting a pair of electrons from a nucleophile

AIIMS 2017

38. Arrange followings in correct decreasing order of pK_a :-

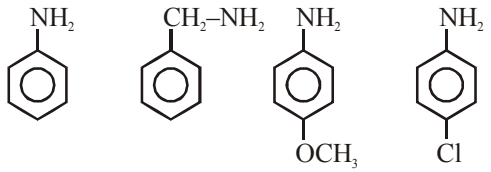


(I) (II) (III) (IV)

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

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

39. Arrange followings in correct decreasing order of pK_b :-

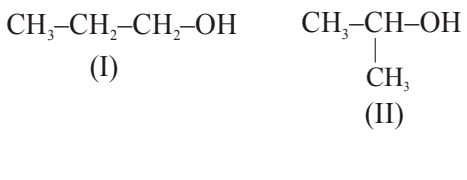


(I) (II) (III) (IV)

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

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

40. Arrange following in correct increasing order of pK_a



(I) (II)

(III) (IV)

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

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

NEET(UG) 2018

41. Which of the following is correct with respect to –I effect of the substituents ? (R = alkyl)

(1) $-NH_2 < -OR < -F$

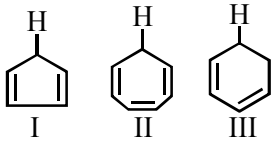
(2) $-NR_2 < -OR < -F$

(3) $-NH_2 > -OR > -F$

(4) $-NR_2 > -OR > -F$

AIIMS 2018

42. Arrange the following compounds in their decreasing order of acidic strength



I II III

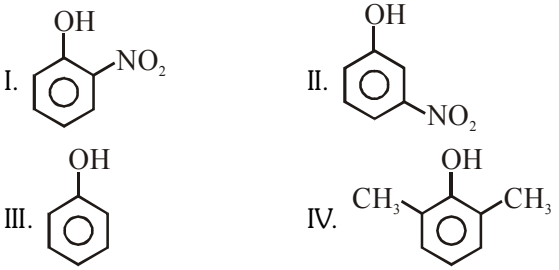
(1) I > II > III

(2) I > III > II

(3) II > III > I

(4) II > I > III

43. Arrange the following decreasing order of their acidic strength



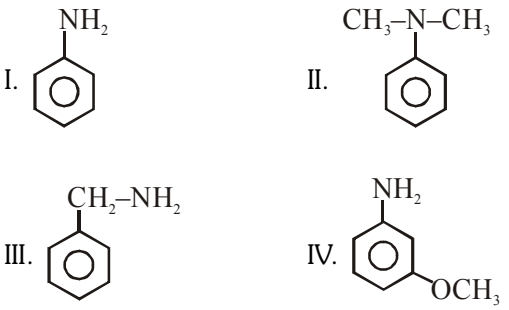
(1) I > II > III > IV

(2) I > II > IV > III

(3) II > I > III > IV

(4) IV > I > II > III

44. Arrange the following in decreasing order of basic strength



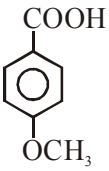
(1) I > II > III > IV

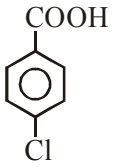
(2) III > II > IV > I

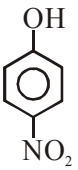
(3) III > II > I > IV

(4) IV > II > III > I

45. Arrange the following acids in decreasing order of their acidic strength :-

(I) 

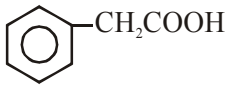
(II) 

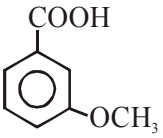
(III) 

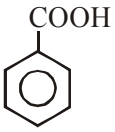
(IV) 

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

46. Compare the acidic strength of the given acids

(I) CH_3CH_2COOH (II) 

(III) 

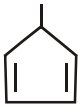
(IV) 

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

47. Which of the following molecule on reaction with $CH_3CH_2\overset{-}{O}\overset{+}{Na}$ gives aromatic species :-

(1) 

(2) 

(3) 

(4) 

EXERCISE-II (Previous Year Questions) ANSWER KEY

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

EXERCISE-III (Analytical Questions) — Check Your Understanding

1. Consider the following statements :-

(a) $CH_3O\overset{\oplus}{C}H_2$ is more stable than $CH_3\overset{\oplus}{C}H_2$

(b) $Me_2\overset{\oplus}{C}H$ is more stable than $CH_3CH_2\overset{\oplus}{C}H_2$

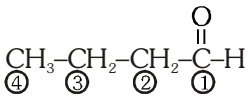
(c) $CH_2=CH-\overset{\oplus}{C}H_2$ is more stable than $CH_3CH_2\overset{\oplus}{C}H_2$

(d) $CH_2=\overset{\oplus}{C}H$ is more stable than $CH_3\overset{\oplus}{C}H_2$

of these statements :-

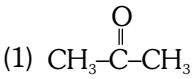
(1) a and b are correct
(2) c and d are correct
(3) a, b and c are correct
(4) b, c and d are correct

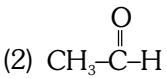
2. Which of the following carbon has most acidic hydrogen.

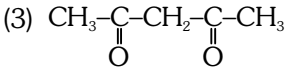


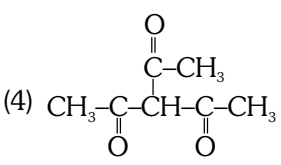
(1) C_1–H (2) C_2–H
(3) C_3–H (4) C_4–H

3. Which of the following has the most acidic proton:

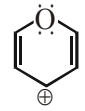
(1) 

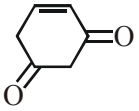
(2) 

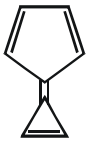
(3) 

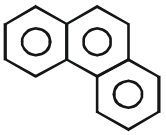
(4) 

4. Which is not aromatic compound :-

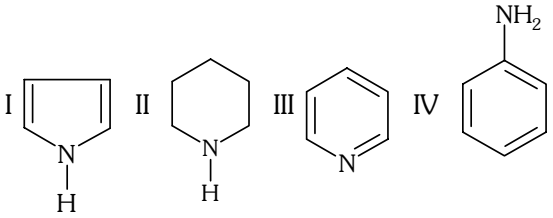
(1) 

(2) 

(3) 

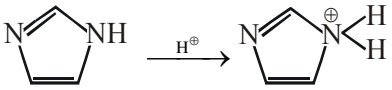
(4) 

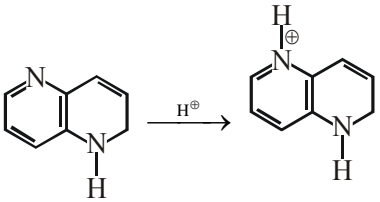
5. The correct order of decreasing basic strength is

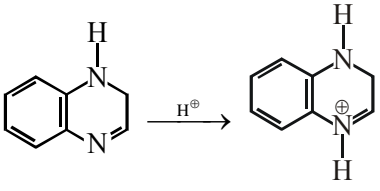


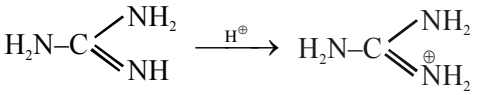
(1) I > II > III > IV (2) II > III > I > IV
(3) II > IV > I > III (4) II > III > IV > I

6. Which of the following acid-base reaction is not feasible :-

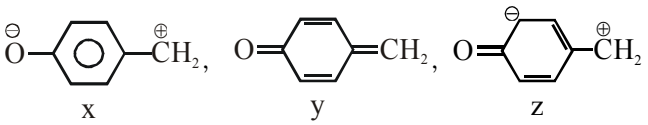
(1) 

(2) 

(3) 

(4) 

7. Select the correct option for stability of following resonance structures :-



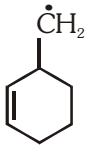
x y z

(1) x > y > z (2) z > y > x
(3) y > x > z (4) y > z > x

8. (a) $CH_2=CH-CH=CH_2$
(b) $CH_3-CH=CH_2$
(c) CH_3-CH_3
C—C single bond distance would be :-
(1) a < b < c
(2) a > b < c
(3) a < b > c
(4) a < b > c

9. Hydrogen attached to sp^3 carbon in cyclopentadiene can be easily removed as what :-
(1) Hydride ion
(2) Hydrogen molecule
(3) Proton
(4) Hydrogen atom

10. Which one is most stable free radical :

(1)  (2) 

(3) $CH_2=CH-\dot{C}H_2$ (4) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{\dot{C}}}}}-CH_3$

11. Which is wrong electromeric effect :

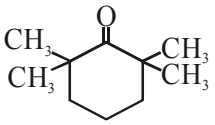
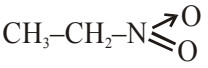
(1) 

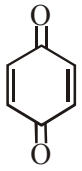
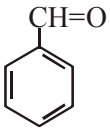
(2) $CH_3-CH=CH_2 \longrightarrow CH_3-\overset{\oplus}{C}H-\overset{\ominus}{C}H_2$

(3) $-C\equiv N \longrightarrow -\overset{\ominus}{C}=\overset{\oplus}{N}$

(4) $CH\equiv CH \longrightarrow \overset{\oplus}{C}H=\overset{\ominus}{C}H$

12. Tautomerism is exhibited by :-

(1)  (2) 

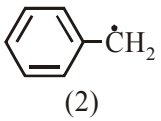
(3)  (4) 

13. Identify the compound that exhibits tautomerism :-
(1) 2-Pentanone (2) Phenol
(3) 2-Butene (4) Lactic acid

14. Arrange the following in correct order of acidic strength :
(I) CH_3-NO_2 (II) $NO_2-CH_2-NO_2$
(III) $CH_3-CH_2-NO_2$ (IV) $NO_2-\underset{\displaystyle NO_2}{\overset{\displaystyle NO_2}{\overset{|}{\underset{|}{CH}}}}-NO_2$

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

15. The correct order of stability of following carbon free radical is :-

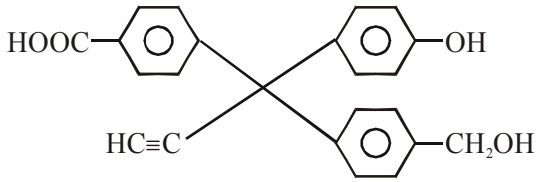
$(CH_3)_3\dot{C}$ (1)  (2)

$CH_3CH_2\dot{C}H_2$ (3) $\dot{C}H_3$ (4)

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

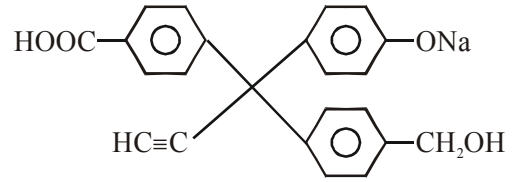
16. Which of the following is the strongest acid :-
(1) Carbolic acid (2) Carbonic acid
(3) Picric acid (4) Acetic acid

17.

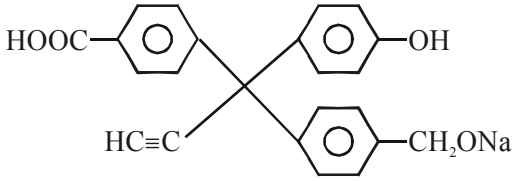


$\xrightarrow[(1\text{mole})]{NaNH_2}$ product is :-

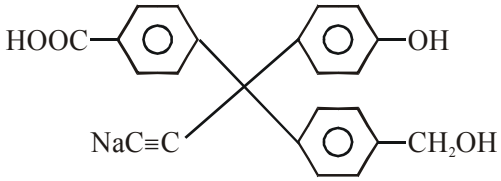
(1)



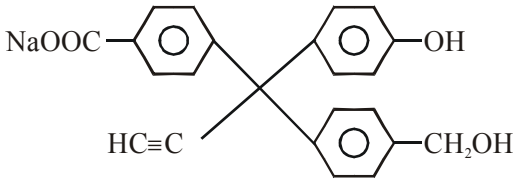
(2)



(3)



(4)



18. The correct order of acidic strength is :-
(1) $CH_3COOH < HCN < H_2O < C_2H_5OH$
(2) $CH_3COOH > HCN > H_2O > C_2H_5OH$
(3) $HCN > CH_3COOH > H_2O > C_2H_5OH$
(4) $CH_3COOH > HCN > C_2H_5OH > H_2O$

19. Which of the follwing orders of acid strength is correct :-
(1) RCOOH > ROH > HOH > HC≡CH
(2) RCOOH > HOH > ROH > HC≡CH
(3) RCOOH > HOH > HC≡CH > ROH
(4) RCOOH > HC≡CH > HOH > ROH

EXERCISE-III (Analytical Questions) ANSWER KEY

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

EXERCISE-IV (Assertion & Reason) — Target AIIMS

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

(A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.

(B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.

(C) If Assertion is True but the Reason is False.

(D) If both Assertion & Reason are false.

1. ***Assertion :–*** Tertiary carbonium ions are generally formed more easily than primary carbonium ions.
Reason :– Hyperconjugative as well as inductive effect of additional alkyl groups stabilize tertiary carbonium ions.
(1) A (2) B (3) C (4) D

2. ***Assertion :–*** Carbanions have ammonia like pyramidal shape.
Reason :– The carbon atom carrying negative charge has an octet of electrons.
(1) A (2) B (3) C (4) D

3. ***Assertion :–*** Pyrrole is a weaker base than its hydrogenated product pyrrolidine.
Reason :– Lone pair of electrons on nitrogen is delocalized in pyrrole.
(1) A (2) B (3) C (4) D

4. ***Assertion :–*** A mixture of o–nitrophenol and p–nitrophenol can be separated by steam distillation.
Reason :– o–nitrophenol is steam volatile but p–nitrophenol is not.
(1) A (2) B (3) C (4) D

5. ***Assertion :–*** The carbocation $CF_3 - \overset{\oplus}{C}H_2$ is less stable than $\overset{\oplus}{C}F_3$.
Reason :– In case of $CF_3 - \overset{\oplus}{C}H_2$, the strongly electron withdrawing $-CF_3$ group intensifies the +ve charge but in case of $\overset{\oplus}{C}F_3$, the lone pairs of electrons on each of the three F–atoms overlap with the empty p–orbital of the carbocation carbon atom, thereby dispersing the +ve charge.
(1) A (2) B (3) C (4) D

6. ***Assertion :–*** Acidity of the following compounds decreases in the order
$HC \equiv CH > CH_2 = CH_2 > CH_3 - CH_3$
Reason :– Acidity of the compounds increase as the electronegativity of the carbon increases to which H is attached.
(1) A (2) B (3) C (4) D

7. ***Assertion :–*** The acidity of alcohols follows the order : 1° > 2° > 3°.
Reason :– The + I effect of the additional alkyl groups favours the cleavage of O–H bond.
(1) A (2) B (3) C (4) D

8. ***Assertion :–*** Phenol is less acidic than p–nitro phenol.
Reason :– Phenolate ion is more stable than p–nitro phenolate ion.
(1) A (2) B (3) C (4) D

9. ***Assertion :–*** Pyrrole is more basic than pyridine.
Reason :– In pyrrole, nitrogen is sp^3–hybridized.
(1) A (2) B (3) C (4) D

10. ***Assertion :–*** Aniline is a weaker base than benzyl amine.
Reason :– In aniline, mesomeric interaction occurs between benzene ring and amino group.
(1) A (2) B (3) C (4) D

11. ***Assertion*** : Cyclopentadienyl anion is much more stable than allyl anion.
Reason : Cyclopentadienyl anion is aromatic in character.
(1) A (2) B (3) C (4) D

12. ***Assertion :*** Acetic acid is stronger acid than ethyl alcohol.
Reason : In acetate ion both C–O bond lengths are equal.
(1) A (2) B (3) C (4) D

13. ***Assertion :*** Tropylium ion is more stable than benzyl cation.
Reason : Tropylium ion is anti-aromatic in nature.
(1) A (2) B (3) C (4) D

14. ***Assertion :–*** Phenol is more acidic than benzyl alcohol.
Reason :– $C_6H_5–O^{\ominus}$ is more stable than $C_6H_5–CH_2–O^{\ominus}$
(1) A (2) B (3) C (4) D

15. ***Assertion :–*** Picric acid is stronger acid than phenol.
Reason :– Picric acid has –COOH group, while phenol has –OH group.
(1) A (2) B (3) C (4) D

16. ***Assertion :-*** Pyridine is less basic than trimethyl amine.
Reason :- Nitrogen atom in pyridine is sp^2 hybridized, while in trimethylamine it is sp^3.
(1) A (2) B (3) C (4) D

17. ***Assertion :–*** Enol form of cyclohexane–1,3,5–trione is more stable than its ketoform.
Reason :– It contains α–hydrogen atoms.
(1) A (2) B (3) C (4) D

18. ***Assertion :–*** $C_2H_5NO_2$ shows functional isomerism as well as tautomerism.
Reason :– Nitroethane shows tautomerism due to presence of α–hydrogens and functional isomerism with ethyl nitrite.
(1) A (2) B (3) C (4) D

19. ***Assertion*** : Tautomers have different functional group.
Reason : Tautomers have same molecular formula.
(1) A (2) B (3) C (4) D

20. ***Assertion :–*** The following compound are given below –

$CH_3CH_2NO_2$, $CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}.NO_2$ &

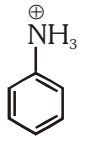
$CH_3—\underset{\displaystyle NO_2}{\overset{\displaystyle |}{CH}}—CH_2—CH_3$

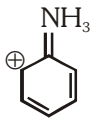
all three compounds are soluble in NaOH.
Reason :– All above compound have lower boiling than CH_3NO_2.
(1) A (2) B (3) C (4) D

21. ***Assertion :–*** Phenol is stronger acid than alcohols.
Reason :– Phenol is stabilized by resonance whereas alcohols are not.
(1) A (2) B (3) C (4) D

22. ***Assertion :–*** Formic acid is a stronger acid than benzoic acid.
Reason :– pK_a of formic acid is higher than that of benzoic acid.
(1) A (2) B (3) C (4) D

23. ***Assertion :–*** Here two structures are given


I


II

I and II are not acceptable canonical structure.
Reason :– Carbonium ions are less stable than ammonium ions.
(1) A (2) B (3) C (4) D

24. ***Assertion :–*** Benzene hexachloride is an aromatic compound.
Reason :– It contain 3π bonds in the ring.
(1) A (2) B (3) C (4) D

25. ***Assertion :-*** $Cl—\underset{\displaystyle C_2H_5}{\overset{\displaystyle H}{C}}—CH_3$ and $H—\underset{\displaystyle CH_3}{\overset{\displaystyle C_2H_5}{C}}—Cl$ are enantiomers.
Reason :- Non-superimposable mirror images are known as enantiomers.
(1) A (2) B (3) C (4) D

26. ***Assertion :-*** Dimethyl amine has more basic strength than trimethyl amine.
Reason :- It is due to solvation effect.
(1) A (2) B (3) C (4) D

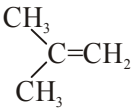
27. ***Assertion :-*** In $\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}=CH_2$, the C–C–C bond angles are different.
Reason :- The C has steric effect of $–CH_3$ group.
(1) A (2) B (3) C (4) D

28. ***Assertion :-*** Benzyl amine is more basic than ethyl amine.
Reason :- Phenyl group has +I effect.
(1) A (2) B (3) C (4) D

29. ***Assertion :-*** o-nitrophenol is more acidic than m-nitrophenol.
Reason :- At o-position, –I effect of $-NO_2$ is more than at m-position.
(1) A (2) B (3) C (4) D

30. ***Assertion :-*** N, N-diethylethane is more basic than N, N-dimethyl methane.
Reason :- +I of ethyl is more than methyl group.
(1) A (2) B (3) C (4) D

31. ***Assertion :-*** Dimethyl amine has more basic strength than trimethyl amine.
Reason :- It is due to solvation effect.
(1) A (2) B (3) C (4) D

32. ***Assertion :-*** In  , the C–C–C bond angles are different.
Reason :- The C has steric effect of $-CH_3$ group.
(1) A (2) B (3) C (4) D

33. ***Assertion :-*** Benzyl amine is more basic than ethyl amine.
Reason :- Phenyl group has +I effect.
(1) A (2) B (3) C (4) D

EXERCISE-IV (Assertion & Reason) ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	**1**	**2**	**1**	**1**	**1**	**1**	**3**	**3**	**4**	**1**	**1**	**2**	**3**	**1**	**3**
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	**1**	**2**	**1**	**2**	**3**	**2**	**3**	**2**	**4**	**1**	**1**	**1**	**4**	**2**	**1**
Que.	31	32	33												
Ans.	**1**	**1**	**4**												

IMPORTANT NOTES