

## Solved Examples

### JEE Main/Boards

**Example 1:** RSH (Thiols or Mercaptans) ( $pK_a = 11$ ) are more acidic than alcohols ( $pK_a = 17$ ).

**Sol:** This can be explained by considering the comparative size of sulphur and oxygen and bond dissociation energies of S-H and O-H.

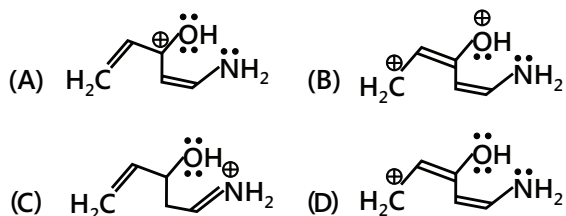
i. The S atom is larger and is more polarised than the O atom. S compounds are more powerful nucleophiles and compounds containing (SH) groups are stronger acids than their oxygen analogues. Also,  $C_2H_5S^-$  ion is a stronger nucleophile than  $C_2H_5O^-$  ion.

ii. Bond dissociation energy of (S-H) bonds of thiols (9~330 kJ) is much less than (O-H) bond of a alcohols (~420 kJ). Thiols undergo oxidative coupling reaction with mild OA alcohol do not undergo such reaction.



In alcohols, the oxidation takes place at the weaker (C-H) (~360 kJ) bond rather than at the stronger (O-H) bond.

**Example 2:** Which of the following is the most stable resonance structure?



**Sol:** (C) Structure (C) is the most stable resonance structure.

i. Number of covalent bonds in (A) and (B) = 13.

ii. Number of covalent bonds in (C) and (D) = 14.

iii. In (C), positive charge is on N, whereas in (D), it is on O atom. Since N is less EN (electronegative) than O, (C) is more stable.

**Example 3:** Give the stability order of the following resonance structures is -



**Sol:** The lesser the charge separation more stable the resonating structure.

(I) and (III) have less charge separation. But in (III), charge is on an electropositive C atom. Therefore, (I) is more stable than (III). Since both have six covalent bonds, so (I) is more stable than (III) (I > III).

Both (II) and (IV) have five covalent bonds, but (II) is more stable than (IV) because in (II) positive charge is on electropositive C atom and negative charge is on EN (electronegative) N atom, whereas in (IV) it is reversed.

Therefore, II > IV.

So, the stability order is I > III > II > IV.

**Example 4:** Dibasic acids are stronger than monobasic acids.

**Sol:** Dicarboxylic acids are stronger than monocarboxylic acids because (-COOH) group is an e-withdrawing group.

Order of acidity: Oxalic > Malonic > Succinic > Glutaric > Adipic > Butanoic acid.

$$pK_{a1} = 1.27 \quad 2.86 \quad 4.21 \quad 4.34 \quad 4.41 \quad 4.82$$

$$pK_{a2} = 4.27 \quad 5.70 \quad 5.64 \quad 5.27 \quad 5.28$$

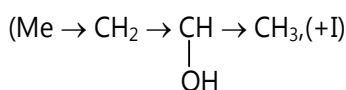
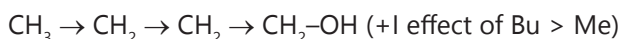
The above order of dibasic acid is due to an increasing number of alkyl group (e-donating group) or increasing number of  $\sigma$ -bonds between (-COOH) and (-COO<sup>-</sup>).

**Example 5:** Arrange the following in the decreasing order of acidity:

- |   |                                       |
|---|---------------------------------------|
| i. 1. n-Butanol                           | 2. Methyl alcohol                     |
| 3. sec-Butanol                            | 4. tert-Butanol                       |
| ii. 1. HCOOH                              | 2. CH <sub>3</sub> COOH               |
| 3. C <sub>2</sub> H <sub>5</sub> COOH     | 4. C <sub>6</sub> H <sub>5</sub> COOH |
| 5. (CH <sub>3</sub> ) <sub>2</sub> CHCOOH | 6. CH <sub>2</sub> ClCOOH             |

**Sol:** Electron withdrawing group increases the acidic character and Electron Donating Group decreases the acidic character.

i. 1 > 4 > 2 > 3



(+I effect of Et and Me > Me)  $\text{Me} \begin{array}{c} \text{Me} \\ | \\ \text{C}-\text{OH} \\ | \\ \text{Me} \end{array}$  +I effect of three Me groups)

ii.  $6 > 1 > 4 > 2 > 3 > 5$

(In (6) -I effect of Cl > (1) (standard) > (4) + R > -I of Ph > (2) +I effect of Me > (3) effect of two Me groups)

**Example 6:** Arrange the following in decreasing order of acidity:

i. 1. o-Hydroxybenzoic acid

2. p-Hydroxybenzoic acid

3. 2,6-Dihydroxybenzoic acid

ii. 1. HCOOH

2.  $\text{C}_6\text{H}_5\text{COOH}$

3.  $\text{C}_6\text{H}_5\text{OH}$

4. HCl

iii. 1. RCOOH

2. ROH

3. RH

4.  $\text{NH}_3$

5. HOH

6. CH=CH

**Sol:** (i)  $3 > 1 > 2$

(3) Intramolecular H-bonding from two sides > (1) Intramolecular H-bonding from one side > (2) -I and +R effects of OH group at p-position; net effect is e-donating.

ii.  $4 > 1 > 2 > 3$

(4) Inorganic acid > (1) Formic acid (standard) > (2) Benzoic acid, -I and +R of Ph group; net e-donating > (3) Phenol.

iii.  $1 > 5 > 2 > 6 > 4 > 3$

(1) Acid > (5)  $\text{H}_2\text{O}$  > (2) Alcohol > (6) HC=CH (sp character) > (4)  $\text{NH}_3$  > (3) Alkane ( $\text{sp}^3$  character)

**Example 7:** Arrange the following in decreasing order of basicity:

i. 1. RCN

2.  $\text{RNH}_2$

3. R-N=CH-R

ii. 1.  $\text{C}_2\text{H}_5\text{NH}_2$

2. (iso- $\text{C}_3\text{H}_7$ ) $_3\text{N}$

3.  $\text{CH}_3\text{CONH}_2$

4.  $\text{CH}_3\text{NHNa}^\oplus$

iii. 1.  $\text{NH}_2^\ominus$

2.  $\text{HC}\equiv\text{C}^-$

3.  $^- \text{OH}$

4.  $^- \text{OR}$

5.  $\text{R}^-$

6.  $\text{RCOO}^-$

**Sol:** i.  $2 > 3 > 1$

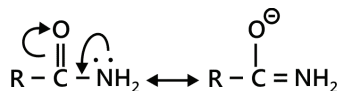
[(2)  $1^\circ\text{R}-\text{NH}_2(\text{sp}^3)$  > (3) R-N=CH-R( $\text{sp}^2$ ) > (1) R-C $\equiv$ N ( $\text{sp}$  character)]

Basicity:  $\text{sp}^3 > \text{sp}^2 > \text{sp}$  character

ii.  $4 > 1 > 2 > 3$

(4) Anion of  $1^\circ$  amine  $\text{CH}_3-\ddot{\text{N}}\text{H}_2^\ominus$

LP e<sup>-</sup>s density increases > (1)  $1^\circ$  amine > (2)  $3^\circ$  amine > (3) amide due to the resonance, non-availability of LP electrons, hence weakest)



iii.  $5 > 1 > 2 > 4 > 3 > 6$

Convert conjugate base into acid by adding  $\text{H}^\oplus$ , find the acidic character and then reverse the order after removing  $\text{H}^\oplus$  ions that would be the order for basic character.

Acidity:  $\text{RCOOH} > \text{H}_2\text{O} > \text{ROH}$

(6) (3) (4)

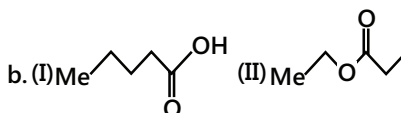
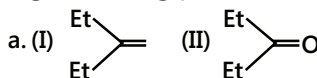
> CH=CH >  $\text{NH}_3$  > RH

(2) (1) (5)

Basicity:  $\text{RCOO}^\ominus < ^-\text{OH} < \text{RO}^- < \text{CH}\equiv\text{C}^\ominus < \overset{\oplus}{\text{N}}\text{H}_2 < \text{R}^-$

(6 < 3 < 4 < 2 < 1 < 5)

**Example 8:** Which of the following pairs would have higher boiling points?



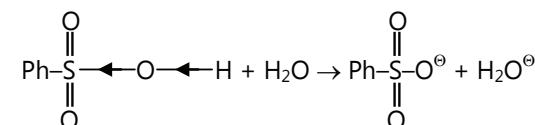
**Sol:** a. (II) because carbonyl group is more polar than double bond.

b. (I) acid forms dimer due to H-bonding.

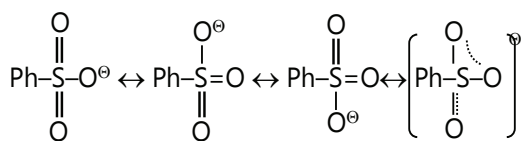
c. (II) cis-compound has high dipole moment ( $\mu$ ), so more polar than trans-compound ( $\mu = 0$ ).

**Example 9:** Sulphonic acids are stronger acids than carboxylic acids

**Sol:**



Benzene sulphuric acid    Benzene sulphonate ion



Oxygen being more EN than S, the sulphonyl group ( $-\text{SO}_2-$ ) having two oxygen atoms greatly facilitates the release of H atom of ( $-\text{SO}_2\text{OH}$ ) group as hydronium ion as shown above.

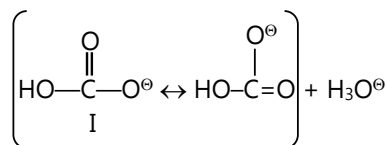
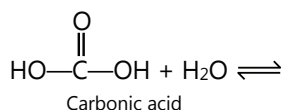
i. Due to the release of a portion, the replacement of ( $-\text{OH}$ ) group is difficult. Hence, esters and amides of sulphuric acids are not formed directly but through their acid chlorides.

ii. Once the sulphonate anion is formed, it is stabilized due to the dispersal of negative charge over three oxygen atoms

Benzene sulphonic acid is a stronger acid than benzoic acid due to greater stabilisation of benzene sulphonate ion than the carboxylate ion.

**Example 10:** Carbonic Acid ( $\text{H}_2\text{CO}_3$ ) is a stronger acid than phenol.

**Sol:** In carbonate anion negative charge is delocalised over two oxygen atom thus it is more stable. As the resonating structure is stable, parent compound is More acidic.



Resonance structure of bicarbonate ion

Resonating structures I and II of the bicarbonate ions are equivalent, whereas the resonating structures of the phenoxide ion are non-equivalent. Hence, the bicarbonate ion is relatively more stable.

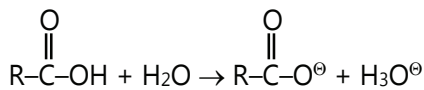
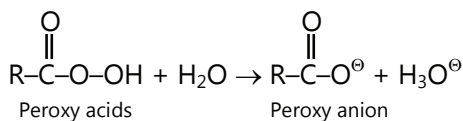
## JEE Advanced/Boards

**Example 1:** Peroxy Acids  $\left( \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{OH} \right)$  are Much Weaker

than Acids  $\left( \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} \right)$

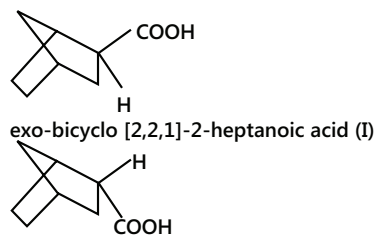
**Sol:** The negative charge on Peroxy anion is localized and hence is not resonance stabilized.

Acid anion is stabilized by resonance as explained earlier.



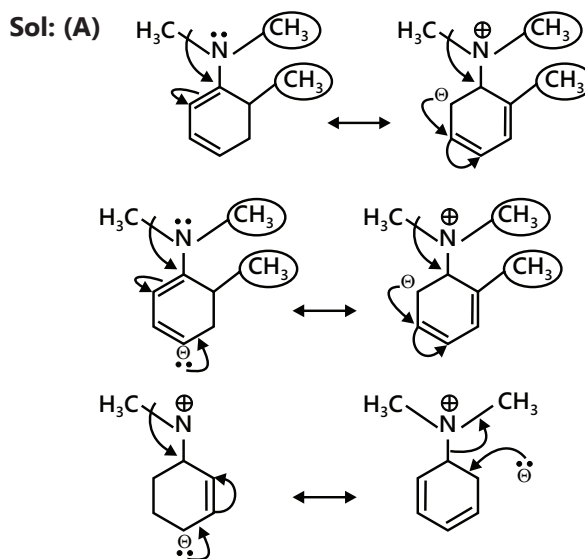
**Example 2:** Exo-2-Norborane Carboxylic Acid (I) is more acidic than endo-Isomer (II)

**Sol:** Exo-bicyclo [2,2,1]-2-heptanoic acid (I)



Here, exo ( $-\text{COO}^-$ ) is less hindered and is thus more exposed to solvent and as a result more acidic.

**Example 3:** Compare the basicity of (a) N,N-dimethyl-o-toluidine and N-dimethyl aniline. (b) Bemzoquinoclidine and N,N-dimethyl aniline. (c) p=Cyanophenol and 5-methyl p-cyanophenol. (d) 2,4,6-DNP and Aniline. (e) Trimethyl amine, pyridine and acetonitrile

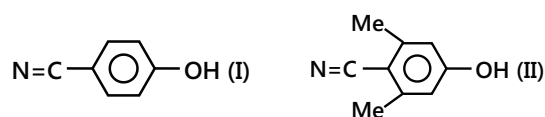


The extent of stabilization due to delocalization is lesser in N, N-dimethyl-o-toluidine than in N, N-dimethyl aniline because in it the  $(-\text{CH}_3)$  group at the o-position and  $(-\text{CH}_3)$  group at nitrogen of the amine group are close enough and the steric hindrance between these groups inhibits the nitrogen atom of the amino group and the benzene ring to become coplanar. Thus, the lone pair of e<sup>-</sup>s over nitrogen is less delocalized in N, N-dimethyl-o-toluidine and therefore, it is more basic of the two.

**(B)** Benzoquinoclidine is a stronger base than N, N-dialkyl aniline derivative, i.e., N, N-dimethylaniline.

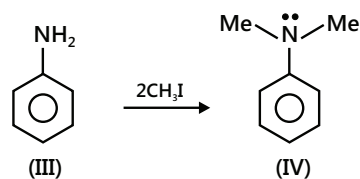
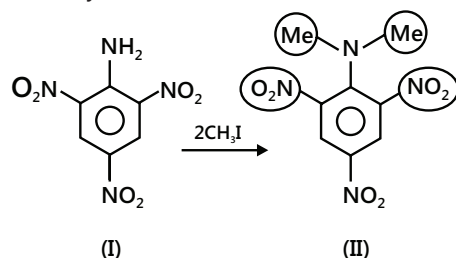
In II, LP of e<sup>-</sup>s on nitrogen is sterically hindered, whereas in I, the groups are only on one side and the pair can be donated comparatively more readily, resulting in (I) being the more basic of the two.

**(C)** The reason why acidity of p-cyanophenol (I) and 3, 5-dimethyl p-cyanophenol (II) is approximately the same is explained below.

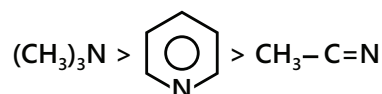


There is no steric inhibition of resonance in both due to the linear cyano group.

**(D)** From the reactions given below it is clear that methylation increases the basicity of 2, 4, 6-trinitroaniline (I) by 40,000 times, whereas nearly triples the basicity of aniline.

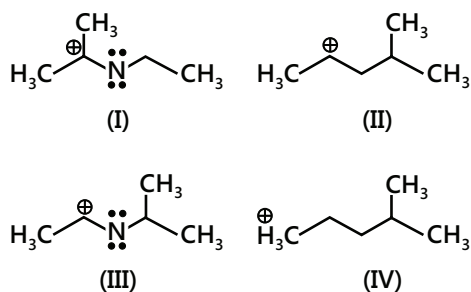


**(E) Basic character:**

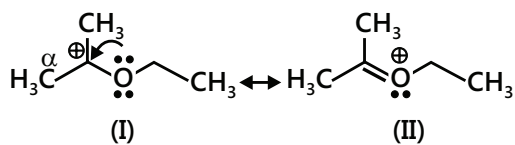


( $sp^3 > so^2 > sp$ , for basic character)

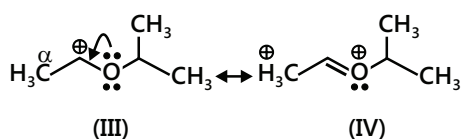
**Example 4:** Gives the correct stability order of the following species:



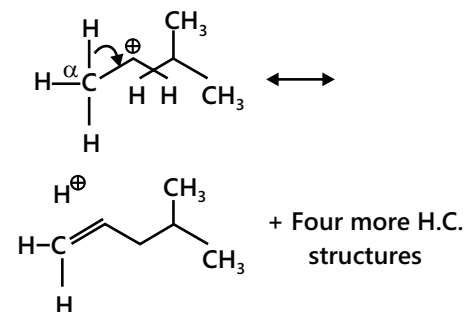
**Sol:** i. (I) is most stable, since it is stabilized by resonance and has six  $\alpha$ -H atoms (hyperconjugation).



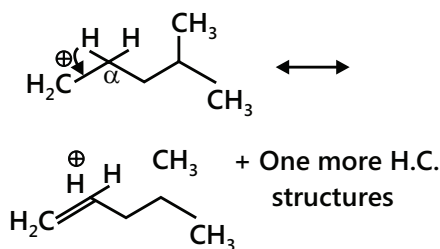
ii. (III) is less stable than (I) but more stable than (II) and (IV), since it is also stabilized by resonance and has three  $\alpha$ -H atoms (hyperconjugation).



iii. (II) is more stable than (IV) and is stabilised only by hyperconjugative structure (five  $\alpha$ -H atoms).

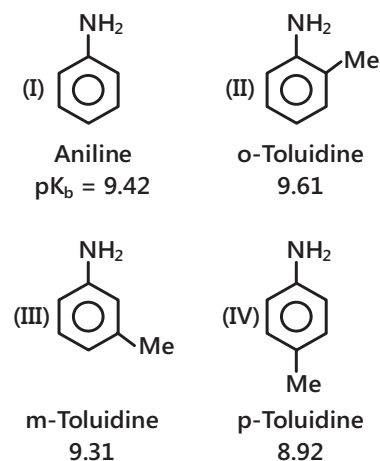


(IV) is least stable; it has only two  $\alpha$ -H atoms.



So, the stability order is  $\text{I} > \text{III} > \text{II} > \text{IV}$ .

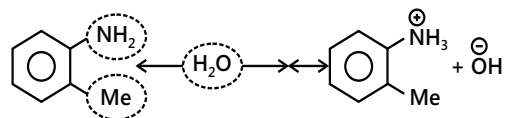
**Example 5:** Compare the basicity of substituted aromatic amines:



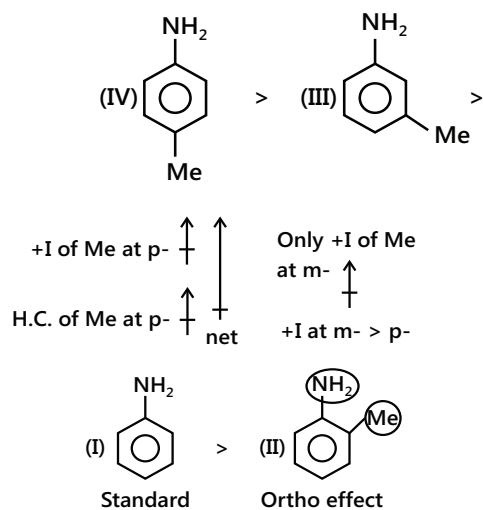
**Sol:** Basic character: IV > III > I > II

(p- > m- > Aniline > o-)

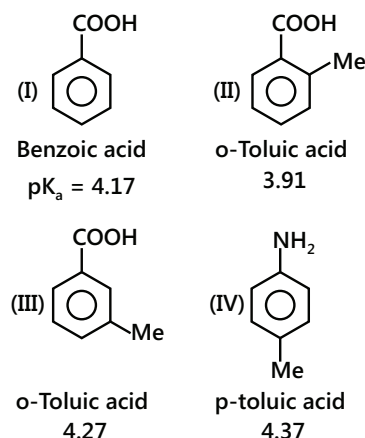
According to +I and H.C. effects, o-isomer (II) should be the strongest base. Due to ortho effect, basic character is decreased. In this case, ortho effect is due to steric hindrance of (Me) group, over the (NH<sub>2</sub>) group; this results in the protonation of (NH<sub>2</sub>) group becoming more difficult (solvation effect), hence the basicity decreases.



In general, basicity order of methyl-substituted aromatic amine is the reverse of the acidic order of methyl-substituted acid.



**Example 6:** Compare the acidity of substituted aromatic acids



**Sol:** Basic character: II > I > III > IV (o- > B.A. > m- > p-).

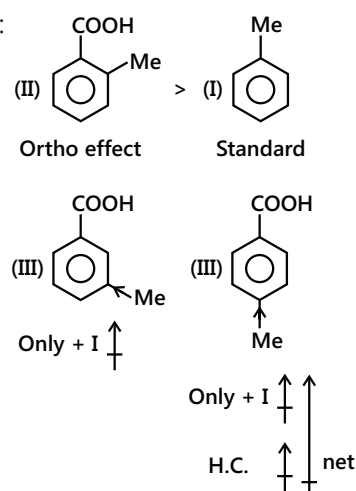
In II, there is ortho effect, strongest acid.

So, o-substituted acid, containing EWG or EDG, is the strongest acid its isomers (except in case of o-amino benzoic acid)

Acidic character of phenolic compound in (a): o- > B.A. > m- > p-

Place o-methyl substituted at the strongest position, keeping the rest of the order same as in Me-substituted phenol.

Explanation:



## JEE Main/Boards

### Exercise 1

**Q.1** Explain tetravalency of carbon.

**Q.2** Why does carbon undergo hybridization prior to bond formation.

**Q.3** Draw the orbital diagram of methane and ethane molecules indicating the hybridization involved.

**Q.4** Which of the following has higher melting point and why?

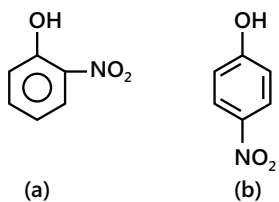
(i) Fumaric acid (ii) Maleic acid

**Q.5** What is the effect of type of hybridization on

(i) Bond length (ii) Bond strength.

**Q.6** Draw bond-line formulae for (a) tert-butylcyclopentane, (b) cyclohexanone.

**Q.7** Which is more soluble and why?



**Q.8** Write condensed and bond-line structural formulae for all the possible isomers of molecular formula

(i)  $C_6H_{14}$

(ii)  $C_6H_{10}$

(iii)  $C_8H_{10}$

(iv)  $C_8H_{18}$

(v)  $C_3H_8O$

(vi)  $C_3H_8O_2$

(vii)  $C_4H_{10}O$

(viii)  $C_6H_{11}NO_2$

**Q.9** What is a functional group? Write the functional groups of the following:

(i) Thioalcohol

(ii) Isothiocyanate

(iii) Thiocyanate and

(iv) Sulphonic acid

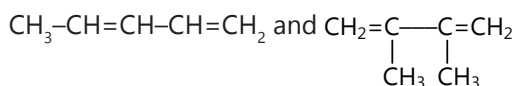
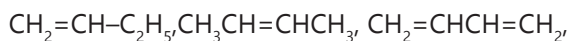
(v) Sulphones

(vi) Sulphoxides

**Q.10** What are homocyclic and heterocyclic compounds? Given two examples with their names.

**Q.11** Hydrazine does not show a positive test for Lassaigne's test of nitrogen. Why?

**Q.12** Giving reason arrange the following in increasing order of reactivity towards HBr.



**Q.13** What is homologous series? Given its important characteristics. Write the first four homologues of alcohols and give their IUPAC names.

**Q.14** Explain in the following terms with one example in each case, (i) word root (ii) primary and secondary suffixes and prefixes.

**Q.15** 0.2018 gm of silver salt of dibasic acid gives 0.1073 gms of silver on complete ignition. What is the molecular weight of the acid?

**Q.16** When is the process of fraction crystallization employed?

**Q.17** 0.3168 gms of the platonic chloride of a mono acidic base gave 0.1036 gms of platinum, what is the molecular weight of the base?

**Q.18** How will you separate two components when: (a) their boiling points differ by a few degrees,

(a) They are soluble in the same solvent.

(b) They are almost immiscible in water but are volatile in steam?

**Q.19** What is resonance effect? What are its various types? In what respects, does the resonance effect differ from inductive effect?

**Q.20** Common upon the statement: 'Usual order of inductive effects of the alkyl groups is often reversed when attached to a double or a benzene ring.' Name the electronic effect and illustrate your answer with suitable examples.

**Q.21** Explain hyperconjugation effect.

**Q.22** What is principle of column chromatograph?

**Q.23** Explain the principle of steam distillation.

**Q.24** When is the process of fractional distillation employed?

## Exercise 2

### Single Correct Choice Type

**Q.1** Which of the following species have a trigonal planar shape?

- (A)  $\text{CH}_3^-$  (B)  $\text{CH}_3^+$  (C)  $\text{BF}_4^-$  (D)  $\text{SiH}_4$

**Q.2** A nucleophile must necessarily have -

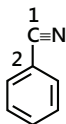
- (A) An overall positive charge  
(B) An overall negative charge  
(C) An unpaired electron  
(D) A lone pair of electrons

**Q.3** Which of the following has a bond formed by overlap of  $\text{sp}^3\text{-sp}^2$  hybrid orbitals?

- (A)  $\text{CH}_3\text{-C}\equiv\text{C-CH}_3$  (B)  $\text{CH}_3\text{-CH=CH-CH}_3$   
(C)  $\text{CH}_2=\text{CH-CH=CH}_2$  (D)  $\text{HC}\equiv\text{C}_2\text{H}_4$

**Q.4** The bond between carbon atoms (1) and carbon atom (2) in compound,

- (A)  $\text{sp}^3$  and  $\text{sp}^2$  (B)  $\text{sp}^2\text{-sp}^3$   
(C)  $\text{sp}$  and  $\text{sp}^2$  (D)  $\text{sp}$  and  $\text{sp}$



**Q.5** In the compound  $\text{CH}_2=\text{CH-CH}_2\text{-CH}_2\text{-CH}_2\text{-C}\equiv\text{CH}$ , the  $\text{C}_2\text{-C}_3$  bond is of the type is -

- (A)  $\text{sp-sp}^2$  (B)  $\text{sp}^3\text{-sp}^3$   
(C)  $\text{sp-sp}^2$  (D)  $\text{sp}^2\text{-sp}^3$

**Q.6** Which of the following species has a trigonal planar shape?

- (A)  $\text{CH}_3^-$  (B)  $\text{CH}_3^+$  (C)  $\text{BF}_4^-$  (D)  $\overset{\cdot}{\text{C}}\text{H}_3$

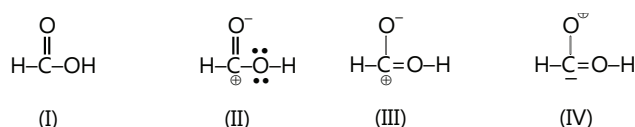
**Q.7** The stability order of alkenes is given as  $\text{CH}_3\text{-CH=CH}_2 > \text{CH}_2=\text{CH}_2$ , the reactivity order towards electrophilic addition reaction is given by

- (A)  $\text{CH}_2=\text{CH}_2 > \text{CH}_3\text{-CH=CH}_2$   
(B)  $\text{CH}_3\text{-CH=CH}_2 > \text{CH}_2=\text{CH}_2$   
(C)  $\text{CH}_3\text{-CH=CH}_2$  equal to  $\text{CH}_2=\text{CH}_2$   
(D) None of these

**Q.8** Carbanion is

- (A) An electrophile (B) A nucleophile  
(C) A zwitter ion (D) A free radical

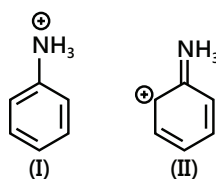
**Q.9** Formic acid is considered as a resonance hybrid of the four structures.



Which of the following order is correct for the stability of the four contributing structures?

- (A)  $\text{I} > \text{II} > \text{III} > \text{IV}$  (B)  $\text{I} > \text{II} > \text{IV} > \text{III}$   
(C)  $\text{I} > \text{III} > \text{II} > \text{IV}$  (D) none of these

**Q.10** Examine the following two structures for the anilinium ion and choose the correct statement from the ones given below.

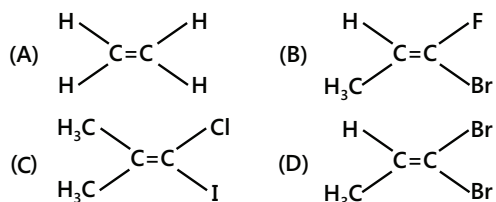


- (A) II is not an acceptable canonical structure because carbonium ions are less stable than ammonium ion  
(B) II is not an acceptable structure because it is non-aromatic  
(C) II is not an acceptable canonical structure because the nitrogen has 10 valence electrons  
(D) II is an acceptable canonical structure

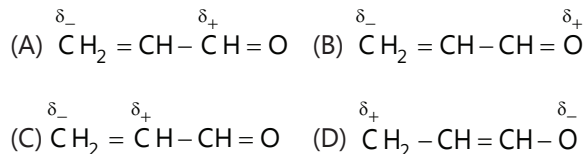
**Q.11**  $\text{HC}\equiv\text{CH} \xrightarrow[\text{H}_2\text{SO}_4]{\text{HgSO}_4} \text{(A)} \xrightarrow[5^\circ\text{C}]{\text{dil. OH}^-} \text{(B)}$ . Give the IUPAC name of B.

- (A) 2-butenal (B) 3-hydroxybutanal  
(C) 3-formyl 2-propanol (D) 4-oxo-2-propanol

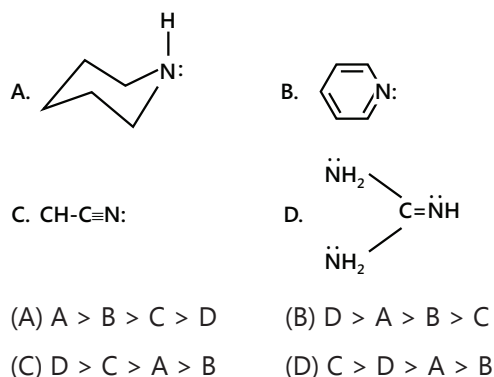
**Q.12** Geometrical isomerism is shown by



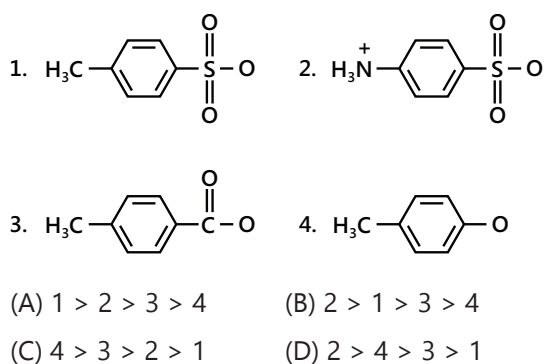
**Q.13** Polarisation of electrons in acrolein may be written as



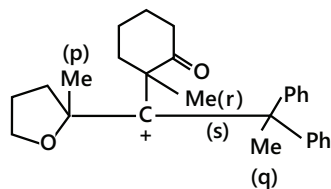
**Q.14** What is the basic strength order



**Q.15** The leaving group ability of the following will be expressed in the order

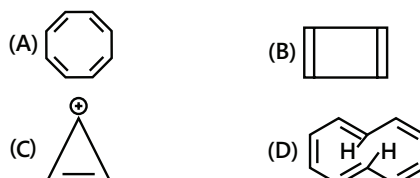


**Q.16** The rearrangement of following carbocation will occur with the shifting of group ... to yield the most stable carbocation



- (A) Me - (p) (B) Me - (q)  
(C) Me - (r) (D) bond - (s)





**Q.17** Which of the following is aromatic



**Q.18** In the identification of phosphorus, the phosphorus in the organic compound is converted to  $\text{PO}_4^{3-}$  using

- (A) NaOH (B)  $\text{Na}_2\text{O}$   
(C)  $\text{Na}_2\text{O}_2$  (D)  $\text{NaO}_2$

**Q.19** The correct reactivity order(s) for  $\text{S}_{\text{N}}1$  reaction is/are

- $\text{Ph}-\text{Br} < \text{Ph}-\text{CH}_2-\text{Br}$
- $\text{Ph}-\text{Br} > \text{PhCH}_2\text{Cl}$
-   $>$  
-   $>$  

- (A) 1, 2, 3 (B) 2, 4 (C) 1, 4 (D) 2, 3, 4

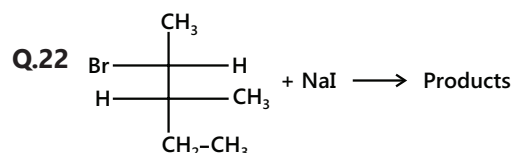
**Q.20** The incorrect statement about  $\text{S}_{\text{N}}1$  reaction is (When only  $\alpha$ -C atom is chiral)

- (A) A stereoisomer is formed  
(B) Two step reaction  
(C) Rearrangement takes place  
(D) The rate is independent of concentration of nucleophile

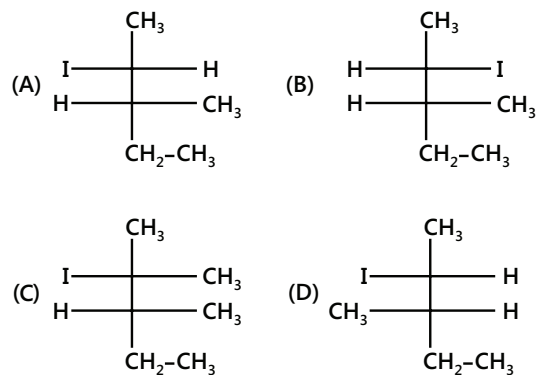
**Q.21** The acidic strength of chloro substituted benzoic acid is

- (A) Benzoic acid  $>$  o-chloro  $>$  m-chloro  $>$  p-chloro  
(B) o-chloro  $>$  m-chloro  $>$  p-chloro  $>$  benzoic acid  
(C) m-chloro  $>$  o-chloro  $>$  p-chloro  $>$  benzoic acid  
(D) None of these

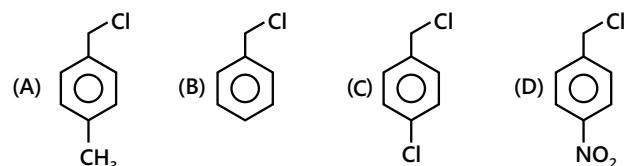




Product of reaction is:



**Q.23** Which of the following is most reactive towards  $S_N2$  reaction?



**Q.24** Magnesia mixture used during estimation of phosphorous is -

- (A)  $MgCl_2 + NH_4Cl$   
 (B)  $HgCl_2 + NH_4Cl + \text{little of } NH_3$   
 (C)  $HgCl_2 + NH_4Cl$   
 (D)  $MgCl_2 + NH_4Cl + \text{little of } NH_3$

**Q.25** In the Kjeldal's estimation of nitrogen in the form of  $NH_3$  small amounts of  $K_2SO_4$  is added to the system -

- (A) Here  $K_2SO_4$  acts as a catalyst  
 (B) To provide common ion effect for dissociation of  $CuSO_3$   
 (C)  $K_2SO_4$  is responsible for converting  $NH_3$  to  $(NH_4)_2SO_4$   
 (D)  $K_2SO_4$  raises the boiling point of  $H_2SO_4$

**Q.26** The compound having maximum enol content -

- (A)  $CH_3CH_2CHO$  (B)  $CH_3COCH_3$   
 (C)  $CH_3CHO$  (D)  $CH_3COCH_2COCH_3$

**Q.27** In which of the following pairs the difference in dipole moment is maximum -

- (A) cis and trans 1,2-Dichloro ethane  
 (B) cis and trans 1-chloropropene  
 (C) o-Xylene, m-xylene  
 (D) Dipole moment does not change with configuration

**Q.28** The stability of carbenes is -

- (A) Singlet carbene > Triplet carbene  
 (B) Singlet carbene = Triplet carbene  
 (C) Singlet carbene < Triplet carbene  
 (D) Cannot be predicted

**Q.29** The number of isomeric chloro butanes formed by the monochlorination of n-butane are -

- (A) 1 (B) 2 (C) 3 (D) None of these

**Q.30** The reactivity order of  $HCHO$ ,  $ArCHO$ ,  $ArCOAr$ ,  $ArCOR$ ,  $RCOR$  is towards nucleophilic attack is -

- (A)  $HCHO > ArCHO > ArCOAr > ArCOR > RCOR$   
 (B)  $HCHO > ArCOAr > ArCHO > ArCOR > RCOR$   
 (C)  $HCHO > ArCHO > RCOR > ArCOAr > RCOAr$   
 (D) None of these

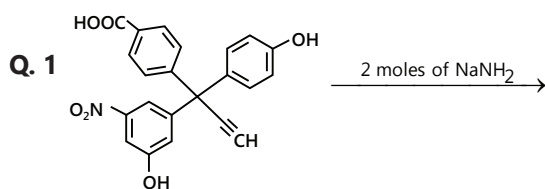
**Q.31** The number of meso forms for glucose are

- (A) 1 (B) 2  
 (C) 3 (D) None of these

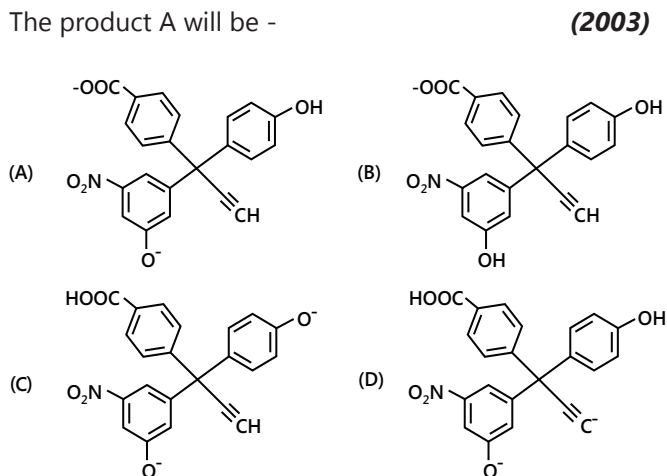
**Q.32** The Lassaigne's extract is boiled with dil.  $HNO_3$  before testing for halogens such that -

- (A)  $AgX$  is soluble in  $HNO_3$   
 (B)  $Na_2S$  and  $NaCN$  are decomposed by  $HNO_3$   
 (C)  $Ag_2S$  is soluble in  $HNO_3$   
 (D)  $AgCN$  is soluble in  $HNO_3$

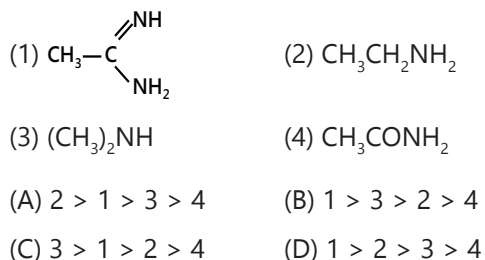
## Previous Years' Questions



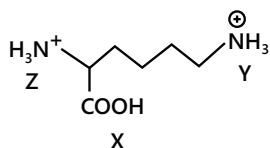
The product A will be -



**Q.2** The correct order of basicity of the following compounds is - (2001)



**Q.3** Arrange in order of increasing acidic strength (2004)

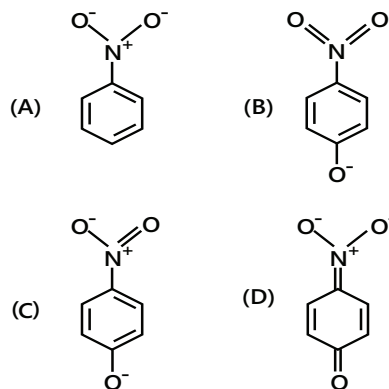


- (A)  $X > Z > Y$  (B)  $Z < X > Y$
- (C)  $X > Y > Z$  (D)  $Z > X > Y$

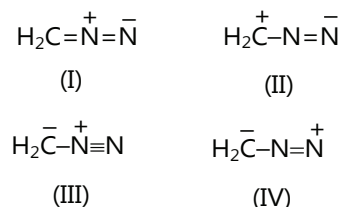
**Q.4** Which of the following, has the most acidic hydrogen? (2000)

- (A) 3-hexanone (B) 2,4-hexanedione
- (C) 2,5-hexanedione (D) 2,3-hexanedione

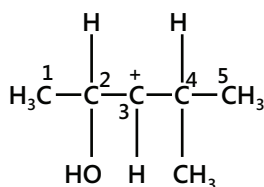
**Q.5** The most unlikely representation of resonance structure of p-nitrophenoxide ion is (1999)



**Q.6** The correct stability order of the following resonance structures is - (2009)



**Q.7** In the following carbocation, H/ $\text{CH}_3$  that is most likely to migrate to the positively charged carbon is (2009)

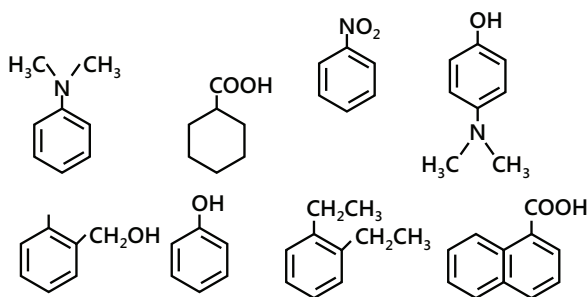


- (A)  $\text{CH}_3$  at C-4 (B) H at C-4
- (C)  $\text{CH}_3$  at C-2 (D) H at C-2

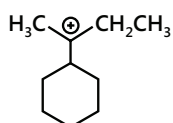
**Q.8** Hyperconjugation involves overlap of the following orbitals - (2008)

- (A)  $\sigma$ -s (B)  $\sigma$ -p (C) p-p (D)  $\pi$ -p

**Q.9** Amongst the following, the total number of compound soluble in aqueous NaOH is – (2010)



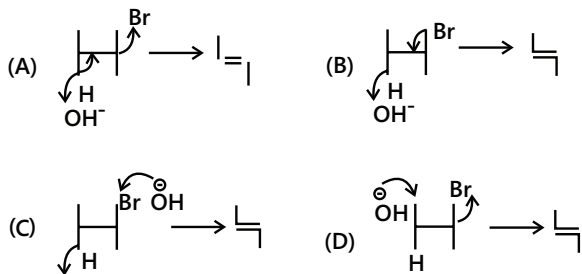
**Q.10** The total number of contributing structures showing hyper conjugation (involving C-H bonds) for the following carbocation is (2011)



**Q.11** The optically active tartaric acid is named as D-(+)-tartaric acid because it has positive (1999)

- (A) Optical rotation and is derived from D-glucose  
 (B) pH in organic solvent  
 (C) Optical rotation and is derived from D(+) glyceraldehydes  
 (D) Optical rotation only when substituted by deuterium

**Q.12** Dehydrohalogenation in presence of OH<sup>-</sup> is correctly represented by – (2004)



**Q.13** Which one of the following species is most stable (1995)

- (A)  $p\text{-O}_2\text{N-C}_6\text{H}_4\text{-CH}_2^+$  (B)  $p\text{-CH}_3\text{O-C}_6\text{H}_4\text{-CH}_2^+$   
 (C)  $p\text{-Cl-C}_6\text{H}_4\text{-CH}_2^+$  (D)  $\text{C}_6\text{H}_5\text{-CH}_2^+$

**Q.14** Which of the following has the highest nucleophilicity – (2000)

- (A) F<sup>-</sup> (B) OH<sup>-</sup> (C) CH<sub>3</sub><sup>-</sup> (D) NH<sub>2</sub><sup>-</sup>

**Q.15** Dipole moment is shown by – (1986)

- (A) 1, 4-dichloro benzene  
 (B) Cis-1, 2-dichloro ethene  
 (C) Trans-1,2dichloro-2-pentene  
 (D) Trans-1,2dichloro ethene

**Q.16** The molecules that will have dipole moment are – (1992)

- (A) 2,2-dimethyl propane  
 (B) Trans-2-pentene  
 (C) Cis-3-hexene  
 (D) 2,2,3,3-tetramethyl butane

**Q.17** Only two isomers of monochloro product is possible of – (1986)

- (A) n-butane (B) 2,4-dimethyl pentane  
 (C) Benzene (D) 1-methyl propane

Each of the questions given below consists of two statements, an assertion (Assertion) and reason (Reason). Select the number corresponding to the appropriate alternative as follows

- (A) If both assertion and reason are true and reason is the correct explanation of assertion.  
 (B) If both assertion and reason are true and reason is not the correct explanation of assertion.  
 (C) If assertion is true but reason is false.  
 (D) If assertion is false but reason is true.

**Q.18 Assertion:** Carbon-oxygen bonds are of equal length in carbonate ion. (1993)

**Reason:** Bond length decreases with the multiplicity of bond between two atoms.

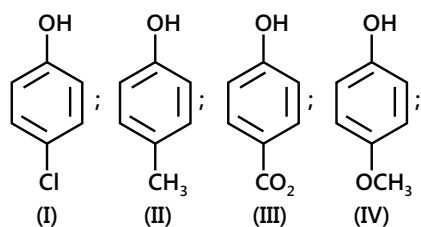
**Q.19 Assertion:** Boiling points of cis-isomers are higher than trans-isomers. (1997)

**Reason:** Dipole moments of cis-isomers are higher than trans-isomers.

**Q.20 Assertion:** Diastereoisomers have different physical properties. (1986)

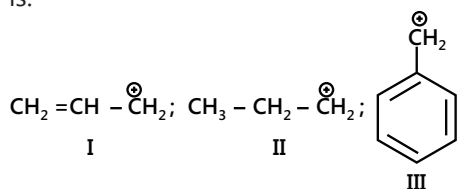
**Reason:** They are non-superimposable mirror images.

**Q.21** Arrange the following compounds in order of decreasing acidity: (2013)



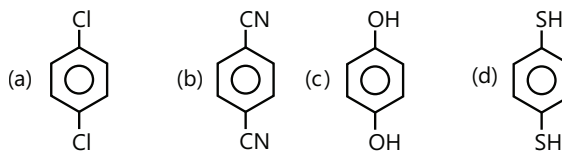
- (A) II > IV > I > III                      (B) I > II > III > IV  
 (C) III > I > II > IV                      (D) IV > III > I > II

**Q.22** The order of stability of the following carbocation is: (2013)



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

**Q.23** For which of the following molecule significant  $\mu \neq 0$ ? (2014)



- (A) Only (c)                      (B) (c) and (d)  
 (C) Only (a)                      (D) (a) and (b)

## JEE Advanced/Boards

### Exercise 1

**Q.1** Explain the term hybridization. Why does carbon undergo hybridization? Explain the different types of hybridizations carbon atom can undergo?

**Q.2** In terms of hybridization of carbon atom, discuss briefly the shapes of methane, ethane, ethene and ethyne?

**Q.3** Explain?

- (a) Although boron trifluoride is insoluble in trimethylamine, it is soluble in triphenylamine.  
 (b) Which  $CX_2$  ( $X = F, Cl, Br, I$ ) is the most stable radical and why?

**Q.4** Discuss classification of hydrocarbons into various types and illustrate each class by taking two examples?

**Q.5** Explain the following giving examples?

- (i) Functional group  
 (ii) Homologous series and its characteristics

**Q.6** Sulphanilic acid although has acidic as well as basic group, it is soluble in alkali but insoluble in mineral acids. Explain.

**Q.7** What is meant by hybridization? Discuss its various type giving at least one example in each case.

**Q.8** Define tautomerism. Discuss briefly keto-enol tautomerism in aldehydes and ketones. Also discuss the conditions under which enol form predominates.

**Q.9** Write equations for the acid base reaction that would occur when each of the following compounds of solution are mixed. In each case label the stronger acid and stronger base and the weaker acid and weaker base.

- (a)  $NaNH_2$  is added to acetylene  
 (b) gaseous  $NH_3$  is added to ethyl lithium in hexane  
 (c)  $C_2H_5OH$  is added to a solution of  $HC \equiv C^-Na^+$  in liquid  $NH_3$ .  
 (d)  $NaH$  is added to  $H_3COH$ .

**Q.10** Give a brief account of the various types of electronic effects in a covalent molecule.

**Q.11** Define and explain the term resonance with suitable examples. Comment upon the relative contributions of the various resonance structures.

**Q.12** What is hyperconjugation effect? How does it differ from resonance effect. Briefly discuss the significance of hyperconjugation effect.

**Q.13** How are free radicals, carbocations and carbanions produced? Discuss their relative stabilities.

**Q.14** Cyclohexanol is more soluble in water than 1-hexanol why?

**Q.15** 1, 5-Pentanediol is soluble and 1-pentanol is slightly soluble in  $H_2O$ . Justify the statement.

**Q.16**  $1^\circ$  and  $2^\circ$  amides tend to exist as dimers in solid and pure liquid state.

**Q.17** Give an account of common types of organic reactions with suitable examples.

**Q.18** Explain the following with one example in each case.

- (i) Homolytic fission
- (ii) Heterolytic fission of covalent bonds.

**Q.19** What are electrophiles and nucleophiles? Explain with examples.

**Q.20** What are reactive intermediates? How are they generated by bond fission?

**Q.21** Discuss the stability of carbanions on the basis of inductive effects.

**Q.22** Explain the following:

(a) p-chlorobenzene is more soluble in n-propyl alcohol than methyl alcohol, while o-dichlorobenzene is less soluble in n-propyl alcohol than methanol.

(b) Heterolytic cleavage requires more energy than homolytic cleavage.

**Q.23** How many isomers of molecular formula  $C_3H_7NO$  are possible when all isomers have 'amide' group. If one of the isomer has different properties, name that isomer and give reason of different characteristics.

**Q.24** Explain the following reactions:

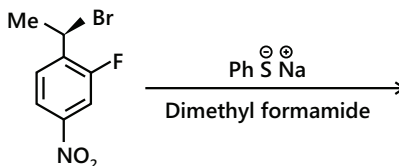
- (i) Substitution
- (ii) Addition
- (iii) Elimination
- (iv) Rearrangement
- (v) Isomerization
- (vi) Condensation
- (v) Pericyclic

**Q.25** Sulphanilic acid although has acidic as well as basic group, it is soluble in alkali but insoluble in mineral acids. Explain.

## Exercise 2

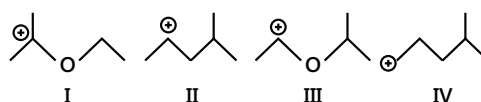
### Single Correct Choice Type

**Q.1** The major product of the following reaction is



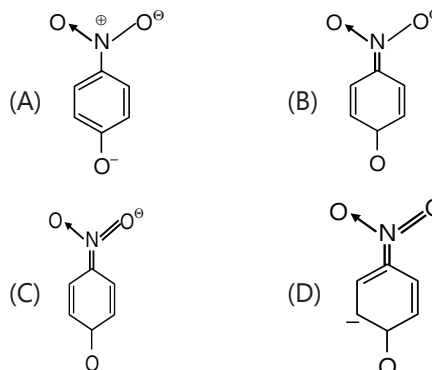
- (A) (B)
- (C) (D)

**Q.2** The correct stability order for the following species is



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

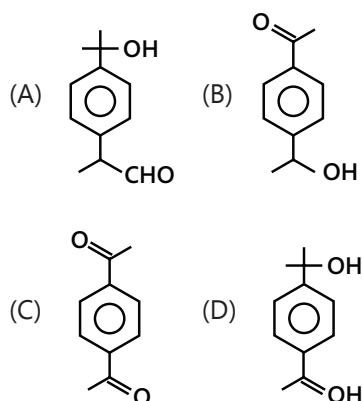
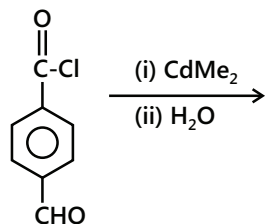
**Q.3** The most unlikely representation of resonance structure of p-nitrophenoxide ion is



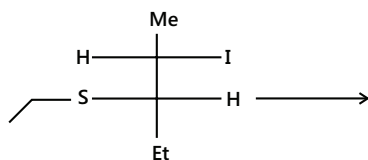
**Q.4** Which of the following is an electrophile?

- (A)  $AlCl_4^-$       (B)  $BCl_3$       (C)  $NH_3$       (D)  $CH_3OH$

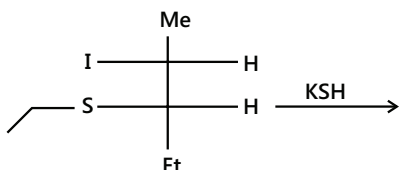
**Q.5** Product of the following reaction is



**Q.6** Reaction A:

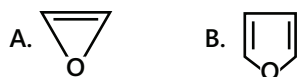


Reaction B:



- (A) Products are same and mechanism is also same  
 (B) Products are same but mechanism is different  
 (C) Products are different but mechanism is same  
 (D) Products are different and mechanism is also different

**Q.7** The stability order of the compounds



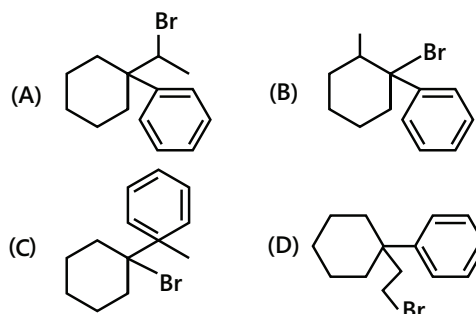
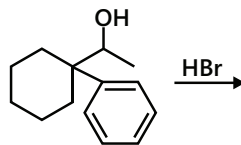
- (A)  $A < B$       (B)  $A > B$   
 (C)  $A = B$       (D) Stabilities cannot be compared

**Q.8** The acidic strength of chloro substituted benzoic acid is

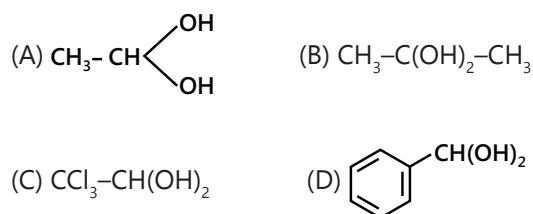
acid is

- (A) Benzoic acid > o-chloro > m-chloro > p-chloro  
 (B) o-chloro > m-chloro > p-chloro > benzoic acid  
 (C) m-chloro > o-chloro > p-chloro > benzoic acid  
 (D) None of these

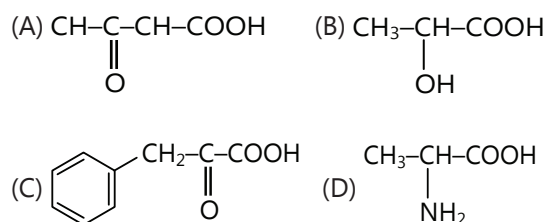
**Q.9** The major product of following reaction is



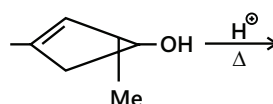
**Q.10** Which one among the following geminal dihydroxy compound is most stable -

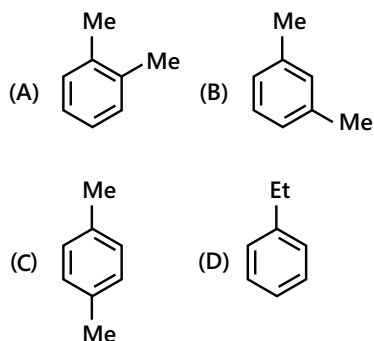


**Q.11** Which of the following can undergo decarboxylation reactions most easily



**Q.12** Write the product of the following reaction:

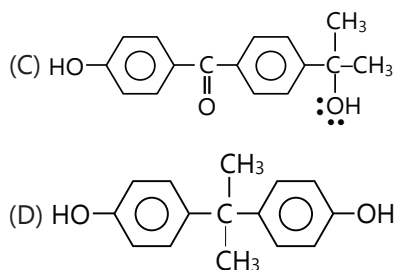
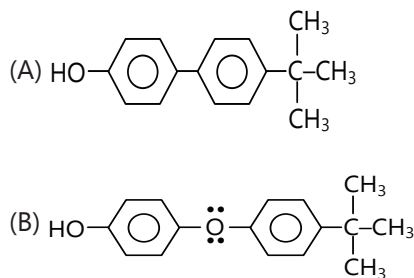
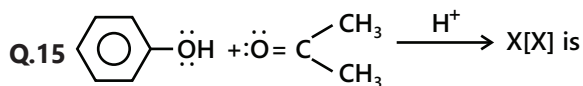
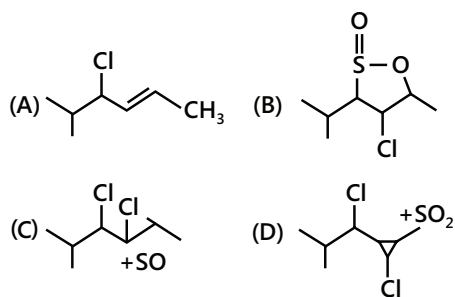
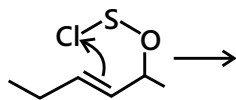




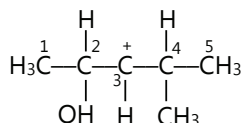
**Q.13** Select the incorrect option amongst the following statements

- (A) Bimolecular elimination of alkyl halides is a stereospecific reaction
- (B) In  $S_N2$  reaction a single isomer is the only product
- (C) n-Propyl alcohol dehydrates in strongly basic conditions by E1cB mechanism
- (D) 3-Hydroxypropanal dehydrates in strongly basic conditions by E1cB mechanism

**Q.14** Which of the following is the most likely product from the reaction illustrated by the curved arrows in the formula?



**Q.16** In the following carbocation, H/CH<sub>3</sub> that is most likely to migrate to the positively charged carbon is



- (A) CH<sub>3</sub> at C-4                      (B) CH<sub>3</sub>COCH<sub>3</sub>
- (C) CH<sub>3</sub>CHO                          (D) H at C<sub>2</sub>

**Q.17** The compound having maximum enol content -

- (A) CH<sub>3</sub>CH<sub>2</sub>CHO                      (B) CH<sub>3</sub>COCH<sub>3</sub>
- (C) CH<sub>3</sub>CHO                          (D) CH<sub>3</sub>COCH<sub>2</sub>COCH<sub>3</sub>

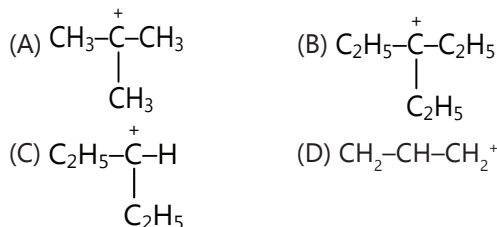
**Q.18** Which of the following statement is correct?

- (A) Trimethylmethyl and triphenylmethyl radicals, both being 3° free radical, equally exist in solution
- (B) Stability order of carbanions always follows reverse order to that of corresponding carbocations
- (C) Among the simple alkyl carbocations, the most stable one is  $CH_3^+$  because here the positive charge is dispersed only to small extent
- (D) None of these

**Q.19** The heat of hydrogenation of benzene is 49.8 Kcal/mole while its resonance energy is 36.0 Kcal/mole. Then the heat of hydrogenation of cyclohexene is -

- (A) 28.6 K cal/mole                      (B) 13.8 K cal/mole
- (C) 85.8 K cal/mole                      (D) 36.0 K cal/mole

**Q.20** Which carbocation among the following is most stable -



**Multiple Correct Choice Type**

**Q.21** Resonance structure of a molecule should have –

- (A) Identical arrangement of atoms
- (B) Nearly the same energy content
- (C) The same number of paired electrons
- (D) Identical bonding

**Comprehension Type****Paragraph 1 (Q.22 to 24)**

Conformation are structures obtained by rotation around  $\sigma$  bonds without breaking and remaking the bonds. Ethane has staggered and eclipsed conformations. Staggered conformation is more stable than eclipsed conformation.

**Q.22** The total number of possible conformation of ethane are –

- (A) 2
- (B) 3
- (C) Infinite
- (D) Zero

**Q.23** Which conformation of cyclohexane is most stable?

- (A) Chair
- (B) Boat
- (C) Half-chair
- (D) Half-boat

**Q.24** Which of the following is correct?

- (A) Conformations cannot be isolated due to less difference in their energy
- (B) Conformations can be isolated
- (C) Conformations are obtained by breaking and remaking the bonds
- (D) Conformations are same as configurational isomers

**Paragraph 2 (Q.25 to 27)**

Those compounds which rotate plane polarised light are optically active compounds. They must be chiral, i.e. should not have any plane of symmetry. They should have chiral carbon atom. Meso compounds have internal plane of symmetry.

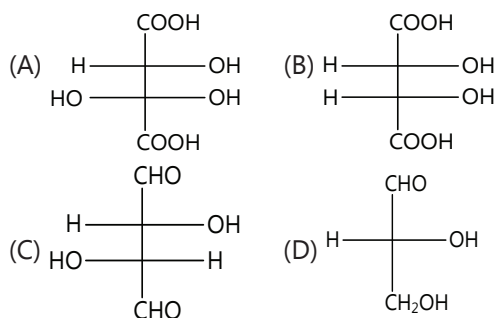
**Q.25** Which of the following alkane shows optical isomerism?

- (A) 2-methyl pentane
- (B) 3-methyl pentane
- (C) 2,3-dimethyl pentane
- (D) Both (B) and (C)

**Q.26** Which the following are pair of enantiomers?

- (A) d-glucose and l-glucose
- (B) Glucose and L-glucose
- (C) Racemic-tartaric acid
- (D) Meso-tartaric acid

**Q.27** Which of the following is meso compounds?

**Assertion Reasoning Type**

Each of the questions given below consists of two statements, an assertion (Assertion) and reason (Reason). Select the number corresponding to the appropriate alternative as follows

- (A) If both assertion and reason are true and reason is the correct explanation of assertion.
- (B) If both assertion and reason are true and reason is not the correct explanation of assertion.
- (C) If assertion is true but reason is false.
- (D) If assertion is false but reason is true.

**Q.28 Assertion:** Trophylum cation is more stable than  $(\text{CH}_3)_3\text{C}^+$ .

**Reason:** It is stabilized by both resonance effect and inductive effect.

**Q.29 Assertion:** In benzyne, two out of six carbon atoms are sp-hybridised.

**Reason:** Benzyne has one  $\text{C} \equiv \text{C}$  bond.

**Q.30 Assertion:**  $\text{PH}_3$  is stronger nucleophile than  $\text{NH}_3$ .

**Reason:**  $\text{PH}_3$  is stronger base than  $\text{NH}_3$ .

**Q.31 Assertion:** The carbocation  $\text{CF}_3 - \overset{\oplus}{\text{C}}\text{H}_2$  is less stable than  $\overset{\oplus}{\text{C}}\text{F}_3$ .

**Reason:** In case of  $\text{CF}_3 - \overset{\oplus}{\text{C}}\text{H}_2$ ,  $\text{CF}_3$  is strong electron withdrawing, therefore increases +ve, charge whereas



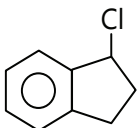
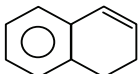
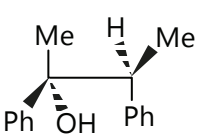
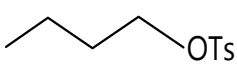
in  $\text{CF}_3^\oplus$ , lone pair of F overlap with vacant p-orbital of carbon reducing +ve charge by  $p\pi-p\pi$  bonding or back bonding.

### Match the Columns

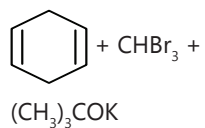
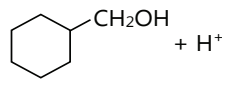
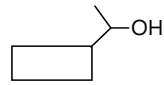
**Q.32** Match the following:

Column I		Column II	
(A)	Carbocations	(p)	E1
(B)	Tetrahedral transition state	(q)	Nucleophilic-addition
(C)	Pentavalent transition state	(r)	$S_N2$
(D)	Carbonyl compounds	(s)	$C=C + HX$

**Q.33** Match the compounds given in column I with their reactions given column II

Column I		Column II	
(A)		(p)	Halogenation
(B)		(q)	Electrophilic addition reactions
(C)		(r)	Nucleophilic addition reactions
(D)		(s)	Elimination reaction $E_1$ or $E_2$
		(t)	Formation of carbocation intermediate

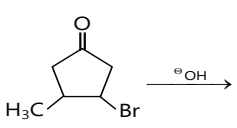
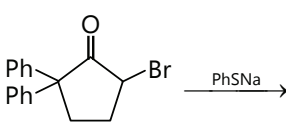
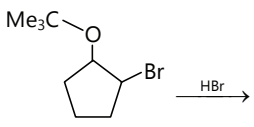
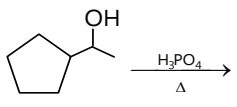
**Q.34** Match the following:

Column I		Column II	
(A)	$(\text{CH}_3)_2\text{C}=\text{CH}_2 + \text{HBr}$	(p)	1° carbocation
(B)		(q)	2° carbocation
(C)		(r)	3° carbocation
(D)		(s)	Carbene

**Q.35** Match the following:

Column I		Column II	
(A)	Carbocation	(p)	Reaction with ethylene
(B)	Carbanions	(q)	Reaction with opposite species
(C)	Carbenes	(r)	Rearrangement
(D)	Free radicals	(s)	Disproportionation

**Q.36** Match the following:

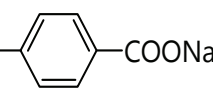
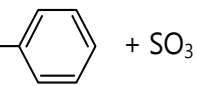
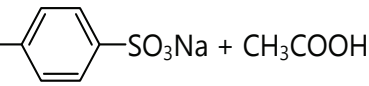
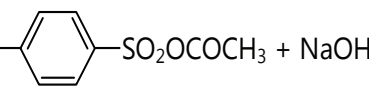
Column I		Column II	
(A)		(p)	$E_2$ (Major)
(B)		(q)	$E_1$ (Major)
(C)		(r)	$S_N1$ (Major)
(D)		(s)	$S_N2$ (Major)
		(t)	$E_1\text{CB}$ (Major)

## Previous Years' Questions

**Q.1** For 1-methoxy-1, 3-butadienium ion which of the following resonating structure is least stable? (2005)

- (A)  $\overset{\ominus}{\text{C}}\text{H}_2 - \overset{\oplus}{\text{C}}\text{H} - \text{CH} = \text{CH} - \text{O} - \text{CH}_3$   
 (B)  $\text{CH}_2 - \text{CH} = \text{CH} - \overset{\oplus}{\text{C}}\text{H} - \text{O} - \text{CH}_3$   
 (C)  $\text{CH}_2 = \text{CH}_2 - \overset{\oplus}{\text{C}}\text{H} = \overset{\ominus}{\text{C}}\text{H} - \text{O} - \text{CH}_3$   
 (D)  $\text{CH}_2 = \text{CH} - \overset{\ominus}{\text{C}}\text{H} - \overset{\oplus}{\text{C}}\text{H} = \text{O} - \text{CH}_3$

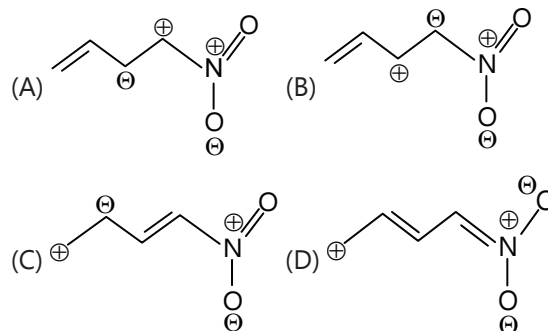
**Q.2** Which of the following is obtained when 4-methylbenzene sulphonic acid is hydrolysed with excess of sodium acetate? (2005)

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

**Q.3** When benzene sulphonic acid and p-nitrophenol are treated with  $\text{NaHCO}_3$ , the gases released respectively are (2006)

- (A)  $\text{SO}_2, \text{NO}_2$  (B)  $\text{SO}_2, \text{NO}$   
 (C)  $\text{SO}_2, \text{CO}_2$  (D)  $\text{CO}_2, \text{CO}_2$

**Q.4** Among the following least stable resonance structure is - (2007)



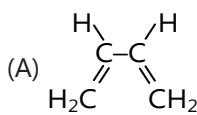
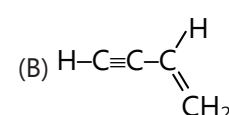
**Q.5** Phenol is less acidic than - (1986)

- (A) Acetic acid (B) p-methoxy phenol  
 (C) p-nitrophenol (D) Ethanol

**Q.6** The compound in which C uses its  $\text{sp}^3$ -hybrid orbitals for bond formation is (2000)

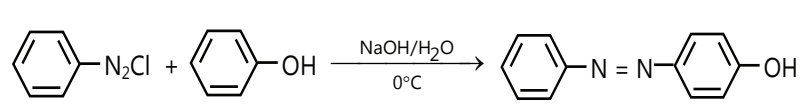
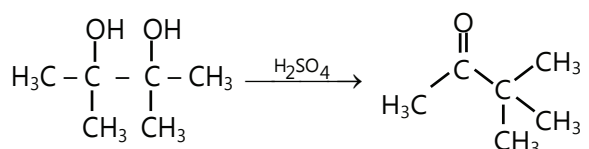
- (A)  $\text{HCOOH}$  (B)  $(\text{H}_2\text{N})_2\text{CO}$   
 (C)  $(\text{CH}_3)_3\text{COH}$  (D)  $\text{CH}_3\text{CHO}$

**Q.7** Amongst the given options, the compound(s) in which all the atoms are in one plane in all the possible conformations (if any), is (are) (2011)

- (A)   
 (B)   
 (C)  $\text{H}_2\text{C}=\text{C}=\text{O}$  (D)  $\text{H}_2\text{C}=\text{C}=\text{CH}_2$

**Q.8**

(2010)

	Column I		Column II
(A)		(p)	Racemic mixture
(B)		(q)	Addition reaction

(C)		(r)	Substitution reaction
(D)		(s)	Coupling reaction
		(t)	Carbocation intermediate

**Q.9** Match the reactions in column I with appropriate type of steps/reactive intermediate involved in these reactions as given in column II **(2011)**

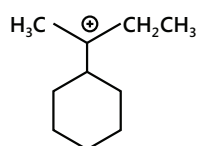
	Column I		Column II
(A)		(p)	Nucleophilic substitution
(B)		(q)	Electrophilic substitution
(C)		(r)	Dehydration
(D)		(s)	Nucleophilic addition
		(t)	Carbanion

**Q.10** Give reasons for the following  $\text{CH}_2=\text{CH}^-$  is more basic than  $\text{HC}\equiv\text{C}^-$ . **(2000)**

**Q.11** Match the following with their  $K_a$  values **(2003)**

(A)	Benzoic acid	(p)	$10.2 \times 10^{-5}$
(B)	p-nitrobenzoic acid	(q)	$3.3 \times 10^{-5}$
(C)	p-chlorobenzoic acid	(r)	$6.4 \times 10^{-5}$
(D)	p-methylbenzoic acid	(s)	$36.2 \times 10^{-5}$

**Q.12** The total number of contributing structures showing hyper conjugation (involving C–H bonds) for the following carbocation is **(2011)**



**Q.13** Among the following compounds, the most acidic is **(2011)**

- (A) p-nitrophenol
- (B) p-hydroxybenzoic acid
- (C) o-hydroxybenzoic acid
- (D) p-toluic acid

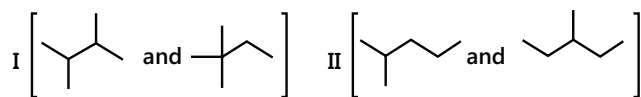
**Q.14** In allene ( $C_3H_4$ ), the type (s) of hybridization of the carbon atoms is (are) **(2012)**

- (A)  $sp$  and  $sp_3$                       (B)  $sp$  and  $sp_2$   
(C) only  $sp^2$                               (D)  $sp^2$  and  $sp^3$

**Q.15** The hyper conjugative stabilities of tert - butyl action and 2 - butane respectively, are due to **(2013)**

- (A)  $\sigma \rightarrow p$  (empty) and  $\sigma \rightarrow \pi$  electron delocalisation  
(B)  $\sigma \rightarrow \sigma$  and  $\sigma \rightarrow \pi$  electron delocalisation's.  
(C)  $\sigma \rightarrow p$  (filled) and  $\sigma \rightarrow \pi$  electron delocalisation's  
(D) P(filled)  $\rightarrow \sigma$  and  $\sigma \rightarrow \pi$  electron delocalisation's

**Q.16** Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure.

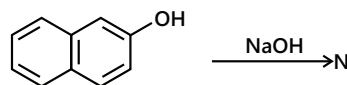


**(2014)**

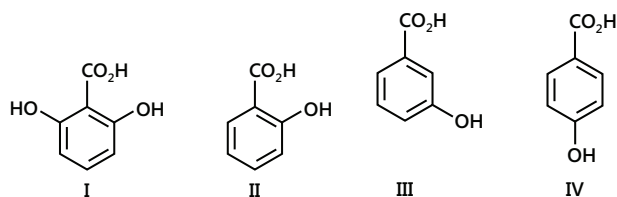
The correct order of their boiling point is

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

**Q.17** The number of resonance structures for N is **(2015)**



**Q.18** The correct order of acidity for the following compounds is **(2016)**



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

# PlancEssential Questions

## JEE Main/Boards

### Exercise 1

- Q.1 (iii)    Q.3                      Q.12 (iii)  
Q.17 (vi, ii)    Q.19 (iv)    Q.22 (ii)    Q.27

### Exercise 2

- Q.2                      Q.14                      Q.19                      Q.27

### Previous Years' Questions

- Q.1                      Q.5                      Q.10

## JEE Advanced/Boards

### Exercise 1

- Q.2                      Q.6(4)                      Q.7(4)  
Q.14                      Q.23                      Q.29

### Exercise 2

- Q.8                      Q.19                      Q.21                      Q.23

### Previous Years' Questions

- Q.2                      Q.4

## Answer Key

### JEE Main/Boards

#### Exercise 1

Q.15 192      Q.26 93.14 g

#### Exercise 2

##### Single Correct Choice Type

Q.1 B	Q.2 D	Q.3 B	Q.4 C	Q.5 D	Q.6 B
Q.7 B	Q.8 B	Q.9 B	Q.10 C	Q.11 B	Q.12 B
Q.13 D	Q.14 B	Q.15 B	Q.16 D	Q.17 C	Q.18 C
Q.19 C	Q.20 A	Q.21 B	Q.22 B	Q.23 D	Q.24 D
Q.25 D	Q.26 D	Q.27 A	Q.28 C	Q.29 B	Q.30 D
Q.31 D	Q.32 B				

##### Previous Years' Questions

Q.1 C	Q.2 A	Q.3 B	Q.4 C	Q.5 A, B, D	Q.6 C
Q.7 D	Q.8 B	Q.9 4	Q.10 B	Q.11 C	Q.12 A
Q.13 B	Q.14 C	Q.15 B	Q.16 C	Q.17 A, D	Q.21 C
Q.22 D	Q.23 B				

### JEE Advanced/Boards

#### Exercise 2

##### Single Correct Choice Type

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

##### Multiple Correct Choice Type

Q.21 A, B, C

##### Comprehension Type

Q.22 C	Q.23 A	Q.24 A	Q.25 C	Q.26 A	Q.27 C
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**Assertion Reasoning Type**

Q.28 A

Q.29 A

Q.30 C

Q.31 A

**Matric Match Type**

Q.32 A → p, s; B → q; C → r; D → q

Q.33 A → p, r, s, t; B → p, q, r, s, t; C → p, r, s, t; D → p, r, t

Q.34 A → p, r; B → r, s; C → p, r; D → q, r

Q.35 A → p, r; B → S; C → p, s; D → q, r, s

Q.36 A → t; B → p; C → r; D → t, b → p; C → r; D → q

**Previous Years' Questions**

Q.1 C

Q.2 C

Q.3 D

Q.4 A

Q.5 B, D

Q.6 C, D

Q.7 B, C

Q.8 A → r, s; B → t; C → p, q; D → r

Q.9 A → r, s, t; B → p, s; C → r, s; D → q, r

Q.11 A → r; B → s; C → p; D → q

Q.12 6

Q.13 C

Q.14 B

Q.15 A

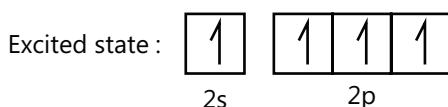
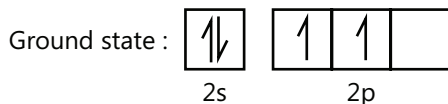
Q.16 B

Q.17 7

Q.18 A

**Solutions****JEE Main/Boards****Exercise 1****Sol 1:** Configuration of C: [He] 2s<sup>2</sup>2p<sup>2</sup>

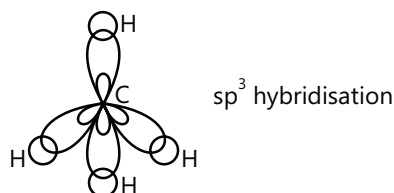
It has four electrons in its outermost shell



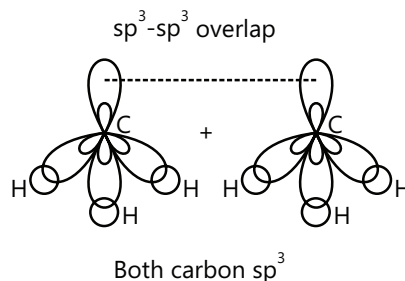
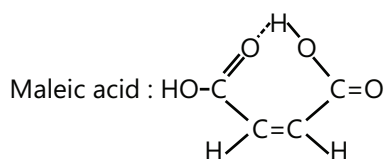
Thus, it has 4 unpaired electrons which it uses in bond forming thus making it tetravalent.

**Sol 2:** Carbon undergoes hybridization due to the following reasons

- Hybridised orbitals are equivalent in energy (degenerate) and have more effective overlapping
- Hybridised orbitals are directional in nature

**Sol 3:** Methane:

Ethane :

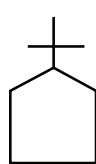
**Sol 4:** Fumaric acid has a higher melting point as maleic acid has intramolecular H-bonding whereas fumaric acid has intermolecular bonding

**Sol 5:** (i) Bond length: Bond length decreases with increasing s character in overlapping orbitals for ex.,  $sp^3$  has the largest bond length and  $sp$  has the least (for carbon compounds)

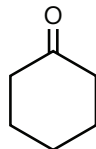
(ii) Bond strength: Bond strength follows opposite order to bond length

**Sol 6:**

(a) Tert-butylcyclopentane



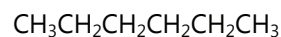
(b) Cyclohexanone



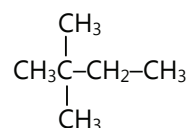
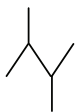
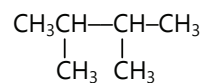
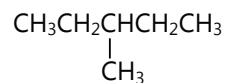
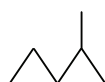
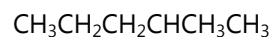
**Sol 7:** (ii) (p-nitrophenol) is more soluble than (i) (o-nitrophenol) as the extent of hydrogen bonding with solvent will be less in (i) due to steric hindrance by a bulky  $NO_2$ -group

**Sol 8:** (i)  $C_6H_{14}$

Condensed

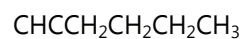


Bond line

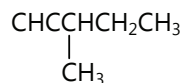
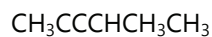
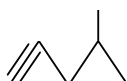
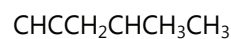
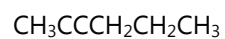


(ii)  $C_6H_{10}$

Condensed



Bond line



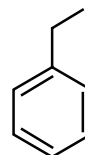
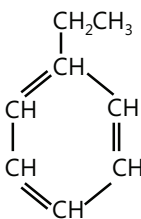
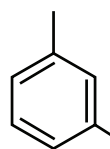
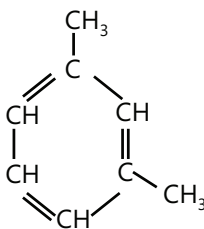
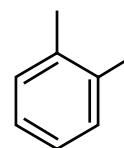
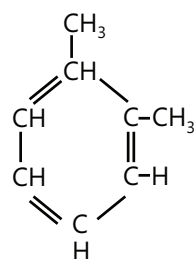
(iii)  $C_8H_{10}$

$$\text{Degree of unsaturation} = 8 - \frac{10}{2} + 1 = 4$$

I am drawing those isomers only which contains a benzene ring.

Condensed

Bond line



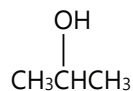
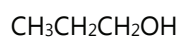
(iv)  $C_8H_{18}$

18 isomers

(v)  $C_3H_8O$

Condensed

Bond line

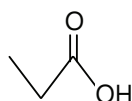
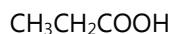
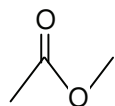
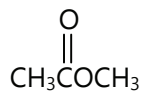
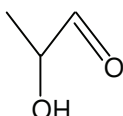
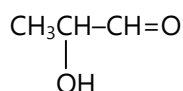
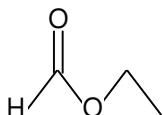
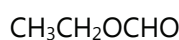
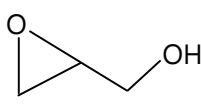
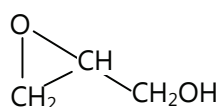
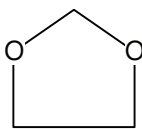
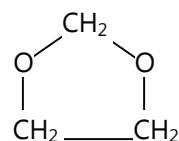
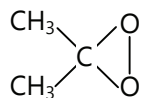


(vi)  $C_3H_6O_2$ 

Degree of unsaturation = 1

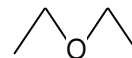
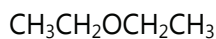
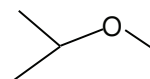
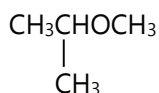
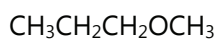
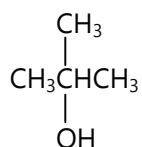
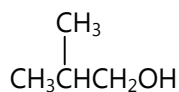
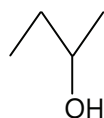
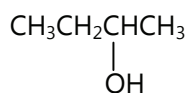
Condensed

Bond line

(vii)  $C_4H_{10}O$ 

Condensed

Bond line

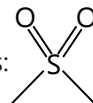
(viii)  $C_6H_{11}NO_2$ 

More than 20 molecules

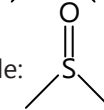
**Sol 9:** Functional group is a specific group of atoms or bonds within molecules that are responsible for the characteristic chemical reaction of those molecules.

(i) Thialcohol:  $-\text{SOH}$ (ii) Isothiocyanate:  $\text{S}=\text{C}=\text{N}-$ (iii) Thiocyanate:  $-\text{S}=\text{C}=\text{N}-$ (iv) Sulphonic acid:  $-\text{SO}_3\text{H}$ 

(v) Sulphones:



(vi) Sulphoxide:



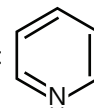
**Sol 10:** Hemicyclic compounds is a cyclic compound that has only one single element as constituent of ring.

E.g.: Cyclopentane :



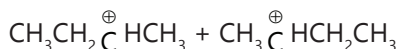
Heterocyclic compounds is a cyclic compound that has atoms of atleast two different elements as members of its ring (s)

E.g.: Pyridine :

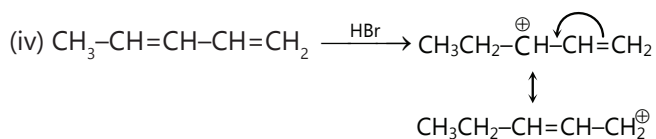
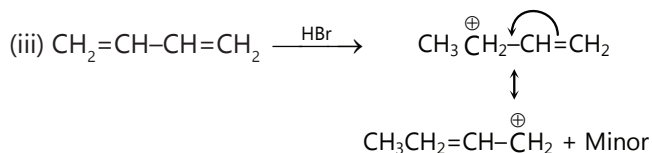


**Sol 11:** Hydrazine ( $\text{H}-\text{N}=\text{N}-\text{H}$ ) does not give a +ve test for Lassaigne's test of Nitrogen because it cannot produce  $\text{NaCN}$ .

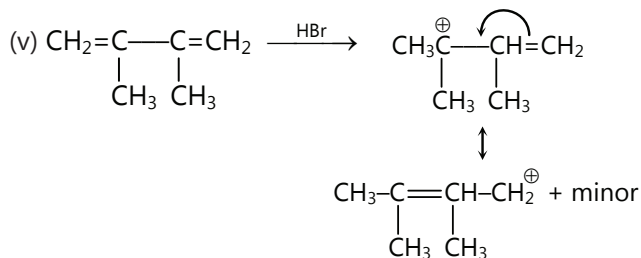
**Sol 12:** (i)  $\text{CH}_2=\text{CH}-\text{C}_2\text{H}_5 \xrightarrow{\text{HBr}}$

(ii)  $\text{CH}_3\text{CH}=\text{CHCH}_3 \xrightarrow{\text{HBr}}$ 





+ minor but stable than III minor



Thus, we see on the basis of resonance and inductive effects (v) > (iv) > (iii) > (ii) > (i)

**Sol 13:** Homologous series is a series of compounds with a similar general formula, usually varying by a single parameter such as the length of the chain.

Members of a homologous series usually have similar physical and chemical properties

Many physical properties, eg. Boiling point gradually increase with molecular mass

Alcohol series:

Methyl alcohol  $\text{CH}_3\text{OH}$

Ethyl alcohol  $\text{C}_2\text{H}_5\text{OH}$

Propyl alcohol  $\text{C}_3\text{H}_7\text{OH}$

Butyl alcohol  $\text{C}_4\text{H}_9\text{OH}$

**Sol 14:** Refer theory

**Sol 15:**  $\text{R}_1\text{Ag}_2 \rightarrow 2\text{Ag} + \text{other}$

Let molecular weight of salt be M.

Then 1 mole of  $\text{R}_2\text{Ag}$  gives 2 moles of Ag

$$\therefore 2 \times \frac{0.2018}{M} = \frac{0.1073}{108} \Rightarrow M = 406.23$$

Molecular weight of organic compound  
=  $406.23 - (2 \times 108) \times 2 = 192.23$

**Sol 16:** Fractional crystallization is a method of refining substances based on difference in solubility (especially when the difference in solubility is low)

**Sol 17:** For platonic chloride method, we have

$$\frac{w}{2M + 410} = \frac{x}{195}$$

$$\frac{w}{2M} \frac{0.3168}{2M + 410} = \frac{0.1036}{195}$$

$$2M + 410 = 596.3$$

$$M = 93.14 \text{ g}$$

**Sol 18:** (a) Fractional Distillation

(b) Crystallisation (c) Steam Distillation

**Sol 19:** For definition and types of resonance effect refer text.

It differs from inductive effect as resonance effects involves actual movement of electrons contrary to inductive effect in which there is no actual movement but just development of polarity.

Because of this, resonance effect is more stronger than inductive effect.

**Sol 20:** The reversal occurs due to hyperconjugation effect, which is an extension of the resonance effect. The inductive effect will depend on the number of hyperconjugation structures which will depend on the number of  $\alpha$ -H

For  $\text{H}_3\text{C}$ - max inductive effect ( $3\alpha\text{H}$ )

$\text{H}_2\text{CH}_3\text{C}$ -2  $\alpha$  H

$(\text{CH}_3)\text{CH}$ -1  $\alpha$  H

$(\text{CH}_3)_3\text{C}$ -0  $\alpha$  H

Thus order of hyperconjugation effect

$\text{CH}_3- > \text{CH}_3\text{CH}_2- > (\text{CH}_3)_2\text{C}- > (\text{CH}_3)_3\text{C}-$

Whereas inductive effect follows reverse order

**Sol 21:** Refer text

**Sol 22:** Chromatography is based upon the principal of distributing the components of a given organic mixture between two medium. One of which is stationary and other is mobile.

**Sol 23:** Refer text

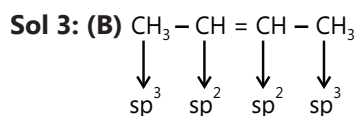
**Sol 24:** Fractional distillation is employed when the liquids which have to be separated have very little difference in their boiling point temperatures (~10–15K)

## Exercise 2

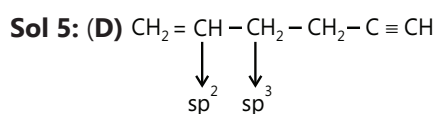
### Single Correct Choice Type

**Sol 1: (B)** In  $\text{CH}_3^+$ , C has a  $\text{sp}^2$  structure, making its shape trigonal planar

**Sol 2: (D)** A nucleophile must have a lone pair of electrons

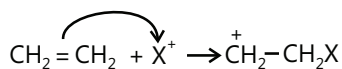
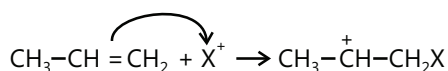


**Sol 4: (C)**  $\text{C}_1$  is  $\text{sp}$  and  $\text{C}_2$  is  $\text{sp}^2$



**Sol 6: (B)** In  $\text{CH}_3^+$ , C has a  $\text{sp}^2$  structure, making its shape trigonal planar

**Sol 7: (B)**



The resulting carbocation is more stable for  $\text{CH}_3-\text{CH}=\text{CH}_2$  due to more number of hyperconjugation structures

**Sol 8: (B)** Carbanion is a nucleophile as it has a negative charge and lone pair of electrons.

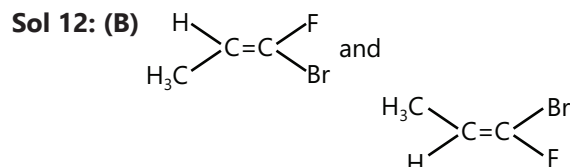
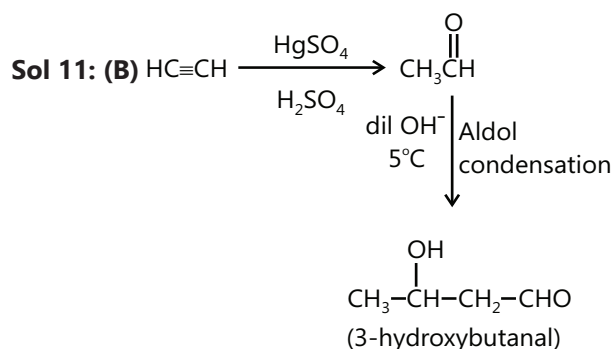
**Sol 9: (C)** In (I)  $\rightarrow$  No charge separation.

(II)  $\rightarrow$  Complete octet on every atom

(III)  $\rightarrow$  Positive charge on Carbon atom

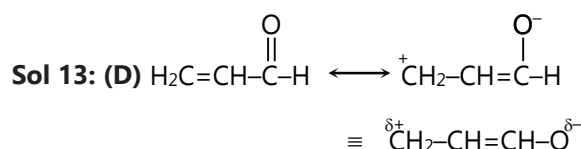
(IV)  $\rightarrow$  Negative charge on Carbon atom

**Sol 10: (C)** In II, N has 10 valence electrons which is not possible, as N is a period 2 element



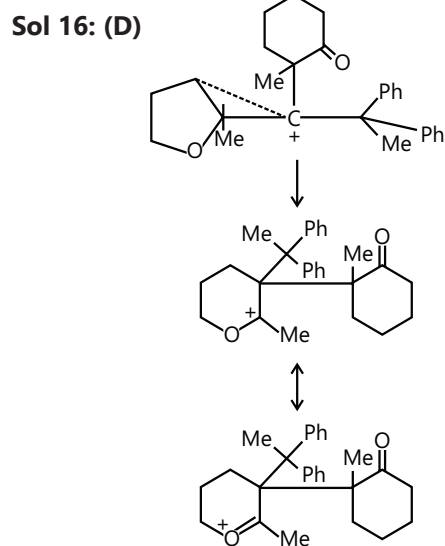
Are geometric isomers

For rest cannot show geometrical isomerism as they contain the same group on C atom.



**Sol 14: (B)** (D) is most stable because of the enhanced stability of the resulting carbocation due to conjugation. In (A) the lone pair of N is not conjugated and also the  $\text{CH}_2-\text{N}$  single bond has more +I effect than the  $\text{C}=\text{N}$  double bond, making it basic than (B)  $\text{CH}_3-\text{C}$  which has the least +I effect.

**Sol 15: (B)**  $\text{RSO}_3^-$  group is the best leaving group. In 1 and 2, 2 will be more stable due to the more -I effect of  $\text{NH}_3^+$  and  $3 > 4$  in stability.  $\therefore 2 > 1 > 3 > 4$



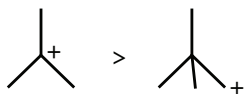
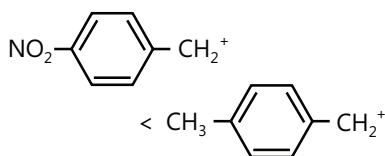
Here the positive charge is greatly stabilised as all the atoms have complete octet.

**Sol 17: (C)** Its ring contains  $2\pi$  electrons, so it follows Huckel's rule

**Sol 18: (C)**  $5\text{Na}_2\text{O}_2 + 2\text{P} \xrightarrow{\text{fuse}} 2\text{Na}_3\text{PO}_4 + 2\text{Na}_2\text{O}$

**Sol 19: (C)** Reactivity order for  $\text{S}_{\text{N}}1$  reaction depends upon the stability of resulting carbocation.

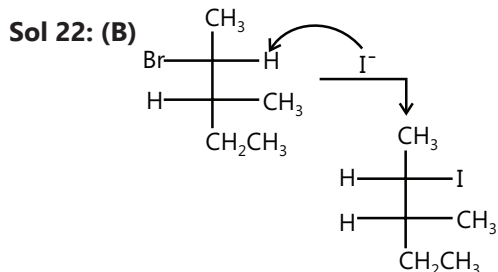
$\text{Ph}\cdot\text{CH}_2^+ > \text{Ph}^+$ , since  $\text{Ph}\cdot\text{CH}_2^+$  is a benzyl cation (due to  $-I$  and  $-M$  effect of  $\text{NO}_2^-$ )



( $\therefore$  tertiary carbocation  $>$  secondary carbocation)

**Sol 20: (A)**  $\text{S}_{\text{N}}1$  reaction yields a racemic mixture

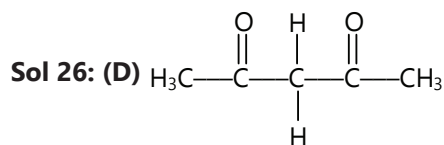
**Sol 21: (B)**  $-\text{Cl}$  group has  $-I$  effect which stabilizes the anion and it decreases with distance.



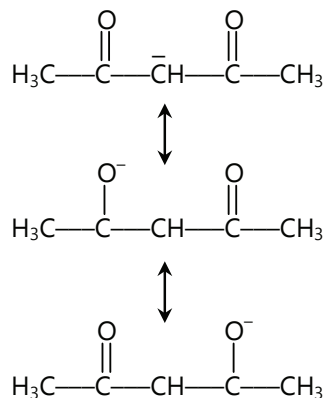
**Sol 23: (D)** For a compound to be reactive towards  $\text{S}_{\text{N}}2$  reaction, the resulting carbocation should be least stable. Here, the resulting carbocation is least stable in (d) due to the strong  $-M$  effect of the  $-\text{NO}_2$  group.

**Sol 24: (D)** Magnesia mixture is  $\text{MgCl}_2 + \text{NH}_4\text{Cl}$  + little of  $\text{NH}_3$

**Sol 25: (D)**  $\text{K}_2\text{SO}_4$  raises the boiling point of water.

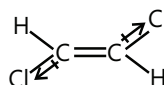


Enolate form is



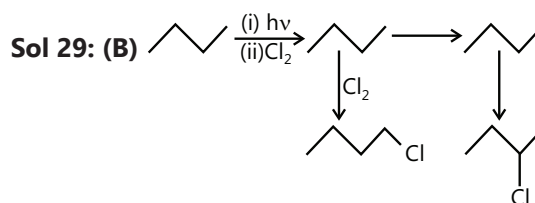
This structure is stabilised most by resonance

**Sol 27: (A)** For trans-1,2-dichloroethene, the dipole moment is 0



Which causes maximum difference in dipole moment between its cis and trans forms. For others, the trans form also has some dipole moment.

**Sol 28: (C)** Triplet carbene is more stable than singlet carbene because of the more repulsion between electrons in singlet carbene compared to triplet carbene.



Total number of isomeric chloro butanes = 2

**Sol 30: (D)** Reactivity will be most for the compound which has the most positive charge density on the carbonyl carbon. Noting this, the order will be:

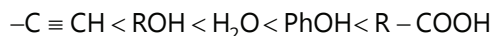
$\text{ArCOAr} > \text{ArCHO} > \text{ArCOR} > \text{HCHO} > \text{ArCOAr}$

**Sol 31: (D)** There are no meso forms for glucose.

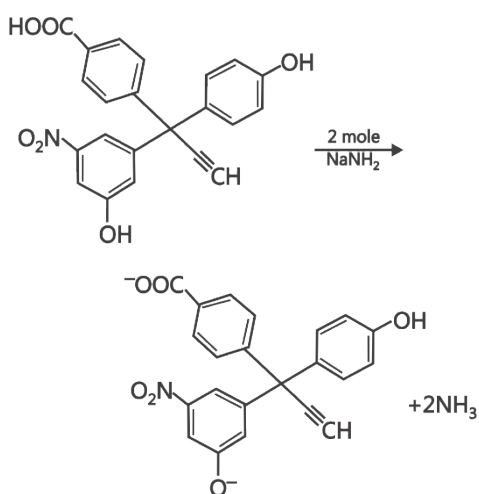
**Sol 32: (B)** It is necessary to remove S and N before testing for halogens.

## Previous Years' Questions

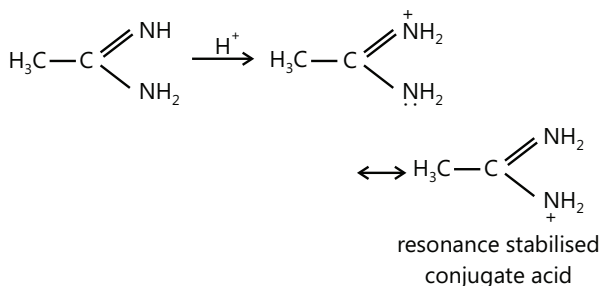
**Sol 1: (C)** In general, the order of acid strength is



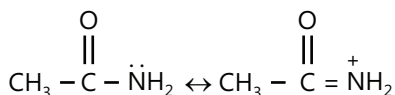
Therefore, during stepwise neutralisation of given acid,  $-\text{COOH}$  will be neutralised first. In the second step, the phenolic  $-\text{OH}$ , assisted by  $-I$  effect of  $-\text{NO}_2$  at Meta position will be neutralised.



**Sol 2: (A)** I is most basic due to formation of resonance stabilised conjugate acid



IV is amide, least basic



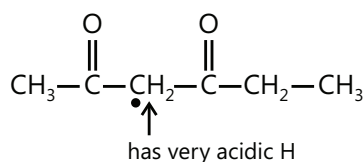
lone pair is part of delocation

Also, among alkyl amines,  $2^\circ$  is more basic than  $1^\circ$  amine. Hence, Overall order of basic strength is  $1 > 3 > 2 > 4$

**Sol 3: (B)** Carboxylic acid is stronger acid than ammonium ion, hence  $-\text{COOH}(X)$  is most acidic.

$Z(\overset{+}{\text{N}}\text{H}_3)$  is more acidic than  $Y(\overset{+}{\text{N}}\text{H}_3)$  due to  $-I$  effect of  $-\text{COOH}$  on Z. Hence, overall acid strength order is  $X > Z > Y$

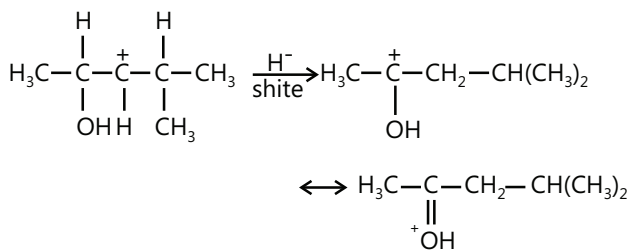
**Sol 4: (C)** A methylene ( $-\text{CH}_2-$ ) with carbonyl on both side is highly acidic.



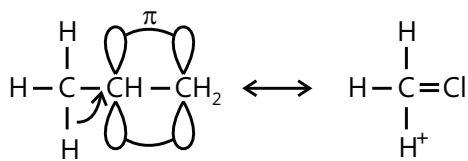
**Sol 5: (A, B, D)** Octet of nitrogen is violated.

**Sol 6: (C)** I is most stable because it has more covalent bonds and negative charge on electronegative nitrogen. III is more stable than II and IV due to greater number of covalent bonds. Between II and IV, II is more stable since, it has negative charge on electronegative atom and positive charge on electropositive atom. Hence, overall stability order is  $I > III > II > IV$

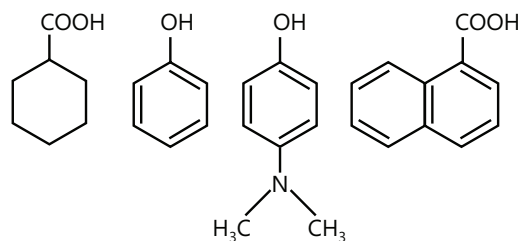
**Sol 7: (D)** H at C-2 will migrate giving resonance stabilised carbocation



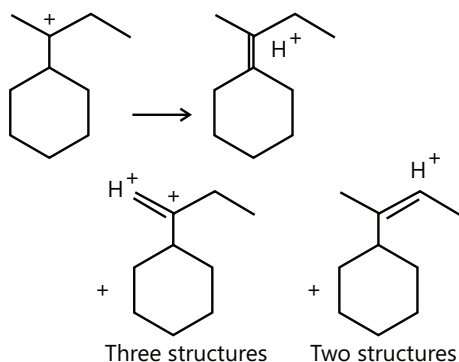
**Sol 8: (B)** The  $\sigma$ -electrons of C-H bond is delocalized with p-orbitals of  $\pi$ -bond.



**Sol 9: (4)** Aromatic alcohols and carboxylic acids forms salt with NaOH, will dissolve in aqueous NaOH:

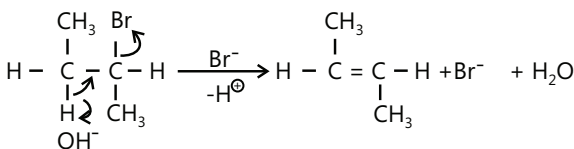
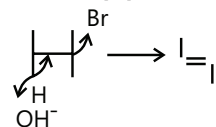


**Sol 10: (B)** These are total  $6\alpha$ -H to  $\text{sp}^2$  carbon and they all can participate in hyper conjugation.



**Sol 11: (C)** D(+)-tartaric acid has positive optical rotation and is derived from D(+) glyceraldehyde.

**Sol 12: (A)**



**Sol 13: (B)**

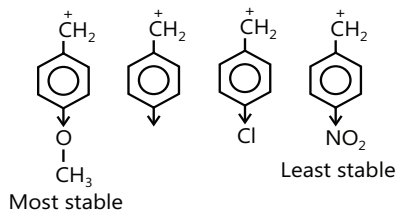
Nitro-group is electron withdrawing therefore decreases stability.

Methoxy group is electron releasing.

Therefore increases stability by donating electron.

Chlorine is also electron withdrawing but its effect is less than  $-\text{NO}_2$  group.

Hence, correct order of stability.

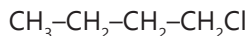


**Sol 14: (C)**  $\text{CH}_3^-$  has the highest nucleophilicity.

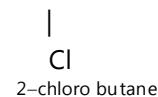
**Sol 15: (B)** In cis isomer the carbon-chlorine dipole reinforces and hence there is a large molecular dipole.

**Sol 16: (C)** (A) and (D) are symmetric alkanes, hence these are non polar, while (B) and (C) are symmetric alkenes hence they possess a dipole moment. But B is trans.

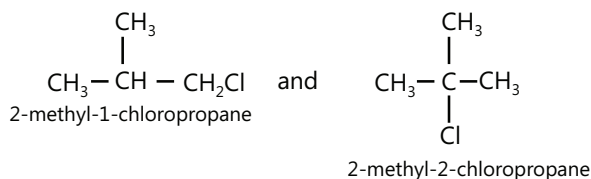
**Sol 17: (A, D)** n-butane has the following two isomeric monochloro derivatives



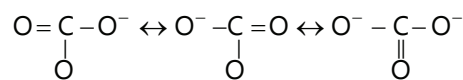
1-chlorobutane and  $\text{CH}_3-\text{CH}_2-\text{CH}(\text{Cl})-\text{CH}_3$



2-methylpropane has the following two isomeric monochloro derivatives.



**Sol 18:**  $\text{CO}_3^{2-}$  shows resonance and thus all the three bonds are of identical bond length.



**Sol 19:** Boiling points of isomeric compounds depend on dipole-dipole interactions and cis-isomers have a greater dipole moment (more polar) than trans-isomers (less polar).

**Sol 20:** Diastereoisomers are mirror images.

**Sol 21: (C)** Acidic nature order (III) > (I) > (II) > (IV)

**Sol 22: (D)** On the basis of the number of resonating structures (III) > (I) > (II)

**Sol 23: (B)** Quinol (c) and thioquinol (d) do not have  $\mu = 0$  due to nonlinear alignment.

## JEE Advanced/Boards

### Exercise 1

**Sol 1:** Hybridisation is the concept of mixing atomic orbitals into new hybrid orbitals suitable for the pairing of electrons to form chemical bonds. Now, talking about carbon, it can hybridize in three different ways, because its valence shell orbitals allow him to do so.

He can hybridize (mix) his valence orbitals to generate sets of equivalent  $sp$ ,  $sp^2$  or  $sp^3$  orbitals.

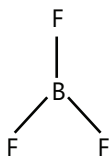
**Sol 2:** Methane: In methane, carbon is  $sp^3$  hybridised making the shape tetrahedral.

Ethane: In ethane, both the carbon atoms are  $sp^3$  hybridised making its shape tetrahedral with respect to each carbon atom

Ethene: In ethene both carbon atoms are  $sp^2$  hybridised making its shape trigonal planar with respect to each carbon atom.

Ethyne: In ethyne both carbon atoms are  $sp$  hybridized making its geometry linear.

**Sol 3:** (a) Boron trifluoride



Here, B has only 2 electrons in its valence shell making a Lewis acid.

On the other hand, nitrogen has a lone pair of electron in both  $(CH_3)_3N$  and  $(PH)_3N$  making them Lewis base.

But, in  $(PH)_3N$  lone pair is resonance stabilised by conjugation with three phenyl rings making availability for lone pair towards co-ordination.

(b)  $:CF_2$  is the most stability due to the back bonding between vacant orbital of C and the filled p orbital of F reducing the electron deficiency on C carbon.

**Sol 4:** The classifications for hydrocarbons, defined by IUPAC nomenclature of organic chemistry are as follows:

(a) Saturated hydrocarbon: The general formula for saturated hydrocarbons is  $C_nH_{2n+2}$

Example: methane, ethane

(b) Unsaturated hydrocarbons: These with one double bond are called alkenes have the formula  $C_nH_{2n}$

Example: Ethene, propene.

Those containing triple bonds are called alkynes, with general formula  $C_nH_{2n-2}$

Example: Acetylene, Propyne

(c) Cycloalkanes are hydrocarbons: The general formula for a saturated hydrocarbon containing one ring is  $C_nH_{2n}$ . Example: cyclopropane, cyclobutane

(d) Aromatic hydrocarbons: Also known as arenes, are hydrocarbons that have at least one aromatic ring. E.g. benzene, naphthalene

**Sol 5:** (i) Functional group is an atom or group of atoms that replaces hydrogen in an organic compound and that defines the structure of a family of compounds and determines the properties of the family. E.g. Alkyl, Phenyl

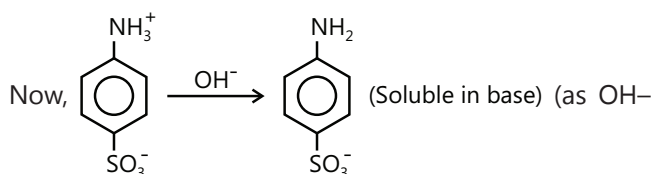
(ii) A homologous series is a group of chemicals which have similar chemical properties and can be represented by a general formula. Homologous series are 'families' of organic compounds

They share common characteristics:

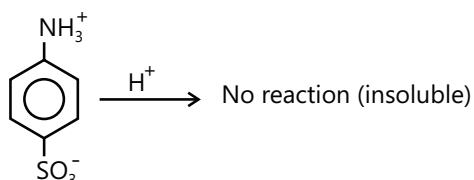
(a) They all contain the same functional group. This gives the homologous series name.

(b) They differ in formula from one member to the next by one  $-CH_2-$  unit

(c) They show a steady change in physical properties from one member to the next. The alkanes, alkenes and cycloalkanes are examples of homologous series



is more basic than  $-NH_2$ )



( $H^+$  is less acidic than  $-SO_3H$ )

**Sol 7:** Hybridization happens when atomic orbitals mix to form new atomic orbitals. The new orbitals have the same total electron capacity as the old ones. The properties and energies of the new, hybridized orbitals are an 'average' of the original unhybridized orbitals

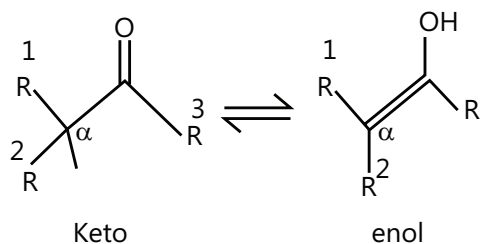
$sp^3$  hybridization: Tetrahedrally coordinated carbon. e.g. Methane

$sp^2$  hybridisation: In ethene molecule carbon  $sp^2$  hybridises, because one  $\pi$  (pi) bond is required for the double bond between the carbons and only three  $\sigma$  bonds are formed per carbon atom.

$sp$  hybridisation: The chemical bonding in acetylene (ethyne) ( $C_2H_2$ ) consists of  $sp-sp$  overlap between the two carbon atoms forming a  $\sigma$  bond and two additional  $\pi$  bonds formed by  $p-p$  overlap.

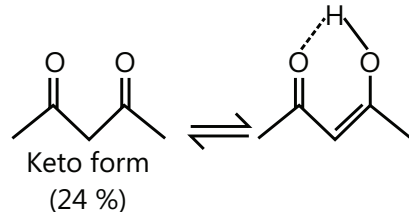
**Sol 8:** Tautomers are constitutional isomers of organic compounds that readily interconvert by chemical reaction called tautomerisation. This reaction commonly results in the formal migration of a hydrogen atom or proton, accompanied by a switch of a single bond and adjacent double bond, The concept of tautomerization is called tautomerism

Keto-enol tautomerism refers to a chemical equilibrium between a keto form (a ketone or an aldehyde) and an enol (an alcohol)



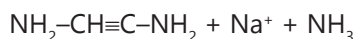
Conditions:

- (i) Presence of conjugated double bonds in enol form
- (ii) Due to favourable hydrogen bonding interactions



- (iii) Sometimes under slightly acidic or basic conditions

**Sol 9:** (a)  $NaNH_2 + C_2H_2 \longrightarrow$

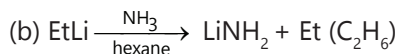


Strong acid:  $NH_2^-$

Weak acid:  $C_2H_2$

Weak base:  $NH_3$

Strong base:  $H-C\equiv C^-$

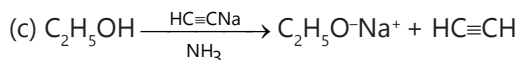


Strong base:  $Et^- (C_2H_5^-)$

Weak acid:  $NH_3$

Strong acid:  $Li^+$

Weak base:  $NH_3$

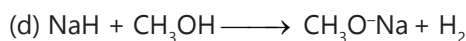


Strong acid:  $Na^+$

Weak acid:  $C_2H_5OH$

Strong base:  $HC\equiv C^-$

Weak base:  $HC\equiv CH$



Strong acid:  $Na^+$

Weak acid:  $CH_3OH$

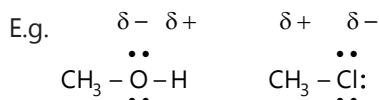
Strong acid:  $H^-$

Weak base:  $H_2$

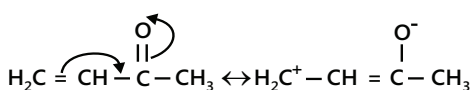
**Sol 10:** The following four types of electronic effects operates in covalent bonds

- (a) Inductive effect
- (b) Mesomeric and Resonance effect
- (c) Electronic effects
- (d) Hyperconjugation

(a) Inductive Effect: In a covalent bond between the two dissimilar atoms, the electron pair forming the bond is never shared absolutely equally between the two atoms but is attracted a little more towards the more electronegative atom of the two.

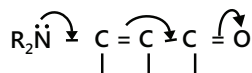


(b) Resonance & Mesomeric Effect: There are many organic molecules which cannot be represented by a single lewis structure. In turn, they are assigned more than one structure called canonical forms or contributing of resonating structures. The phenomenon exhibited by such compounds is called resonance. For example,



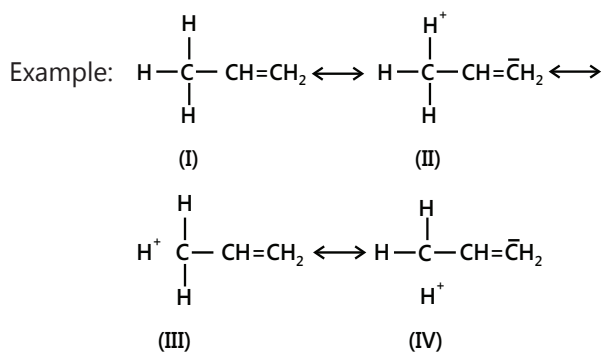


(c) Electromeric Effect: It is a temporary effect in which a shared pair of electron ( $p$  - electron pair) is completely transferred from a double bond or triple bond to one of the atoms joined by the bond at the requirement of attacking reagent.

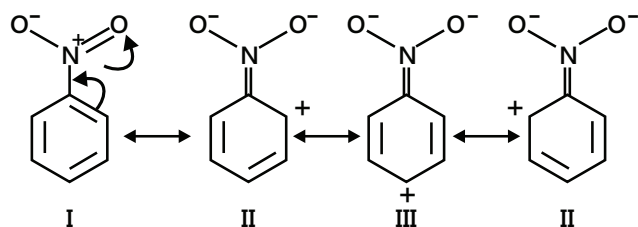


(d) Hyperconjugation: It is the delocalisation of sigma electron. Also known as sigma-pi conjugation or no bond resonance

Condition: Presence of  $\text{-H}$  with respect to double bond, triple bond carbon containing positive charge (in carbonium ion)



**Sol 11:** Resonance or mesomeric effect (on reaction rates, ionization equilibria, etc.) is attributed to a substituent due to the overlap of its  $p$ - or  $\pi$ -orbitals with the  $p$ - or  $\pi$ -orbitals of the rest of the molecular entity. There are many organic molecules which cannot be represented by a single lewis structure. In turn, they are assigned more than one structure called canonical forms or contributing of resonating structures. The phenomenon exhibited by such compounds is called resonance. For example, The nitro group,  $-\text{NO}_2$ , in nitrobenzene shows  $-\text{M}$  effect due to the delocalization of conjugated  $\pi$  electrons as shown below. Note that the electron density on the benzene ring is decreased particularly on ortho and para positions.



This is the reason for why nitro group deactivates the benzene ring towards the electrophilic substitution reaction.

**Sol 12:** The displacement of  $\sigma$ -electrons towards the multiple bond occurs when there are hydrogens on the  $\alpha$ -carbon (which is adjacent to the multiple bond).

This results in the polarization of the multiple bond. In the formalism that separates bonds into  $\sigma$  and  $\pi$  types, hyper conjugation is the interaction of  $\sigma$ -bonds (e.g.  $\text{C-H}$ ,  $\text{C-C}$ , etc.) with a  $\pi$  network. This conjugation between electrons of single ( $\text{H-C}$ ) bond with multiple bonds is called hyper conjugation. Hyperconjugation is a permanent effect whereas resonance effect is temporary.

Significance of hyperconjugation:

**Bond Length:** Like resonance, hyperconjugation also affects bond lengths because during the process the single bond in compound acquires some double bond character and vice-versa. E.g.  $\text{C-C}$  bond length in propene is  $1.488 \text{ \AA}$  as compared to  $1.334 \text{ \AA}$  in ethylene.

**Dipole moment :** Since hyperconjugation causes the development of charges, it also affects the dipole moment of the molecule.

**Sol 13:** Free radical :These are neutral intermediates, formed due to homolytic cleavage of a single bond. Some common bonds which cleave to give free radicals in organic chemistry are shown:  $\text{C-O}$ ,  $\text{C-Cl}$ ,  $\text{C-Br}$ ,  $\text{C-I}$ ,  $\text{C-C}$ ,  $\text{C-H}$ . Carbon free radicals are mainly generated by:

- Photolysis (action of light) like acetone alpha cleavage
- Other radical initiator like allylic bromination by  $\text{N-Bromosuccinimide}$  (NBS)

**Carbocations:** Carbocations are formed from the heterolytic cleavage of a carbon-heteroatom. These are mainly generated by:

Formed due to heterolysis of a  $\text{C-X}$  bond (where  $\text{X}$  is more electronegative) and thus has a positive charge.

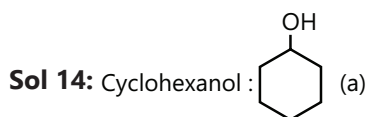
Planar in shape ( $\text{sp}^2$  hybridized carbon), with empty  $p$  orbital perpendicular to the plane of the molecule.

Reactive towards electron rich species

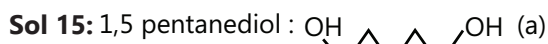
**Carbanion:** These are intermediates also formed as a result of heterolysis, but here the electron pair from the bond is kept by the carbon atom.

- Formed due to heterolysis of a  $\text{C-X}$  bond (where  $\text{X}$  is less electronegative) and thus has a negative charge.
- Pyramidal in shape ( $\text{sp}^3$  hybridized) with the excess electrons placed in one  $\text{sp}^3$  hybrid orbital.
- Reactive towards positively charged (electron deficient species).



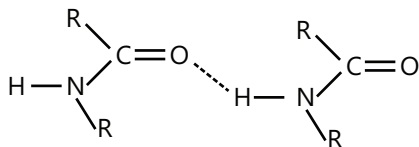


(a) Is more soluble than (b) due to greater extent of H-bonding due to its compact structure and less steric hindrance



(a) Is more soluble than (b) because of greater extent of H-bonding in (a) due to 2-OH groups compared with 1 in (b)

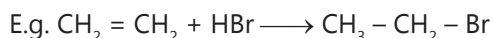
**Sol 16:** 1° and 2° amides tend to exist as dimer in solid and pure liquid state, because of H-bonding between them.



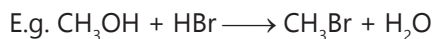
But this cannot happen in 3° amides as there is no hydrogen available for H-bonding

### Sol 17:

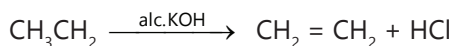
**1. Addition Reactions:** The reactions in which the attacking reagent adds up to the substrate molecule is called an addition reaction.



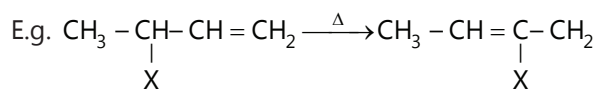
**2. Substitution Reaction:** The replacement of an atom or a group from a molecule by a different atom or group is known as a substitution reaction



**3. Elimination Reactions:** These reactions are the reverse of the addition reaction and involve the loss of atoms or a group of atoms from a molecule to form a multiple linkage. Most commonly, loss of atoms or groups occurs from adjacent carbon atoms to yield an olefin.



**4. Rearrangement:** Rearrangement reactions involve either the migration of a functional group to another position in the molecule containing a double bond or change the sequences of atoms forming the basic carbon skeleton of the molecule to form a product with a new structure.



### Sol 18:

(i) Homolytic cleavage is the breaking of a covalent bond in such a way that each fragment gets one of the shared electrons.

(ii) Heterolytic or ionic fission is the breaking of a covalent bond in such a way that one atom gets both of the shared electrons.

**Sol 19:** Electrophile: The species which carry +ve charge or are electron deficient are called electrophiles. These species attack regions of high electron density in a molecule.

Two types

(i) Positively charged electrophile:  $\text{H}^+$ ,  $\text{CH}_3^+$

(ii) Neutral electrophiles:  $\text{SO}_3$ ,  $\text{RCOCl}$

Nucleophiles: Those species which carry a negative charge / electron rich species or which have some pair of electrons are called nucleophiles. They attack regions of low electron density.

Two types

(i) Negatively charged:  $\text{Br}^-$ ,  $\text{CH}_3^-$

(ii) Neutral electrophiles:  $\text{NH}_3$ ,  $\text{ROH}$

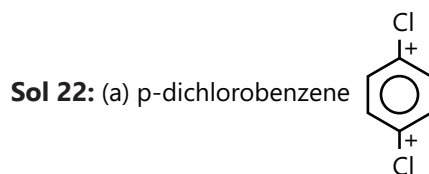
**Sol 20: Free radical:** Photolysis (action of light) like acetone alpha cleavage. Other radical initiator like allylic bromination by N-bromosuccinimide (NBS)

**Carbocations:** Formed due to heterolysis of a C-X bond (where X is more electronegative) and thus

**Carbanion:** Formed due to heterolysis of a C-X bond (where X is less electronegative) and thus has a negative charge.

**Sol 21:** Carbanions will be more stable if they are attached to a group which withdraws electrons (-I).


Therefore, the more the -I effect of surrounding atoms, the more stable the carbanion will be



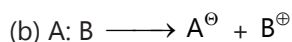
has a dipole moment which makes this compound non-polar and therefore, its solubility will be more in a polar solvent compared to a non-polar one. Now polarity of methyl alcohol ( $\text{CH}_3\text{OH}$ ) > n-propyl alcohol



∴ Its solubility is more in n-propyl alcohol than methyl alcohol.

o-dichlorobenzene  has a non zero dipole

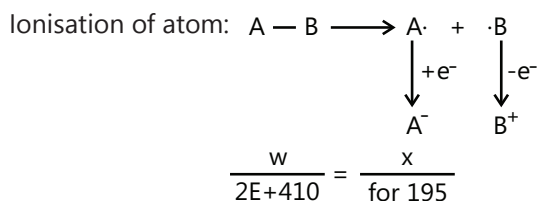
moment and therefore its solubility will be more in a polar solvent.



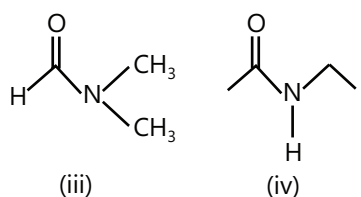
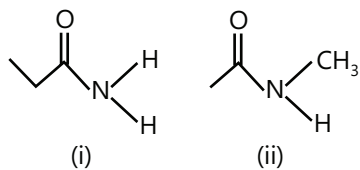
Heterolytic bond fission requires higher energy compared to homolytic bond fission as it involves separation of opposite charges which will be hindered by electrostatic force of attraction between ions.

If we study heterolytic cleavage step wise

If is first homolytic cleavage and then



**Sol 23:** 4 isomers are possible



Out of these four isomers, only (iii) cannot do hydrogen bonding and therefore exhibits different characteristics than the other three.

Name of (iii): Dimethyl formamide

**Sol 24:**

(i) Substitution reaction (also known as single displacement reaction or single replacement reaction) is a chemical reaction during which

one functional group in a chemical compound is replaced by another functional group.

(ii) An addition reaction, in organic chemistry, is in its simplest terms an organic reaction where two or more molecules combine to form a larger one (the adduct).

(iii) An elimination reaction is a type of organic reaction in which two substituents are removed from a molecule in either a one or two-step mechanism. The one-step mechanism is known as the E2 reaction, and the two-step mechanism is known as the E1 reaction.

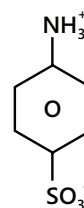
(iv) A rearrangement reaction is a broad class of organic reactions where the carbon skeleton of a molecule is rearranged to give a structural isomer of the original molecule.

(v) Isomerization: The chemical process by which a compound is transformed into any of its isomeric forms

(vi) Condensation: It is a chemical reaction in which two molecules or functional groups combine to form a large molecule, together with the loss of a small molecule.

(vii) Pericyclic: It is a chemical reaction where in the transition state of the molecule has a cyclic geometry, and the reaction progress in a concerted fashion.

**Sol 25:** Sulphanilic acid exists as Zwitter ion as :



In the presence of dil. NaOH the weakly acidic  $-\text{NH}_3^+$  group transfers its  $\text{H}^+$  to  $\text{OH}^-$  to form soluble salt  $\text{P}^- - \text{NH}_2\text{C}_6\text{H}_4\text{SO}_3^- \text{Na}^+$ . On the other hand,  $-\text{SO}_3^+$  group is a very weak base and does not accept  $\text{H}^+$  from dil HCl to form  $\text{NH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$  and therefore, it does not dissolve in dil HCl.

## Exercise 2

### Single Correct Choice Type

**Sol 1: (A)**  $\text{Ph}^-$  will attack  $\text{C}-\text{Br}$  bond (because carbocation formed from this carbon will have most stability due to conjugation with the ring) and from opposite side of Br

**Sol 2: (B)** I and III are stabilized by +M effect of O, I is further stabilized as it is tertiary carbocation.

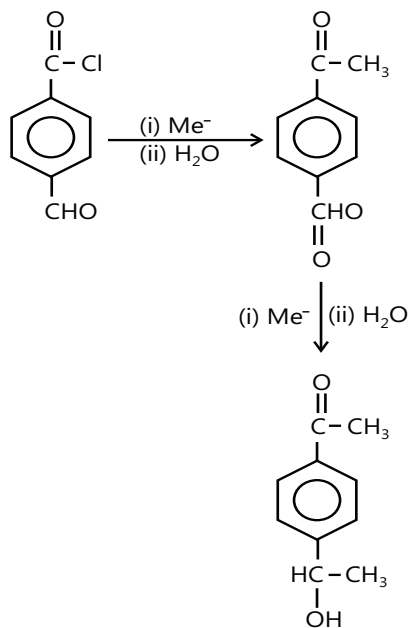
II is secondary carbocation

IV is primary carbocation.

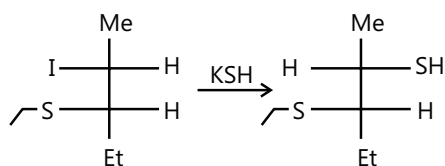
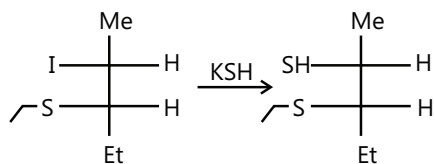
**Sol 3: (C)** In this structure O contains 10 valence electrons, which is not possible

**Sol 4: (B)**  $\text{BCl}_3$  is an electrophile as B has only 6 valence electrons and needs electrons to complete its octet.

**Sol 5: (B)**



**Sol 6: (C)** Mechanism is same for both (nucleophilic substitution), But products will be isomers

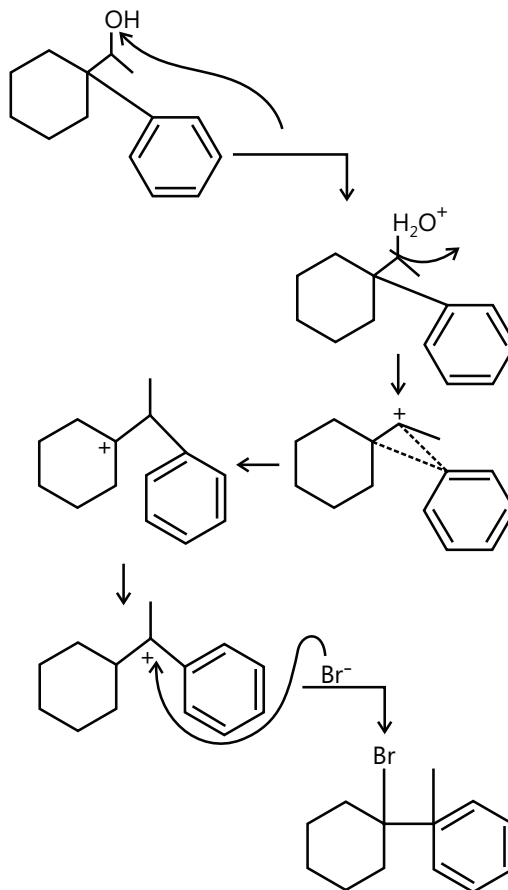


**Sol 7: (A)** (A) is antiaromatic ( $4\pi$  electrons)

(B) is aromatic ( $6\pi$  electrons)

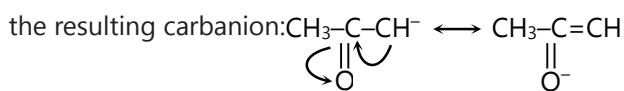
**Sol 8: (B)**  $-\text{Cl}$  group have  $-\text{I}$  effect which stabilizes the anion and it decreases with distance.

**Sol 9: (C)**

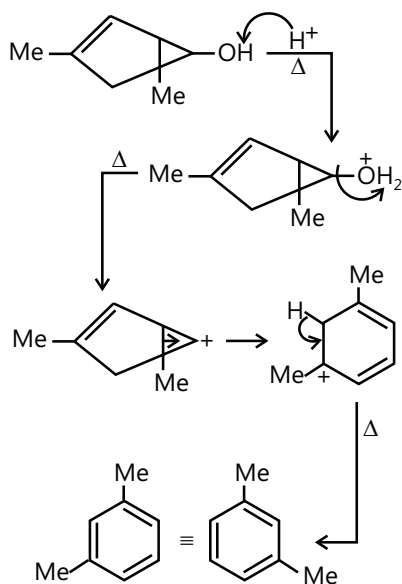


**Sol 10: (C)**  $\text{CCl}_3-\text{CH}(\text{OH})_2$  is most stable as it can form hydrogen bonding most effectively due to more  $-\text{I}$  effect of  $\text{CCl}_3-$  group

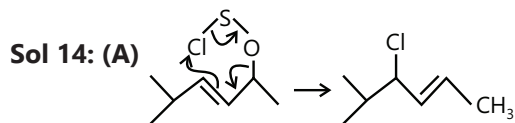
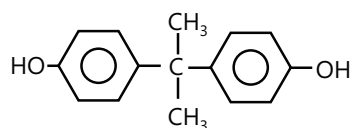
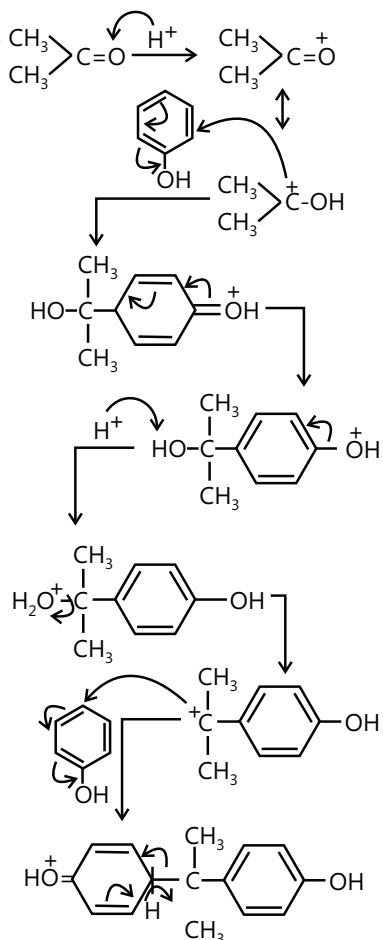
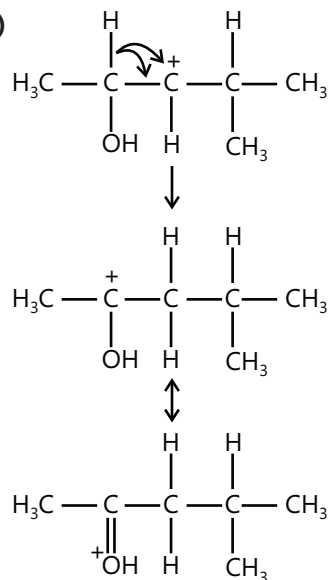
**Sol 11: (A)**  $\text{CH}_3-\text{C}(=\text{O})-\text{CH}_2-\text{COOH}$  has most reactivity as



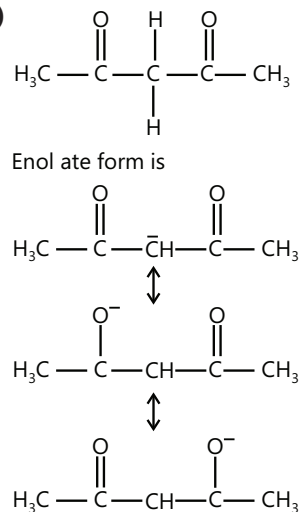
This is stabilized by resonance

**Sol 12: (B)**

**Sol 13: (C)** n-propyl alcohol will dehydrate by E2 mechanism. Rest statements are correct)

**Sol 15: (D)****Sol 16: (D)**

(This is very stable as it contains octet for all elements)

**Sol 17: (A)**

This structure is stabilised most by resonance

**Sol 18: (D)** (A) Triphenylmethyl radical is more stable than trimethyl radical due to more conjugation (increasing stability) in the former.

(B) This trend is not always necessarily followed

(C)  $^+\text{CH}_3$  is the least stable one as the positive charge needs to be dispersed to increase stability.

**Sol 19: (A)** Heat of hydrogenation of Benzene involves hydrogenation of 3 normal  $\pi$  bonds – the resonance energy of benzene.

$\therefore$  Heat of hydrogenation of  $3\pi$  bonds

$$= (49.8 + 36) \text{ K cal./mol} = 85.8 \text{ k cal/mol}$$

Heat of hydrogenation of cyclohexene involves.

Hydrogenation of 1  $\pi$  bonds, therefore,

$$\text{Heat of hydrogenation} = \frac{85.8}{3} \text{ k cal/mole}$$

$$= 28.6 \text{ k cal/mole}$$

**Sol 20: (A)** + H effect 9  $\alpha$  – H in  $(\text{CH}_3)_3\text{C}^+$

### Multiple Correct Choice Type

**Sol 21: (A, B, C)** These are the characteristics of resonance structures

### Comprehension Type

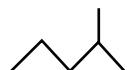
#### Paragraph 1

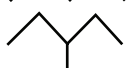
**Sol 22: (C)** Infinite orientations are possible and each orientation represents one conformation.

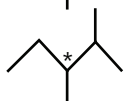
**Sol 23: (A)** Chair forms has least strain

**Sol 24: (A)** Conformation have very less difference in energy and are easily transformed into one another at room temperature.

#### Paragraph 2

**Sol 25: (C)** (A):   $\rightarrow$  No chiral carbon

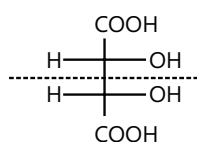
(B):  : No chiral carbon

(A):  : \* C is chiral

Making it optically active

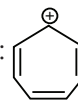
**Sol 26: (A)** d-glucose and  $\ell$ -glucose are enantiomers

**Sol 27: (B)** Meso compounds contain internal plane of symmetry which is only in C



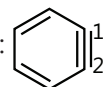
### Assertion Reasoning Type

**Sol 28: (A)** Tropylium cation:



This cation is aromatic and hence very stable due to resonance  $(\text{CH}_3)_3\text{C}^+$  is stabilized only by +I effect

**Sol 29: (A)** Benzyne:



$\text{C}_1$  and  $\text{C}_2$  are sp hybridized as  $\text{C}_1\text{--C}_2$  is triple bond

**Sol 30: (C)**  $\text{PH}_3$  is stronger nucleophile than  $\text{NH}_3$  due to big size of P and increased polarisability

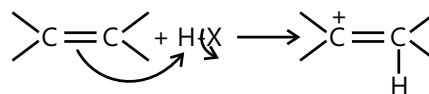
$\text{PH}_3$  is weak base than  $\text{NH}_3$  as lone pair density is more in  $\text{NH}_3$  due to its small size making it a better electron donor and hence better base

**Sol 31: (A)** R is the correct explanation for A

### Match the Columns

**Sol 32:** A  $\rightarrow$  p, s ; B  $\rightarrow$  q ; C  $\rightarrow$  r ; D  $\rightarrow$  q

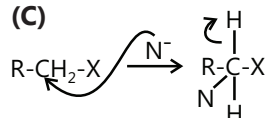
(A) Carbocations are formed in E1 reaction and halagenation of alkenes



(B)



(C)



(Pentavalent transition state)

(D) Carbonyl compounds undergo nucleophilic addition

**Sol 33:** A  $\rightarrow$  p, r, s, t ; B  $\rightarrow$  p, q, r, s, t ; C  $\rightarrow$  p, r, s, t ; D  $\rightarrow$  p, r, t

(A) Cannot undergo electrophilic addition as there is electron rich centre except benzene ring which does not undergo addition Nucleophilic addition can occur due to electron withdrawing effect of

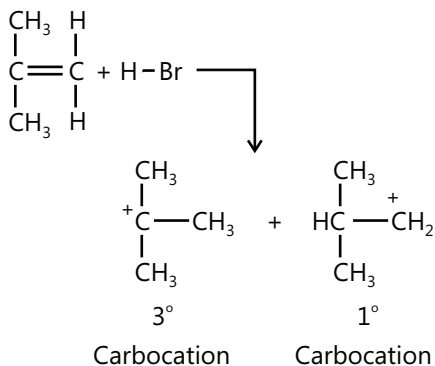
(B) It can undergo all reaction at different sites

(C) Cannot undergo electrophilic addition, no  $\pi$  bonds which can be broken

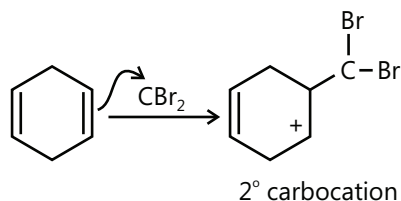
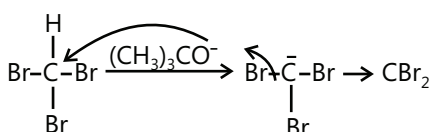
(D) Cannot undergo electrophilic addition reaction and elimination reaction

**Sol 34:** A → p, r; b → r, s; C → p, r; D → q, r

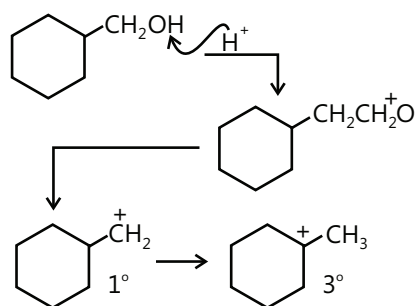
(A)



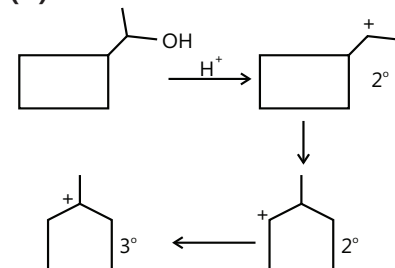
(B)



(C)



(D)



**Sol 35:** A → p, r; B → s; C → p, s; D → q, r, s

(A) Carbocations can undergo reaction with ethylene and rearrangement

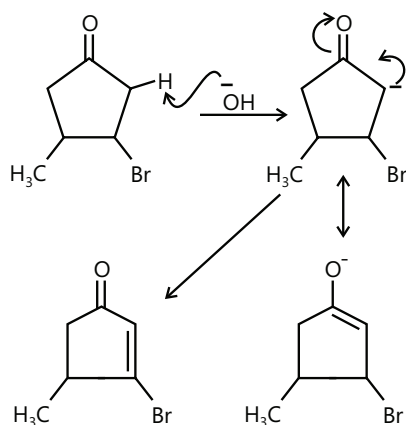
(B) Carbanions undergo disproportionation

(C) 2 carbenes can combine to form ethane. Carbenes can also react with ethylene

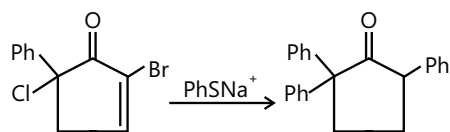
(D) Free radicals can combine and they also undergo rearrangement

**Sol 36:** A → t; B → p; C → r; D → q

(A) E<sub>1</sub> CB mechanism

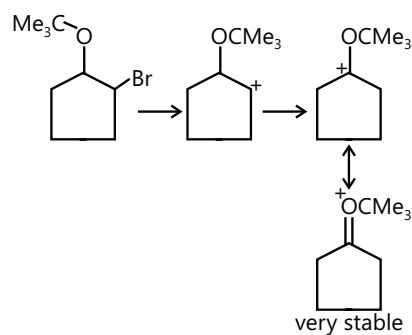


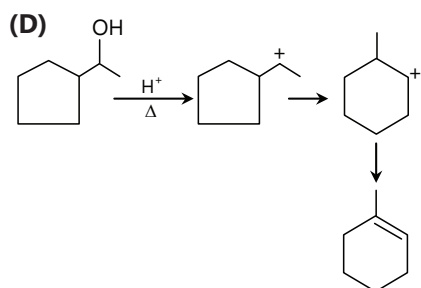
(B)



Will undergo E2 because of sterical hindrance and nucleophile PhS<sup>-</sup>

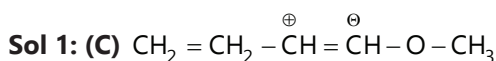
(C) Will undergo S<sub>N</sub>1 due to stability of carbocation and weaker nucleophile





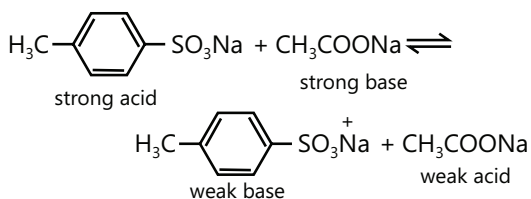
Can't undergo  $E_{cb}$  as no acidic hydrogen.

## Previous Years' Questions



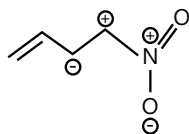
Lone pair of oxygen is not the part of this mode of delocalisation.

**Sol 2: (C)** A spontaneous neutralisation will occur between strong acid and strong base as



**Sol 3: (D)**

**Sol 4: (A)** The following structure has like charge on adjacent atoms, therefore, least stable.



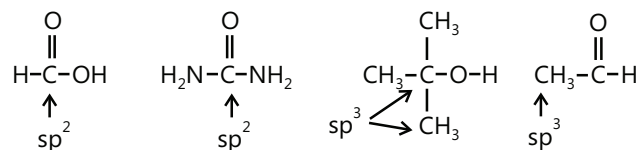
**Sol 5: (B, D)** Phenol is less acidic than a carboxylic acid (acetic acid). Nitro group from para position exert electron withdrawing resonance effect, increases acid strength. Therefore, phenol is less acidic than p-nitro phenol.

On the other hand, methoxy group from para position, donate electrons by resonance effect, decreases acid strength of phenol. Also ethanol is weaker acid than phenol due to resonance stabilisation in phenoxide ion. Hence,

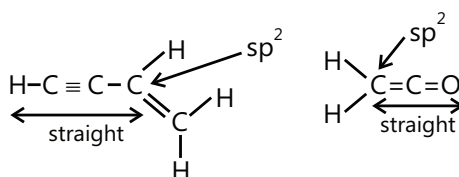
ethanol < p-methoxyphenol < phenol < p-nitrophenol < acetic acid

—increasing acid strength —>

**Sol 6: (C, D)**



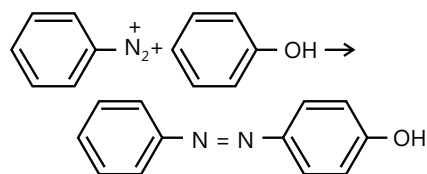
**Sol 7: (B, C)** In both (B) and (C), all the atoms are present in one single plane



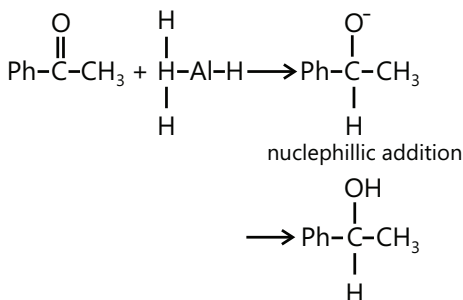
In (A) 1,3-butadiene, conformational change is possible between  $C_2-C_3$  bond in which atoms will be present in more than one single plane.

In (D) allene, the terminals  $H-C-H$  planes are perpendicular to one another.

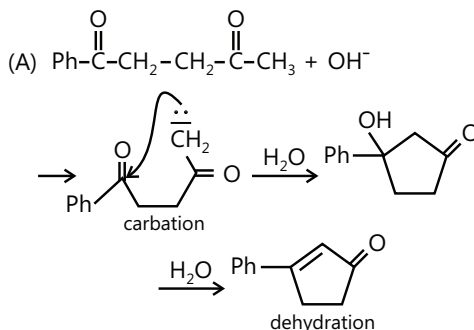
**Sol 8: A → r, s; B → t; C → p, q; D → r**

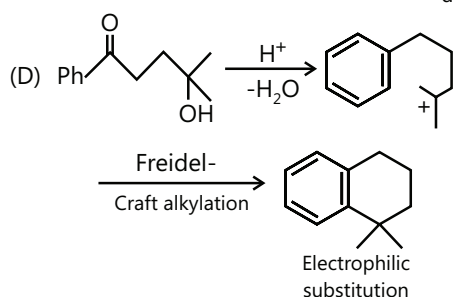
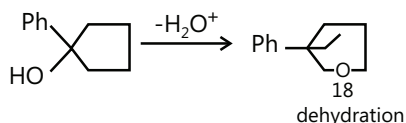
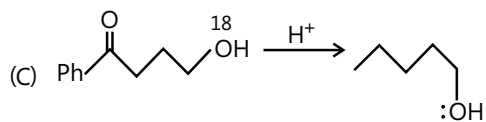
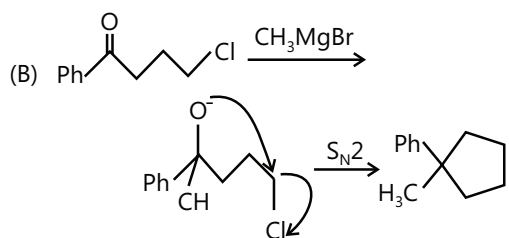


this is an example of electrophilic substitution at para position of phenol, giving a coupling product.



**Sol 9: A → r, s, t; B → p, s; C → r, s; D → q, r**





**Sol 10:**  $\text{H}-\text{C}\equiv\text{C}-\text{H}$  is more acid than  $\text{CH}_2=\text{CH}_2$ .

**Sol 11:** A  $\rightarrow$  r; B  $\rightarrow$  s; C  $\rightarrow$  p; D  $\rightarrow$  q

p-methoxy benzoic acid is the weakest and p-nitrobenzoic acid is the strongest acid among these acids. Chloro group has overall electron withdrawing effect on ring, therefore, increases acid strength of benzoic acid. Methyl group decreases acid strength of benzoic acid by +I effect. Therefore,

p-methylbenzoic acid  $3.3 \times 10^{-5}$

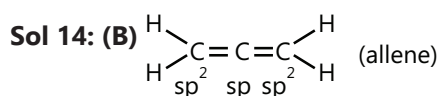
benzoic acid  $6.4 \times 10^{-5}$

p-chlorobenzoic acid  $10.2 \times 10^{-5}$

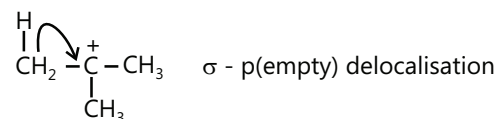
p-nitrobenzoic acid  $36.2 \times 10^{-5}$

**Sol 12:** No. of hyper conjugative structure = 6

**Sol 13: (C)** The most acidic compound is ortho-hydroxy benzoic acid due to ortho effect.



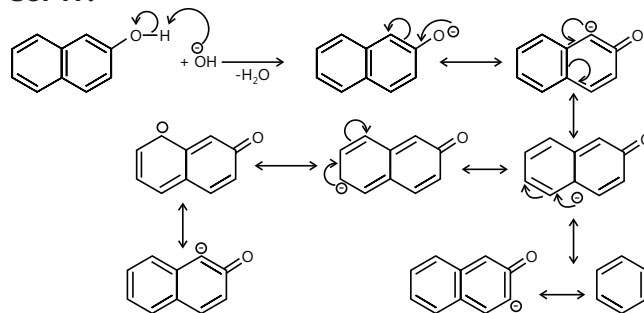
**Sol 15: (A)**



$\text{CH}_3-\text{CH}=\text{CH}_2$  ( $\sigma$  -  $\pi^*$  electron) delocalisation

**Sol 16: (B)** With increase in branching boiling point decreases.

**Sol 17:**



**Sol 18: (A)**

