CHAPTER

13 Some Basic Principles and Techniques: General Organic Chemistry

BOND FISSION

Breaking of a covalent bond of the compound is known as bond fission. A bond can be broken by two ways

1. **Homolytic Fission:** Occurs in gas phase or in non-polar solvents in the presence of peroxide, UV light, heat (≥ 500°C) or presence of electricity and free radical. The process is known as initiation of free radical reaction. In such fission, free radicals are formed. Here the bond pair is equally shared after the fission.

   $A–B \longrightarrow \overset{\bullet}{A} + \overset{\bullet}{B}$ (free radicals)

   $CH_3—H \rightarrow \overset{\bullet}{CH_3} + \overset{\bullet}{H}$

   (i) Homolytic bond fission gives free radical as the reaction intermediate.

   (ii) Reaction mechanism of the reaction is known as **free radical or homolytic mechanism**.

2. **Heterolytic Fission:** Occurs in polar solvents, catalysed by acids or bases and greatly influenced by polarity of solvents. In an organic compound such as R - G, two types of ions are formed.

   $R–G \longrightarrow R^+ + G^-$

   (R^+ is known as carbocation)

   $R–G \longrightarrow R^- + G^+$

   (R^- is known as carbanion)

   The factor which favours heterolysis is a greater difference of electronegativity between A and B.

   Thus,

   (i) Heterolytic bond fission gives carbocation or carbanion as reaction intermediate.

   (ii) Mechanism of the reaction in which heterolytic bond fission takes place is known as heterolytic mechanism or ionic mechanism.

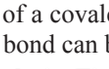
REACTION INTERMEDIATES

In the study of organic chemistry, following intermediates are important:

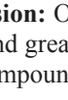
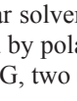
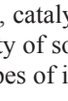
(i) Carbocation (ii) Carbanion

(iii) Carbon free radical (iv) Carbene

(v) Nitrene

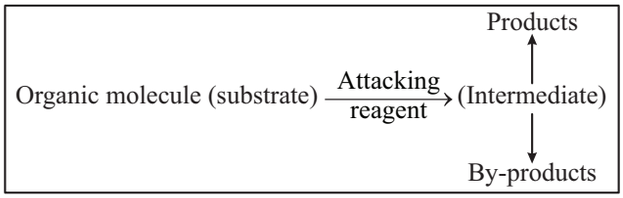
Property	Carbocation	Carbanion	Carbon Free Radical
Representation			
Bond fission	Heterolysis	Heterolysis	Homolysis
Electrical nature	Positive	Negative	Neutral
No. of electrons in valence shell of carbon	6	8	7
Hybridisation	sp^2	sp^3	sp^2
Shape	Planar	Pyramidal	Planar

Carbene and Nitrene are of following Two Types

Property	Singlet Carbene	Triplet Carbene	Singlet Nitrene	Triplet Nitrene
Representation				
Electrical nature	Neutral	Neutral	Neutral	Neutral
No. of electrons in valence shell	6	6	6	6
Hybridisation	sp^2	sp	sp^2	sp
Shape	V-shape	Linear	Linear	Linear

FUNDAMENTAL CONCEPTS IN ORGANIC REACTION MECHANISM

In an organic reaction, the reactant organic molecule is known as substrate which reacts with an attacking reagent and leads to the formation of one or more intermediates and finally forms the products. The general reaction may be represented as follows:



The substrate is that reactant which provides carbon to form the new bond and the other reactant is called reagent. However, if both the reactant supply carbon to the new bond then choice of substrate is arbitrary and in that case, the molecule which we are interested to study is the substrate.

During organic reactions, a covalent bond between two carbon atoms or a carbon atom and some other atom is broken and a new bond is formed. The detailed study of stepwise description of a reaction, electron movement, energetics during bond breaking and bond formation and the details of time required for the steps, when a reactant is transformed into the product is called Reaction Mechanism. The knowledge of reaction mechanism is very important because it helps to understand the reactivity of organic compounds.

Reaction Reagents

Organic reagents can be classified in two categories:

(A) Electrophile: Electron deficient species or electron acceptor.

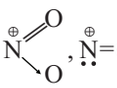
(B) Nucleophile: Electron rich species or electron donor.

(A) Electrophiles: It can be classified into two categories:

(I) Charged electrophiles

(II) Neutral electrophiles

(I) Charged electrophiles: Positively charged species in which central atom has incomplete octet is charged electrophile.

e.g.: $H^{\oplus}$, $R^{\oplus}$, , $\overset{\oplus}{N}{=}O$, $\overset{\oplus}{S}O_3H$

Key Note

Almost all cations are charged electrophiles except cations like Na^+, K^+, Al^{3+} and $\overset{+}{N}H_4$ etc.

(II) Neutral electrophiles: They can be classified into three categories:

(i) Neutral covalent compounds in which central atom has incomplete octet are neutral electrophiles.

e.g.: $BeCl_2$, AlX_3, $\ddot{C}H_2$, $\ddot{C}X_2$

(ii) Neutral covalent compounds in which central atom has complete or expanded octet and central atom has unfilled valence p or d-subshell are neutral electrophiles.

e.g.: $SnCl_4$, $SiCl_4$, PCl_5, SF_6, IF_7, BX_3, $ZnCl_2$, FeX_3

(iii) Neutral covalent compounds in which central atom is multiply bonded with two or more than two highly electronegative atoms are neutral electrophiles.

e.g.: CO_2, SO_3, CS_2

Key Note

- Cl_2, Br_2 and I_2 also behave as neutral electrophiles.
- Electrophiles are Lewis acids.

(B) Nucleophiles: Nucleophiles can be classified into three categories:

(I) Charged nucleophiles: Almost all Negatively charged species are charged nucleophiles.

e.g.: $\overset{\ominus}{H}$, $\overset{\ominus}{O}H$, $R\overset{\ominus}{O}$, $\overset{\ominus}{C}H_3$, $\overset{\ominus}{X}$, $\overset{\ominus}{S}H$, $R\overset{\ominus}{S}$

(II) Neutral nucleophiles: Neutral covalent compounds, in which central atom has complete octet, has at least one lone pair of electrons and none of the atoms present on central atom are electronegative, are called neutral nucleophiles.

e.g.: $\ddot{N}H_3$, $R\ddot{N}H_2$, $R_2\ddot{N}H$, $R_3\ddot{N}$, $\ddot{N}H_2\ddot{N}H_2$

(Nitrogen nucleophiles)

$H_2\ddot{O}$, $R\ddot{O}H$, $R_2\ddot{O}$

(Oxygen nucleophiles)

$H_2\ddot{S}$, $R\ddot{S}H$, $R_2\ddot{S}$

(Sulphur nucleophiles)

$\ddot{P}H_3$, $R\ddot{P}H_2$, $R_2\ddot{P}H$, $R_3\ddot{P}$

(Phosphorus nucleophiles)

Key Note

Organic compounds containing carbon–carbon multiple bonds behave as nucleophiles.

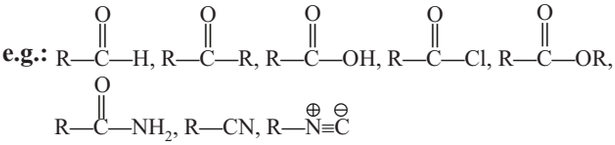
e.g.: Alkenes, Alkynes, Benzene,

(III) Ambident nucleophiles: Species having two nucleophilic centres, one neutral (complete octet and has at least one lone pair of electrons) and other charged (negative charge) behave as ambident nucleophiles.

e.g.: $\overset{\ominus}{C}{\equiv}\ddot{N}$, $\overset{\ominus}{O}{-}\ddot{N}{=}O$

Key Note

- Organometallic compounds are nucleophiles.
- Nucleophiles are Lewis bases.
- **Ambiphiles: Organic compounds which behave as electrophile as well as nucleophile:** Organic compound in which carbon is bonded with electronegative atom (O, N, S) by multiple bond.

e.g.: 

Note: During the course of chemical reaction electrophile reacts with nucleophile.

NUCLEOPHILICITY AND BASICITY

- If the nucleophilic atoms are from the same period of the periodic table, strength as a nucleophile parallels strength as a base. E.g.: $H_2O < NH_3$

$$H_2\ddot{O} < R\ddot{O}H < R{-}C(=O){-}\ddot{O}^{\ominus} < H{-}\ddot{O}^{\ominus} < R{-}\ddot{O}^{\ominus}$$

Increasing basic strength,
increasing nucleophilic strength

- Nucleophilic strength increases down a column of the periodic table (in protic solvents that can have hydrogen bond, such as water and alcohols).

e.g.: $RO^{\ominus} < RS^{\ominus}$ & $F^{\ominus} < Cl^{\ominus} < Br^{\ominus} < I^{\ominus}$

Increasing nucleophilic strength
& decreasing basic strength

- In aprotic solvents such as DMF, DMA, DMSO, nucleophilic strength decreases down the group.

$$I^{\ominus} < Br^{\ominus} < Cl^{\ominus} < F^{\ominus}$$

Increasing basic strength and
increasing nucleophilic strength

- Steric bulk decreases nucleophilicity.

e.g.: $H_3C{-}C(CH_3)_2{-}O^{\ominus}$ < $HO^{\ominus}$

Weaker nucleophile
Stronger base

Stronger nucleophile
Weaker base

ELECTRONIC DISPLACEMENT IN ORGANIC COMPOUNDS

Electronic displacement

- Permanent
  - Inductive effect
  - Resonance effect
  - Mesomeric effect
  - Hyperconjugation effect
- Temporary
  - Electromeric effect

INDUCTIVE EFFECT

- It involves partial displacement of σ electrons towards more electronegative atom or group. It is permanent effect.

$$\text{I – effect} \propto \frac{1}{\text{distance}}$$

- I-effect is of two types: + I effect and – I effect

1. **–I effect:** The element or group which attracts σ electrons as compared to hydrogen shows this effect. Order of – I effect of some standard species is:

$$-\overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3 > -NO_2 > -CN > -COOH > -F > -Cl > -Br > -I > -OH > -NH_2 > -OR > -CH \equiv CH > -Ph > -HC = CH_2 > -H$$

2. **+I effect**: The element or groups which repels σ electrons as compared to the hydrogen shows this effect. Order of +I effect of some standard species is:

$$-\overset{\ominus}{N}H > -\overset{\ominus}{O} > -COO^{-} > -C(CH_3)_3 > -CH(CH_3)_2 > -CH_2CH_3 > -CH_3 > -D > -H$$

Applications of Inductive Effect

1. **Stability of intermediates:**

$$\text{Stability of carbocation} \propto +I \propto \frac{1}{-I}$$

$$\text{Stability of carbanion} \propto -I \propto \frac{1}{+I}$$

e.g.:

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

(ii) $CH_3{-}\overset{\ominus}{C}(CH_3)_2{-}CH_3 < CH_3{-}\overset{\ominus}{C}H{-}CH_3 < CH_3{-}\overset{\ominus}{C}H_2 < \overset{\ominus}{C}H_3$

(iii) $ClH_2C-\overset{\oplus}{C}H_2 > Cl_2HC-\overset{\oplus}{C}H_2 > Cl_3C-\overset{\oplus}{C}H_2$

(iv) $CH_3{-}CH_2{-}\underset{F}{CH}{-}\overset{\ominus}{C}H_2 > CH_3{-}\underset{F}{CH}{-}CH_2{-}\overset{\ominus}{C}H_2 > CH_2(F){-}CH_2{-}CH_2{-}\overset{\ominus}{C}H_2$

(v) $HC\equiv\overset{\ominus}{C}$ > $H_2C=\overset{\ominus}{C}H$ > $H_3C-\overset{\ominus}{C}H_2$

$HC\equiv\overset{\ominus}{C}$: sp-carbon; More EN due to more s character

$H_2C=\overset{\ominus}{C}H$: sp^2—carbon

$H_3C-\overset{\ominus}{C}H_2$: sp^3—carbon

2. **Acidic strength:** The proton donating tendency of any compound is called its acidic strength.

Generally, Acidic strength ∝ Stability of anion (Conjugate Base)

e.g.:

(i) $CH_3OH > CH_3CH_2OH > CH_3{-}CH(CH_3){-}OH$

$\downarrow -H^+$ $\downarrow -H^+$ $\downarrow -H^+$

$CH_3O^- > CH_3CH_2O^- > CH_3{-}\overset{\ominus}{C}H{-}CH_3$

(Stability)

(ii) $CH_3OH > CH{\equiv}CH > CH_3NH_2 > CH_2{=}CH_2$

$\downarrow -H^{\oplus}$ $\downarrow -H^{\oplus}$ $\downarrow -H^{\oplus}$ $\downarrow -H^{\oplus}$

$CH_3{-}O^{\ominus} > HC{\equiv}C^{\ominus} > CH_3{-}NH^{\ominus} > CH_2{=}CH^{\ominus}$

EN = 3.5 | EN = 3.25 (sp-carbon) | EN = 3.0 | EN = 2.75 (sp^2–carbon)

(Stability)

3. **Basic Strength:** The lone-pair donating tendency of the atom in any compound is called as basic strength.

Generally, $\boxed{\text{Basic strength} \propto +I \propto \frac{1}{-I}}$

e.g.:

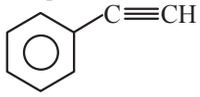
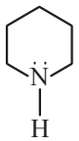
(i) $CH_3-\ddot{N}H_2 > \ddot{N}H_3 > Cl-\ddot{N}H_2$

(ii) $CH_3-\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{C}}}-\ddot{N}H_2 > CH_3-\underset{CH_3}{\underset{|}{CH}}-\ddot{N}H_2 > CH_3CH_2CH_2-\ddot{N}H_2$

(iii) $CH_3-\underset{CH_3}{\underset{|}{CH}}-\ddot{O}H > CH_3-CH_2-\ddot{O}H > CH_3-\ddot{O}H$

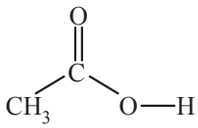
Train Your Brain

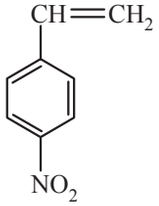
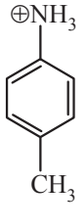
Example 1: Show the direction of inductive effect in following compounds:

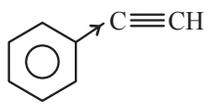
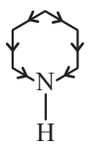
(I)  (II) 

(III) $CH_3-CH=CH_2$ (IV) $CH_3-CH_2-CH_2-Li$

(V) $CH_3-CH_2-CH_2-MgBr$ (VI) CH_3-CH_2-OH

(VII) (VIII) 

(IX)  (X) 

Sol. (I)  (II) 

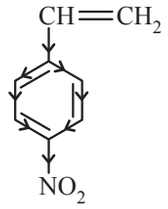
(III) $CH_3 \rightarrow CH=CH_2$

(IV) $CH_3 \leftarrow CH_2 \leftarrow CH_2 \leftarrow Li$

(V) $CH_3 \leftarrow CH_2 \leftarrow CH_2 \leftarrow MgBr$

(VI) $CH_3 \rightarrow CH_2 \rightarrow OH$

(VII) (VIII) $CH_3 \rightarrow COOH$

(IX)  (X)

Concept Application

1. Which of the following group shows +I-effect?
   (*a*) –Br (*b*) –COOH
   (*c*) –OR (*d*) $-COO^-$
2. Which of the following alkyl group has the maximum +I effect ?
   (*a*) $(CH_3)_2CH-$ (*b*) $(CH_3)_3C-$
   (*c*) CH_3CH_2- (*d*) CH_3-
3. Decreasing –I effect of given groups is:
   (i) –CN (ii) $-NO_2$
   (iii) $-NH_2$ (iv) –F
   (*a*) iii > ii > i > iv (*b*) ii > iii > iv > i
   (*c*) iii > ii > iv > i (*d*) ii > i > iv > iii
4. Which of the following is the strongest –I group?
   (*a*) $-\overset{+}{N}(CH_3)_3$ (*b*) $-\overset{+}{N}H_3$
   (*c*) $-\overset{+}{S}(CH_3)_2$ (*d*) –F

RESONANCE EFFECT

When a molecule or ion can be represented by two or more structures which have the same arrangement of atomic nuclei but differ in distribution of electrons, the phenomenon is called as Resonance. The various structures are called contributing or resonating structures. None of these structures truly represents all the properties of that molecule or ion. The actual structure is a resonance hybrid of several contributing structures. Resonance generally occurs when there is a conjugation of π-electrons (alternate double–single–double bond arrangement) known as conjugated system.

Conjugate positions of the molecule: Alternate positions of the molecule having π bond with positive charge or negative charge or odd electron or lone pair of electrons are known as conjugative positions.

$\underset{1}{CH_2}=CH-\underset{3}{CH}=CH-\underset{5}{CH}=CH_2$

1, 3 and 5 are conjugate positions.

$\underset{1}{CH_2}=CH-\underset{3}{CH}=CH-\overset{\oplus}{\underset{5}{CH}}-CH_3$

1, 3 and 5 are conjugate positions.

$CH_2 = CH - CH = CH - CH = CH - \ddot{N}H_2$

1, 3, 5 and 7 are Conjugate positions

Key Note

Compound having at least two conjugate positions is known as conjugated compound.

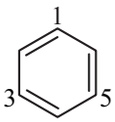
Type of Conjugation

1. **π, π conjugation:** If all conjugate positions have π bonds, then conjugation is known as π, π conjugation.

   e.g.:

   $CH_2 = CH - CH = CH_2$;

   $CH_3 - CH_2 - CH = CH - CH = CH - CH = CH_2$;

2. **Positive charge, π conjugation:** In this case, all but one conjugate positions have π bonds and only one conjugate position has positive charge. If this is the case, then conjugation is known as positive charge, π conjugation.

   e.g.: $CH_2 = CH - \overset{\oplus}{C}H_2$

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

3. **Negative charge, π conjugation:** If all but one conjugate positions have π bonds and only one conjugate position has negative charge, then conjugation is known as negative charge, π conjugation.

   e.g.: $CH_2{=}CH{-}\overset{\ominus}{C}H_2$; $CH_2 = CH - CH = CH - \overset{\ominus}{C}H_2$

4. **Odd electron, π conjugation:** If all but one conjugate positions have π bonds and only one conjugate position has odd electron, then conjugation is known as odd electron, π conjugation.

   e.g.: $CH_2{=}CH{-}\dot{C}H_2$; $CH_2{=}CH{-}CH{=}CH{-}\dot{C}H_2$

5. **Lone pair, π conjugation:** If all but one conjugate positions have π bonds and only one conjugate position has lone pair then conjugation is known as lp, π conjugation.

   e.g.: $CH_2{=}CH{-}\ddot{N}H_2$; $CH_2 = CH - \ddot{X}:$

Resonance Stabilisation Energy or Resonance Energy or Delocalization Energy

The resonance hybrid is always more stable than any one of its canonical form. The stability of resonance hybird is attributed to resonance energy which is equal to difference in energy of resonance hybird and its most stable canonical form. The stability of resonance hybrid increases with increasing number of equivalent contributing resources.

Important Characteristic Features of Resonance

(i) The resonance structures should differ only in position of electrons and not in the relative position of atom.

(ii) The number of unpaired electrons should be same in all canonical forms.

(iii) The various forms in which octet rule is violated for elements of second period are not considered as resonating structure.

For Example:

$CH_2 = CH - \overset{\oplus}{N}H_3 \longleftrightarrow \overset{\oplus}{C}H_2 - CH = NH_3$

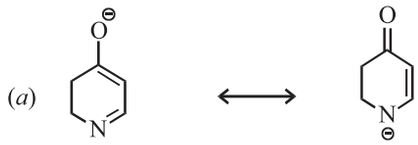
I II

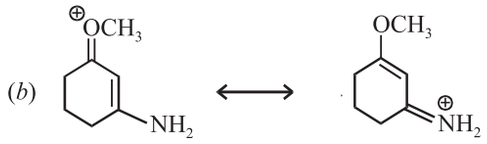
Since in structure-II, N violates octet rule, therefore this structure is invalid.

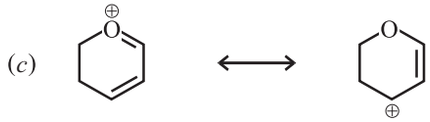
Train Your Brain

Example 2: Write the stability order of following resonating structures:

I II

(*a*) 

(*b*) 

(*c*) 

(*d*)

Sol. (*a*) I > II (*b*) II > I

(*c*) I > II (*d*) II > I

Concept Application

5. Resonance structures of the molecule does not have
(*a*) Higher energy than their hybrid structure.
(*b*) Identical arrangement of atoms.
(*c*) The same number of paired electrons.
(*d*) Always equal contribution to the resonance hybrid.

6. Which of the following species can not show resonance?

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

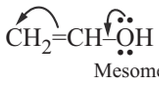
7. Which of the following does not have conjugated system?

(*a*) $CH_2=CHCl$ (*b*) $CH_2=CHCHO$

(*c*) $CH_3CH=CH_2$ (*d*)

MESOMERIC EFFECT

Groups or atoms which release or withdraw π-electron density from the conjugated system are called mesomeric group and this effect is called mesomeric effect.

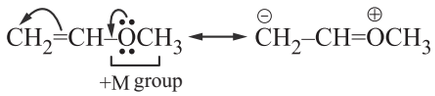


Key Note

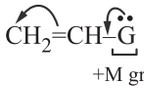
- It is distance independent effect.
- It is permanent and strong effect.
- It operates along π-bonds.

It is of two types:

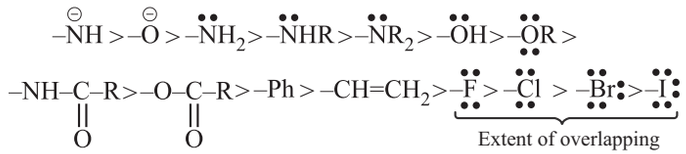
(i) +M effect: Groups or atoms which release π-electrons to the conjugated system are known as +M group and the effect is called +M effect.



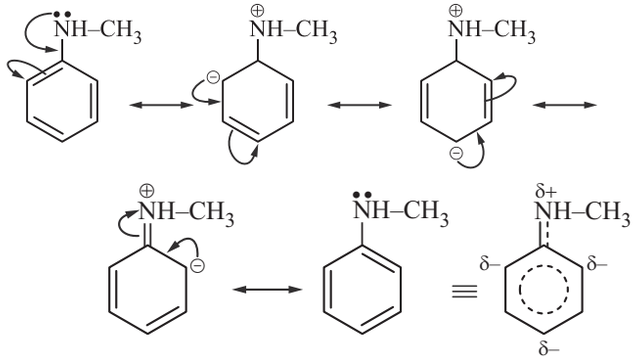
- **Conditions:** To show +M effect, the key atom of the group should have at least one lone pair.



- **Order of +M effect:**



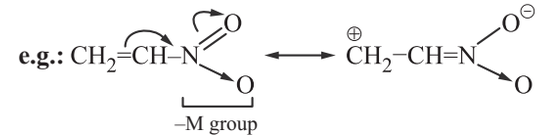
e.g.:



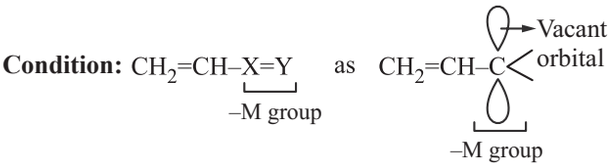
- +M group increases electron density in benzene ring, so they activate the benzene ring towards electrophilic substitution reaction and are known as activating groups.
- +M groups increase rate of ESR.
- +M groups are ortho, para directing.

(ii) –M effect: Groups or atoms which withdraw π-electrons from the conjugated system are known as –M groups and this effect is called –M effect.

e.g.:

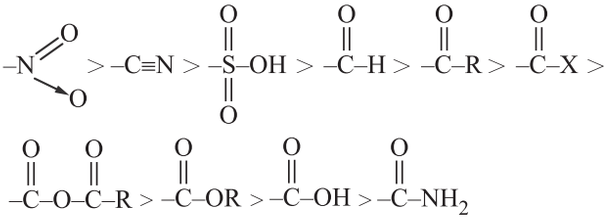


- **Condition:**

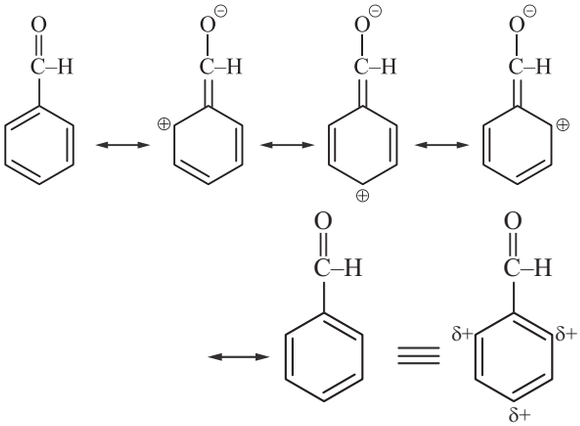


The first atom of the group must have either vacant orbital or is attached to more electronegative atom via multiple bonds.

- **Order of –M effect:**



e.g.:



- –M group decreases electron density in benzne ring, so rate of ESR decreases.
- –M groups are deactivating groups
- –M groups are meta directing.
- **Some important points:**
  - Some groups show both +M as well as –M effect.
    e.g.: –Cl:, –SH, –N=O, etc.
  - Generally, mesomeric effect dominates over inductive effect but in case of halogen, and NO inductive effect dominates over mesomeric effect.
  - **Priority:** Mesomeric > Resonance > Inductive
  - Mesomeric effect does not operate at meta position.

Train Your Brain

Example 3: Arrange the following groups in the increasing order of +M.

(*i*) –I, –Cl, –F, –Br (*ii*) $-NH_2$, –OH, $-O^{\ominus}$

Sol. (*i*) +M: – I < – Br < – Cl < – F

(*ii*) +M: –OH < $-NH_2$ < $-O^{\ominus}$

Concept Application

8. Which of the following groups show +M effect ?

(*a*) –CN (*b*) –O–NO

(*c*) $-CCl_3$ (*d*) –CHO

9. Which of the following groups show –M effect?

(*a*) $-CMe_3$ (*b*) $-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-R$

(*c*) $-NH-\overset{\overset{O}{\|}}{C}-CH_3$ (*d*) $-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-R$

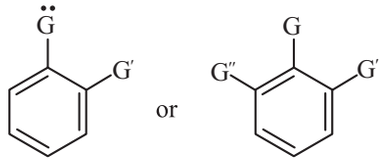
10. Which of the following group shows both +M and –I effect?

(*a*) $-\overset{\overset{O}{\|}}{C}-F$ (*b*) $-\overset{\overset{O}{\|}}{C}-OR$

(*c*) $-O^{\ominus}$ (*d*) –OH

Steric Inhibition of Resonance (SIR effect)

- In case of 1,2 - disubstituted benzene, if the substituents are bulky then due to steric repulsion (vanderwaal repulsion) the groups go out of plane with respect to benzene ring.
- Due to this change in planarity, the conjugation between the substituent and benzene ring is slightly diminished, this effect is called steric inhibition of resonance.

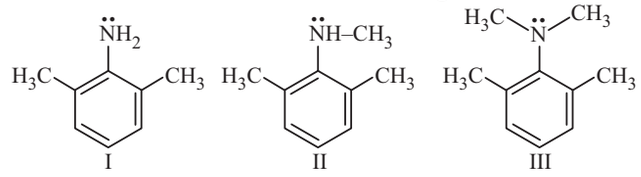


If G = OH, $-NH_2$ or –CN, SIR does not operate.

SIR effect ∝ size of group

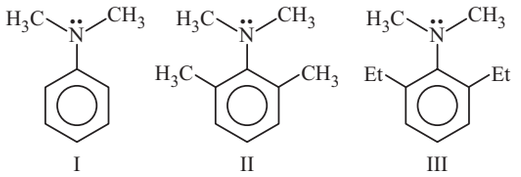
e.g.: Give order of SIR effect in the following:

(*a*)



SIR: I < II < III

(*b*)



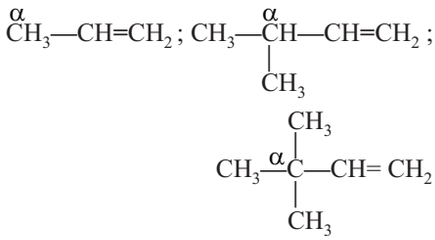
SIR: I < II < III

HYPERCONJUGATION EFFECT

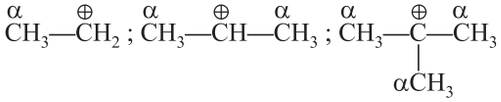
When (C–H) sigma electrons are in conjugation to π bond or pure p-orbitals, the conjugation is known as σ(C–H), π conjugation, no bond resonance or hyperconjugation.

- **Structural requirement for hyperconjugation:**
  - (i) Compound should have at least one sp^2-hybrid carbon of either alkene or alkyl carbocation or alkyl free radical.
  - (ii) Saturated α-carbon with respect to sp^2 hybrid carbon should have at least one hydrogen.

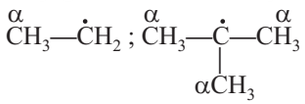
    If both these conditions are fulfilled then hyperconjugation will take place in the molecule.
- **Hyperconjugation is of three types:**
  - (i) **σ (C–H), π conjugation:** This type of conjugation occurs in alkenes.



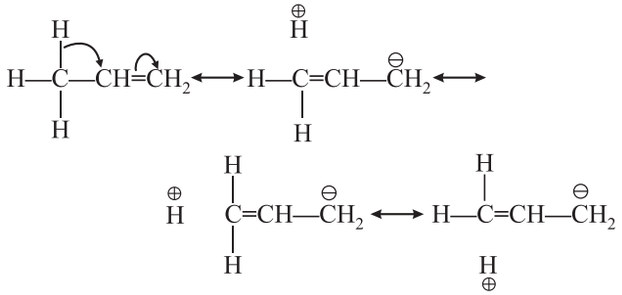
  - (ii) **σ (C–H), positive charge conjugation:** This type of conjugation occurs in alkyl carbocation.



  - (iii) **σ (C–H), odd electron conjugation:** This type of conjugation occurs in alkyl free radicals.



- Resonating structures due to hyperconjugation may be written involving "no bond" between the alpha carbon and hydrogen atoms.



In the above resonating structures there is no covalent bond between carbon and hydrogen. From this point of view, hyperconjugation may be regarded as **"no-bond resonance"**.

Application of Hyperconjugation

1. **Stability of Alkenes:** Stability of alkenes ∝ Number of α– hydrogens ∝ Number of resonating structures

   e.g.:

   (i) $CH_3—CH=CH_2 > CH_3—CH_2—CH=CH_2 >$ $CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}—CH=CH_2$

   (ii) $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C=C\!<\!\begin{matrix}CH_3\\CH_3\end{matrix} > \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C=CH—CH_3 > \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C=CH_2$

2. **Stability of Alkyl Carbocations:** Stability of alkyl carbocations ∝ Number of resonating structures ∝ Number of α-hydrogens.

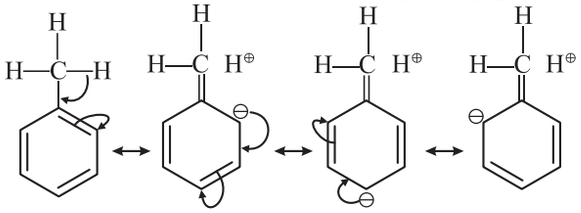
   e.g.:

   $\overset{\oplus}{C}H_3 < CH_3—\overset{\oplus}{C}H_2 < CH_3—\overset{\oplus}{C}H—CH_3 < CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle \oplus}{\overset{\displaystyle |}{C}}}—CH_3$

3. **Stability of Alkyl free radicals:** Stability of alkyl free radicals depend on the number of resonating structures or number of α-Hydrogens.

   $\dot{C}H_3 < CH_3—\dot{C}H_2 < CH_3—\dot{C}H—CH_3 < CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle |}{\dot{C}}}—CH_3$

4. **Electron releasing (or donating) power of R in alkyl benzene:** CH_3– (or alkyl group) is +R group, ortho-para directing group and activating group for electrophilic aromatic substitution reaction because of the hyperconjugation.



The electron donating power of alkyl group will depend on the number of resonating structures, this depends on the number of hydrogens present on α-carbon. The electron releasing power of some groups (when directly attached to unsaturated system) are as follows:

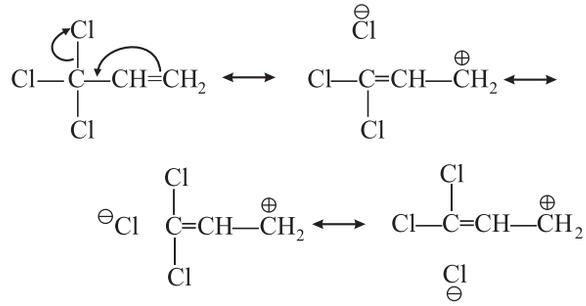
$CH_3— > CH_3—CH_2— > CH_3—\underset{\displaystyle |}{CH}—CH_3 > CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}}—$

REVERSE HYPERCONJUGATION

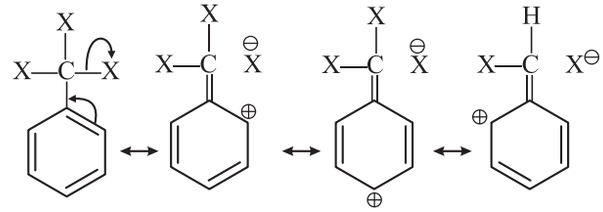
The phenomenon of hyperconjugation is also observed in the system given below:

$—\underset{\displaystyle |}{\overset{\displaystyle X}{\overset{\displaystyle |}{C}}}—C=C$ (where X=halogen atom)

In such systems the effect operates in the reverse direction. Hence the hyperconjugation in such systems is known as reverse hyperconjugation.



The meta directing and deactivating effect of $—CX_3$ group for electrophilic aromatic substitution reaction can be explained by this effect.



Train Your Brain

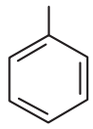
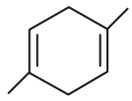
Example 4: In the following molecules or ions, write the number of hyperconjugable hydrogen atoms.

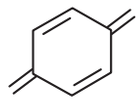
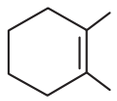
(I) $C_6H_5–CH=CH_2$ (II) $CH_3–CH_2–CH=CH_2$

(III) $CH_2=CH_2$ (IV) $CH_3–\overset{\ominus}{C}H_2$

(V) $CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}}—CH=CH_2$ (VI) $CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}}—\overset{\oplus}{C}H_2$

(VII) $C_2H_5—\underset{\displaystyle C_2H_5}{\overset{\displaystyle \oplus}{C}}$ (VIII) $CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle \oplus}{C}}$

(IX)  (X) 

(XI)  (XII) 

Sol. (I) 0 (II) 2

(III) 0 (IV) No hyperconjugation

(V) 0 (VI) 0

(VII) 6 (VIII) 9

(IX) 3 (X) 10

(XI) 0 (XII) 10

Concept Application

11. In hyperconjugation, there is overlap between:

(*a*) p- and π-orbitals (*b*) 2π-orbitals

(*c*) d- and π-orbtials (*d*) σ- and p-orbitals

12. Which of the following cannot exhibit hyperconjugation?

(*a*) $CH_3\dot{C}H_2$ (*b*) $CH_3-\overset{+}{C}H-CH_3$

(*c*) $CH_3CH=CH_2$ (*d*) $(CH_3)_3C-\overset{+}{C}H_2$

13. Which of the following alkenes will show maximum number of hyperconjugation forms?

(*a*) $CH_2=CH_2$ (*b*) $CH_3-CH=CH_2$

(*c*) $CH_3-CH_2-CH=CH_2$ (*d*) $CH_3-\underset{CH_3}{CH}-CH=CH_2$

14. Which one of the following has inductive, mesomeric as well as hyperconjugation effect?

(*a*) CH_3Cl (*b*) $CH_3-CH=CH_2$

(*c*) $CH_3CH=CH-\underset{O}{\overset{\|}{C}}-CH_3$ (*d*) $CH_2=CH-CH=CH_2$

ELECTROMERIC EFFECT

- Electromeric effect is a temporary effect in which a shared pair of electrons (π–electron pair) is completely transfered from a double or a triple bond to one of the atoms joined by the bond at the requirement of attacking reagent.
- If the attacking reagent is removed, charge disappears and substrate attains its original form. Thus, this effect is reversible and temporary.
- The electromeric effect can be decided by other permanent effects in various conditions as follows:

Case-I: Electromeric effect may be decided by I–effect as –

E.g. $CH_3\rightarrow CH=CH_2 \xrightleftharpoons{\text{Reagent}} CH_3-\overset{\oplus}{C}H-\overset{\ominus}{C}H_2$

$Cl_3C\leftarrow CH=CH_2 \xrightleftharpoons{\text{Reagent}} Cl_3C-\overset{\ominus}{C}H-\overset{\oplus}{C}H_2$

Case-II: If the multiple bond is present between two different atoms, the electromeric shift will take place in the direction of the more electronegative atom.

e.g.: $>C=O \xrightleftharpoons{\text{Reagent}} >\overset{\oplus}{C}-\overset{\ominus}{O}$

$-C\equiv N \xrightleftharpoons{\text{Reagent}} -\overset{\oplus}{C}=\overset{\ominus}{N}$

TYPES OF ORGANIC REACTIONS

Organic reactions can be classified into the following categories:

(i) Substitution reactions
(ii) Addition reactions
(iii) Elimination reactions
(iv) Rearrangement reactions

Substitution Reactions

- A reaction in which one group or atom is replaced by another is called a substitution reaction.
- The incoming group is bonded to the same carbon to which the leaving group was bonded.
- The substituting species may be either a nucleophile, an electrophile or a free radical.

$$HO^{\ominus} + CH_2(CH_3)-Br: \longrightarrow HO-CH_2(CH_3) + :Br:^{\ominus}$$

(Nucleophile) (1° alkyl halide) Substitution product (Leaving group)

Addition Reactions

- A reaction in which the reagent is added to the substrate to form a product is called addition reaction.
- It is characteristic of compounds containing multiple bonds

(> C = C <, – C ≡ C –, > C = O, –C ≡ N etc.).
- The reactivity of these compounds is due to the loosely held π electrons which are particularly available to a reagent that is seeking electrons like an electrophile or a free radical.
- As for example, hydrogen halides (HCl, HBr and HI) add to the double bond of alkenes.

$$R-C=C + HX \longrightarrow -\underset{X}{\overset{R}{C}}-\underset{H}{C}-$$

- Mechanisms for addition of hydrogen halide to an alkene involves the following two steps:

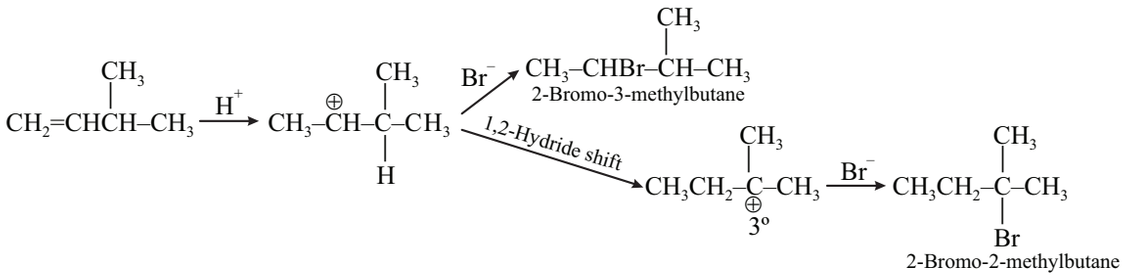
Step-I:

$$R-C=C + H-X \xrightarrow[(RDS)]{\text{Slow}} -\underset{\oplus}{\overset{R}{C}}-\underset{H}{C}- + X^-$$

Step-II:

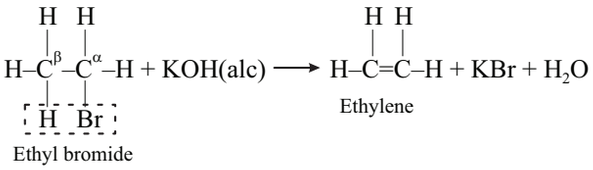
$$-\underset{\oplus}{\overset{R}{C}}-\underset{H}{C}- + X^- \xrightarrow{\text{Fast}} -\underset{X}{\overset{R}{C}}-\underset{H}{C}-$$

- The addition of HX to some alkenes give a mixture of the expected alkyl halide and an isomer formed by rearrangement.



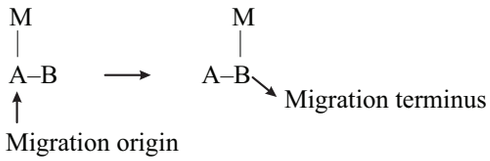
Elimination Reactions

- When two atoms or groups from adjacent carbons are eliminated with the formation of unsaturated compounds (alkene or alkyne), the reaction is called elimination reaction.
- Most commonly a leaving group (from the α– carbon) and a proton from the β– carbon are eliminated. Hence, the reaction is known as 1,2– or α,β– elimination or simply β–elimination.
- For example, dehydrohalogenation of alkyl halides with alcoholic solution of KOH.

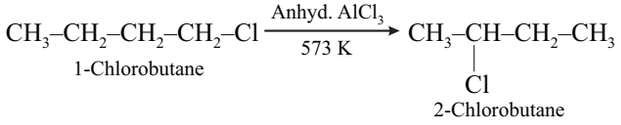


Rearrangement Reactions

- It involves the migration of an atom or a group from one atom to another within the molecule.
- The most common type are 1, 2– rearrangements in which the migrating group moves to the adjacent atom with its bonding pair of electron (nucleophilic rearrangement).



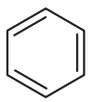
- For example, 1-chlorobutane rearranges to form 2-chlorobutane when heated in the presence of anhydrous $AlCl_3$ at 573K.



AROMATICITY

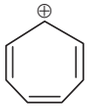
Aromatic Compounds:

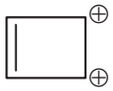
1. Molecule should be cyclic and planar (i.e. all ring-atoms of the molecule should be sp^2 hybridised).
2. Complete cyclic conjugation should be present in molecule.
3. The number of π-electrons which take part in conjugation in the ring should be equal to 4n + 2, where n = 0, 1, 2, 3.....

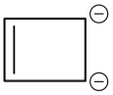
(i)  4n + 2 = 6 Aromatic benzenoid
n = 1

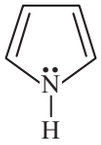
(ii) 4n + 2 = 2 Aromatic Non-benzenoid
n = 0

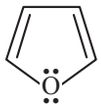
(iii) 4n + 2 = 6 Aromatic Non-benzenoid
n = 1

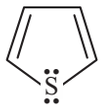
(iv)  4n + 2 = 6 Aromatic Non-benzenoid
n = 1

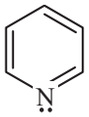
(v)  4n + 2 = 2 Aromatic Non-benzenoid
n = 0

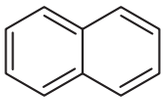
(vi)  4n + 2 = 6 Aromatic Non-benzenoid
n = 0

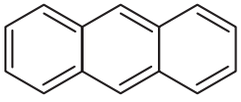
(vii)  4n + 2 = 6 Aromatic Non-benzenoid
n = 1

(viii)  4n + 2 = 6 Aromatic Non-benzenoid
n = 1

(ix)  4n + 2 = 6 Aromatic Non-benzenoid
n = 1

(x)  4n + 2 = 6 Aromatic Non-benzenoid
n = 1

(xi)  4n + 2 = 10 Aromatic benzenoid
n = 2

(xii)  4n + 2 = 14 Aromatic benzenoid
n = 3

Aromatic compounds burn with sooty flame due to high percentage of carbon.

Anti-aromatic compounds:

1. Molecule should be cyclic and planar.
2. Complete cyclic conjugation should be present in a molecule.

3. No. of π-electron which take part in conjugation in the ring should be equal to 4n, where n = 1, 2, 3.....

(i)
4n = 4
n = 1
Anti Aromatic

(ii)
4n = 4
n = 1
Anti Aromatic

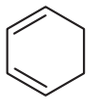
(iii)
Anti Aromatic
4n = 4
n = 1

Key Note

Anti Aromatic compounds do not exist at room temp. i.e., they are not stable at room temp.

Non-Aromatic compounds:

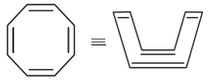
1. → Non planar

2.  → Incomplete conjugation

Annulenes: Monocyclic conjugated polyenes are called annulenes.

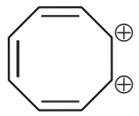
(i) annulene [4] → Anti Aromatic

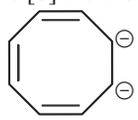
(ii) annulene [6] → Aromatic

(iii) annulene [8] →  Non-Aromatic

Key Note

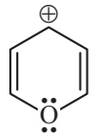
Following derivatives of Annulene [8] are aromatic.

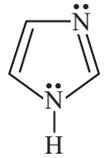

Planar
Aromatic

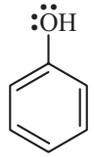

Planar
Aromatic

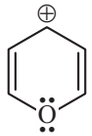
Train Your Brain

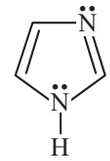
Example 5: Identify the nature of following compounds as Aromatic or non-aromatic.

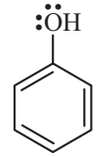
1. 

2. 

3. 

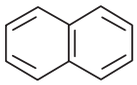
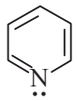
Sol. 1.  4n + 2 = 6 Aromatic
n = 1

2.  4n + 2 = 6 Aromatic
n = 1

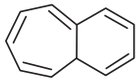
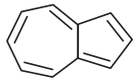
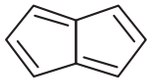
3.  4n + 2 = 6 Aromatic

Concept Application

15. Which of the following is aromatic hydrocarbon?

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

16. Identify the aromatic compound amongst the following:

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

17. Aromatic compounds burn with sooty flame because:

(*a*) They have a ring structure of carbon atoms.
(*b*) They have relatively high percentage of hydrogen.
(*c*) They resist reaction with oxygen or air.
(*d*) They have relatively high percentage of carbon.

ACIDIC AND BASIC STRENGTH

Basic Strength

(a) Arrhenius base: Base is a substance that can donate OH^- ions in H_2O.

(b) The Bronsted Lowry definition of bases: A base is a substance that can accept a proton (H^+).

(c) The Lewis definition of acids and bases: Lewis proposed that acids are electron pair acceptors and bases are electron pair donors.

Key Note

Base dissociation constant:

$$\ddot{B} + H_2O \longrightarrow BH^+ + OH^-$$

$$K_b = \frac{[BH^+][OH^-]}{[B]} \Rightarrow pK_b = -\log K_b$$

BASIC STRENGTH OF ORGANIC BASES

- Strength of bases is related to the ease of accepting a proton, which in turn depends on the availability of electron pair on the donor atom.
- More is the availability of electron pair, more easily the proton will be accepted and more will be the basic strength.

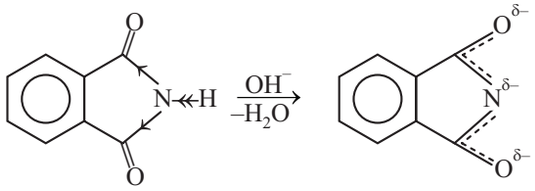
Aliphatic Amines

- If we compare the basicities of NH_3, $MeNH_2$, Me_2NH and Me_3N, then at a glance it would seem like $NH_3 < MeNH_2 < Me_2NH < Me_3N$ is the basicity order but the result is quite different in aqueous media.
  - The correct order is $Me_2NH > MeNH_2 > Me_3N > NH_3$. This order can be explained considering the solvation effect of the protonated amines.
  - But in absence of a polar protic solvent i.e. in the presence of non-polar solvent or gaseous phase, the order of basicity is $Me_3N > Me_2NH > MeNH_2 > NH_3$.
- Tetraalkylammonium salts, e.g. $R_4N^+I^-$ on treatment with moist silver oxide (AgOH) yield basic solutions comparable in strength with the mineral alkalies. This is readily understandable as $R_4N^+OH^-$ formed is completely ionized to give R_4N^+ and free OH^-.
- The effect of introducing electron–withdrawing groups, e.g. –Cl, $–NO_2$, close to a basic centre decreases the basicity, due to their electron–withdrawing inductive effect. Thus, the amine Tr is (trifluoro methyl) amine is found to be virtually non–basic due to the presence of three powerful electron–withdrawing $–CF_3$ groups.

Amides

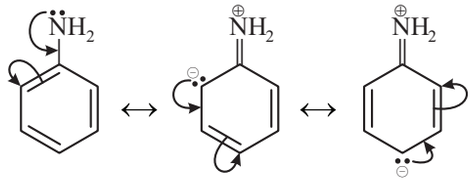
- The amides are found to be only very weakly basic in water because of the –I and –R effect of RCO^- group which makes the electron pair very slightly available on nitrogen atom.

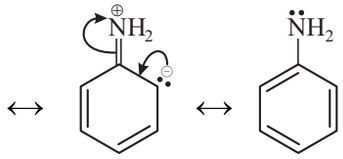
- If two >C=O groups are present, the resultant imides often become sufficiently acidic to form alkali metal salts. For example, benzene–1,2–dicarboximide is not basic but is acidic in nature because of the presence of two electron–withdrawing >C=O groups.



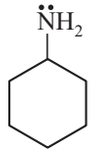
Aromatic Amines

- In aniline, owing to resonance, the lone pair of electrons on the nitrogen atom is less available for co-ordinating with a proton and at the same time, small positive charge on the nitrogen atom would tend to repel a proton. Alternatively, since there are more resonating structures possible for aniline itself than for the cation $C_6H_5NH_3$ the former will be stabilized with respect to the latter.





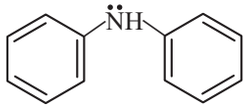
- Aniline is a weaker base than ammonia or cyclohexylamine. It is because of the fact that the electron pair on nitrogen is involved in delocalization, making it less available for donation.



Cyclohexylamine

Ammonia

- Diphenylamine is even a weaker base than aniline due to the presence of another phenyl group.

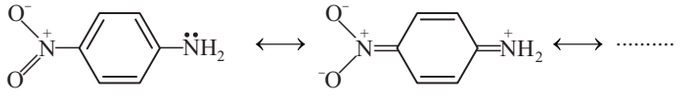


and triphenylamine (Ph_3N) is not basic at all by any means

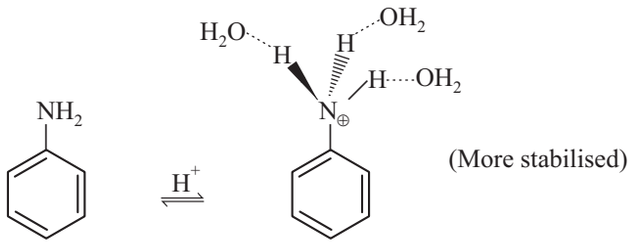
  - Introduction of alkyl group (like Me) on the nitrogen atom of aniline results in small increase in the basic strength. $C_6H_5NH_2 < C_6H_5NHMe < C_6H_5NMe_2$

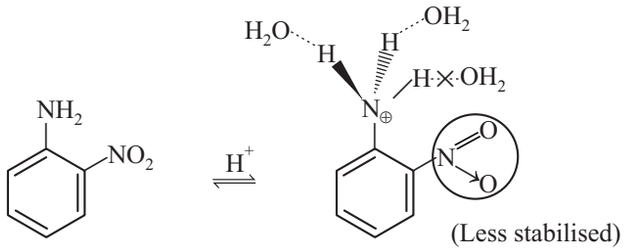
Substituted Aromatic Amines

- The effect of a ring substituent on basicity depends on whether the substituent is electron attracting or releasing, its ability to enter into resonance with the amino–group and its position.
- All the nitroanilines are weaker bases than aniline. The nitro–group has a strong –R effect and o– and p– nitroaniline are therefore, more resonance stabilised than aniline itself.

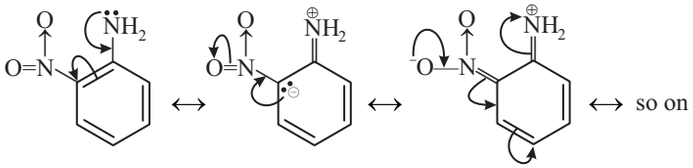


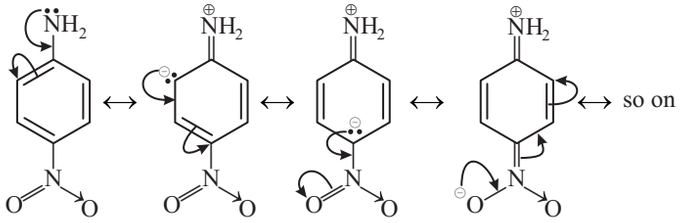
  - A m-nitro group cannot enter into resonance with the amino-group, but nevertheless m-nitroaniline is a much weaker base than aniline. In this case, nitro-group has a strong –I effect. This –I effect tends to draw into the ring the lone pair of N, thus decreasing its basicity.
- In ortho-nitro substituted aniline, the ortho effect is observed in the conjugate acid, which leads to decrease in basic strength of o-nitro aniline with respect to aniline and m- and p- nitro aniline.



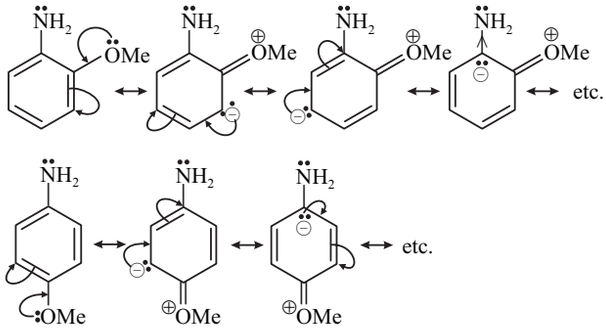


Thus, the order of basicity of nitroanilines is $C_6H_5NH_2 > m–NO_2C_6H_4NH_2 > p–NO_2C_6H_4NH_2 > o–NO_2C_6H_4NH_2$.





- When the ring contains an electron–releasing group, this reduces resonance of the NH_2 group with the ring and consequently should increase basicity. The methyl group raises the electron density more at the o– and p-positions than at the m-position. Thus, the carbon atom para to the methyl group has a high electron density and the lone pair on the nitrogen atom is therefore prevented to some extent from entering into resonance with the ring. A methyl group raises the electron density at the m-position only to a very small extent. Hence, resonance with the ring of NH_2 group at this position is prevented less than for the p-position. Consequently, a methyl group in the ring increases the basicity of the aniline, more so from the p–position than from the m-position. Thus, order of basicity of methyl anilines is $p–CH_3C_6H_4NH_2 > m-CH_3C_6H_4NH_2 > C_6H_5NH_2 > o–CH_3C_6H_4NH_2$. (Ortho effect is observed in the conjugate acid of o-methyl aniline, which decreases the basic strength.)
- The p–OMe group has a +R effect and its presence increases basicity. In the m–position, it can exert only –I effect and this decreases the basicity. The order of basicity of methoxy anilines is $p–CH_3OC_6H_4NH_2 > C_6H_5NH_2 > o–CH_3OC_6H_4NH_2 > m–CH_3OC_6H_4NH_2$. (Ortho effect is observed in the conjugate acid of o-methoxy aniline, which decreases the basic strength but not lower than m-methoxy aniline.)



Train Your Brain

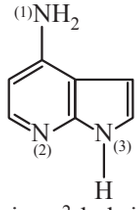
Example 6: Compare the basic strength of the following compounds:

(*i*) $C_2H_5O^-$ (*ii*) $C_2H_5^-$ (*iii*) $C_2H_5NH^-$

(*iv*) NH_2^- (*v*) F^-

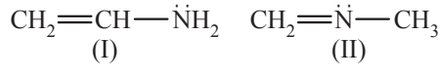
Sol. (*ii*) > (*iii*) > (*iv*) > (*i*) > (*v*)

Example 7: Which of the following group is most basic in the given compound?



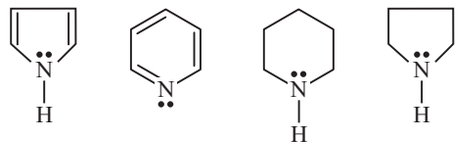
Sol. As the nitrogen is sp^2 hybridized, the lone pair is localised and hence it is most basic.

Example 8: Which of the following is a stronger base? Give reason to justify your answer.



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

Example 9: Compare the basicities of following compounds:



Sol. In pyrrole(I), the lone pair on nitrogen is involved in resonance, while in other three, it is free of resonance. So, (I) is least basic. Among (II), (III) and (IV), the lone pair on nitrogen in (II) lies in sp^2 hybrid orbital (which is smaller than sp^3 hybrid orbital and is held more strongly by the nucleus, so the electron pair is less available for donation), while in (III) and (IV) it lies in sp^3 hybrid orbital. Among (III) and (IV), (III) has greater electron releasing groups by positive inductive effect than (IV). So, the correct order of basicity is (III) > (IV) > (II) > (I).

Concept Application

18. The correct basic strength order of following anions is:

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

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

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

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

19. Find the order of basic strength if (R = Me)

(I) $R_4N^+OH^-$ (II) R_3N

(III) R_2NH (IV) RNH_2

(*a*) I > III > IV > II (*b*) IV > III > I > II

(*c*) II > IV > III > I (*d*) II > IV > I > III

Acidic Strength

(a) Arrhenius acid: An acid is a substance that can donate a proton (H^+) in H_2O.

(b) The Bronsted Lowry definition of acids: An acid is a substance that can donate a proton (H^+).

(c) The Lewis definition of acids and bases: Lewis proposed that acids are electron pair acceptors and bases are electron pair donors.

Acid dissociation constant (K_a):

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

$$K_{eq} = \frac{[A^-]\,[H_3O^+]}{[HA]\,[H_2O]}$$

$$K_a = \frac{[A^-]\,[H_3O^+]}{[HA]}$$

$$pK_a = -\log K_a$$

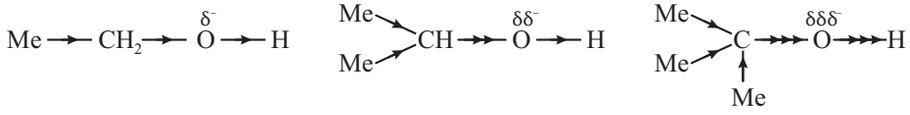
ACIDIC STRENGTH OF ORGANIC ACIDS

The factors responsible for influencing the acidity of an organic compound, H–X are

- The strength of the H–X bond
- The electronegativity of X
- Factors stabilizing X^- as compared to HX and the nature of the solvent.
- The most important factors among all is (c).
- More stable (less basic) the conjugate base is, more acidic the compound will be.
- On comparing the acidic strength of two compounds, the compound having greater acidity will have higher value of K_a and lower pK_a value.
- Now let us see using any of these factors, how we can predict the order of acidic strength for organic acids.

Alcohols

If we were to predict the order of acidic strength of ethanol, iso-propanol and tert-butanol,

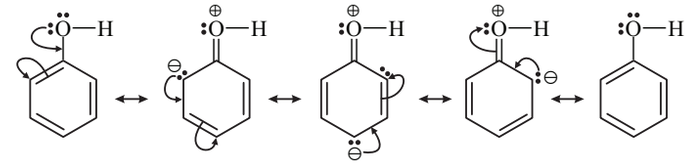


- As alkyl groups (methyl group) have a +I effect, the electron density at the oxygen atom will increase. More the number of alkyl groups, more will be the intensity of negative charge on oxygen.
- Greater the negative charge on the oxygen atom, the closer is the electron pair in the O-H bond driven to the hydrogen atom and consequently separation of a proton becomes increasingly difficult.
- Thus, the acidic strength of given alcohols will be in the order Ethanol > iso – propanol > t – butanol
- In general, electron releasing groups decreases the acidity while electron withdrawing group increases the acidity of a compound.

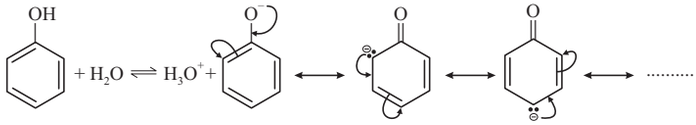
Phenols and Substituted Phenols

Phenol

- Because of resonance in phenol, the oxygen atom of the OH group acquires a positive charge and so proton release is facilitated, compared to an alcohol.



- When phenol ionizes, the phenoxide ion is also a resonance hybrid, but it is more stabilised by resonance than is the unionized phenol molecule because of spreading of negative charge only.
- In the unionized phenol, unlike charges are spread and so is less stable.



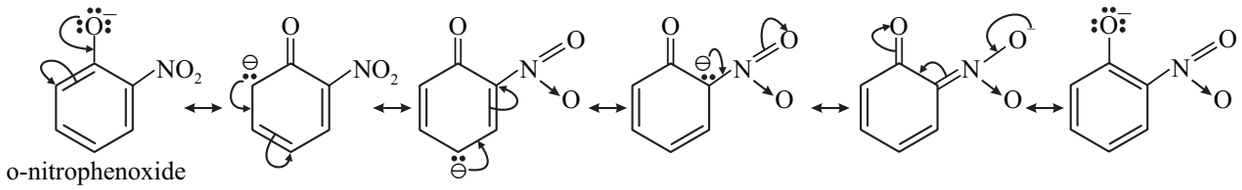
Phenols are stronger acids than alcohols. This is attributed to the fact that in phenoxide anion (obtained by the loss of proton from phenol), there is possibility of the delocalization of its negative charge through interaction with the p-orbitals of the aromatic

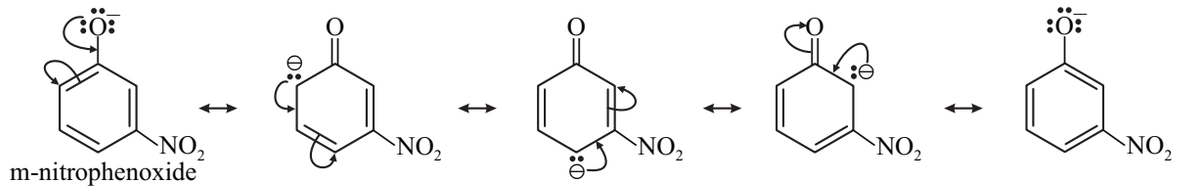
nucleus while alkoxide cannot be stabilized by such effect. Thus phenoxide is a weaker base than alkoxide. Consequently, the phenol would be stronger acid than alcohol.

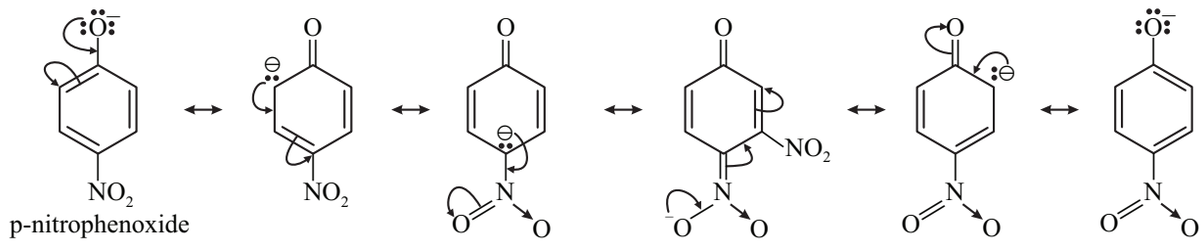
Substituted phenols

The effect of a ring substituent on the acid strength of phenol depends on whether the group is electron attracting or releasing, its ability to enter into resonance with the hydroxyl group and its position.

- Effects in the o-position are similar to those in the p-position, but there are added complications due to the steric effect and hydrogen bonding (when this is possible). Effects from meta position are altogether different from ortho and para position.
- In general, the presence of electron withdrawing groups in phenol increases its acidity while the presence of electron releasing groups decreases the acidity of phenol.
- Let us compare the acidic strength of o–, m– and p–methylphenols.
- The methyl group decreases the acid strength of phenol from all ring positions. The methyl group is electron releasing and so release of a lone pair from oxygen of the OH group in the unionized phenol or from the O^- in the phenoxide ion into the ring is opposed. This results in diminished resonance in the contributing structures and consequently the phenoxide ion is more resonance stabilised with respect to phenol than is the methylphenoxide ion with respect to methylphenol.
- Hence, phenol is a stronger acid than all methylphenols. The order of acidity of methyl phenols is phenol > m–methyl phenol > p–methylphenol > o–methyl phenol.
  - Now, let us compare the acidic strength of o–, m– and p– nitrophenols. The corresponding phenoxide ions obtained from the three nitrophenols would be stabilized by delocalization as







- From the structures of phenoxide ions, it is evident that o– and p–nitrophenoxides are more extensively stabilized with respect to m–nitro phenoxide (as additional contributing structure is obtained by the dispersal of negative charge over oxygen atom of NO_2 group in o– and p– nitrophenoxide but not in m–nitrophenoxide).
- Thus, corresponding o– and p-nitrophenols are much stronger acids than m-nitrophenol.
- A meta–nitro group cannot enter into resonance with the hydroxyl group but can exert –I effect for this position. Hence, meta-nitrophenol is also stronger acid than phenol.
- Out of o– and p–nitrophenols, p–nitrophenol is slightly stronger acid than o– isomer as o– isomer involves intramolecular hydrogen bonding, thus having a reduced tendency to release proton.
- The order of acidic strength of the nitrophenols is **p–nitrophenol > o–nitrophenol > m–nitrophenol > phenol**
  - The cumulative effect of three nitro groups in the 2, 4, 6 positions is shown by the fact that 2, 4,6– trinitrophenol (picric acid) is a very strong acid.

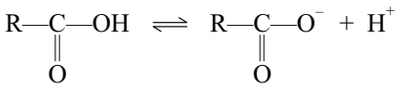
Key Note

- All the halophenols are stronger acids than phenol and it follows that the –I effect of halogen atom is greater than its +R effect.
- The order of acidity of halophenols is **o–halophenol > m–halophenol >p–halophenol > phenol**.
- Among methoxy phenols, the order of acidity is: **o–methoxyphenol > phenol > m–methoxy phenol > p–methoxy phenol.**

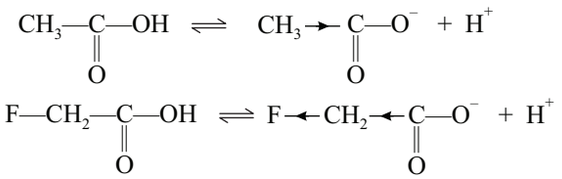
Aliphatic Carboxylic Acids

- The aliphatic carboxylic acids are much stronger acids than phenols and alcohols.

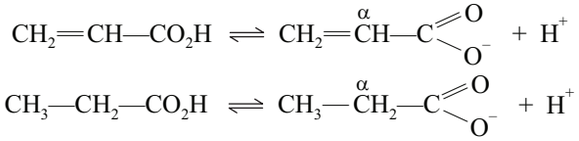
- This is attributed to the fact that the carboxylate ion (obtained by the loss of proton from carboxylic acid) is relatively more stabilized by delocalization than the phenoxide and alkoxide ions with respect to their undissociated molecules.



- The delocalization of the negative charge in the carboxylate anion involves structures of identical energy content (as the negative charge resides on more electronegative atom, oxygen) while in phenoxide anion, the negative charge also resides on the less electronegative atom (carbon) making these structures of high energy content with respect to those structures in which the negative charge is on oxygen.
  - The presence of electron-withdrawing substituents in simple aliphatic acids increases their acidity while the electron-releasing substituents have reverse effect.
  - For instance, let us compare the acidic strength of fluoroacetic acid and acetic acid.



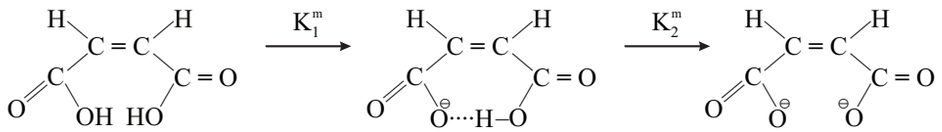
  - The fluoro acetate ion is stabilized more due to strong –I effect of fluorine, with respect to acetate ion. Hence, fluoro acetate ion is less basic than acetate ion, thereby making fluoroacetic acid stronger than acetic acid.
  - If there is a doubly bonded carbon atom adjacent to the carboxyl group, the acidic strength is increased. This will be evident if we compare the acidic strength of propanoic acid and propenoic (acrylic) acid.



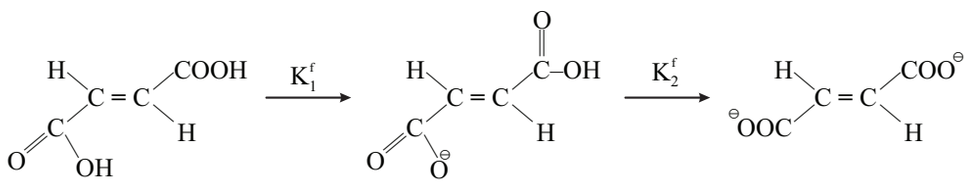
- As we know that unsaturated α-carbon atom in propenoate ion is sp^2 hybridised, which means that electrons are drawn closer to the carbon nucleus than in a saturated, sp^3 hybridised α–carbon atom, due to greater s-contribution in the sp^2 hybrid orbital.
- The result is that sp^2 hybridised carbon atoms are less electron-donating than saturated hybridised ones, thus, propanoate ion will be comparatively less stabilized than propenoate ion, thereby making propenoic acid stronger than propanoic acid (but propanoic acid will still be weaker than methanoic acid).
  - If there is a triply bonded carbon atom adjacent to carboxyl group, the acidic strength is greater with respect to the presence of a doubly bonded carbon atom adjacent to $–CO_2H$ group.
- This is attributed to the fact that sp hybridized carbon atoms are less electron–releasing than sp^2 hybridized carbon atoms.
- Some other trends of acidity are:
  (a) $HCO_2H > CH_3CO_2H > CH_3CH_2CO_2H > \ldots\ldots$
  (b) $HO_2C–CO_2H > HO_2C–CH_2–CO_2H > HO_2C–CH_2CH_2–CO_2H > \ldots$
- These trends reflect that in any homologous series, when we move from lower members to higher members, the acidity decreases.

Comparison between two Geometrical Isomers

Maleic acid:



Fumaric acid:



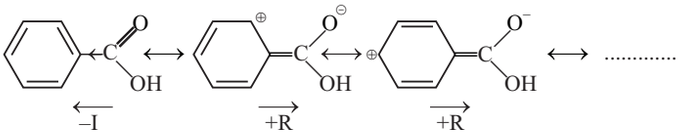
- $K_1^m > K_1^f$, since the conjugate base of maleic acid is stabilised by intramolecular H bonding but not that of fumaric acid.
- But $K_2^f > K_2^m$ since in maleate ion, after donation of $H^{\oplus}$ two $–COO^{\ominus}$ groups face each other and would be destabilised due to repulsion making the system unstable. In fumarate ion, this repulsion is minimised because two CO_2^- groups are on opposite side.

Aromatic Carboxylic Acids

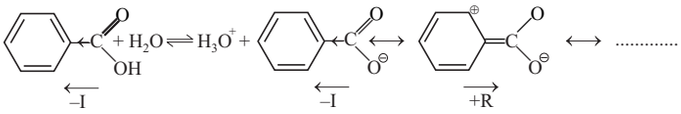
- It has been pointed out that replacement of the hydrogen atom in formic acid by an alkyl group weakens the strength of the acid and the greater the +I effect of the R group, the weaker is the acid.
- Phenylacetic acid, $PhCH_2CO_2H$ is stronger than acetic acid and therefore the phenyl group has an overall –I effect.

Benzoic acid

On the other hand, benzoic acid is weaker than formic acid. In this case, the phenyl group has an overall electron releasing effect (which is smaller than that of methyl group). These apparently contradictory results may be explained as follows. When the carboxyl group is directly attached to the nucleus, the resonance effect (+R) overcomes the -I effect (in phenylacetic acid, the phenyl group is insulated from the carboxyl group by a CH_2 group and so the +R effect is not possible):

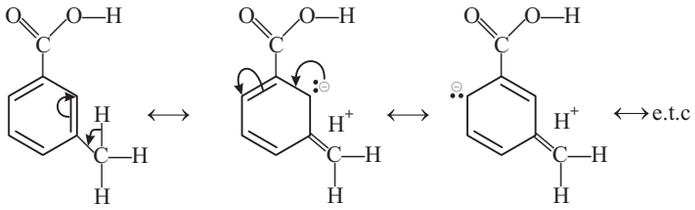


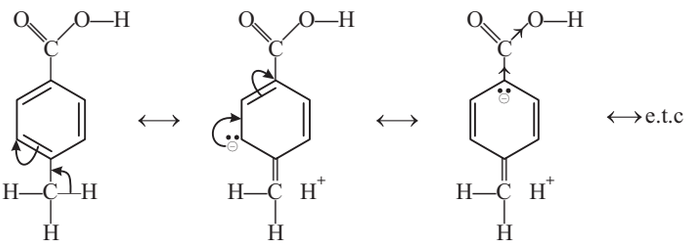
- This prevents to a large extent, the lone pair on the O atom of the OH group from entering into resonance with the CO group.
- The result is a smaller positive charge on the O atom of the OH group and so proton release is more difficult than in formic acid.
- The fact that benzoic acid is stronger than acetic acid means that [–I+(+R)] of phenyl group < [+I+(+H)] of the methyl group.
- The same arguments may be applied to ionised benzoic acid.



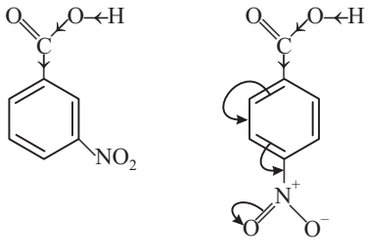
Substituted Benzoic acids

- Now let us consider substituted benzoic acids. At this point, we will consider the effect of substituents from m–and p–positions only.
- First let us take methyl substituted benzoic acids. As the methyl group has +I effect, so the net result will be to increase the +R effect in the m– or p–tolyl group.
  - Since, the inductive effect decreases with distance, so the +I effect of CH_3 from para position would be less than the +I effect of CH_3 group from meta position. Thus, the electron–density in the O–H bond of m–methyl benzoic acid would be greater than that in p–methyl benzoic acid. Accordingly, the p–isomer should be more acidic than the m–isomer. But in real practice, the order is reverse.
  - Actually, we have ignored the hyperconjugation effect of CH_3 group. Due to hyperconjugation effect of CH_3 in p–isomer, the electron density in the O–H bond would be increased greatly with respect to that in m–isomer.

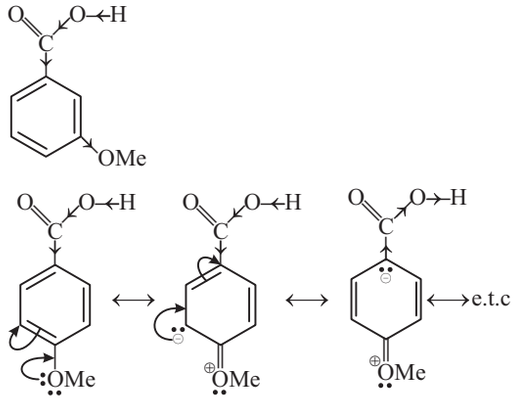




  - Thus, the release of proton is facilitated easily in m–isomer than in p–isomer.
- Secondly, let us take nitro substituted benzoic acids. As the $–NO_2$ group exerts –I and –R effect (both reinforcing each other), the electron–density from the O–H bond would be withdrawn, thus destabilizing the O–H bond and making m– and p– nitro benzoic acids stronger than benzoic acid.



  - As it is clear that $–NO_2$ group exerts its electron withdrawing resonance effect from the p–position and not from m–position, thus withdrawal of electron density from the O–H bond is greater in p-nitrobenzoic acid than m–nitrobenzoic acid. Thus, **p–nitrobenzoic acid is stronger acid than m–nitrobenzoic acid**.
- Thirdly, we compare the acid strength of m– and p– methoxy benzoic acid. –OMe group exerts –I and +R effects. The electron–releasing resonance effect (+R) is operative in p–methoxy benzoic acid and not in m–methoxy benzoic acid while – I effect is operative in both the isomers. Thus, the electron density is greatly increased in the –O–H bond in p–isomer than in m–isomer, thereby making m–isomer stronger acid than p–isomer

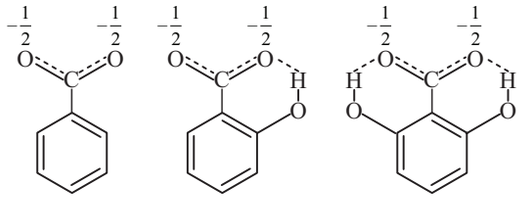


Ortho-effect

- This is a steric effect that is shown by o–substituted benzoic acids. **Nearly all o–substituted benzoic acids are stronger than benzoic acid due to ortho effect irrespective of the polar nature of the o–substituent**.
  - As we have seen that benzoic acid is a resonance hybrid and so the carboxyl group is coplanar with the ring. An o–substituent tends to prevent this coplanarity. Thus, resonance is diminished (or prevented) and so the O atom of the OH group has a greater positive charge, resulting in increased acid strength. It follows from this that greater the steric inhibition of resonance, the stronger is the acid. Support for this is the following order of strengths of substituted benzoic acids.: 2, 6–di–Me > 2– t–Bu > 2–Me
  - Here again, if we consider the stability of the anion, steric inhibition of resonance prevents the +R effect of the ring coming into operation and since this weakens acid strength, its absence results in increased acid strength.
- o–Hydroxybenzoic acid (salicylic acid) is far stronger than the corresponding m– and p– isomers. Steric inhibition of resonance cannot explain this very large increase, since the

corresponding methoxybenzoic acids all have almost similar acid-strengths. The carboxylate ions of o–hydroxybenzoic acid is stabilised by intramolecular hydrogen bonding while such hydrogen bonding is not feasible in o–methoxy benzoic acid and support for this is given by the following order of acid strength, 2, 6–di–OH > 2–OH > benzoic acid

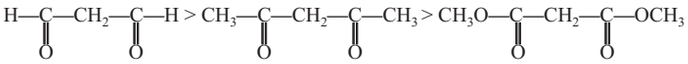
It can be seen that two hydrogen bonds would be expected to bring about more stabilization than one hydrogen bond.

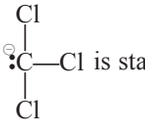
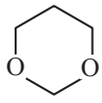


- Including ortho effect, the order of acidity of some substituted benzoic acids is given as:
  - **o-nitro benzoic acid > p-nitrobenzoic acid > m-nitro benzoic acid > benzoic acid.**
  - **o-methyl benzoic acid > benzoic acid > m–methyl benzoic acid > p-methyl benzoic acid**
  - **o-methoxy benzoic acid > m-methoxy benzoic acid > benzoic acid > p-methoxy benzoic acid.**

Carbon Acids

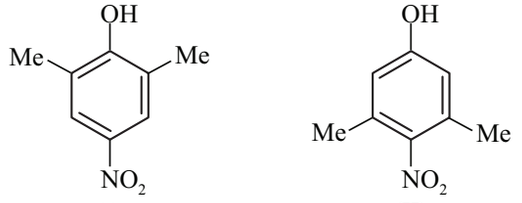
- Carbon acids are those compounds in which H^+ is lost from a carbon. Generally, **C-acids are weaker than most O-acids**.
- A CH_2 group flanked between two electron withdrawing groups has acidic hydrogen. Aldehydic group is more electron withdrawing than ketonic group, which is more electron attracting than ester groups. Thus, order of acidity of carbon acids is



- $CHCl_3$ is more acidic than CHF_3 because the conjugate base of $CHCl_3$ i.e.  is stabilised by - I effect of Cl as well as by pπ – dπ delocalization (which is absent in $\overset{\ominus}{C}F_3$: due to the absence of d–orbital in F).
- For the same reason, is more acidic than .

Train Your Brain

Example 10: Which of the following phenol is more acidic?

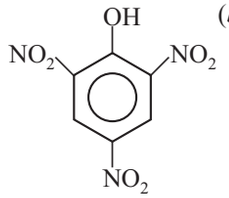
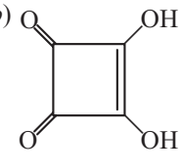


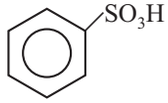
(I) (II)

Sol. Compound (I) is more acidic than compound (II) because NO_2 group can show –I and –R effects in compound (I) while NO_2 group will show only –I effect in compound (II). NO_2 group in compound (II) is unable to show resonance effect because of the steric crowding by adjacent methyl groups.

Example 11: Which of the following would produce effervescence with sodium bicarbonate?

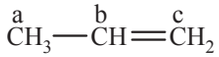
(pK_{a1} of H_2CO_3 = 6.3)

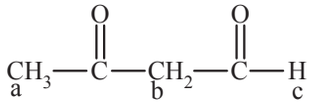
(*a*)  (*b*) 

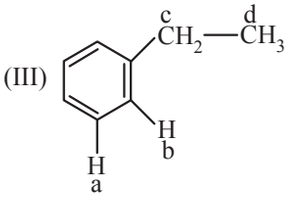
(*c*)  (*d*) All of these

Sol. All the given acids are stronger than carbonic acid and will thus produce effervescence on reacting with sodium bicarbonate as HCO_3^- will pull out H^+ from them to form H_2CO_3 or CO_2 gas as effervescences.

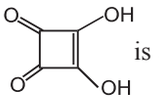
Example 12: Which 'H' atom is most acidic in the following compounds?

(I) 

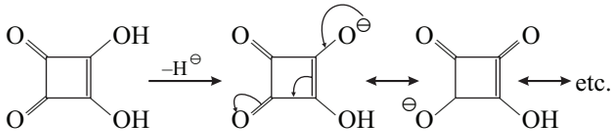
(II) 

(III) 

Sol. I - a, II - b, III - c; (acidic strength ∝ stability of conjugate base)

Example 13: The given compound; X =  is a strong acid. Justify this statement.

Sol.



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

Concept Application

20. Among the following compounds, the strongest acid is:

(*a*) $HC \equiv CH$ (*b*) C_6H_6

(*c*) C_2H_6 (*d*) CH_3OH

21. Which of the following is not correct decreasing order of K_a?

(*a*) $CH_4 > NH_3 > H_2O > HF$

(*b*) $CH_3–OH > CH_3–NH_2 > CH_3–F > CH_3–CH_3$

(*c*) $HI > HBr > HCl > HF$

(*d*) $PhOH > H_2O > C_2H_5OH > CH_3–C\equiv CH$

22. Which of the following acid has the smallest dissociation constant?

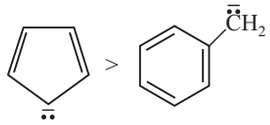
(*a*) $CH_3–\underset{\displaystyle NO_2}{\underset{|}{CH}}–COOH$

(*b*) $O_2N–CH_2–CH_2–COOH$

(*c*) $Cl–CH_2–CH_2–COOH$

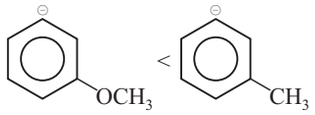
(*d*) $NC–CH_2–CH_2–COOH$

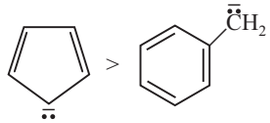
1. Which of the following is/are correct order of stability of carbanion?

(*a*)  >

(*b*) $CH_3—CH_2—\overset{\ominus}{C}H_2 > CH_3—\underset{CH_3}{\overset{\ominus}{C}H}$

(*c*) $\overset{\ominus}{C}F_3 > \overset{\ominus}{C}Cl_3$

(*d*) 

Sol. (*a*) 

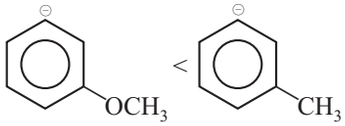
(Due to aromatic nature of former)

(*b*) $CH_3—CH_2—\overset{\ominus}{C}H_2 > CH_3—\underset{CH_3}{\overset{\ominus}{C}H}$

(1° carbanion is more stable than 2° carbanion)

(*c*) $\overset{\ominus}{C}F_3 > \overset{\ominus}{C}Cl_3$

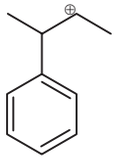
(Due to delocalization of e^- in vacant d-orbital of –Cl atom)

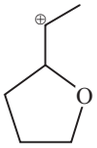
(*d*) 

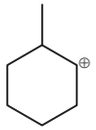
(Due to –I effect)

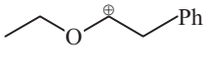
Therefore, option (*a,b*) are the correct answers.

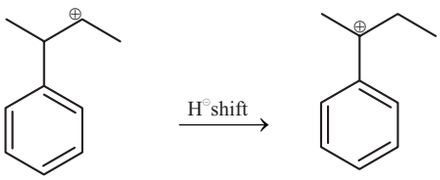
2. In which of the following, carbocation/s rearrangement takes place?

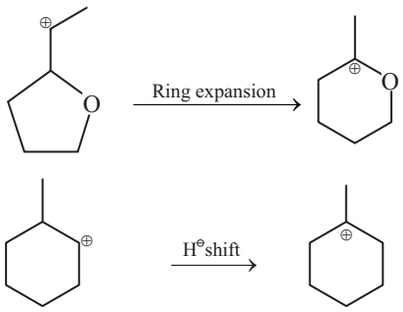
(*a*) 

(*b*) 

(*c*) 

(*d*) 

Sol. 



Therefore, option (*a,b,c*) are the correct answers.

3. Which of the following acid has highest tendency to ionise in aqueous solution?

(*a*) HCOOH (*b*) CH_3COOH

(*c*) FCH_2COOH (*d*) $BrCH_2COOH$

Sol. Acidity $\propto$ –I effect

F shows greater –I effect, hence acidity increases.

Therefore, option (*c*) is the correct answer.

4. Among α-nitro acetic acid (1), α-fluoroacetic acid (2) α-bromoacetic acid (3), α-cyanoacetic acid (4), the correct order of increasing acidic strength is:

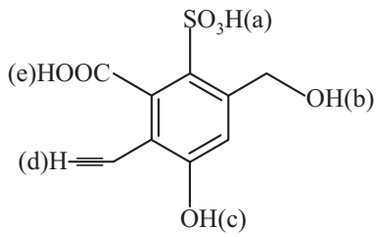
(*a*) 3 < 2 < 4 < 1 (*b*) 1 < 2 < 3 < 4

(*c*) 2 < 1 < 3 < 4 (*d*) 4 < 1 < 2 < 3

Sol. Due to –I effect order: $–NO_2 > –CN > –F > –Br$

Therefore, option (*a*) is the correct answer.

5. Ease of proton release in decreasing order is:



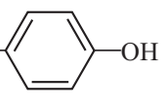
(*a*) a > c > e > d > b (*b*) a > e > c > b > d

(*c*) a > d > c > b > e (*d*) a > c > b > d > e

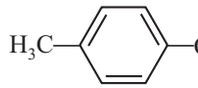
Sol. Due to corresponding order of stability of conjugate base.

Therefore, option (*b*) is the correct answer.

6. Which of the following phenols has the largest pK_a value?

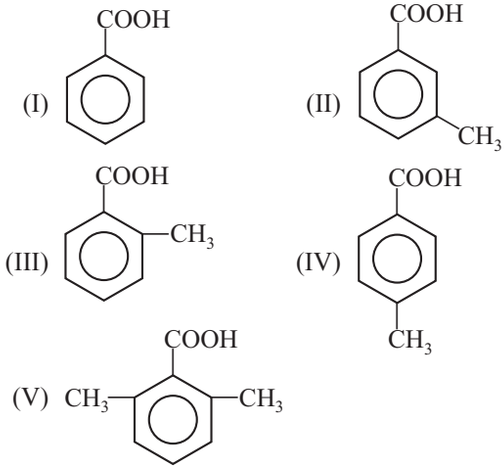
(*a*)  (*b*)

(*c*) (*d*)

Sol.  is least acidic & hence has lowest K_a value, so this compound has largest pK_a value.

Therefore, option (*c*) is the correct answer.

7. What is the correct acidity order of the following compounds?



(*a*) I > II > III > IV > V (*b*) II > III > IV > V > I

(*c*) V > III > I > II > IV (*d*) V > III > II > I > IV

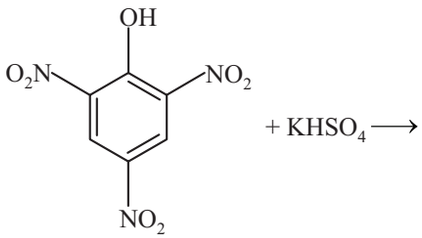
Sol. Due to ortho effect in ortho substituted benzoic acids, acidity increases.

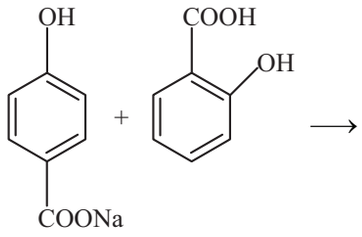
Therefore, option (*c*) is the correct answer.

8. The feasible reaction among the following is:

(*a*) $CH_3COOH + NaCl \rightarrow$

(*b*) $C_6H_5COOH + KBr \rightarrow$

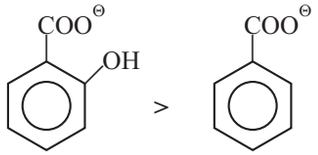
(*c*) 

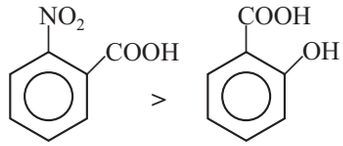
(*d*) 

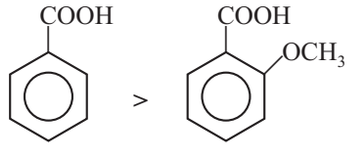
Sol. Salicylic acid is more acidic than p-hydroxy benzoic acid.

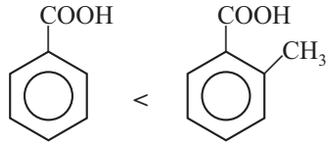
Therefore, option (*d*) is the correct answer.

9. Select the incorrect order amongst the following:

(*a*)  .....(Stability)

(*b*)  .....(Acidic-strength)

(*c*)  .....(Acidic-strength)

(*d*)  .....(Acidic-strength)

Sol. (*a*) → Intramolecular H-bonding

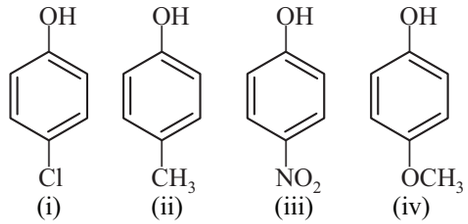
(*b*) → NO_2 is more e^- withdrawing group.

(*c*) → Due to ortho effect.

(*d*) → Due to ortho effect.

Therefore, option (*c*) is the correct answer.

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



(*a*) (i) > (ii) > (iii) > (iv) (*b*) (iii) > (i) > (ii) > (iv)

(*c*) (iv) > (iii) > (i) > (ii) (*d*) (ii) > (iv) > (i) > (iii)

Sol. Electron withdrawing group increases acidic strength and electron releasing group decreases acidic strength.

– NO_2 exerts –I, –R

– Cl exerts predominant –I along with +R

– CH_3 exerts +I, +H

– OCH_3 exerts predominant +R along with –I.

Therefore, option (*b*) is the correct answer.

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

(*a*) B > A > D > C (*b*) B > D > C > A

(*c*) A > B > C > D (*d*) A > C > B > D

Sol. CF_3-COOH > CCl_3-COOH > HCOOH > CH_3COOH (decreasing acidity order).

Therefore, option (*a*) is the correct answer.

12. In which of the following, delocalisation of π-electron is possible?

(*a*) $CH_2 = CH - CH_2 - CHO$

(*b*) $CH_2 = CH - CH = O$

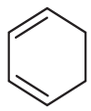
(*c*) $CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$

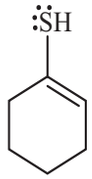
(*d*) $CH_2 = CH - CH_2 - CH = CH_2$

Sol. Due to presence of conjugated system.

Therefore, option (*b*) is the correct answer.

13. Which of the following species has conjugation?

(*a*) 

(*b*) 

(*c*) $CH_2 = C = CH - \ddot{N}H_2$ (*d*) All of these

Sol. (*a*), (*b*) and (*c*) all are conjugated.

Therefore, option (*d*) is the correct answer.

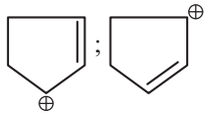
14. Which of the following is not a pair of resonating structures?

(*a*) $H - C \equiv \overset{\oplus}{N}H$; $H - \overset{\oplus}{C} = \ddot{N}H$

(*b*) $CH_3CH = CHCH_3$; $CH_3CH_2CH = CH_2$

(*c*) $CH_3 - \underset{\underset{O^{\ominus}}{|}}{C} = CH - \underset{\underset{O}{||}}{C} - CH_3$;

$CH_3 - \underset{\underset{O}{||}}{C} - \overset{\ominus}{C}H - \underset{\underset{O}{||}}{C} - CH_3$

(*d*) 

Sol. These are positional isomers

Therefore, option (*b*) is the correct answer.

15. $CH_2 = CH - CH = CH - CH_3$ (I) is more stable than $CH_3 - CH = C = CH - CH_3$ (II) because

(*a*) There is resonance in I but not in II.

(*b*) There is tautomerism in I but not in II.

(*c*) There is hyperconjugation in I but not in II.

(*d*) II has more canonical structures than I.

Sol. (I) $\overset{\curvearrowleft}{CH_2}=CH-\overset{\curvearrowleft}{CH}=CH-CH_3 \longleftrightarrow$

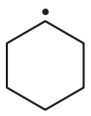
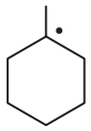
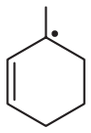
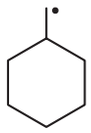
$\overset{\ominus}{C}H_2 - CH = CH - \overset{\oplus}{C}H - CH_3$

(II) $CH_3-CH = C = CH-CH_3$

Here in structure (I) resonance occurs but not in II[nd].

Therefore, option (*a*) is the correct answer.

16. Most stable radical among the following is:

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

Sol. CH_3 resonance stabilised 3º free radical is more stable.

Therefore, option (*c*) is the correct answer.

INTRODUCTION, INDUCTIVE EFFECT

1. A straight chain hydrocarbon has the molecular formula C_8H_{10}. The hybridisation for the carbon atoms from one end of the chain to the other are respectively sp^3, sp^2, sp^2, sp^3, sp^2, sp^2, sp and sp. The structural formula of the hydrocarbon would be

(*a*) $CH_3—C \equiv C—CH_2—CH = CH—CH = CH_2$

(*b*) $CH_3—CH_2—CH = CH—CH_2—C \equiv C—CH = CH_2$

(*c*) $CH_3—CH = CH—CH_2—C \equiv C—CH = CH_2$

(*d*) $CH_3—CH = CH—CH_2—CH = CH—C \equiv CH$

2. Carbon atoms in the compound, $(CN)_4C_2$ are

(*a*) *sp* hybridized (*b*) sp^2 hybridized

(*c*) *sp* and sp^2 hybridized (*d*) *sp*, sp^2 and sp^3 hybridized

3. Toluene has

(*a*) 6σ and 3π-bond (*b*) 9σ and 3π-bond

(*c*) 9σ and 6π-bond (*d*) 15σ and 3π-bond

4. Which one of the following order is correct regarding the negative inductive effect of the substituents?

(*a*) $-NR_2 < -OR > -F$

(*b*) $-NR_2 > -OR > -F$

(*c*) $-NR_2 < -OR < -F$

(*d*) $-NR_2 > -OR < -F$

5. The order of decreasing stability of the carbanions is

(I) $(CH_3)_3\ddot{\underset{\cdot\cdot}{C}}$ (II) $(CH_3)_2\ddot{\underset{\cdot\cdot}{C}}H$

(III) $CH_3\ddot{\underset{\cdot\cdot}{C}}H_2$ (IV) $C_6H_5\ddot{\underset{\cdot\cdot}{C}}H_2$

(*a*) I > II > III > IV

(*b*) IV > III > II > I

(*c*) IV > I > II > III

(*d*) I > II > IV > III

6. Decreasing order of –I effect of the triad

[$-NO_2$, $-\overset{\oplus}{N}H_3$, –CN] is:

(*a*) $-\overset{\oplus}{N}H_3 > -NO_2 > -CN$ (*b*) $-\overset{\oplus}{N}H_3 > -CN > NO_2$

(*c*) $-CN > -NO_2 > -\overset{\oplus}{N}H_3$ (*d*) $-NO_2 > -CN > -\overset{\oplus}{N}H_3$

7. Which of the following carbocation is least stable?

(*a*) $CH_3—\overset{\oplus}{C}H—CH_3$ (*b*) $CH_3—CH_2—\overset{\oplus}{C}H_2$

(*c*) $CH_3—\overset{\oplus}{\underset{\displaystyle CH_3}{\underset{|}{C}}}—CH_3$ (*d*) $CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}—\overset{\oplus}{C}H—C_6H_5$ (CH_3 below C)

8. Which of the following can act as an electrophile?

(*a*) H_2O (*b*) SO_3 (*c*) NH_3 (*d*) ROR

9. Which of the following can act as an electrophile?

(*a*) $AlCl_3$ (*b*) CN^- (*c*) NH_3 (*d*) CH_3OH

10. Strongest nucleophile among the following is

(*a*) RNH_2 (*b*) ROH (*c*) $C_6H_5O^-$ (*d*) CH_3O^-

11. Inductive effect involves:

(*a*) Delocalisation of σ - electrons

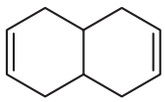
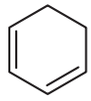
(*b*) Partial displacement of σ - electrons

(*c*) Delocalisation of π - electron

(*d*) Displacement of lone pair electrons

RESONANCE, HYPERCONJUGATION, AROMATICITY

12. Which of the following will show aromatic behaviour?

(*a*)  (*b*) 

(*c*) (*d*)

13. Which of the following is the most stable cation?

(*a*) $Ph_3\overset{+}{C}$ (*b*) $Ph_2\overset{+}{C}H$

(*c*) $Ph_3C\overset{+}{C}H_2$ (*d*) $Ph\overset{+}{C}H_2$

14. Which of the following resonating structures of 1-methoxy-1, 3-butadiene is least stable?

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

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

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

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

15. Which of the following is the decreasing order of stability?

(i) $CH_3–\overset{\oplus}{C}H–CH_3$

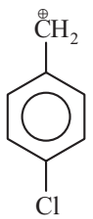
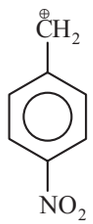
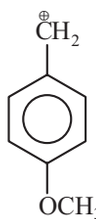
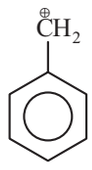
(ii) $CH_3–\overset{\oplus}{C}H–O–CH_3$

(iii) $CH_3–\overset{\oplus}{C}H–CO–CH_3$

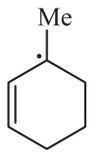
(*a*) (ii) > (i) > (iii) (*b*) (i) > (ii) > (iii)

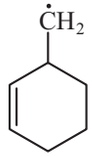
(*c*) (iii) > (ii) > (i) (*d*) (ii) > (iii) > (i)

16. Most stable carbocation amongst the following is:

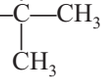
(*a*)  (*b*)  (*c*)  (*d*) 

17. Which one is the most stable free radical?

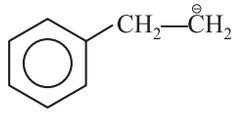
(*a*) 

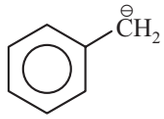
(*b*) 

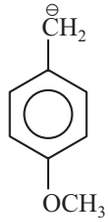
(*c*) $CH_2 = CH—\dot{C}H_2$

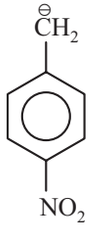
(*d*) 

18. The most stable carbanion among the following is

(*a*) 

(*b*) 

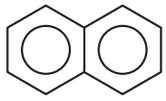
(*c*) 

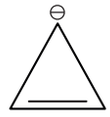
(*d*) 

19. Among the following, the aromatic compound/species is

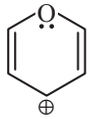
(*a*)

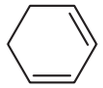
(*b*)

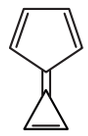
(*c*) 

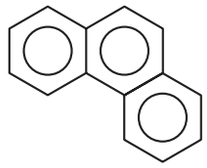
(*d*) 

20. Which of the following is not an aromatic compound?

(*a*) 

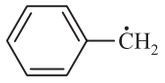
(*b*) 

(*c*) 

(*d*) 

21. The correct order of stability of following carbon free radicals is:

$(CH_3)_3\dot{C}$
(I)


(II)

$CH_3CH_2\dot{C}H_2$
(III)

$\dot{C}H_3$
(IV)

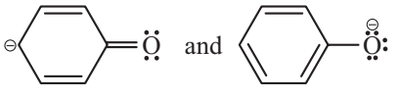
(*a*) I > II > III > IV

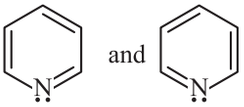
(*b*) IV > III > II > I

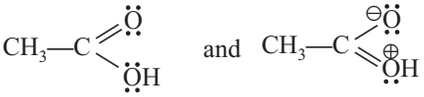
(*c*) II > III > I > IV

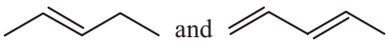
(*d*) II > I > III > IV

22. Which of the following is not a pair of resonating structures?

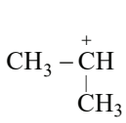
(*a*) 

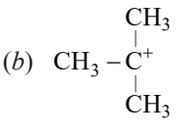
(*b*) 

(*c*) 

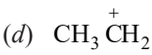
(*d*) 

23. Which amongst the following is the most stable carbocation?

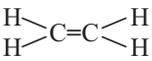
(*a*) 

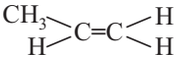
(*b*) 

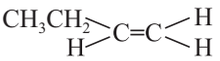
(*c*)

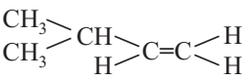
(*d*) 

24. Which of the following is most stable alkene?

(*a*) 

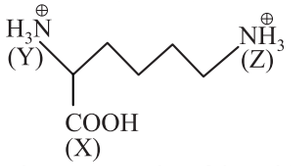
(*b*) 

(*c*) 

(*d*) 

ACIDIC STRENGTH AND BASIC STRENGTH

25. In the compound given below

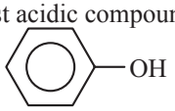


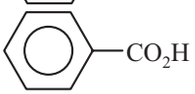
The correct order of the acidity of the positions (X), (Y) and (Z) is

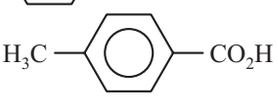
(*a*) (Z) > (X) > (Y) (*b*) (X) > (Y) > (Z)

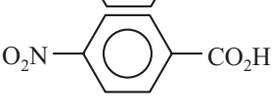
(*c*) (X) > (Z) > (Y) (*d*) (Y) > (X) > (Z)

26. Most acidic compound among the following is:

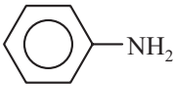
(*a*) 

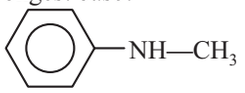
(*b*) 

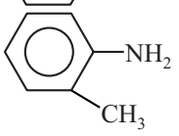
(*c*) 

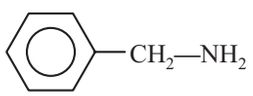
(*d*) 

27. Which of the following is the strongest base?

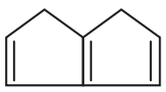
(*a*) 

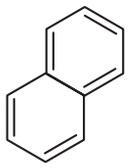
(*b*) 

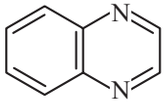
(*c*) 

(*d*) 

28. Which of the following is an aromatic compound?

(*a*) 

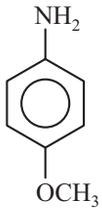
(*b*) 

(*c*) 

(*d*) Both (*b*) and (*c*)

29. Which of the following compound is least basic?

(*a*)

(*b*) 

(*c*)

(*d*)

30. Which of the following orders of acidic strength is correct?

(*a*) RCOOH > ROH > HOH > HC ≡ CH

(*b*) RCOOH > HOH > ROH > HC ≡ CH

(*c*) RCOOH > HOH > HC ≡ CH > ROH

(*d*) RCOOH > HC ≡ CH > HOH > ROH

31. Find the strongest acid among the following compounds:

(*a*) $CH_3\underset{\displaystyle NO_2}{\underset{|}{C}}HCOOH$ (*b*) $CH_3—\underset{\displaystyle Cl}{\underset{|}{C}}H—COOH$

(*c*) CH_3CH_2COOH (*d*) $CH_3\underset{\displaystyle C\equiv N}{\underset{|}{C}}HCOOH$

32. Find the correct order of K_a among the following compounds

$HC \equiv C—CH_2—COOH$ (I) $CH_2 = CHCH_2COOH$ (II)

$CH_3CH_2CH_2COOH$ (III)

(*a*) I > II > III (*b*) II > I > III

(*c*) III > II > I (*d*) I > III > II

INTRODUCTION TO REACTION MECHANISM

33. Conversion of alkane into alkyl halide is an example of which of the following reaction?

(*a*) Electrophilic substitution

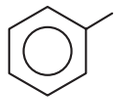
(*b*) Free radical addition

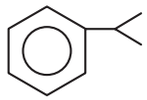
(*c*) Nucleophilic substitution

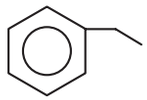
(*d*) Free radical substitution

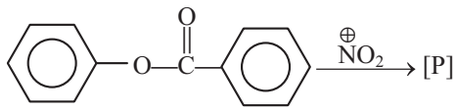
34. Which of the following is most reactive towards E.S.R.?

(*a*)

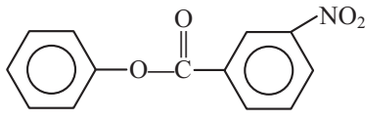
(*b*) 

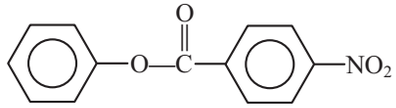
(*c*) 

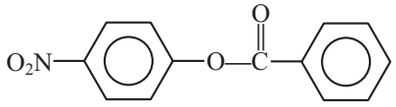
(*d*) 

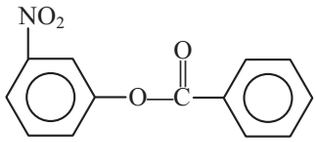
35. 

The product [P] is:

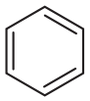
(*a*) 

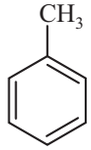
(*b*) 

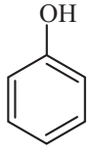
(*c*) 

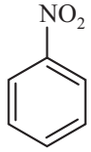
(*d*) 

36. Consider the following compounds:

(I) 

(II) 

(III) 

(IV) 

Correct order of their reactivity in electrophilic substitution reaction would be:

(*a*) I > II > III > IV (*b*) IV > III > II > I

(*c*) III > II > I > IV (*d*) III > IV > I > II

MISCELLANEOUS

37. How many π-electrons are there in the following species?

(*a*) 2 (*b*) 4 (*c*) 6 (*d*) 8

38. The number of benzylic hydrogen atoms in ethylbenzene are:

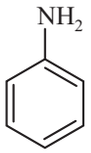
(*a*) 3 (*b*) 5 (*c*) 2 (*d*) 7

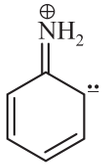
39. Which of the following is most basic?

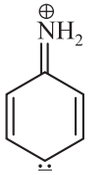
(*a*) Aniline (*b*) o–Nitroaniline

(*c*) m–Nitroaniline (*d*) p–Nitroaniline

40. The most stable resonating structure of aniline is

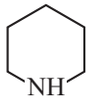
(*a*) 

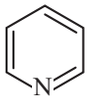
(*b*) 

(*c*) 

(*d*) All are equally stable

41. Which of the following is most basic?

(*a*) 

(*b*) 

(*c*) RCN (*d*) $C_6H_5NH_2$

42. The correct order of basic strength of substituted aniline is:

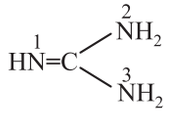
(*a*) p–methylaniline > p–chloroaniline > p–aminoaceto phenone

(*b*) p–methylaniline > p–aminoacetophenone > o–chloro aniline

(*c*) p–aminoacetophenone > p–methylaniline > p–chloroaniline

(*d*) p–aminoacetophenone > p–chloroaniline > p–methylaniline

43. Which of the nitrogen is protonated most readily in guanidine?



(*a*) 1 (*b*) 2

(*c*) 3 (*d*) All are equally protonated

44. Which of the following compound is most acidic?

(*a*) Picric acid

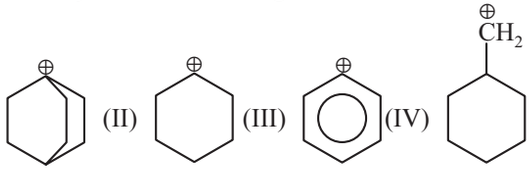
(*b*) *p*-nitrophenol

(*c*) *m*-nitrophenol

(*d*) *o,p*-dinitrophenol

PRABAL (JEE MAIN LEVEL)

1. The stability order of following carbocation is:



(*a*) I > II > IV > III

(*b*) III > I > II > IV

(*c*) IV > II > III > I

(*d*) II > IV > III > I

2. When $-CH_3$, $CH_3-\underset{\displaystyle CH_3}{\overset{}{CH}}-$ and $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-$ groups are introduced on benzene ring, then correct order of their e^- releasing effect is

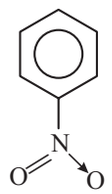
(*a*) $CH_3- > CH_3-\underset{\displaystyle CH_3}{\overset{}{CH}}- > CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-$

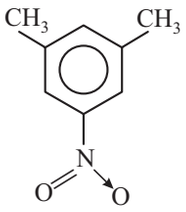
(*b*) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}- > CH_3-\underset{\displaystyle CH_3}{\overset{}{CH}}- > CH_3-$

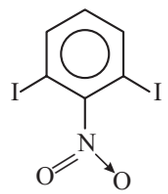
(*c*) $CH_3-\underset{\displaystyle CH_3}{\overset{}{CH}}- > CH_3- > CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-$

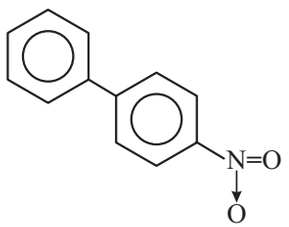
(*d*) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}- > CH_3- > CH_3-\underset{\displaystyle CH_3}{\overset{}{CH}}-$

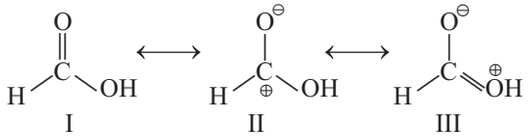
3. In which of the following molecules, $-NO_2$ group is not coplanar with phenyl ring?

(*a*) 

(*b*) 

(*c*) 

(*d*) 

4. 

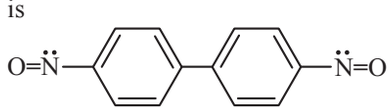
I II III

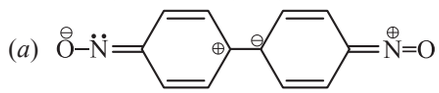
Among these canonical structures, the correct order of stability is

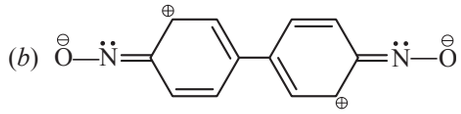
(*a*) I > II > III (*b*) III > II > I

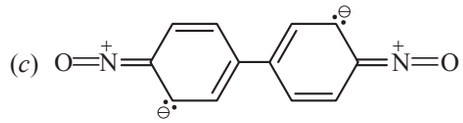
(*c*) I > III > II (*d*) II > I > III

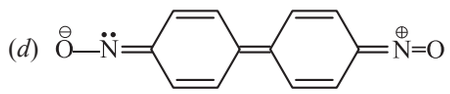
5. The most stable resonating structure of following compound is



(*a*) 

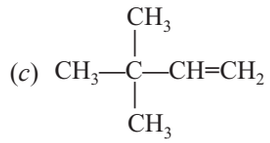
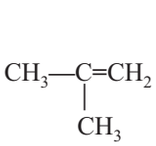
(*b*) 

(*c*) 

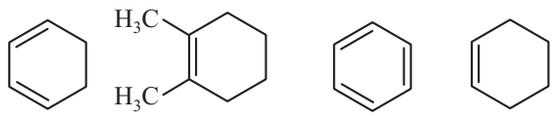
(*d*) 

6. Which of the following molecule has longest C = C bond length?

(*a*) $CH_2 = C = CH_2$ (*b*) $CH_3 — CH = CH_2$

(*c*)  (*d*) 

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

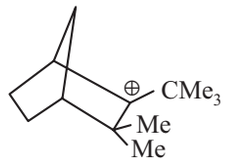
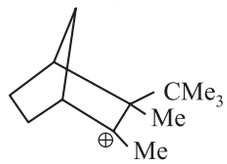


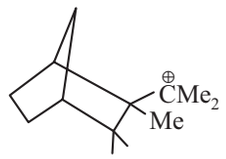
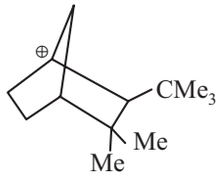
I II III IV

(*a*) II > I > IV > III (*b*) III > I > II > IV

(*c*) IV > II > I > III (*d*) IV > I > II > III

8. Write correct order of stability of following carbocations:

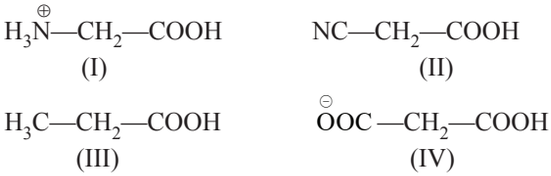
(I)  (II) 

(III)  (IV) 

(*a*) I > II > III > IV (*b*) III > II > I > IV

(*c*) III > I > II > IV (*d*) III > II > IV > I

9. Order of K_a of following acids is:



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

(*a*) I > II > III > IV (*b*) II > I > III > IV

(*c*) I > III > II > IV (*d*) IV > III > II > I

10. Find the strongest acid among the following compounds.

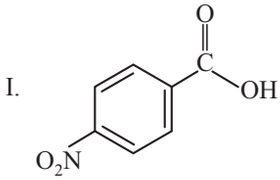
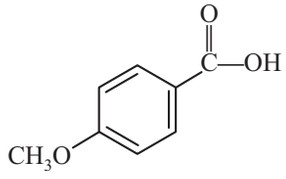
(*a*) $HOOC – (CH_2)_2 – COOH$

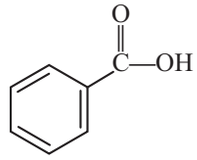
(*b*) $H_3N^{\oplus} – (CH_2)_2 – COOH$

(*c*) $F – (CH_2)_2 – COOH$

(*d*) $CH_3 – (CH_2)_2 – COOH$

11. Find the correct order of K_a, among the following compounds.

I.  II. 

III. 

(*a*) I > II > III (*b*) II > I > III

(*c*) I > III > II (*d*) III > I > II

12. Which one of the following has maximum nucleophilicity?

(*a*) $CH_3S^{\ominus}$ (*b*) $C_2H_5 — O^{\ominus}$

(*c*) Et_3N (*d*) $F^{\ominus}$

13. Correct arrangement of the following nucleophiles in the order of their nucleophilic strength is

(*a*) $C_6H_5O^- < CH_3O^- < CH_3COO^- < OH^-$

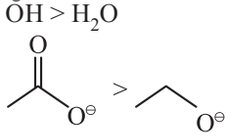
(*b*) $CH_3COO^- < C_6H_5O^- < CH_3O^- < OH^-$

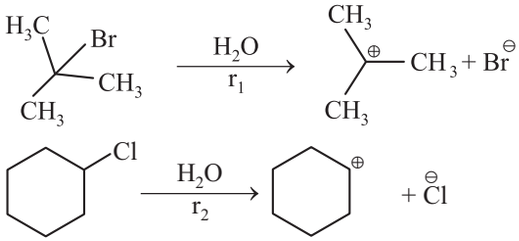
(*c*) $C_6H_5O^- < CH_3COO^- < CH_3O^- < OH^-$

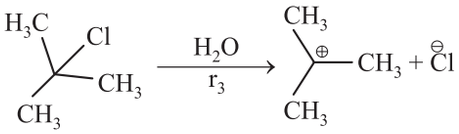
(*d*) $CH_3COO^- < C_6H_5O^- < OH^- < CH_3O^-$

14. The correct order of leaving ability is:

(*a*) $\overset{\ominus}{O}H > H_2O$ (*b*) $\overset{\ominus}{O}H > \overset{\ominus}{S}H$

(*c*)  (*d*) $\overset{\ominus}{Cl} > \overset{\ominus}{I}$

15. 



The rates r_1 , r_2 and r_3 are in the order:

(*a*) $r_1 = r_3 > r_2$ (*b*) $r_3 > r_1 > r_2$

(*c*) $r_1 > r_3 > r_2$ (*d*) $r_2 > r_1 > r_3$

16 The increasing order of reactivity of the following isomeric halides with $AgNO_3$ (H_2O + alcohol) is:

(I) $C_6H_5 - CH = CH - CH_2 - CH_2 - Cl$

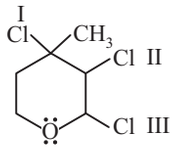
(II) $C_6H_5—CH=CH—\underset{\displaystyle Cl}{\underset{|}{CH}}—CH_3$

(III) $C_6H_5—\underset{\displaystyle Cl}{\underset{|}{C}}=CH—CH_2—CH_3$

(IV) $C_6H_5—\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle C_6H_5}{\overset{|}{C}}}}—CH=CH_2$

(*a*) III < IV < II < I (*b*) I < III < IV < II

(*c*) III < I < II < IV (*d*) I < II < IV < III

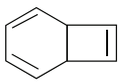
17. 

The correct order of rate of reaction with $AgNO_3$ will be:

(*a*) I > II > III (*b*) III > I > II

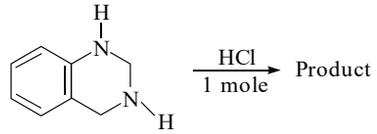
(*c*) III > II > I (*d*) I > III > II

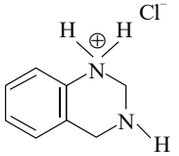
18. The number of $sp^2 - sp^2$ sigma bonds in the compound given below is

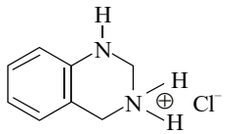


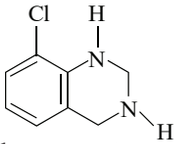
(*a*) 1 (*b*) 3 (*c*) 4 (*d*) 5

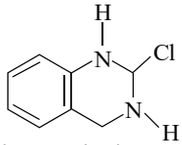
19. Which is the major product of the following reaction?



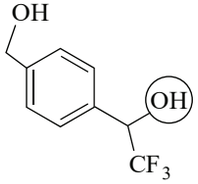
(*a*) 

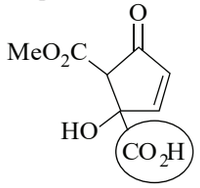
(*b*) 

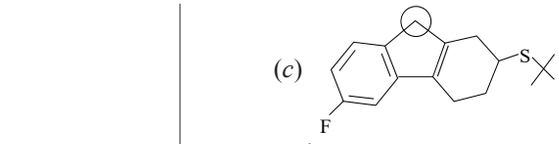
(*c*) 

(*d*) 

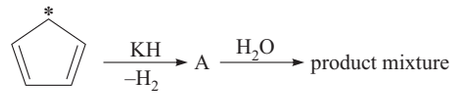
20. Circle represents most acidic hydrogens in these molecules. Which of the following is correct representation?

(*a*) 

(*b*) 

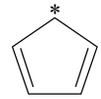
(*c*) 

(*d*) All of these

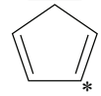
21. 

($\overset{*}{C} = C^{14}$)

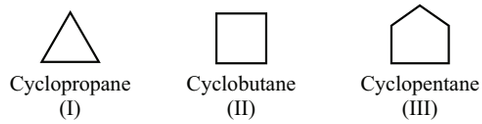
The product mixture contains.

(*a*) 

(*b*)

(*c*) 

(*d*) All of these

22. 

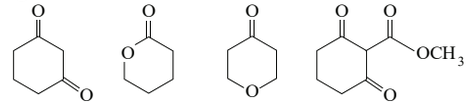
Cyclopropane (I) Cyclobutane (II) Cyclopentane (III)

The correct order of heat of combustion of above compounds is

(*a*) I > II > III (*b*) II > I > III

(*c*) III > II > I (*d*) III > I > II

23. Arrange the following in increasing order of their acidic strength.

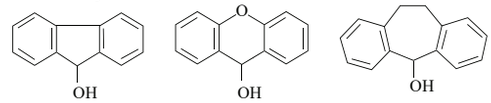


(I) (II) (III) (IV)

(*a*) III < I < IV < II (*b*) II < I < IV < III

(*c*) I < III < IV < II (*d*) II < III < I < IV

24. Arrange the following alcohols in decreasing order of the ease of dehydration under acidic conditions.

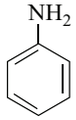
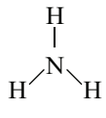
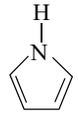
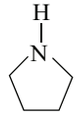


(I) (II) (III)

(*a*) I > III > II (*b*) I > II > III

(*c*) II > III > I (*d*) II > I > III

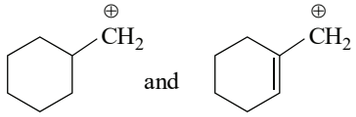
25. Which of the following is the strongest Bronsted base?

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

26. Some pairs of ions are given below. In which pair, first ion is more stable than second?

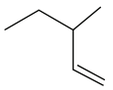
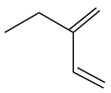
(*a*) $CH_3 - \overset{\oplus}{C}H - CH_3$ and $CH_3 - \overset{\oplus}{C}H - OCH_3$

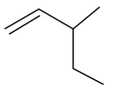
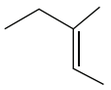
(*b*) $CH_3 - CH_2 - \overset{\oplus}{C}H - CH_3$ and $CH_2 = CH - CH_2 - \overset{\oplus}{C}H_2$

(*c*) 

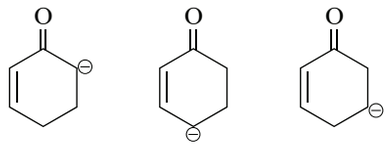
(*d*) $CH_3 - \underset{\displaystyle CH_3 - \overset{\oplus}{C} - CH_3}{\underset{|}{CH}} - CH_3$ and $CH_3 - \underset{\displaystyle CH_3 - \overset{\oplus}{C} - CH_3}{\underset{|}{N}} - CH_3$

27. Which of the following alkenes is the most stable?

(*a*)  (*b*) 

(*c*)  (*d*) 

28. Compare basic strengths of the below compounds:

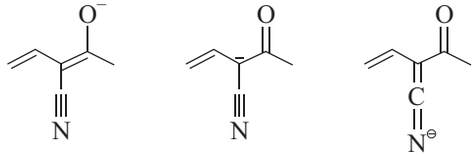


(A) (B) (C)

(*a*) A > B > C (*b*) B > A > C

(*c*) C > A > B (*d*) C > B > A

29. Compare relative stability of the following resonating structures.



(p) (q) (r)

(*a*) p > q > r (*b*) q > p > r

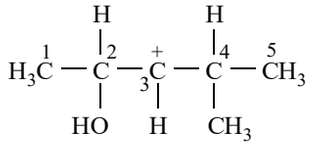
(*c*) q > r > p (*d*) p > r > q

30. Among the following compounds, the most acidic is

(*a*) p-nitrophenol (*b*) p-hydroxybenzoic acid

(*c*) o-hydroxybenzoic acid (*d*) p-toluic acid

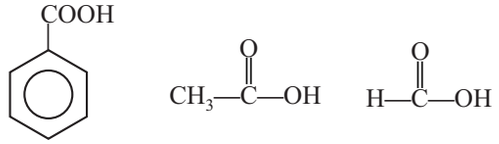
31. In the following carbocation, H/CH_3 that is most likely to migrate to the positively charged carbon is



(*a*) CH_3 at C – 4 (*b*) H at C – 4

(*c*) CH_3 at C – 2 (*d*) H at C – 2

32. The correct acidity order is:

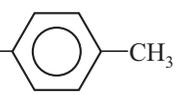


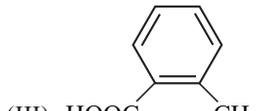
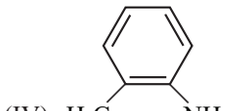
(X) (Y) (Z)

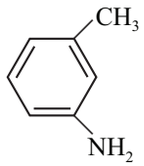
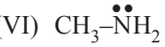
(*a*) X > Z > Y (*b*) Z > X > Y

(*c*) Y > Z > Y (*d*) X > Y > Z

33. The compound in which the CH_3-group causes increase in acidic strength and decrease in basic strength are, respectively:

(I) CH_3–COOH (II) 

(III)  (IV) 

(V)  (VI) 

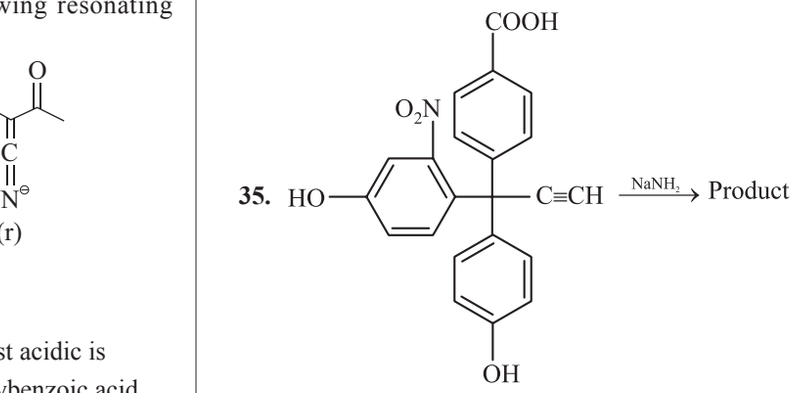
(*a*) III and V (*b*) I and VI

(*c*) III and IV (*d*) II and V

INTEGER TYPE QUESTIONS

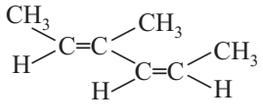
34. How many of the given compounds are electrophiles?

CO_2, $SnCl_2$, $FeCl_3$, NH_4^+, BF_3, $\overset{\oplus}{N}O_2$, :CCl_2, $AlCl_3$, $\overset{\ominus}{C}Cl_3$, SO_3

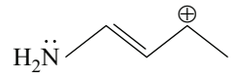
35. 

How many mole of $NaNH_2$ completely react in above reaction?

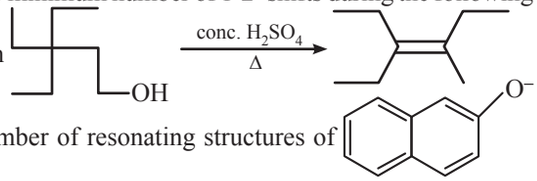
36. The number of hyperconjugating structure (involving C–H bonds) for the given compound are:



37. How many resonating structures can be drawn for the following molecule?

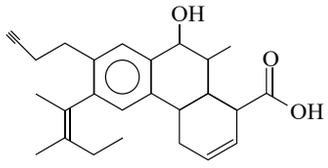


38. Find the minimum number of 1-2- shifts during the following reaction



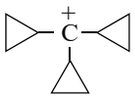
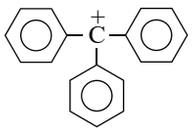
39. The number of resonating structures of is

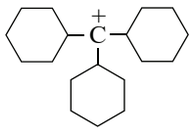
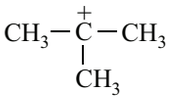
40. How many degree of unsaturation are there in the following compounds?



SINGLE CORRECT TYPE QUESTIONS

1. Which one among the following carbocations has the longest half-life?

(*a*)  (*b*) 

(*c*)  (*d*) 

2. Identify electron - donating groups in resonance among the following:

(I) $-CONH_2$ (II) $-NO_2$

(III) $-OCOCH_3$ (IV) $-COOCH_3$

(V) $-CHO$ (VI) $-NHCOCH_3$

(*a*) (III), (VI) (*b*) (II), (III), (V)

(*c*) (III), (IV), (V) (*d*) (I), (II), (III)

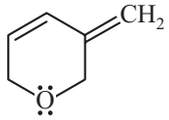
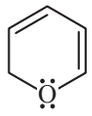
3. In which of the following, lone-pair indicated is not involved in resonance?

(I) $CH_2 = CH - \ddot{N}H - CH_3$

(II) $CH_2 = CH - CH = \ddot{O}$

(III) $CH_2 = CH - \ddot{O} - CH = CH_2$

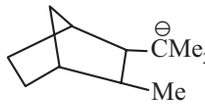
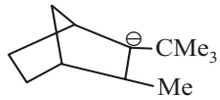
(IV) $CH_2 = CH - C \equiv \ddot{N}$

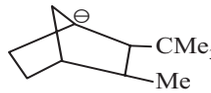
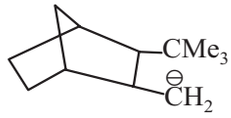
(V)  (VI) 

(*a*) (III), (VI) (*b*) (II), (IV), (V)

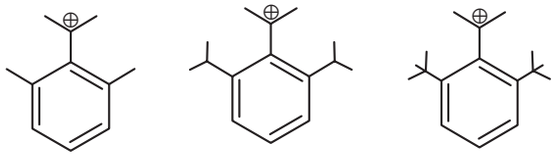
(*c*) (III), (IV), (V) (*d*) (I), (II), (III)

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

(*a*)  (*b*) 

(*c*)  (*d*) 

5. The stability order of following carbocations is



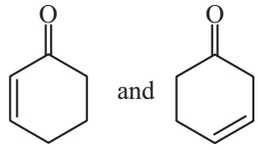
I II III

(*a*) I > II > III (*b*) II > I > III

(*c*) III > I > II (*d*) II > III > I

MULTIPLE CORRECT TYPE QUESTIONS

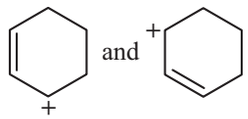
6. Which of the following pair represent resonating structures?

(*a*) 

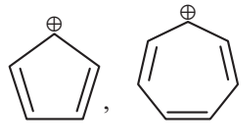
(*b*) $CH_3CH = CH\dot{C}HCH = CH_2$

and $CH_3\dot{C}HCH = CHCH = CH_2$

(*c*) $CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3$ and $CH_2{=}\underset{\underset{OH}{|}}{C}{-}CH_2{-}CH_3$

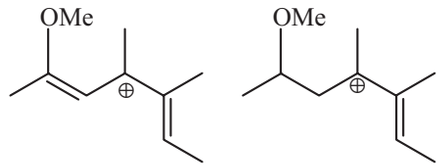
(*d*) 

7. In which of the following, first carbocation is more stable than second one?

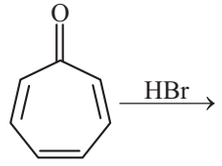
(*a*) 

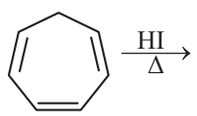
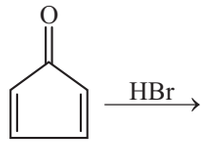
(*b*)

(*c*) $CH_3{-}O{-}\overset{\oplus}{C}H{-}CH_3$, $CH_3{-}\overset{\oplus}{C}H{-}\underset{\underset{CH_3}{|}}{CH}{-}CH_3$

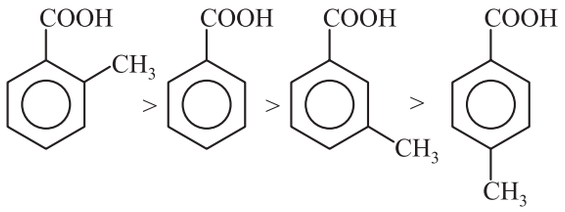
(*d*) 

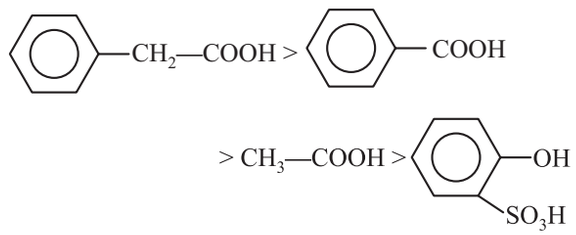
8. Which of the following reactions give aromatic compound?

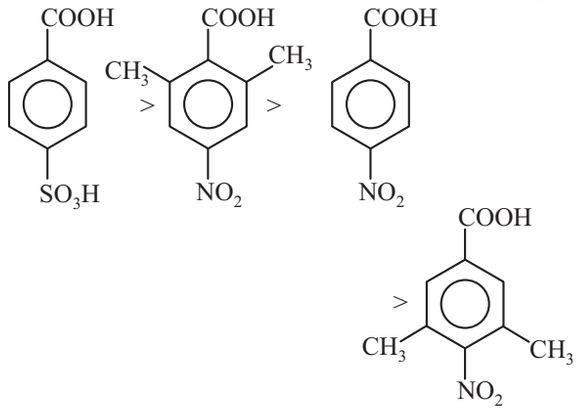
(*a*) (*b*) 

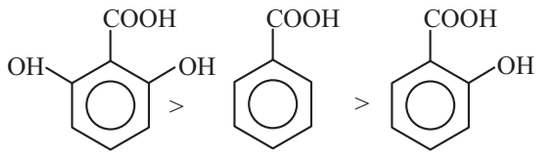
(*c*)  (*d*) 

9. Which of the following is/are correct order of K_a of the given compounds?

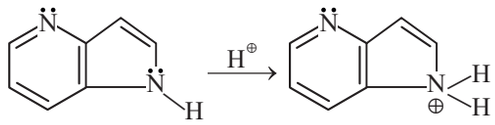
(*a*) 

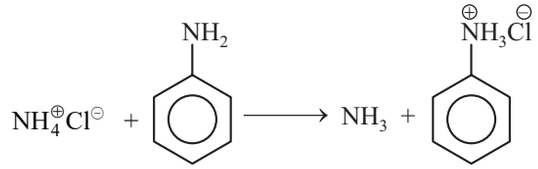
(*b*) 

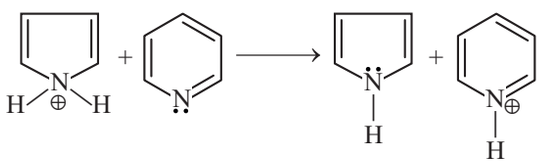
(*c*) 

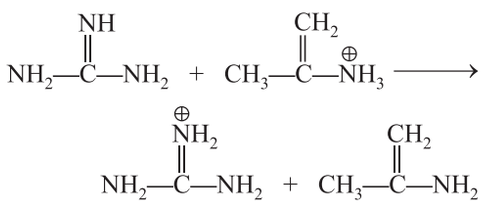
(*d*) 

10. Which of the following reactions are feasible?

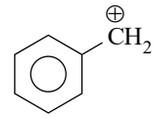
(*a*) 

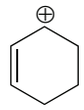
(*b*) 

(*c*) 

(*d*) 

11. Which of the following carbocations is/are resonance stabilized?

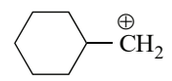
(*a*) 

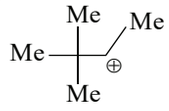
(*b*) 

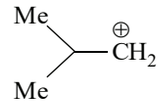
(*c*)

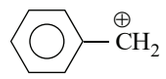
(*d*)

12. In which of the following carbocation, ΔG decreases if there is some intramolecular rearrangement?

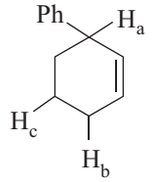
(*a*) 

(*b*) 

(*c*) 

(*d*) 

13. Select the correct statements about the given compound:

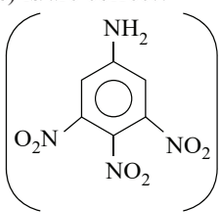
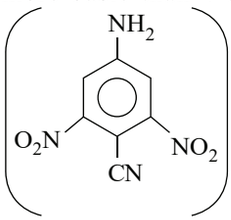


(*a*) H_a is abstracted by bromine radical most rapidly.
(*b*) H_b is abstracted by bromine radical rapidly.
(*c*) H_b is more acidic than H_c.
(*d*) H_b is less acidic than H_c.

14. Which of the following statements is/are correct?
(*a*) pK_{a_1} of maleic acid is less than pK_{a_1} of fumaric acid.
(*b*) pK_{a_2} of maleic acid is less than pK_{a_2} of fumaric acid.
(*c*) Phthalic acid is a stronger acid than isophthalic acid.
(*d*) Isopthalic acid is a stronger acid than terephthalic acid.

15. Which of the following statement(s) is/are correct?
(*a*) HCOOH is stronger acid than PhCOOH.
(*b*) Oximes ($R_2C = N - OH$) are more acidic than hydroxylamine (NH_2OH).
(*c*) R_3SiCH_2COOH is more acidic than R_3CCH_2COOH.
(*d*) Highly branched carboxylic acids are less acidic than unbranched acids.

16. Which of the following statement(s) is/are correct?

(*a*) 3, 4, 5-Trinitroaniline (I)  is more basic than 4-cyano-3, 5-dinitroaniline (II) 

(*b*) (II)is more basic than (I).

(*c*) (I) is more basic than (II) due to steric inhibition to resonance in (I)

(*d*) There is no steric inhibition to resonance in (II).

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 17 to 19):

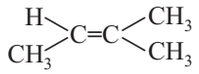
Hyperconjugation: It is delocalisation of sigma electron with p-orbital. Also known as σ, π-conjugation or no bond resonance.

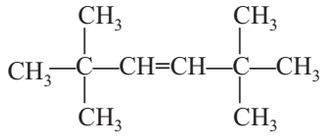
May take place in alkenes, alkynes, carbocations, free radicals and benzene nucleus.

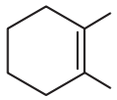
Necessary Condition: Presence of atleast one hydrogen at saturated carbon which is α with respect to alkenes, alkynes, carbocations, free radicals and benzene nucleus.

17. Which of the following alkene have maximum number of hyperconjugation structures?

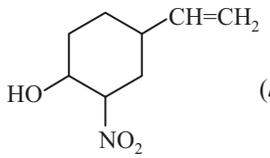
(*a*) $CH_3–CH=CH–CH_3$

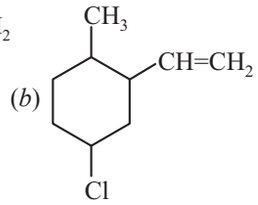
(*b*) 

(*c*) 

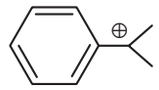
(*d*) 

18. In which of the following species, hyperconjugation is not possible?

(*a*) 

(*b*) 

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

(*d*) 

19. Select the incorrect statement.

(*a*) Hyperconjugation is a permanent effect.

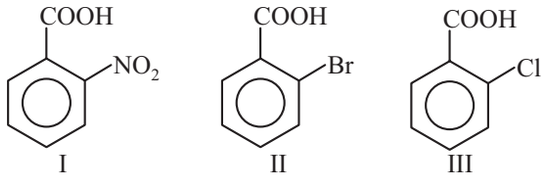
(*b*) $CH_2=CH—CH_3$ shows hyperconjugation.

(*c*) Stability of alkenes is directly related to number of hyperconjugation structures.

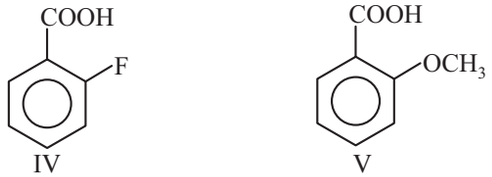
(*d*) $C_6H_5–CH_3$ does not show hyperconjugation.

Comprehension (Q. 20 to 22): Ortho effect is a special type of effect that is shown by o-substituents, but it is not necessarily just a steric effect. The basicities of some o-substituted aniline are explained in terms of steric effect and differences in crowding around the nitrogen atom. This ortho-effect also operates in the ortho substituted benzoic acids. Irrespective of the polar type, nearly all o-substituted benzoic acids are stronger than benzoic acid. Benzoic acid is resonance stabilised and so the carboxyl group is coplanar with the ring. An o-substituent tends to prevent this coplanarity.

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



I II III

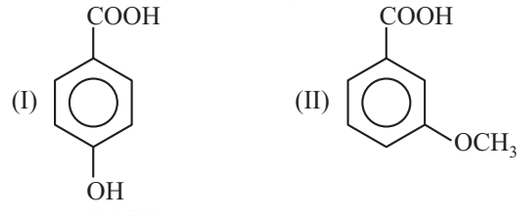


IV V

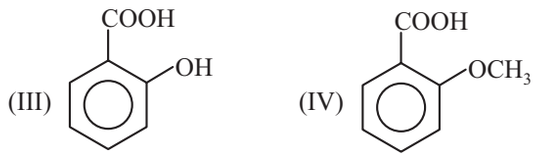
(*a*) I > II > III > IV > V (*b*) II > I > III > IV > V

(*c*) V > IV > III > I > II (*d*) III > II > I > V > IV

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



(I) (II)



(III) (IV)

(*a*) I (*b*) II (*c*) III (*d*) IV

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

(i) 2–nitrobenzoic acid (ii) 3–nitrobenzoic acid

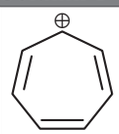
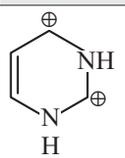
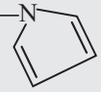
(iii) 4–nitrobenzoic acid (iv) benzoic acid

(*a*) i > ii > iii > iv (*b*) iii > i > ii > iv

(*c*) i > iii > iv > ii (*d*) i > iii > ii > iv

MATCH THE COLUMN TYPE QUESTIONS

23. Match the column.

Column-I		Column-II	
A.		p.	Six π-electrons
B.		q.	Four π-electrons
C.		r.	Aromatic Compound
D.		s.	Anti-aromatic compound

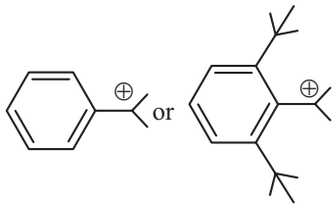
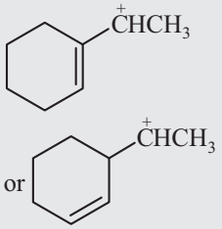
(*a*) A → r; B → q,s; C → p; D → p,r

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

(*c*) A → p,r; B → q; C → p, r; D → p

(*d*) A → p,r; B → s; C → p; D → p,r

24. Match the column:

Column-I		Column-II	
A.	$CH_3O\overset{+}{C}H_2$ or $CH_3N\overset{+}{H}\overset{+}{C}H_2$	p.	First is more stable than second
B.	$CH_3OCH_2\overset{+}{C}H_2$ or $CH_3O\overset{+}{C}H_2$	q.	Second is more stable than first
C.		r.	Not resonating structure of each other
D.		s.	Resonance is present in both carbocations

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

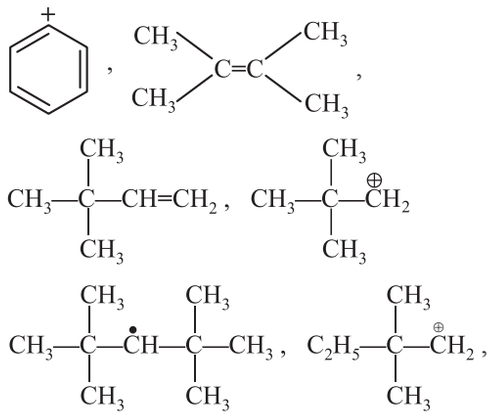
(*b*) A → q,s; B → q,r; C → p,r; D → p

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

(*d*) A → q,r,s; B → q,r; C → r; D → r

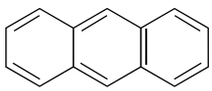
INTEGER TYPE QUESTIONS

25. How many of the following compounds do not show hyperconjugation?

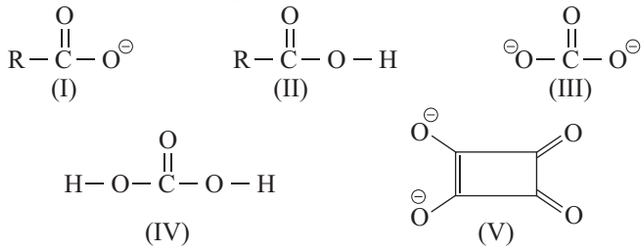


$(CH_3)_3C - CH = CH - C(CH_3)_3$

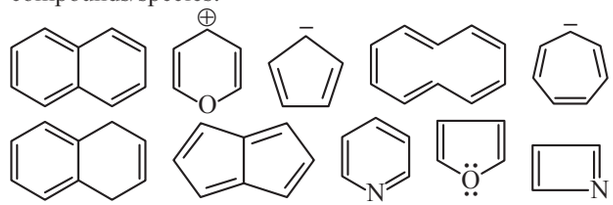
26. How many uncharged resonance structures are there for anthracene?



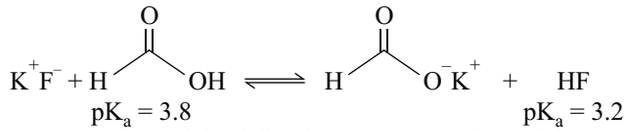
27. The total number of compounds which contain identical (C – O) bond lengths are



28. Some compounds/species are given below, select aromatic compounds/species:



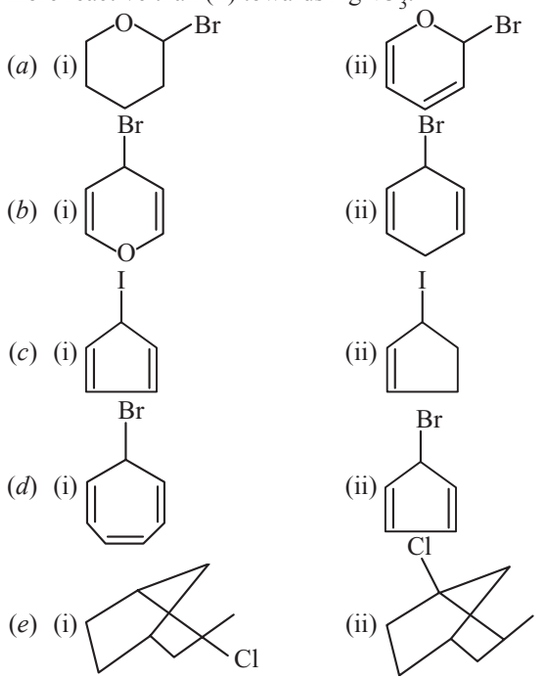
29. Consider the following reaction involving two acids shown below: Formic acid and HF.



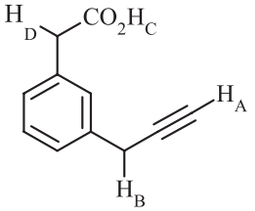
How many of the following statements about this reaction are true?

(*a*) Formic acid is the strongest Bronsted acid in the reaction.
(*b*) HF is the strongest Bronsted acid of the reaction.
(*c*) KF is the strongest Bronsted base in the reaction.
(*d*) KO_2CH is the strongest Bronsted base in the reaction.
(*e*) The equilibrium favours the reactants.
(*f*) The equilibrium favours the products.
(*g*) Formic acid has a weaker conjugate base.
(*h*) HF has a weaker conjugate base.

30. Among given pairs, find how many pairs has compound (i) more reactive than (ii) towards $AgNO_3$:



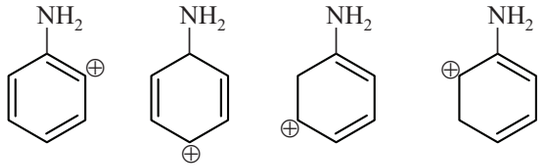
1. What is the correct order of acidity of the protons marked A-D in the given compounds? **[30 Jan, 2023 (Shift-I)]**



(*a*) $H_C > H_D > H_B > H_A$ (*b*) $H_C > H_D > H_A > H_B$

(*c*) $H_D > H_C > H_B > H_A$ (*d*) $H_C > H_A > H_D > H_B$

2. The most stable carbocation for the following is:

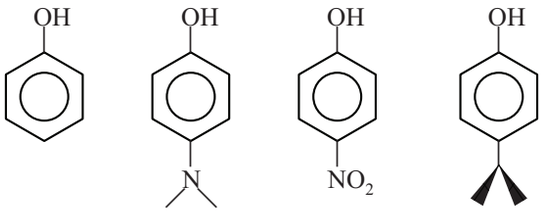


(a) (b) (c) (d)

[30 Jan, 2023 (Shift-II)]

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

3. The correct order of pK_a values for the following compounds is: **[30 Jan, 2023 (Shift-II)]**

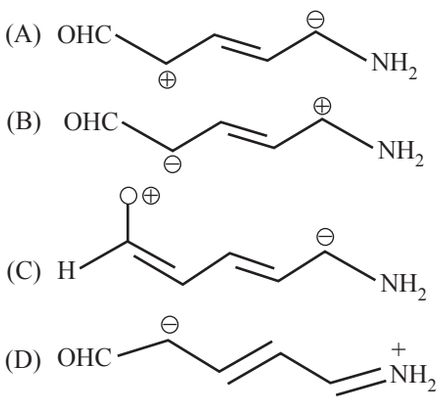


(i) (ii) (iii) (iv)

(*a*) (iii), (i), (iv), (ii) (*b*) (ii), (iv), (i), (iii)

(*c*) (ii), (i), (iv), (iii) (*d*) (i), (ii), (iii), (iv)

4. Increasing order of stability of the resonance structure is: **[24 Jan, 2023 (Shift-I)]**



(*a*) (C), (D), (B), (A) (*b*) (C), (A), (B), (D)

(*c*) (D), (C), (A), (B) (*d*) (D), (C), (B), (A)

5. The pair from the following pairs having both compounds with net non-zero dipole moment is **[10 April, 2023 (Shift-I)]**

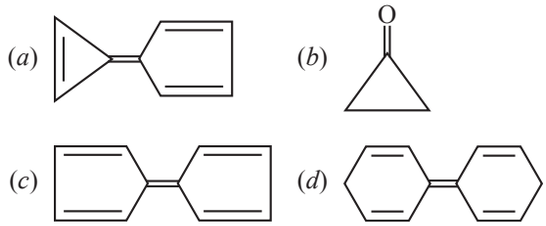
(*a*) Benzene, anisidine

(*b*) 1, 4 -Dichlorobenzene, 1,3-Dichlorobenzene

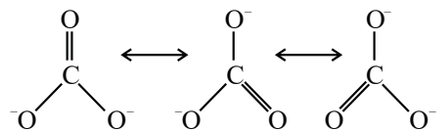
(*c*) CH_2Cl_2, $CHCl_3$

(*d*) cis-butene, trans-butene

6. Among the following compounds, the one which shows highest dipole moment is **[13 April, 2023 (Shift-I)]**



7. Resonance in carbonate ion (CO_3^{2-}) is



Which of the following is true? **[1 Feb, 2023 (Shift-I)]**

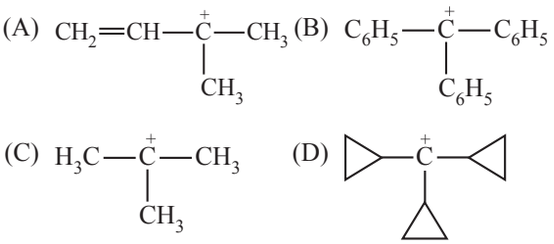
(*a*) It is possible to identify each structure individually by some physical or chemical method

(*b*) All these structures are in dynamic equilibrium with each other

(*c*) Each structure exists for equal amount of time

(*d*) CO_3^{2-} has a single structure i.e., resonance hybrid of the above three structures

8. The decreasing order of hydride affinity for following carbocations is: **[10 April, 2023 (Shift-II)]**



Choose the correct answer from the options given below:

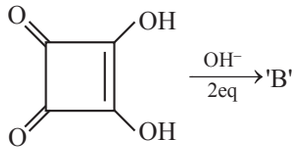
(*a*) (A), (C), (B), (D)

(*b*) (C), (A), (B), (D)

(*c*) (C), (A), (D), (B)

(*d*) (A), (C), (D), (B)

9. Correct statements for the given reaction are:

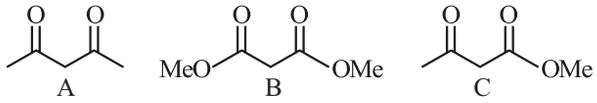


(A) Compound 'B' is aromatic
(B) The completion of above reaction is very slow
(C) 'A' shows tautomerism
(D) The bond lengths C-C in compound B are found to be same

Choose the correct answer from the options given below:
[12 April, 2023 (Shift-I)]

(*a*) (A), (B) and (D) only
(*b*) (A), (B) and (C) only
(*c*) (B), (C) and (D) only
(*d*) (A), (C) and (D) only

10. Which will undergo deprotonation most readily in basic medium? **[24 Jan, 2023 (Shift-II)]**

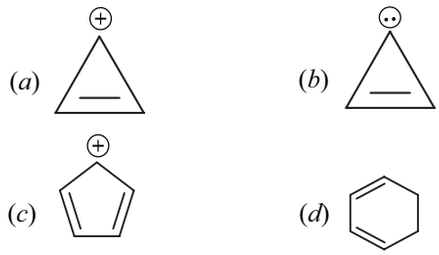


(*a*) A only (*b*) C only
(*c*) Both A and C (*d*) B only

11. The correct order of nucleophilicity is
[26 June, 2022 (Shift-II)]

(*a*) $F^- > OH^-$ (*b*) $H_2O > OH^-$
(*c*) $R\ddot{O}H > RO^-$ (*d*) $NH_2^- > NH_3$

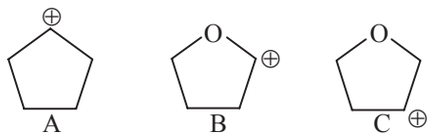
12. Which of the following is most stable?
[27 June, 2022 (Shift-II)]



13. The difference in the reaction of phenol with bromine in chloroform and bromine in water medium is due to:
[26 July, 2022 (Shift-I)]

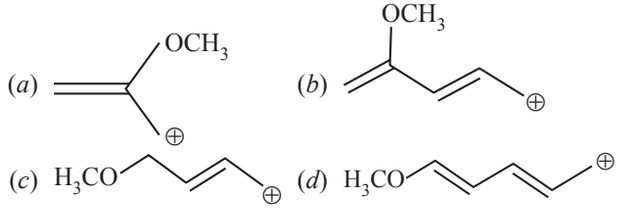
(*a*) Hyperconjugation in substrate
(*b*) Polarity of solvent
(*c*) Free radical formation
(*d*) Electromeric effect of substrate

14. Arrange the following carbocations in decreasing order of stability. **[24 June, 2022 (Shift-II)]**



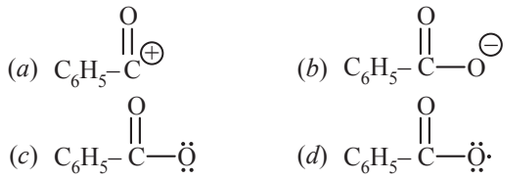
(*a*) A > C > B (*b*) B > A > C
(*c*) C > B > A (*d*) C > A > B

15. Which of the following carbocations is most stable?
[29 June, 2022 (Shift-II)]

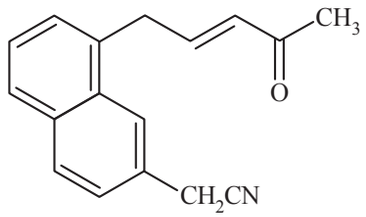


16. $(C_7H_5O_2)_2 \xrightarrow{h\nu} [X] \rightarrow 2\dot{C}_6H_5 + 2CO_2$

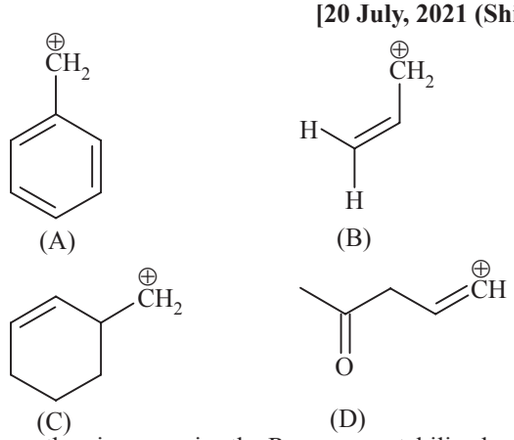
Consider the above reaction and identify the intermediate 'X' **[26 June, 2022 (Shift-I)]**



17. Number of electrophillic centres in the given compound is_____. **[24 June, 2022 (Shift-I)]**



18. **[20 July, 2021 (Shift-I)]**



Among the given species the Resonance stabilized carbocations are:

(*a*) (A), (B) and (C) only (*b*) (C) and (D) only
(*c*) (A), (B) and (D) only (*d*) (A) and (B) only

19. Given below are two statements:

Statement-I: Hyper conjugation is permanent effect.

Statement-II: Hyper conjugation in ethyl cation ($CH_3 - CH_2$) involves the overlapping of $C_{sp^2}H_{1s}$ bond with empty 2p orbital of other carbon. **[27 July, 2021 (Shift-II)]**

Choose the correct option:

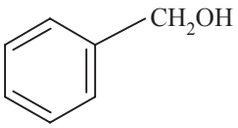
(*a*) Statement-I is incorrect but Statement-II is true.
(*b*) Statement-I is correct but Statement-II is false.
(*c*) Both Statement-I and Statement-II are false.
(*d*) Both Statement-I and Statement-II are true.

20. Which one of the following compounds does not exhibit resonance? **[22 July, 2021 (Shift-II)]**

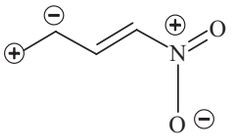
(*a*) $CH_3CH_2CH_2CONH_2$

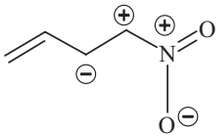
(*b*) $CH_3CH_2CH = CHCH_2NH_2$

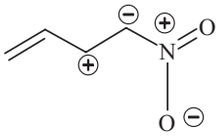
(*c*) $CH_3CH_2OCH = CH_2$

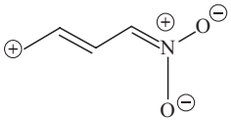
(*d*) 

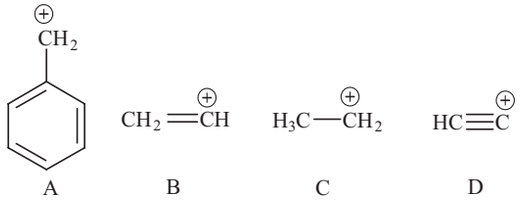
21. Which one among the following resonating structure is not correct? **[25 July, 2021 (Shift-I)]**

(*a*) 

(*b*) 

(*c*) 

(*d*) 

22. 

A B C D

The correct order of stability of given carbocations is:

[27 July, 2021 (Shift-I)]

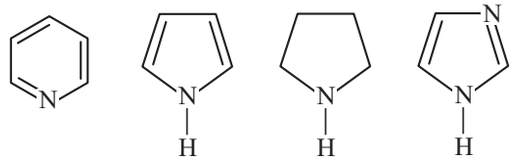
(*a*) A > C > B > D

(*b*) D > B > C > A

(*c*) C > A > D > B

(*d*) D > B > A > C

23. The increasing order of basicity of the following compounds is **[5 Sept, 2021 (Shift-I)]**



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

(*a*) (A) < (B) < (C) < (D)

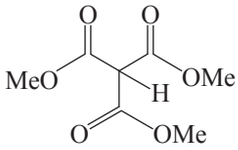
(*b*) (D) < (A) < (B) < (C)

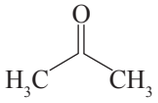
(*c*) (B) < (A) < (C) < (D)

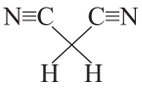
(*d*) (B) < (A) < (D) < (C)

24. Which one of the following compounds possesses the most acidic hydrogen? **[3 Sept, 2021 (Shift-I)]**

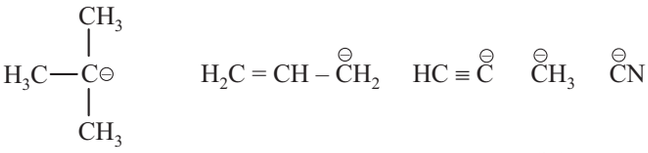
(*a*) $H_3C–C\equiv C–H$

(*b*) 

(*c*) 

(*d*) 

25. The increasing order of basicity for the following intermediates is (from weak to strong) **[9 Jan, 2020 (Shift-I)]**



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

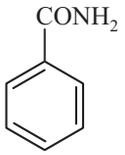
(*a*) (v) < (iii) < (ii) < (iv) < (i)

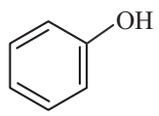
(*b*) (iii) < (i) < (ii) < (iv) < (v)

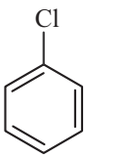
(*c*) (v) < (i) < (iv) < (ii) < (iii)

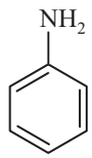
(*d*) (iii) < (iv) < (ii) < (i) < (v)

26. Which of these will produce the highest yield in Friedel Crafts reaction? **[9 Jan, 2020 (Shift-I)]**

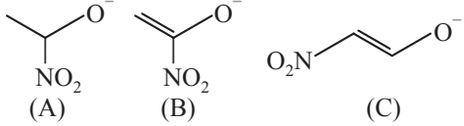
(*a*) 

(*b*) 

(*c*) 

(*d*) 

27. The correct order of stability for the following alkoxides is **[7 Jan, 2020 (Shift-II)]**



(A) (B) (C)

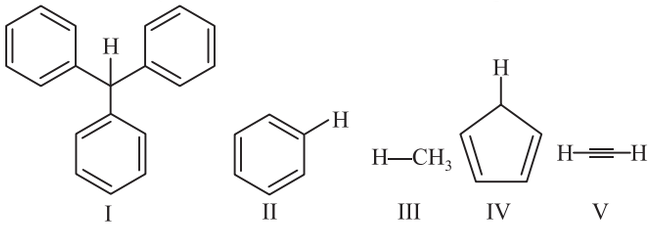
(*a*) (B) > (C) > (A)

(*b*) (C) > (A) > (B)

(*c*) (C) > (B) > (A)

(*d*) (B) > (A) > (C)

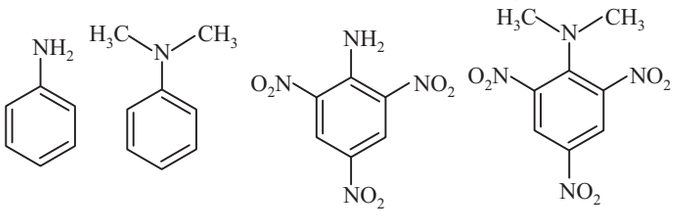
28. With respect to the compounds I-V, choose the correct statement(s). **[JEE Adv 2020]**



I II III IV V

(*a*) The acidity of compound-I is due to delocalization in the conjugate base.
(*b*) The conjugate base of compound-IV is aromatic.
(*c*) Compound-II becomes more acidic, when it has a $-NO_2$ substituent.
(*d*) The acidity of compounds follows the order: I > IV > V > II > III

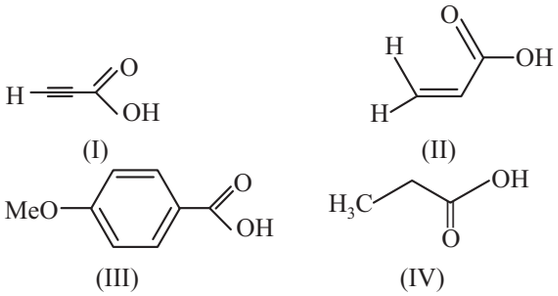
29. Consider the following four compounds **I, II, III**, and **IV.** **[JEE Adv 2020]**



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

Choose the correct statement(s).
(*a*) The order of basicity is II > I > III > IV.
(*b*) The magnitude of pK_b difference between I and II is more than that between III and IV.
(*c*) Resonance effect is more in III than in IV.
(*d*) Steric effect makes compound IV more basic than III.

30. The correct order of acid strength of the following carboxylic acids is **[JEE Adv 2019]**



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

(*a*) (I) > (III) > (II) > (IV)
(*b*) (III) > (II) > (I) > (IV)
(*c*) (II) > (I) > (IV) > (III)
(*d*) (I) > (II) > (III) > (IV)

31. Match the following: **[6 Sept, 2020 (Shift-II)]**

Test/Method		Reagent	
A.	Lucas Test	p.	$C_6H_5SO_2Cl$/aq.kOH
B.	Dumas method	q.	$HNO_3/AgNO_3$
C.	Kjeldahl's method	r.	CuO/CO_2
D.	Hinsberg Test	s.	Conc. HCl and $ZnCl_2$
		t.	H_2SO_4

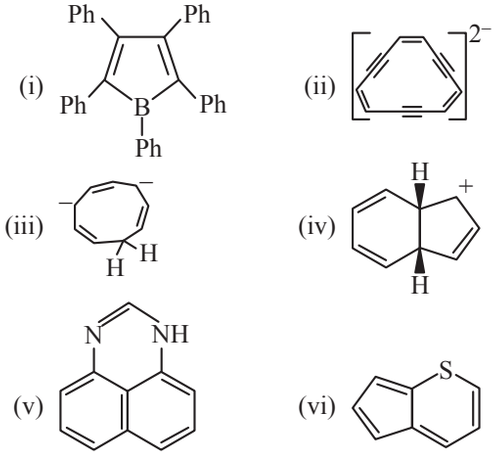
(*a*) (A)-(s), (B)-(r), (C)-(q), (D)-(t)
(*b*) (A)-(q), (B)-(s), (C)-(t), (D)-(p)
(*c*) (A)-(s), (B)-(r), (C)-(t), (D)-(p)
(*d*) (A)-(q), (B)-(p), (C)-(r), (D)-(s)

PW CHALLENGERS

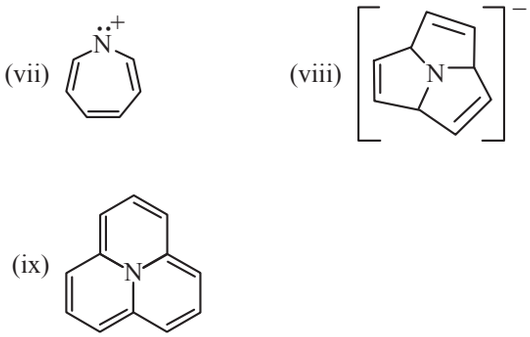
1. Arrange in order of resonance energy per ring
Benzene, Naphthalene, Anthracene, Phenanthrene

2. Arrange in order of resonance energy:
Pyrrole, Furan, Pyridine, Thiophene, Benzene

3. Which of the following are aromatic species?

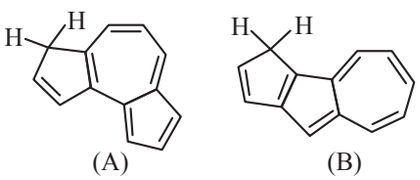


(i) (ii) (iii) (iv) (v) (vi)



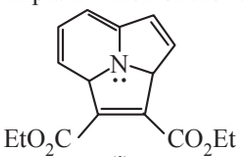
(vii) (viii) (ix)

4. Explain which is more acidic: (A) or (B)?

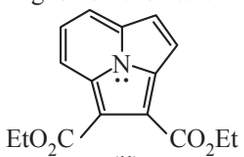


(A) (B)

5. Explain which of the following is non-aromatic?

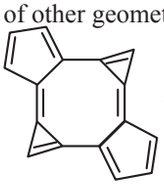


(i)

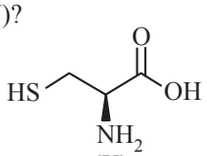


(ii)

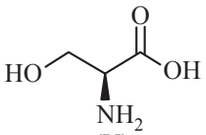
6. Explain that one of the geometrical isomer of following compound, Bicalicene is aromatic. Also identify the nature of other geometrical isomer.


(Q) = trans-Bicalicene

7. Explain which is more acidic among cysteine (X) and serine (Y)?

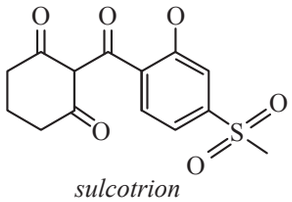


(X)



(Y)

8. The structure of the herbicide *sulcotrion* is shown below and is found to have a pK_a of 3.13. Draw the structure of the conjugate base and explain the unusual acidity of this 'carbon acid'.



sulcotrion

9. Explain the following

(i) All aminobenzoic acids are less acidic than simple benzoic acid.

(ii) para-Aminobenzoic acid is more acidic than ortho-aminobenzoic acid.

10. Lithium deltate, $Li_2C_3O_3$ is a water-soluble white solid having pronounced aromatic character of its anion. Find structure of its anion.

Answer Key

CONCEPT APPLICATION

1. (*d*)	**2.** (*b*)	**3.** (*d*)	**4.** (*a*)	**5.** (*d*)	**6.** (*a*)	**7.** (*c*)	**8.** (*b*)	**9.** (*d*)	**10.** (*d*)
11. (*d*)	**12.** (*d*)	**13.** (*b*)	**14.** (*c*)	**15.** (*c*)	**16.** (*b*)	**17.** (*d*)	**18.** (*c*)	**19.** (*a*)	**20.** (*d*)
21. (*a*)	**22.** (*c*)								

PRARAMBH (TOPICWISE)

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

PRABAL (JEE MAIN LEVEL)

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

PARIKSHIT (JEE ADVANCED LEVEL)

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

PYQ's (PAST YEAR QUESTIONS)

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

PW CHALLENGERS

1. Benzene > Naphthalene > Phenanthrene > Anthracene

2. Benzene > Pyridine > Thiophene > Pyrrole > Furan